

Structural and magnetic studies of pseudohalide bridged di and polynuclear Ni(II) complexes with N,O donor Schiff base ligand

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**Thesis Submitted for the Award of the Degree
of Doctor of Philosophy in Science**

* * *

March-2022

*Dedicate to My
Parents & Respected Sir*

CERTIFICATE

This is to certify that the thesis entitled “*Structural and magnetic studies of pseudohalide bridged di and polynuclear Ni(II) complexes with N, O donor Schiff base ligand*” submitted by **Mrs. Sarmistha Adak** who got her name registered on November 11, 2016, for the award of Ph.D. (Science) degree from Jadavpur University, is absolutely based upon her own work under the joint supervision of **Dr. Anangamohan panja**, Gokhale Memorial Girls’ College (formerly Panskura Banamali College) and **Dr. Amrita Saha**, Jadavpur University, and that neither her thesis nor any part of it has been submitted for either any degree / diploma or any other academic award anywhere before.

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Forewords

This dissertation includes design and synthesis of di and polynuclear Ni(II) complexes with various flexible ligands followed by their proper characterization by various techniques and the study of magneto-structural correlation of the resulted complexes. The major task in designing these compounds largely depends on the judicial choice of the blocking ligands. Schiff-base ligands are extremely useful for this purpose due to their ease of synthesis and tremendous structural diversities. A large number of coordination compounds with Schiff base ligands prepared by condensation of N-substituted diamine at one end, namely *N,N*-dimethylethylenediamine with salicylaldehyde or pyridine-2-aldehyde, have been developed with interesting magnetic properties. Surprisingly, only fewer report of structurally characterized complexes with the Schiff base derived from an unsymmetrical triamine namely, *N,N*-dimethyldipropylenetriamine, is available in the literature. In this context, we intended to systematically develop the coordination chemistry of the transition metals derived from this triamine, with the goal of their applications in diverse fields including magnetic materials. Accordingly, in this present endeavour, we carried out the synthesis of tetradentate Schiff base ligands derived from *N,N*-dimethyldipropylenetriamine and salicylaldehyde/pyridine-2-aldehyde. Moreover, binucleating Schiff base ligands derived from 2,6-diformyl-4-methylphenol (DFMP) and *N,N*-dimethyldipropylenetriamine were employed to obtain high nuclearity clusters especially in the presene of azide bringig ligands. Efforts were made to prepare various ligands taking different substituted derivatives of salicylaldehyde. Synthesized di and polynuclear Ni(II) complexes of these ligands were characterized by elemental analysis and IR spectroscopy and finally by X-ray diffraction study. After the structural caracterization, the magnetic properties of these compounds were examined. Finally, the magneto-structural correlation provides us enough information to understand the basic magnetic phenomenon in these complexes and in turn enriched the field of molecular magnetism.

Abbreviation

AEP	: 2-aminoethylpyridine
AF	: Antiferromagnetic
AMP	: 2-aminomethylpyridine
ATHAc	: 2-acetyl-2-thiazoline acetylhydrazone
ATsc	: 2-acetyl-2-thiazoline semicarbazone
bipy	: 2,2'-bipyridine
bpa	: 2,2'-Bipyridyl amine
BQMI	: <i>o</i> -benzoquinone monoamine
ca.	: About
CCD	: Cambridge Crystallographic data
CCDC	: Cambridge Crystallographic data Centre
dca	: dicyanamide
DFMP	: 2,6-diformyl-4-methylphenol
DFT	: Density functional theory
TD-DFT	: time-dependent density functional theory
DMF	: <i>N, N</i> - Dimethylformamide
DMSO-d6	: Deuterated dimethyl sulfoxide
EE	: End-to-End
eg	: ethylene glycol
en	: ethylenediamine
EPR	: Electron paramagnetic resonance
EO	: End-on
ESI-MS	: Electrospray ionization-Mass spectrometry
ESR	: Electron spin resonance
EXAFS	: Extended X-ray Absorption Fine Structure

F	: Ferromagnetic
FT-IR	: Furrier Transform Infrared Spectroscopy
HOBz	: Benzoic acid
HOMO	: Highest occupied molecular orbital
<i>hs</i> / HS	: high spin
JT	: Jahn-Teller distortion
<i>ls</i> / LS	: low spin
LUMO	: Lowest occupied molecular orbital
LMCT	: Ligand-to-metal charge transfer
MLCT	: Metal-to-ligand charge transfer
Near-IR	: Near-infrared
NMR	: Nuclear magnetic resonance
OBz	: Benzoate
ORTEP	: Oak Ridge Thermal Ellipsoid Plot
PXRD	: Powder X-ray diffraction
py	: Pyridine
rt	: room temperature
S-dept	: N,N,N',N'-tetraethylpyridine-2,6-dithiocarboxamide
SCMs	: Single chain magnets
SC-XRD	: Single Crystal X-Ray Diffraction
SMMs	: Single molecular magnet
SQUID	: Superconducting Quantum Interference Device
T _B	: Blocking Temperature
TEA	: triethylamine
Terpy	: 2,2';6',2''-Terpyridine
TGA	: Thermogravimetric analyses
THF	: Tetrahydrofurane

THMAM	: tris- (hydroxymethyl)aminomethane
TMS	: Tetramethylsilane
TPA	: tris-(2-pyridylmethyl)amine
tren	: 2,2',2''-triaminotriethylamine
TTF	: 4,5-bis(2-pyridylmethylsulfanyl)-4',5'-ethylenedithiotetrathiafulvene
UV-Vis	: Ultraviolet-visible
VSM	: Vibrating Sample Magnetometer
XANES	: X-ray Absorption Near Edge Structure
ZFS	: Zero-field splitting

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CHAPTER 1

CHAPTER-1

General Introduction

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1.1 General Introduction: Reviews of structural and magnetic properties of di and polynuclear complexes

The development of di and polynuclear paramagnetic transition metal complexes are of current interest due to their wide range of applications in various fields such as magnetism [1,2], catalysis [3-5], luminescence [5-7], storage [8-9], nonlinear optics and sensors [10-13]. Studies of the magnetic interactions involving paramagnetic metal centers have become an intense research area in recent years because some of these can function as single molecule magnets (SMMs), which show magnetic hysteresis arising from slow magnetization reversal due to a high energy barrier and thus behave as magnets below a certain blocking temperature (T_B) [14]. Such tiny magnets have attracted particular interest in chemistry, physics, and materials sciences because they show novel phenomena at the classical/quantum interface, and because they are considered as promising nanoscale objects for, inter alia, future high-density memory storage devices, spintronics, and quantum computing technologies [15].

Since the discovery of the first SMM, the dodecanuclear mixed-valent manganese complex $[\text{Mn}_{12}\text{O}_{12}(\text{OAc})_{16}(\text{OH}_2)_4]$ with $S_T = 10$ ground state by R. Sessoli and coworkers in 1993 [16], various derivatives of this so-called Mn_{12} archetype have been investigated, and much effort has been devoted to the synthesis and characterization of new polynuclear clusters that display slow magnetic relaxation behavior [17]. To date, the majority of SMMs have been found among homometallic manganese clusters containing at least some Mn(III) atoms as a transition metal, which is because such clusters often have large spin ground states as well as large negative magneto-anisotropy associated with the presence of Jahn-Teller-distorted Mn(III) atoms [18].

For obtaining a larger magnetic anisotropy, higher spin states and for a better understanding of quantum tunneling effects, preparative chemists moved beyond the manganese complex.

Herein we focused on di and polynuclear Ni(II) based complexes which may behave as SMMs.

1.2 Choice of metal:

Here we carried out the synthesis and characterization of di and polynuclear complexes of Ni(II) with some monoimine and di-imine based Schiff base ligands in presence of azido and different pseudohalides bridged ligands. Choice of this transition element to prepare di and polynuclear complexes have been made due to the presence of partially field d-orbitals, variable oxidation states and ability to form different coordination geometries with mono, di and polynuclear complexes [19-20]. Among the transition metals, Ni(II) deserves special mention due to its large single-ion zero-field splitting, and as a consequence numerous di- and polynuclear Ni(II) complexes with interesting magnetic properties have been derived [21-23]. Furthermore, due to the presence of unpaired electron in d-orbital of Ni(II) centre and also the presence of azido and different pseudohalides bridging ligands with their various coordination mode allowed the spin-spin interaction within the di or polynuclear Ni(II) centre in the complexes resulting the formation of complexes with significant diversity in structure and magnetic properties such as complexes with ferromagnetism [21], antiferromagnetism [22], ferrimagnetism [23] etc. Moreover, eminent choice of Ni(II) complexes are also due to their various application such as catalysis [24], remarkable role in biochemical process (as the nickel centers are present in the active site of the enzyme urease) [25] and anticancer activities and different technological and industrial application [26].

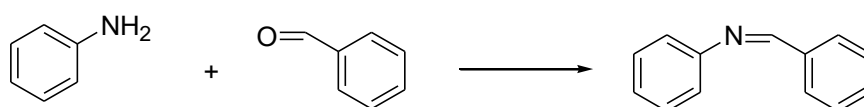
A remarkable evolution has been taken place in recent era in the field of single molecular magnetisms (SMMs). Researchers shifted their attention towards the understanding of the mechanism of magnetic coupling [14-15] in SMMs and the development of the process to prepared new paramagnetic di and polynuclear metal clusters with high spin and strong anisotropy. [16-17]

Pseudohalide bridging ligands are excellent for obtaining these types of metal clusters. Among all the pseudohalide bridging ligands, the azido ligand is the most common in linking divalent transition metal ion and other pseudohalide anions are very few.

Hence in the present work we focused on the synthesis and characterisation of di and polynuclear Ni(II) complexes with various Schiff base ligands in presence of pseudohalides as exogenous bridging ligands.

1.3 Choice of Ligands:

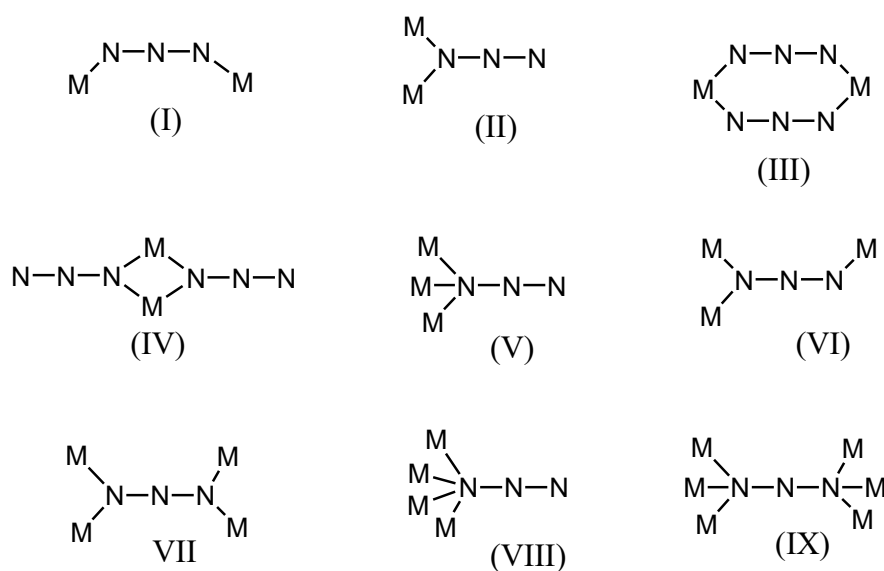
Different Schiff mono- and di-base ligands have been used to synthesize di and polynuclear Ni(II) complexes by various research groups worldwide. Schiff base ligand was first synthesized by Hugo Schiff in 1864 using condensation reaction between aniline and different aldehyde including acetaldehyde, valeraldehyde, benzaldehyde and cinnamaldehyde etc (Scheme 1.1) [27].



Scheme 1.1: Schematic diagram of synthesis of Schiff base ligand

After that the name “Schiff base” was used for the above type of imine-based ligands for the honor of the chemist Hugo Schiff. In coordination chemistry Schiff base ligand was first used by Middleton *et al.* [28] in 1923 and since that this type of ligands became preeminent choice to the chemist to prepared different type organometalic complexes. Several works have been carried out by different groups of chemists taking this type of ligand and for this purpose they prepared different type of Schiff base ligand varying amine and aldehyde. Diversities in structural and magnetic properties of Ni(II) complexes depends on various factors. Stereochemical orientation created by the blocking ligand around the metal centre is one of them and that’s why choice of blocking ligand is very important. Schiff base ligands has a ability to form di and polynuclear Ni(II) complexes with diverse decoration and

magnetic properties [29]. Their paramount choice is also due to their ease of synthesis and chemist can also bring varieties by varying the substituent either in amine part or in aldehyde part of the Schiff base ligands. Metal complexes decorated with Schiff base ligands has also wide application like in model study for biological oxygen carrier, oxygen transport, metallo-enzyme, anti neoplastic [30], antibacterial, antifungal, in catalysis [31] and magnetism [32] and in medical imaging [33]. Diverse magnetic behavior of Ni(II) complexes not only depends on the Schiff base ligand but also in the nature, bridging mode and orientation of the different exogenous bridging ligands like pseudohalide ions. In our work azido and different pseudohalides bridged ligands were employed for the synthesis of di- and polynuclear Ni(II) complexes due to their diverse magnetic properties. These ligands also show varieties of coordination fashion which enable us to prepare the Ni(II) complexes with versatile magnetic properties. The important coordination modes of azido ligand are $\mu_{1,3}$ -N₃ (end-to-end) and $\mu_{1,1}$ -N₃ (end-on), $\mu_{1,1,3}$ -N₃, $\mu_{1,1,1}$ -N₃, $\mu_{1,1,1,1}$ -N₃, $\mu_{1,1,2,2}$ -N₃, and $\mu_{1,1,1,3,3,3}$ -N₃ (Scheme 1.2) [34].



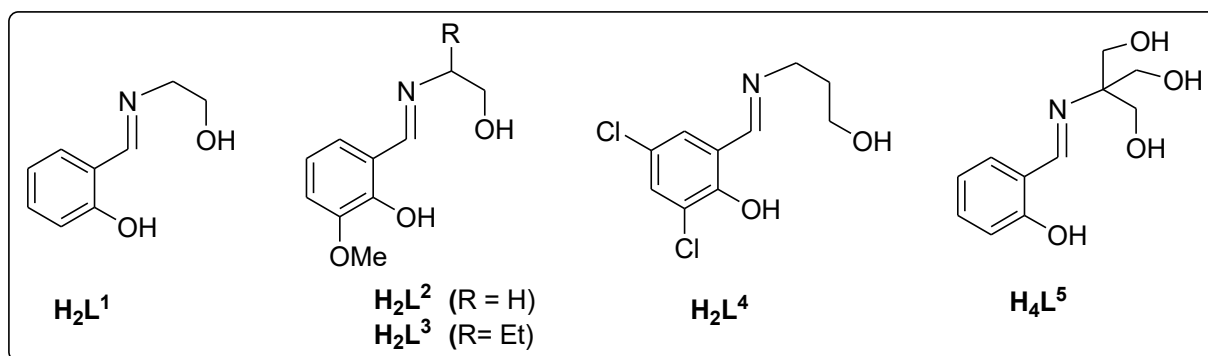
Scheme 1.2: Different azido bridging mode

Among the above-mentioned co-ordination mode, end-on (IV) and end-to-end (III) coordination modes are frequently observed in di and polynuclear complexes of paramagnetic

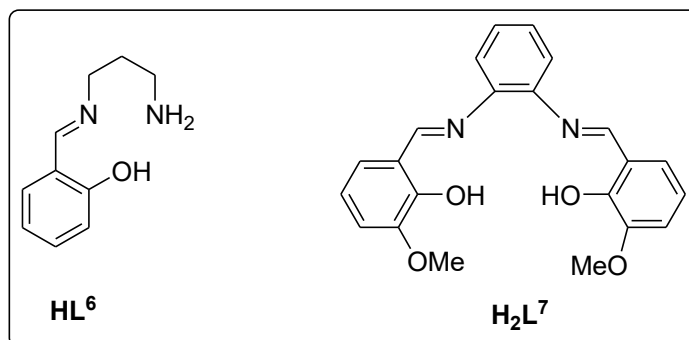
metal ions. The magneto-structural correlation of polynuclear and dinuclear Ni(II) complexes with pseudohalides bridging ligands have been extensively studied as they mediate an efficient magnetic coupling interaction between the paramagnetic metal ions [35-36]. Furthermore, investigation by various research groups revealed that the end-on azido bridging mode ($\mu_{1,1}$) shows ferromagnetic coupling whereas end-to-end mode ($\mu_{1,3}$) shows an antiferromagnetic coupling interaction between the Ni(II) ions [37]. However, $\mu_{1,3}$ bridging mode of thiocyanato ligand with Ni(II) ions exhibit a weak ferromagnetic interaction [38-46], and $\mu_{1,3}$ bridged cyanato ligand shows mixed behavior [47-50]. Magnetic susceptibility studies have been established that the $\mu_{1,5}$ dicyanamide bridges mediate a very weak antiferromagnetic interaction between the Ni(II) centers [51]. Thus, the diverse magnetic properties of molecular materials can be achieved by incorporation of the various bridging modes of the pseudohalide ligands. Different type of Schiff base ligands used for the synthesis of different di and polynuclear Ni(II) complexes reported in the literature classified in the following subsections.

1.3.1. Monoformyl phenol based ligand:

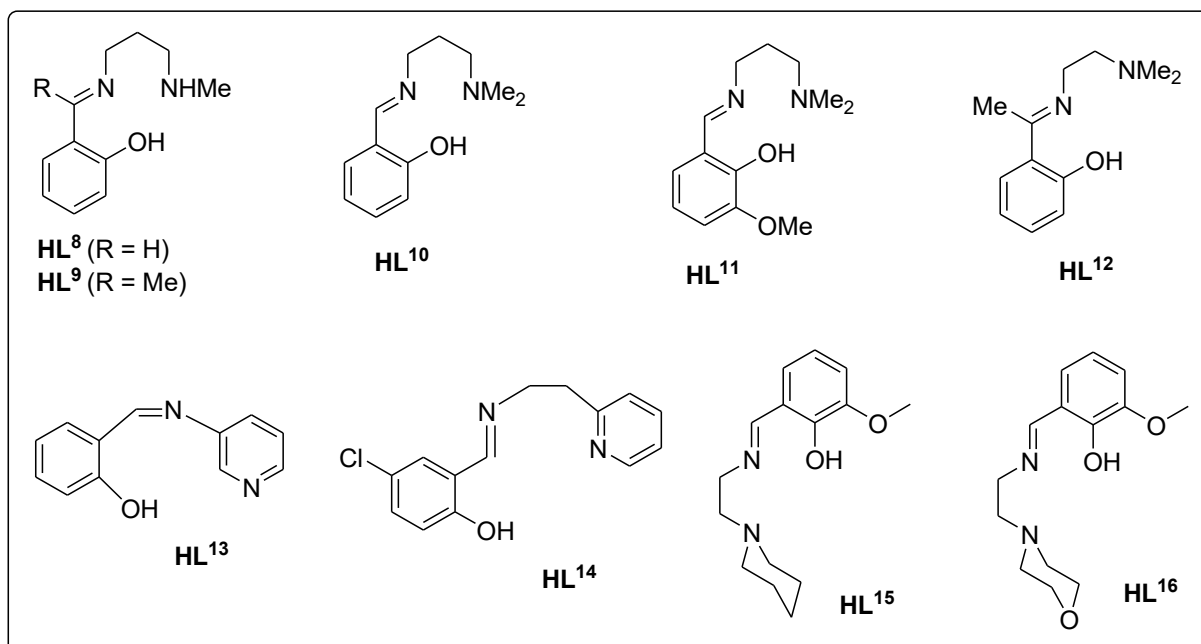
1.3.1.1. Monoamine based ligand:



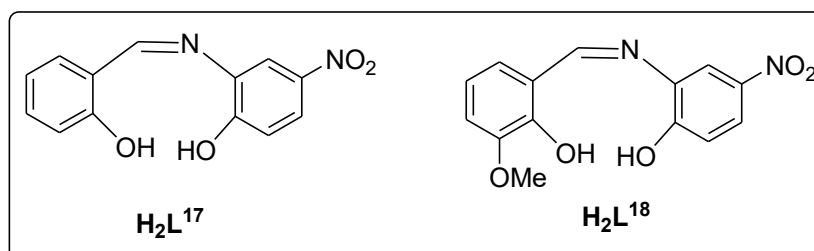
1.3.1.2. Symmetric diamine based ligand:



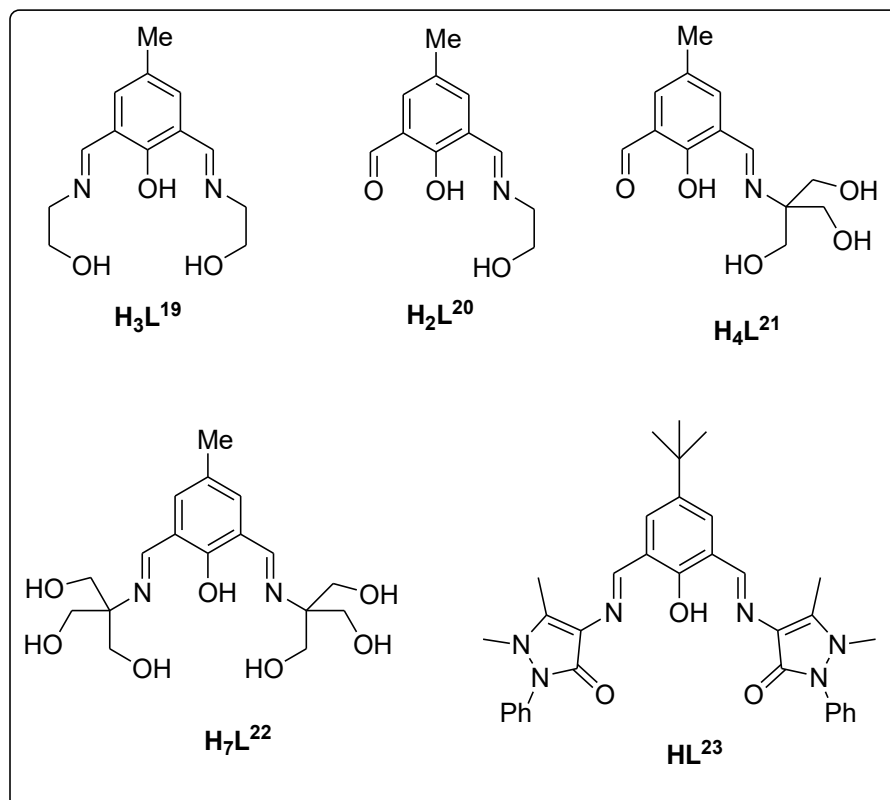
1.3.1.3. Unsymmetric diamine based ligand:



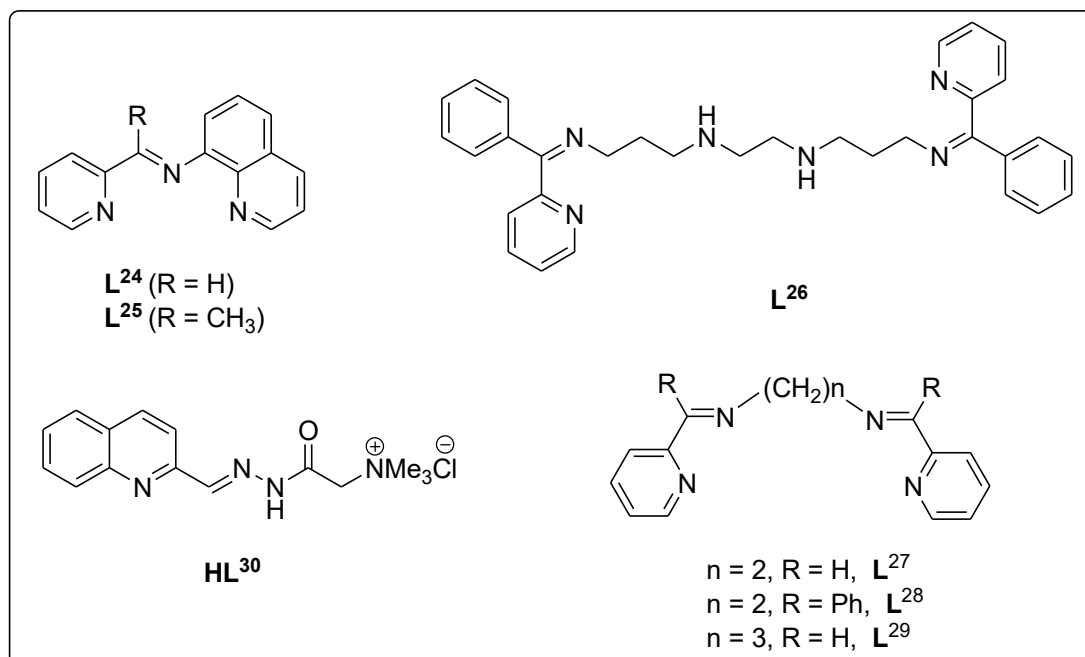
1.3.1.4. Amino-phenolate based ligand:



1.3.2. Diformyl phenol based ligand:



1.3.3. Pyridine-2-aldehyde based ligand:

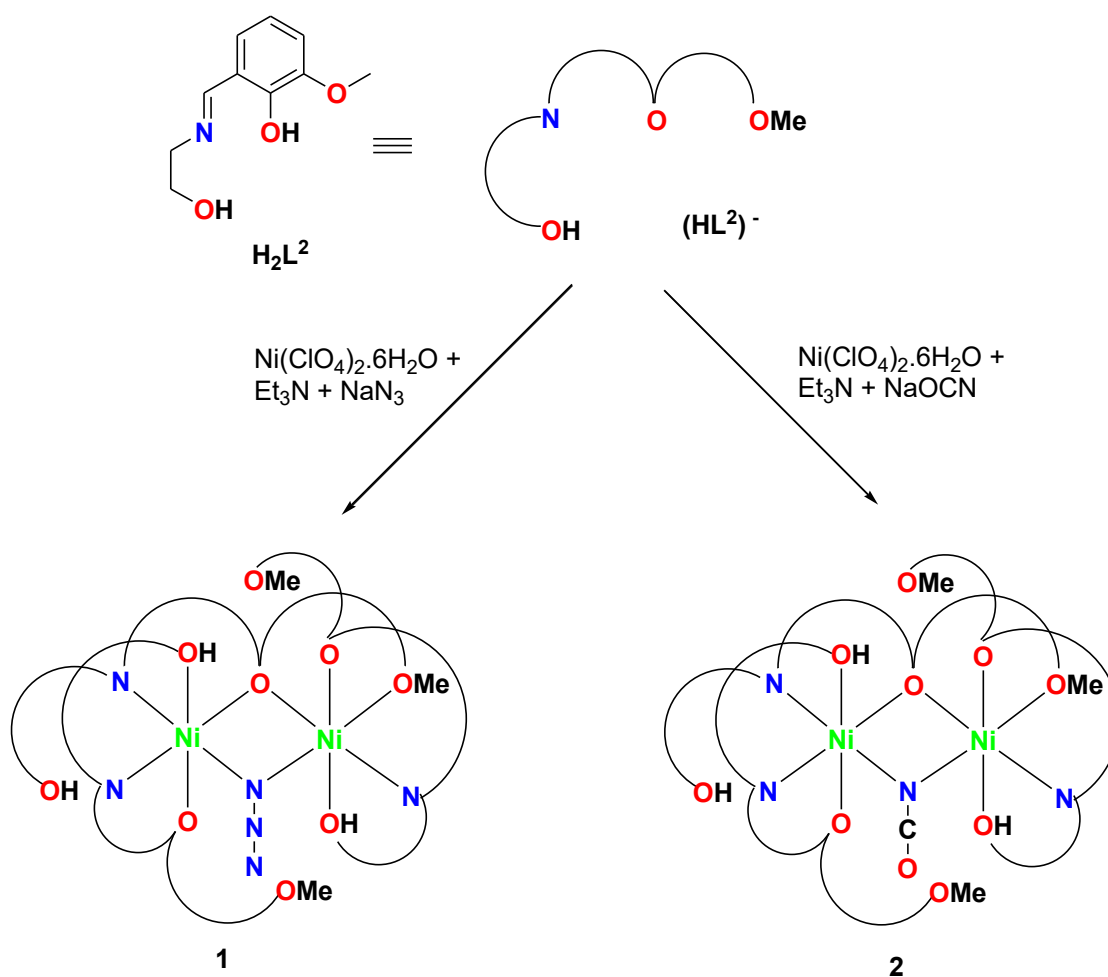


1.4. Different dinuclear Ni(II) complexes:

1.4.1. Di-nuclear Ni(II) complexes with monoformyl phenol based Schiff based ligand:

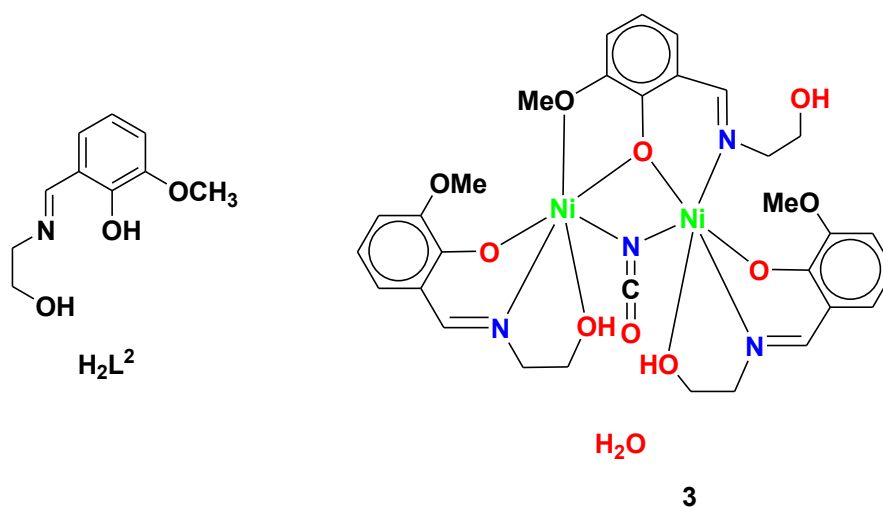
1.4.1.1. Dinuclear Ni(II) complexes with monoformyl phenol based Schiff base ligand derived from monoamine base:

Mohanta *et al.* [52] reported the structures and magnetic properties of pseudohalide bridged dinuclear Ni(II) complexes in which the blocking ligand H_2L^2 was prepared by condensation of 3-methoxysalicylaldehyde with 2-aminoethanol (Scheme 1.3). The dinuclear complex $[Ni_2(HL^2)_3(\mu_{1,1}-N_3)] \cdot 3H_2O$ (**1**) consists of an end-on (μ -1,1) azide bridging and a phenoxo bridging between the two Ni(II) centre, and in the dinuclear Ni(II) complex $[Ni_2(HL^2)_3(\mu_{1,1}-NCO)] \cdot 2H_2O$ (**2**), μ -1,1 cyanato and phenoxo bridge the metal centres. Magnetic study reveals that complexes **1** and **2** show ferromagnetic interaction between the Ni(II) centres.



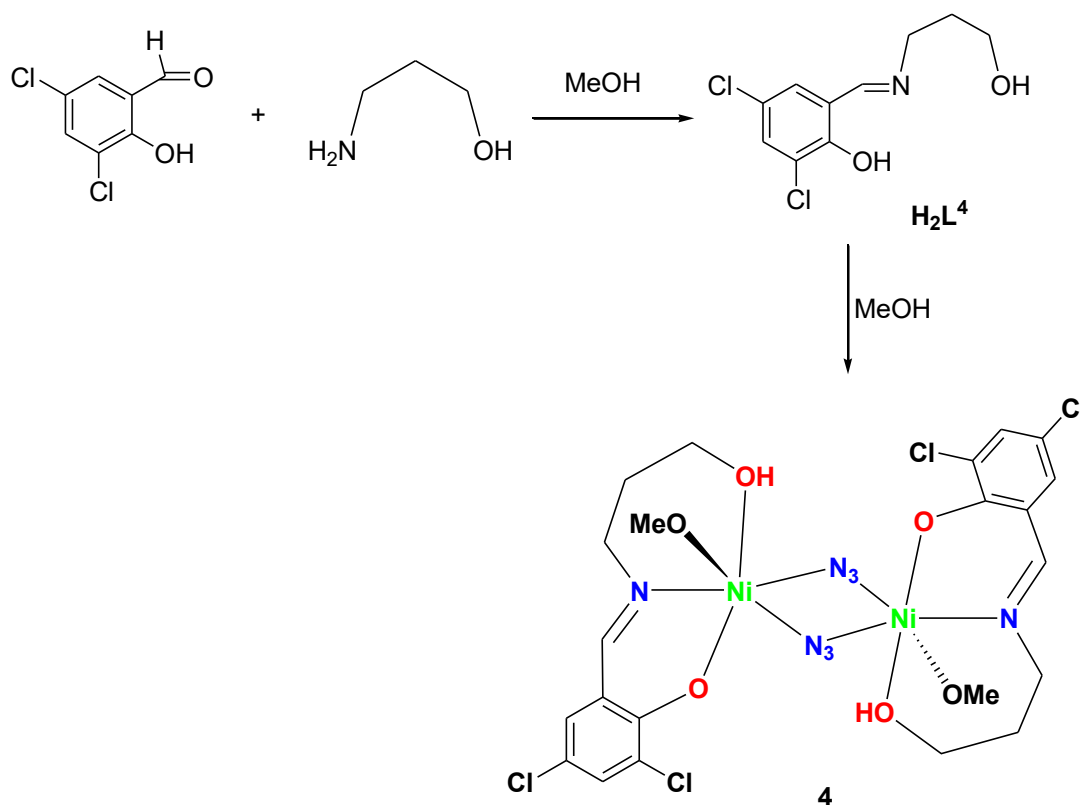
Scheme1.3: Synthesis of **1** and **2**

Hazra *et al.* [53] also reported the synthesis, structure and magnetism of a dinuclear Ni(II) complex $[\text{Ni}_2(\text{HL}^2)_3(\mu_{1,1}\text{-NCO})]\cdot 2\text{H}_2\text{O}$ (**3**) using the Schiff base ligand *N*-(2-hydroxyethyl)-3-methoxysalicylaldehyde (H_2L^2). In complex $[\text{Ni}_2(\text{HL}^2)_3(\mu_{1,1}\text{-NCO})]\cdot 2\text{H}_2\text{O}$ (**3**), two Ni(II) centers are held together by an exogenous $\mu_{1,1}\text{-NCO}$ bridging unit together with endogenous bridging phenolate group (Scheme 1.4). Complex **3** shows weak ferromagnetic interaction between the two Ni(II) centers.



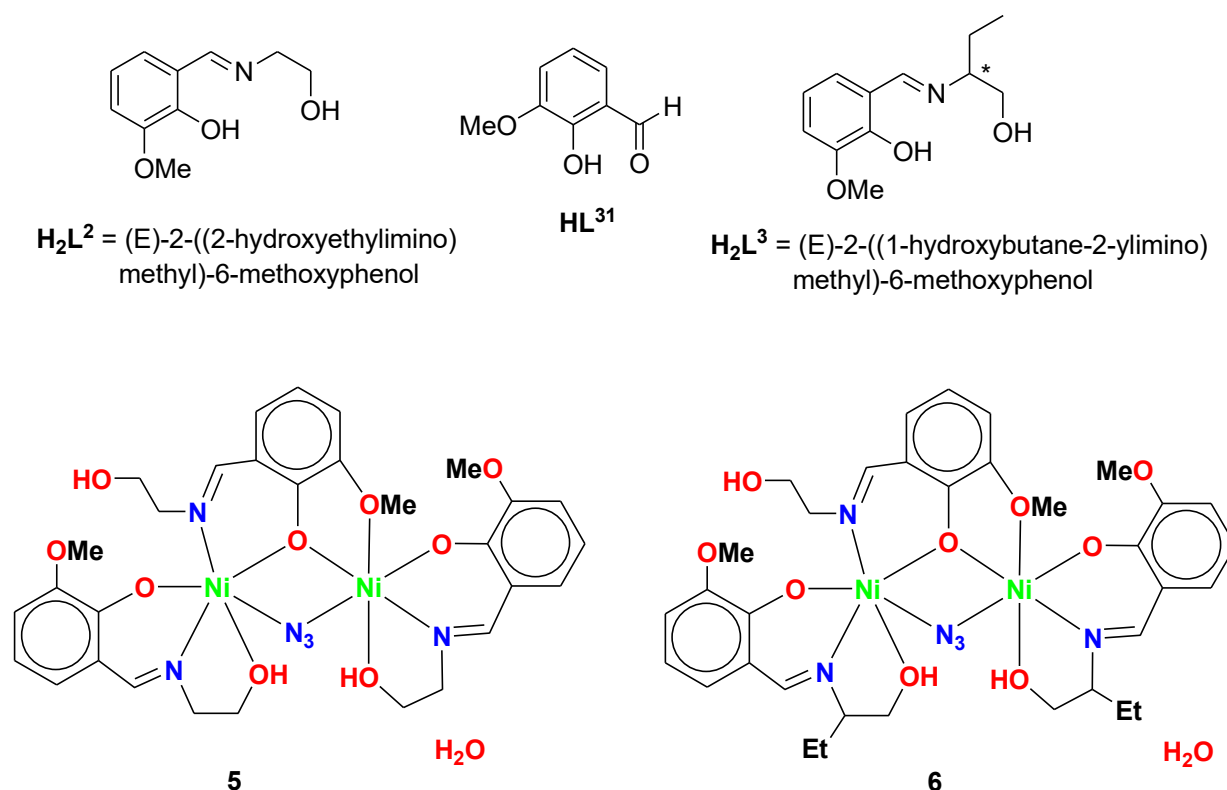
Scheme 1.4: Structure of the ligand H_2L^2 and the complex **3**

Donmez and his group [54] reported the synthesis of a dinuclear Ni(II) complex, $[\text{Ni}_2(\mu_{1,1}\text{-N}_3)_2(\text{HL}^4)_2(\text{MeOH})_2]$ (**4**), using Schiff baser ligand H_2L^4 (Scheme 1.5). H_2L^4 was prepared by the condensation between 3,5-dichlorosalisaldehyde and 3-aminopropanol. Single crystal X-ray diffraction study revealed that double end-on azide-bridge is present in the complex between the two Ni(II) centre. They also reported variable temperature magnetic susceptibility measurements that reveal the presence of a ferromagnetic interaction between the metal centres through double end-on azide-bridges. They also performed solid state photoluminescence measurements at room temperature for the Ni(II) complex. From this experiment, it was observed that the complex shows a strong green emission at $\lambda_{\text{max}} = 508$ nm whereas the free ligand H_2L^4 shows a broad yellow emission band at $\lambda_{\text{max}} = 594$ nm.



Scheme 1.5: Synthesis of the complex **4**

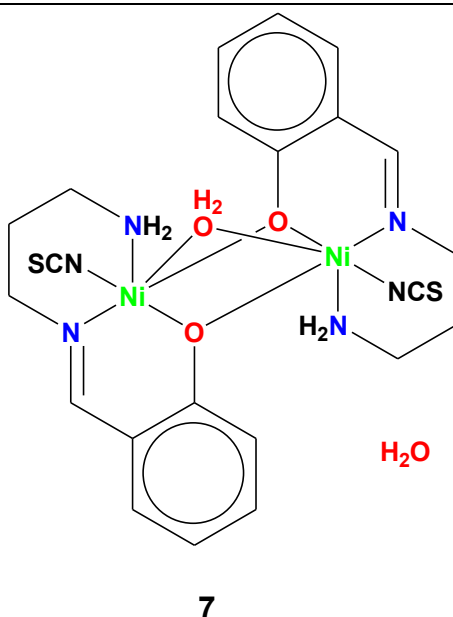
Liu and his co-workers [55] reported the synthesis of pseudohalide bridged Ni(II) dinuclear complexes along with their magnetic studies. They prepared two tridentate ligand H_2L^2 and H_2L^3 by condensation between *o*-vanillin and 2-aminoethanol or 2-aminobutan-1-ol respectively. These ligands were subjected to react separately with $NiCl_2$ in presence of azide to prepare two Ni(II) dinuclear complexes $[Ni_2(HL^2)_3(\mu_{1,1}-N_3)] \cdot 2H_2O$ (**5**) and $[Ni_2(L^{31})(HL^3)_2(\mu_{1,1}-N_3)] \cdot H_2O$ (**6**) (Scheme 1.6). In these two complexes azide ion was bridged as an end-on ($\mu_{1,1}-N_3$) mode between the two Ni(II) centers. Magnetic susceptibility measurement indicates that all these complexes show ferromagnetic coupling between the metal centres.



Scheme 1.6: Relative structure of the ligands and complex **5** and **6**

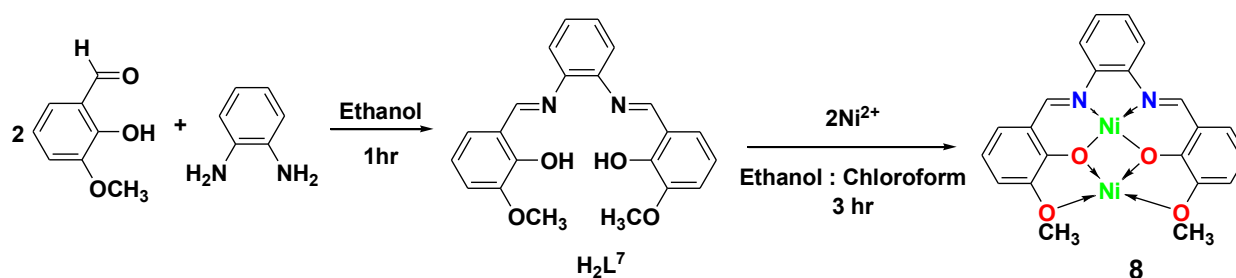
1.4.1.2. Dinuclear Ni(II) complexes with monoformyl phenol based Schiff base ligand derived from symmetric diamine base:

Banerjee *et al.* [56] synthesized a dinuclear Ni(II) complex, $[\text{Ni}_2(\text{L}^6)_2(\text{H}_2\text{O})(\text{NCS})_2] \cdot 3\text{H}_2\text{O}$ (**7**) (Scheme 1.7). The tridentate Schiff base ligand $[\text{HL}^6 = \text{N}-(3\text{-aminopropyl})\text{salicylaldehyde}]$ was derived from the condensation reaction between salicylaldehyde and 1,3-diaminopropane. In the said complex, two Ni(II) metal centres were linked by two μ_2 -phenoxo bridges together with a bridging aqua ligand. Each Ni(II) atom in the dinuclear complex possesses a distorted octahedral geometry where the Ni–O bond distance and the Ni–O–Ni bond angle related to bridging aqua ligand were 2.240(11) Å and 82.5(5)°, respectively. The magnetic susceptibility measurement reveals that the ferromagnetic coupling is operative between two Ni(II) metal centres in the complex **7** with $J = 3.1 \text{ cm}^{-1}$.



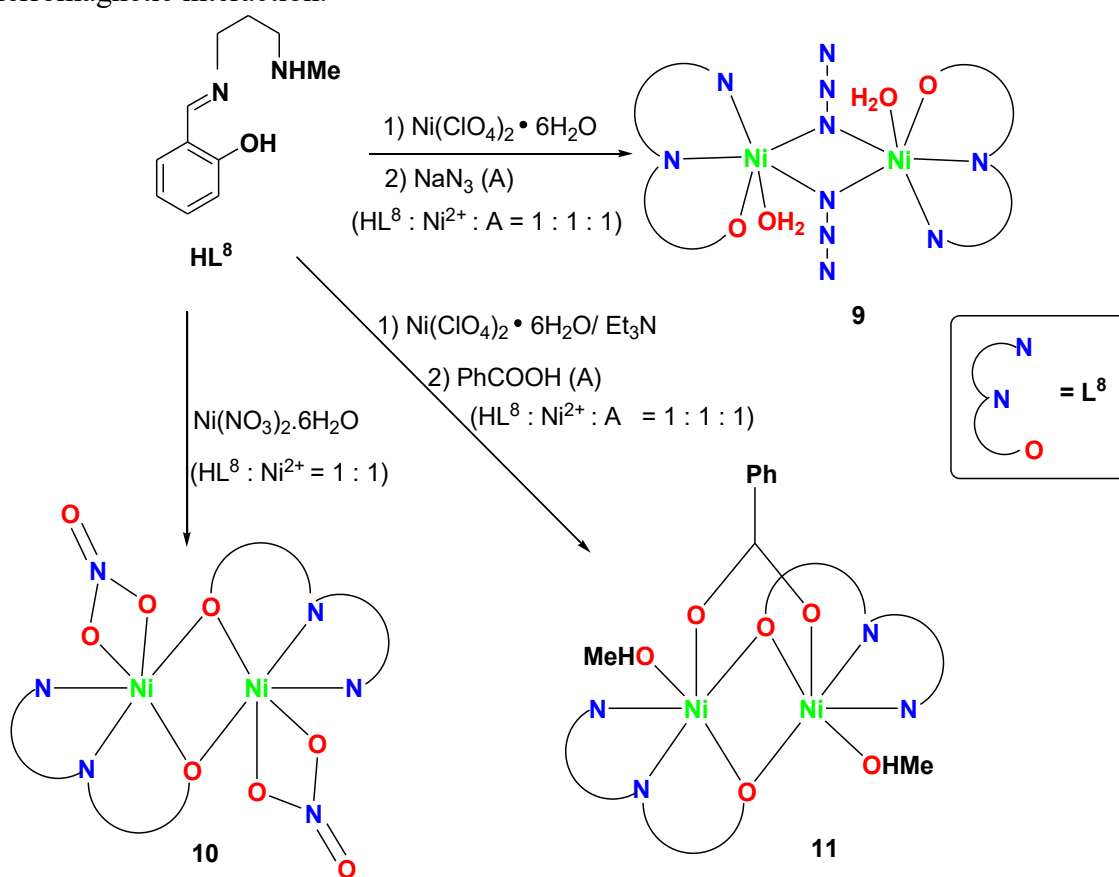
Scheme 1.7: structure of the complex 7

Bahron and his group [57] reported the synthesis and medicinal application of the dinuclear Ni(II) complex $\text{Ni}_2(\text{L}^7)$ (8) [L^7 = 6,6'-dimethoxy-2,2'-[o-phenylenebis(nitrilomethylidyne)]diphenolato] in which two Ni(II) centre posses square planar geometry as shown in Scheme 1.8. The $\text{Ni}_2(\text{L}^7)$ complexe showed diamagnetic character and it has low molar conductivities in acetonitrile solvent which indicate nonelectrolytic behaviour of the complex. They also examined the anticancer activity of the complex in human colorectal cancer HCT116 cell lines and ovserved the potency of the complex with an IC50 value of 0.81 μM .

Scheme 1.8: Synthesis of dinuclear complex $\text{Ni}_2(\text{L}^7)$ (8)

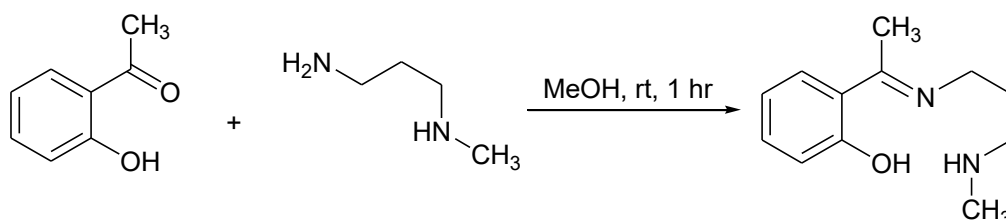
1.4.1.3. Dinuclear Ni(II) complexes with monoformyl phenol based Schiff base ligand derived from unsymmetrical diamines:

Recently Ghosh *et al.* [58] prepared a series of dinuclear Ni(II) complexes using a Schiff base ligand, HL^8 (2-[(3-Methylamino-propylimino)-methyl]-phenol), and some polyatomic monoanions like N_3^- , NO_2^- , NO_3^- , PhCOO^- etc (Scheme 1.9). Among all these complexes, the dinuclear complex $[\text{Ni}_2(\text{L}^8)_2(\text{N}_3)_2(\text{H}_2\text{O})_2]$ (**9**) has di- $\mu_{1,1}$ -azido bridges between the two Ni(II) centers. Both complexes $[\text{Ni}_2(\text{L}^8)_2(\text{NO}_3)_2]$ (**10**) and $[\text{Ni}_2(\text{L}^8)_2(\text{O}_2\text{CPh})(\text{CH}_3\text{OH})_2]\text{ClO}_4 \cdot 0.5\text{CH}_3\text{OH}$ (**11**) consist of di- μ_2 -phenoxo bridging units where as an additional bridging benzoate ligand is present in complex **11**. Both the Ni(II) centers in this complexes have distorted octahedral geometry and a ferromagnetic coupling was operating between two metal centers within the dimer and a intradimer antiferromagnetic interaction was observed in **9**. Complexes **10** and **11** experience an intradimer antiferromagnetic interaction.

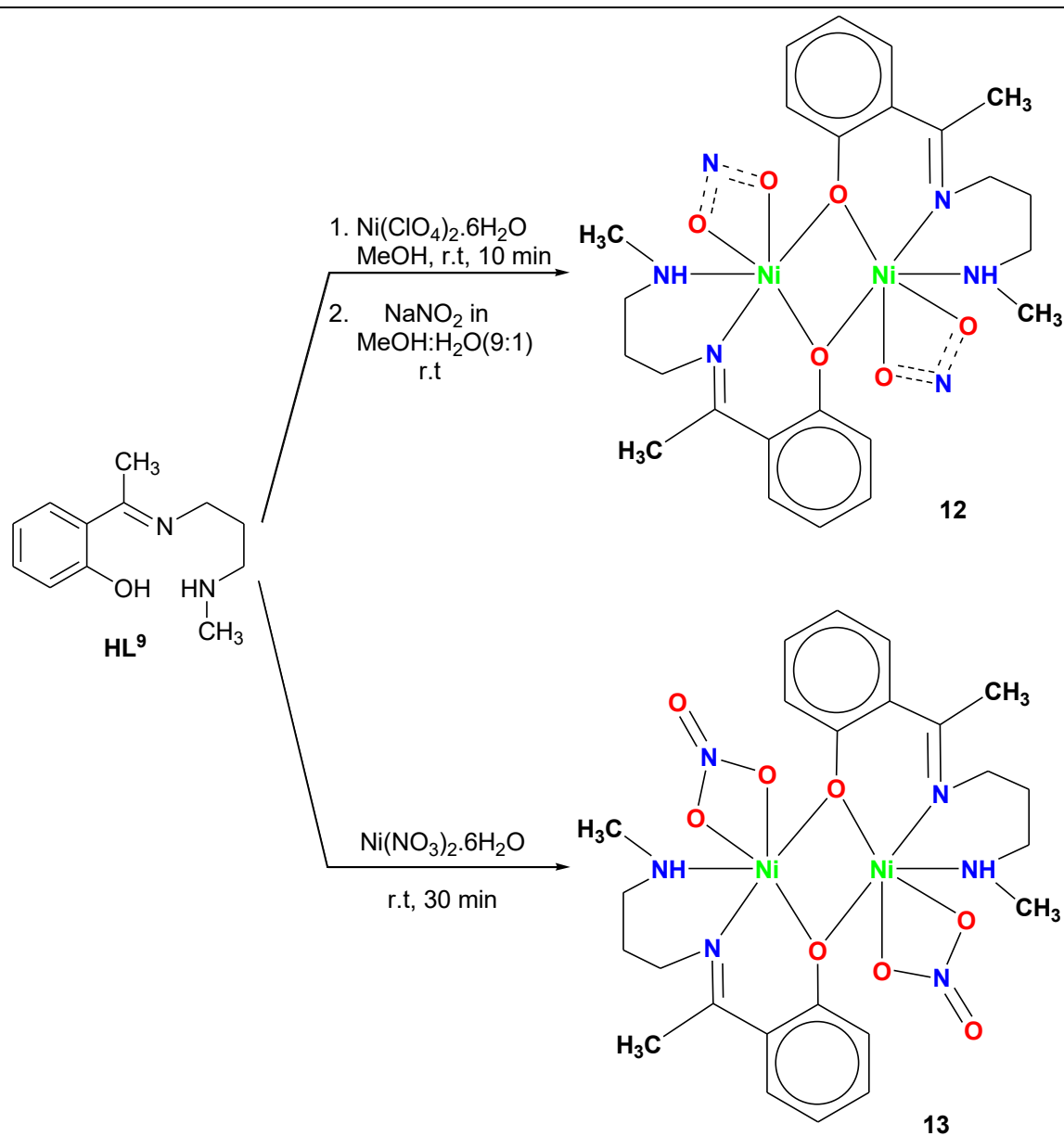


Scheme 1.9: Synthesis of complex 9-11

Naiya *et al.* [59] reported the synthesis of a Schiff base ligand, HL⁹ and two dinuclear Ni(II) complexes, [Ni₂(L⁹)₂(NO₂)₂] (**12**) and [Ni₂(L⁹)₂(NO₃)₂] (**13**) (Scheme 1.10 and Scheme 1.11). The Schiff base ligand, was prepared by a general condensation reaction between 2-hydroxy acetophenone and *N*-methyl-1,3-diaminopropane (Scheme 1.10). The two Ni(II) ions possess distorted fac- and mer-octahedral geometries in complexes **12** and **13**, respectively. In both the complexes, two Ni(II) ions were bridged by two μ₂-phenolate ions where bidentate nitrite and nitrate co-ligand were present in the complexes **12** and **13**, respectively. X-ray diffraction study revealed that the central Ni₂O₂ core remains in the same plane with the phenyl rings of the Schiff base ligand in complex **12** whereas in the complex **13** they are almost perpendicular to each other. This observation was correlated by DFT calculations.



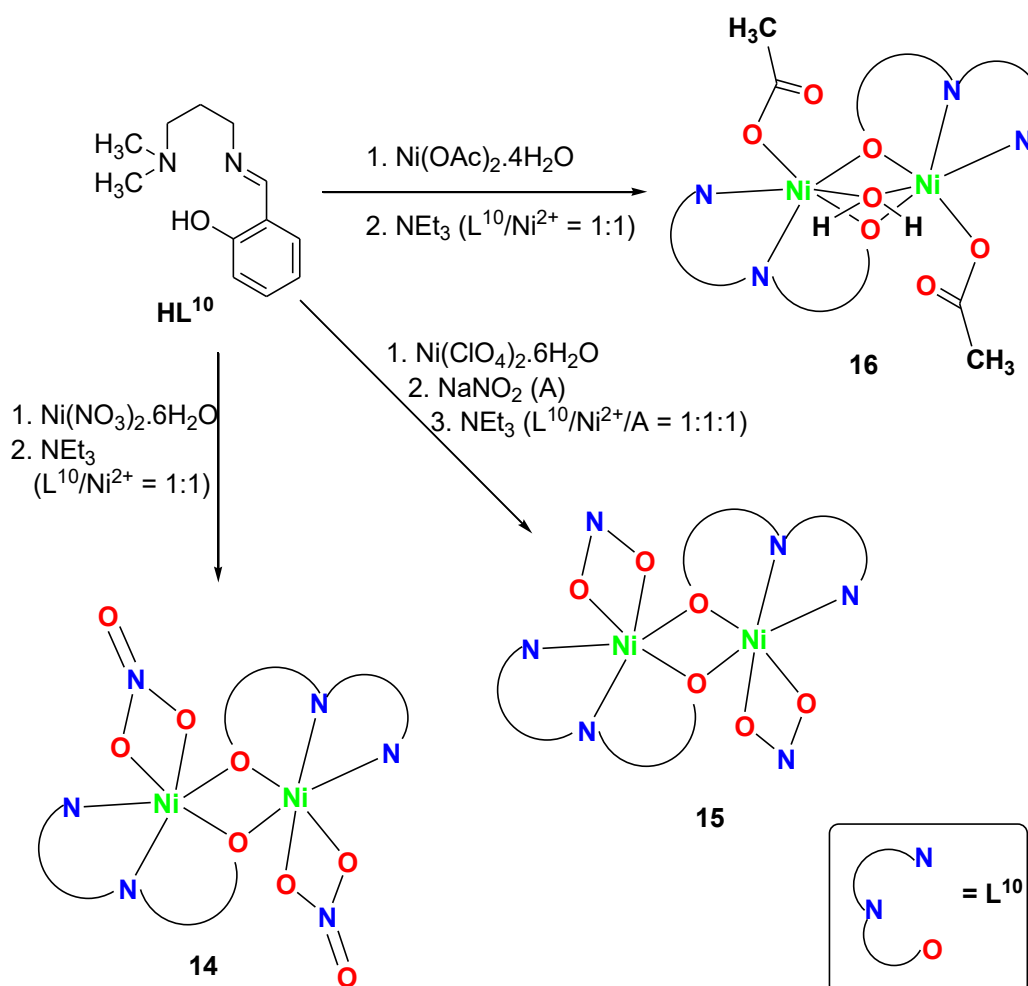
Scheme 1.10: Synthesis of the ligand HL⁹



Scheme 1.11: Synthesis of the complex **12** and **13**

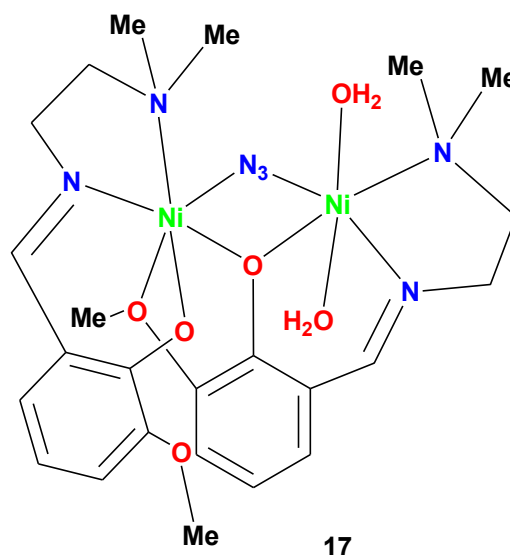
Biswas *et al.* [60] prepared three dinuclear Ni(II) complexes, $[\text{Ni}_2(\text{L}^{10})_2(\text{NO}_3)_2]$ (**14**), $[\text{Ni}_2(\text{L}^{10})_2(\text{NO}_2)_2]$ (**15**) and $[\text{Ni}_2(\text{L}^{10})_2(\text{CH}_3\text{COO})_2(\text{H}_2\text{O})]$ (**16**), using a tridentate ligand HL^{10} which was synthesised by the condensation between *N,N*-dimethylpropane-1,3-diamine and salisaldehyde (Scheme 1.12). The co-ligand nitrate, nitrite or acetate ion was used during the synthesis of these complexes. X-ray diffraction study revealed that the Ni(II) ions in all the

three complexes present in distorted octahedral environment. In complexes **14** and **15**, two Ni(II) atoms were joined by two μ_2 -phenoxido-bridging ligands, and nitrate and nitrite ions act as bidentate co-chelating ligands. Whereas in complex **16** two Ni(II) atoms are coordinated by two μ_2 -phenoxido bridging ligands and a bridging aqua ligand and monodentate acetate anion as a co-ligand. Magnetic susceptibility measurements revealed that complexes **14** and **15** exhibit the antiferromagnetic behavior whereas complex **16** show the ferromagnetic coupling between the metal centres. They also established a nice magnetostructural correlation considering bond lengths and bond angles, which was further supported by the DFT study.



Scheme 1.12: Synthesis of complex 14-16

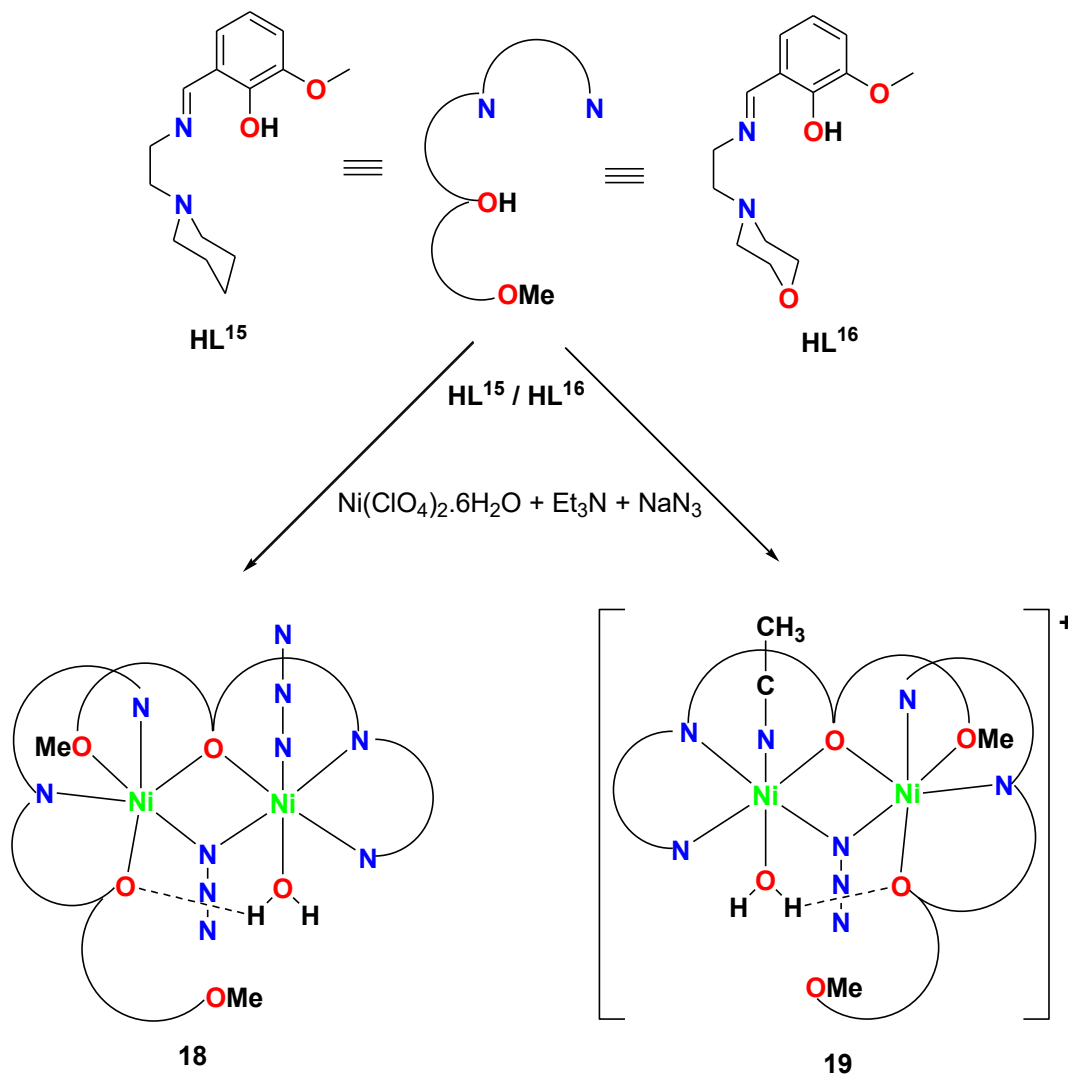
Sinha and his co-workers [61] synthesized Ni(II) dinuclear complex bridged by the end-on azide ion and reported the magnetism and biological study of the synthesized complex. They reported that when Ni(II) perchlorate was subjected to react with the ligand HL¹¹ (a condensation product of *o*-vanillin and *N,N*-dimethylethylenediamine) and NaN₃ in methanol at room temperature, it afforded dark brown crystalline compound of [Ni(L¹¹)(μ_{1,1}-N₃)Ni(L¹¹)(OH₂)₂].ClO₄ (**17**) where HL¹¹ = Me₂N(CH₂)₂N=CH-C₆H₃(OH)(OCH₃) after slow evaporation (Scheme 1.13). The geometry of the complex is distorted octahedron around the Ni(II) centres and a ferromagnetic interaction between the two Ni(II) centers prevails. They also reported that the complex exhibits anti-cancer and anti-microbial activities.



Scheme 1.13: Structure of the complex **17**

Mohanta *et al.* [52] reported pseudohalide bridged dinuclear Ni(II) complexes with their structures and magnetic properties. In this context, they prepared different Schiff base ligands by condensation procedure. Ligands HL¹⁵ and HL¹⁶ were prepared by condensation of 3-methoxysalicylaldehyde separately with 1-(2-aminoethyl)-piperidine and 4-(2-aminoethyl)-morpholine, respectively (Scheme 1.14). In dinuclear complexes [Ni₂(L¹⁵)₂(μ_{1,1}-N₃)(N₃)(H₂O)]·CH₃CH₂OH (**18**) and

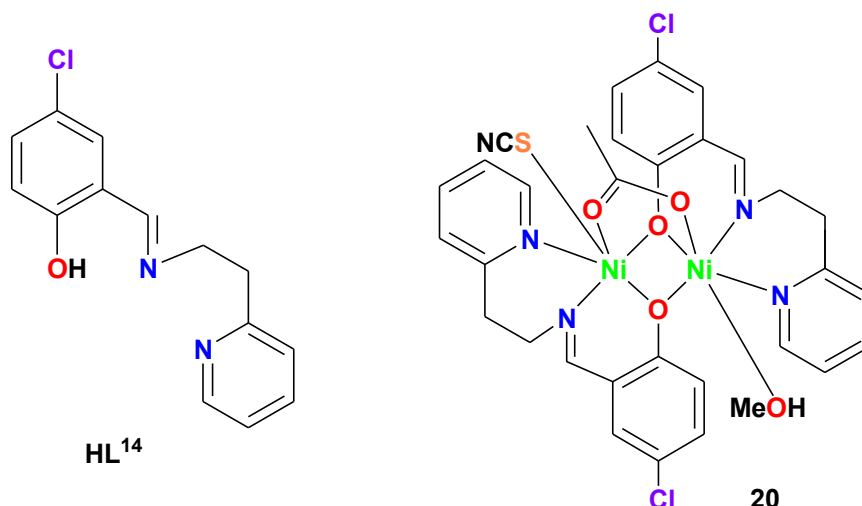
$[\text{Ni}_2(\text{L}^{16})_2-(\mu_{1,1}\text{-N}_3)(\text{CH}_3\text{CN})(\text{H}_2\text{O})](\text{ClO}_4)\cdot\text{H}_2\text{O}\cdot\text{CH}_3\text{CN}$ (**19**), two Ni(II) centres are held together by an end-on (μ -1,1) azide bridge and a phenoxo bridge. Magnetic study revealed that complexes **18** and **19** show the ferromagnetic interaction between the Ni(II) centre.



Scheme 1.14: Synthesis of the complex **18** and **19**

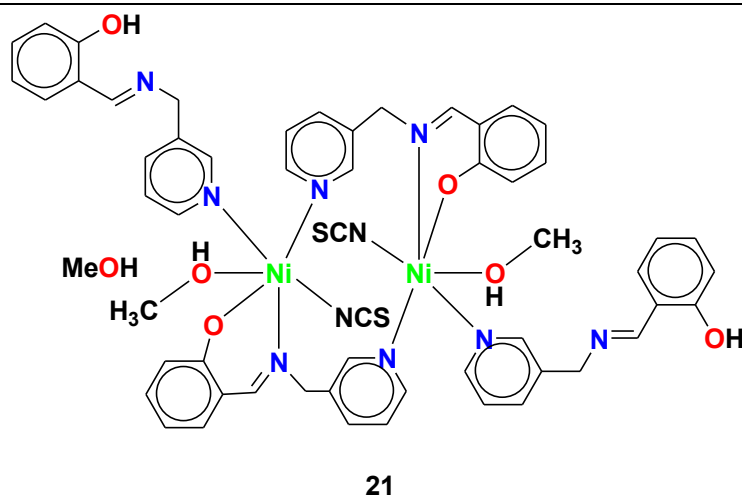
Das and his research group [62] developed a method to synthesise a novel dinuclear Ni(II) complex, $[\text{Ni}_2(\text{L}^{14})_2(\text{NCS})(\text{AcO})(\text{H}_2\text{O})_{0.5}(\text{MeOH})_{0.5}] \cdot 1.25\text{H}_2\text{O}$ (**20**), using ligand **HL**¹⁴ (**HL**¹⁴ = 2-((E)-(2-(pyridin-2-yl)ethylimino)methyl)-4-chlorophenol) (Scheme 1.15). Structural analysis showed that two Ni(II) ions are linked two μ_2 -diphenoxo bridging groups and one

μ -acetato bridging ligand with the metal-metal separation of 3.099 Å. Magnetic susceptibility measurements indicate that the complex exhibits an intramolecular ferromagnetic interaction through the diphenoxido and a syn-syn acetato bridges.



Scheme 1.15: Showing the structure of the ligand HL^{14} and the complex **20**

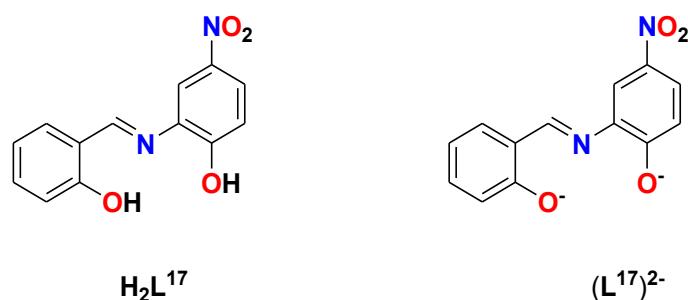
Garcia and his co-worker [63] prepared a dinuclear Ni(II) complex, $[Ni_2(L^{13})_2(HL^{13})_2(NCS)_2(CH_3OH)_2] \cdot 2CH_3OH$ (**21**) using Schiff base ligand HL^{13} which was prepared by condensation between salicylaldehyde and 3-aminomethylpyridine (Scheme 1.16). A distorted octahedral coordination environment was developed around each Ni(II) centre by a methanol molecule, a linear isothiocyanato co-ligand and the Schiff base ligand.



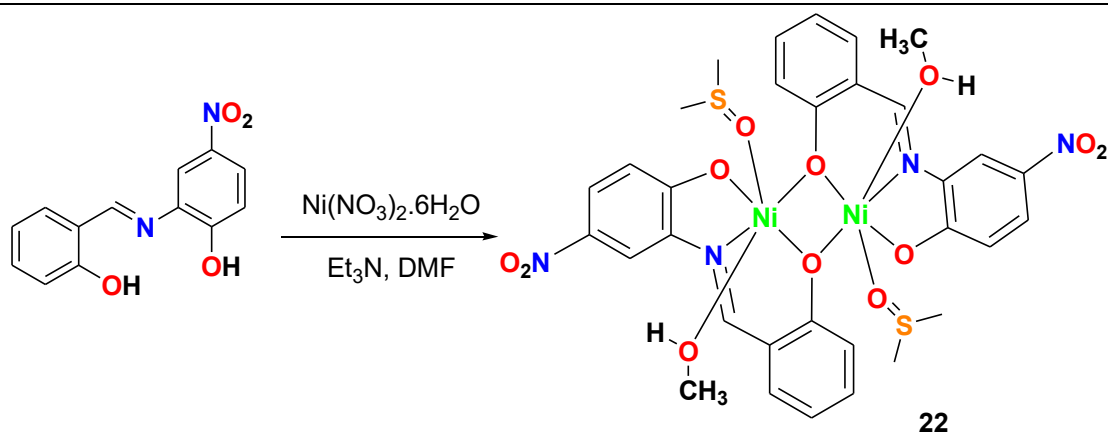
Scheme 1.16: Showing the structure of the complex **21**

1.4.1.4. Dinuclear Ni(II) complexes with monoformyl phenol based Schiff base ligand derived from aminophenol:

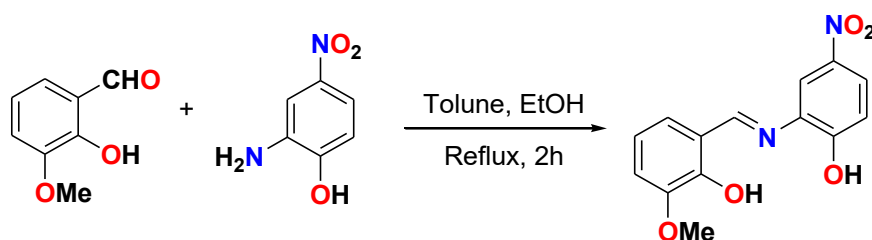
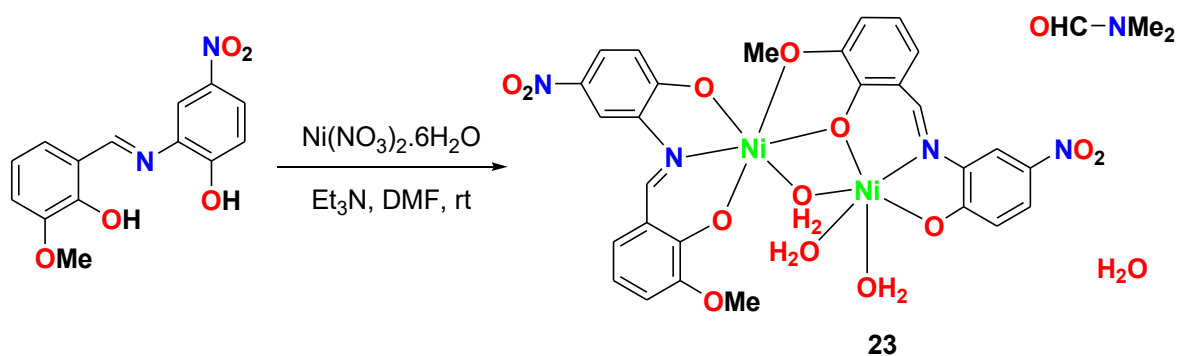
Nayek *et al.* [64] prepared a new Schiff base ligand (H_2L^{17}) from Salicylaldehyde and 2-amino-4-nitrophenol (Scheme 1.17). When $Ni(NO_3)_2 \cdot 6H_2O$ was subjected to react with the Schiff base ligand in DMF in presence of Et_3N base, a precipitate was obtained which on recrystallisation from CH_2Cl_2 -MeOH-DMSO generated a dinuclear Ni(II) complex, $[Ni_2(L^{17})_2(DMSO)_2(MeOH)_2]$ (**22**) (Scheme 1.18). Single crystal X-ray diffraction study explored the structure of complex **22** in which Ni(II) ions were joined by two μ_2 -phenoxo bridging ligands. The complex shows the ferromagnetic coupling between the two Ni(II) ions present in the complex. They also investigated its thermal stability and optical properties.



Scheme 1.17: neutral and deprotonated form of H_2L^{17}

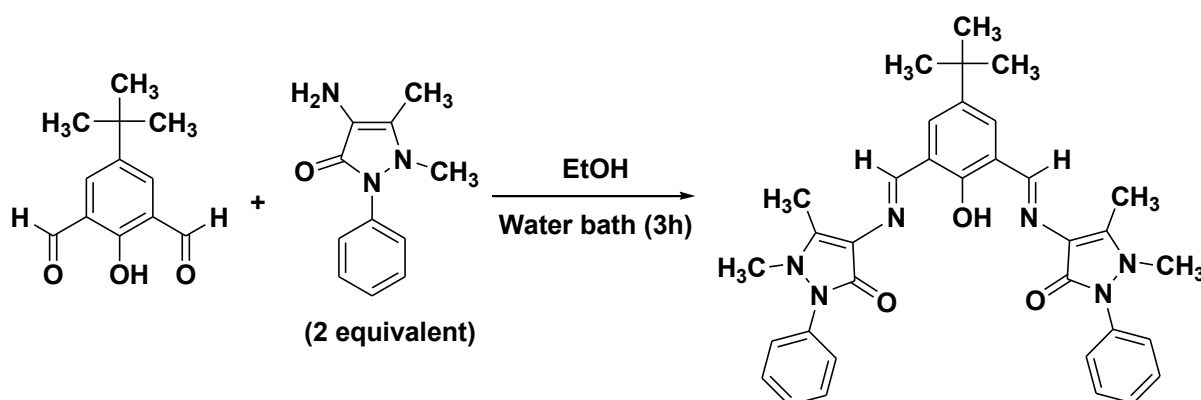
Scheme 1.18: Synthesis of the complex **22**

The same group also [65] reported synthesis of similar type of Schiff base ligand (H_2L^{18}) from *o*-vanillin and 2-amino-4-nitrophenol (Scheme 1.19). By employing this Schiff base ligand, they prepared a dinuclear Ni(II) complex, $[Ni_2 (L^{18})_2(H_2O)_3] \cdot 2DMF \cdot 3H_2O$ (**23**) in which Ni(II) ions were joined by phenoxo and aqua bridging ligands (Scheme 1.20). They also investigated its thermal stability and optical properties.

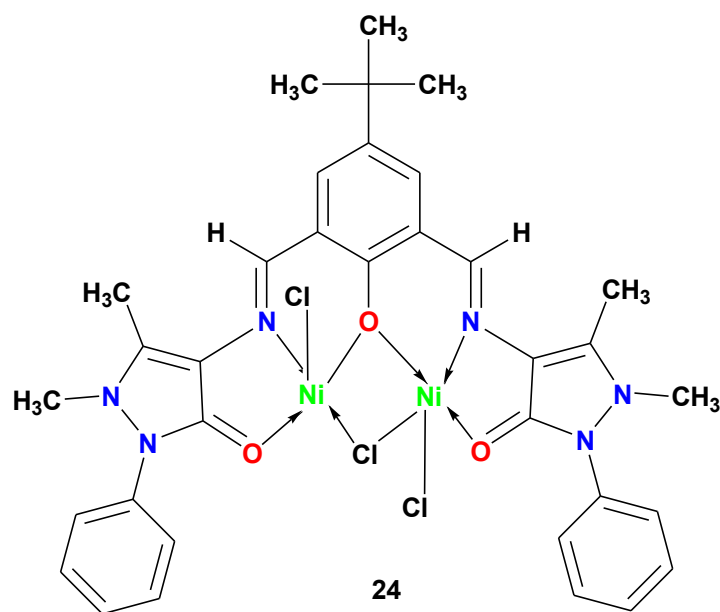
Scheme 1.19: Synthesis of the ligand H_2L^{18} Scheme 1.20: Synthesis of the complex **23**

1.4.2. Dinuclear Ni(II) complexes with diformyl phenol based Schiff base ligand:

Abid *et al.* [66] developed a procedure for the synthesis of a Ni(II) binuclear complex (**24**) with a dinucleating Schiff base ligand having N_2O_3 donor sites (Scheme 1.21 and Scheme 1.22). The ligand was prepared using 2,6-diformyl-4-*tert*-butylphenol and 4-aminoantipyrine. In the complex, the Ni(II) centres reside in square pyramidal environment where two Ni(II) centres are joined by μ_2 -phenoxo bridging unit. The complex was found to be a non-electrolyte as suggested by the molar conductivity measurement in DMF solvent, which indicates that the all chloride ions present inside the first coordination sphere.

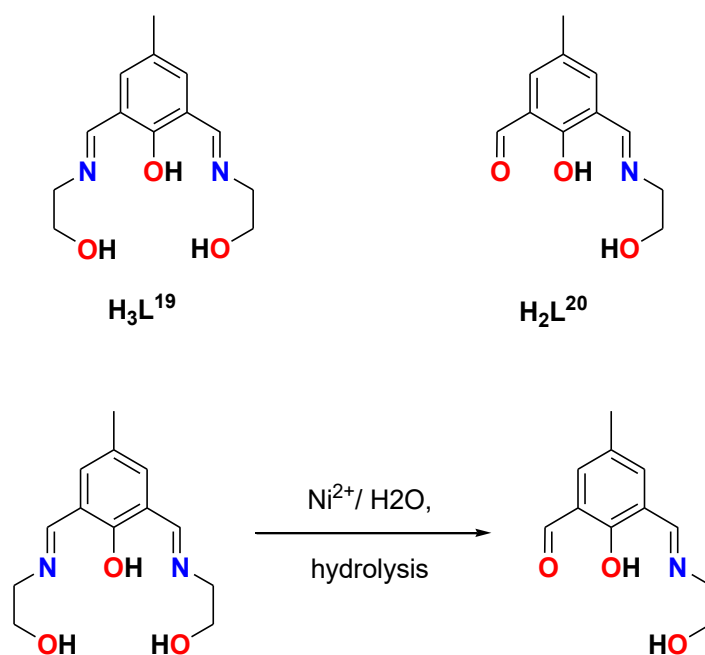


Scheme 1.21: Synthesis of the ligand HL²³



Scheme 1.22: Structure of the complex **24**

Ray *et al.* [67] also employed diformyl based Schiff based ligand (H_3L^{19}) for the synthesis of Ni(II) dinuclear complexes $[Ni_2(HL^{20})_2(H_2O)_4](OOCCH_3)_2$ (25) $[Ni_2(HL^{20})_2(H_2O)_4](OOCCH_2Cl)_2$ (26). The Schiff base ligand was prepared from DFMP (2,6-diformyl-4-methylphenol) and 2-aminoethanol. They reported that Schiff base ligand H_2L^{20} was generated *in situ* during the reaction course via hydrolysis of one arm of H_3L^{19} ligand in presence of Ni(II) salt in aqueous medium (Scheme 1.23). Both complexes have similar structures and Ni(II) ions have octahedral geometry with O_5N hexa-coordination environments (Figure 1.1). Two Ni(II) centres in both the complexes were joined by two μ_2 -phenoxo bridging groups. Both the complexes show strong antiferromagnetic coupling.



Scheme 1.23: Synthesis of the ligand H_2L^{20} from H_3L^{19}

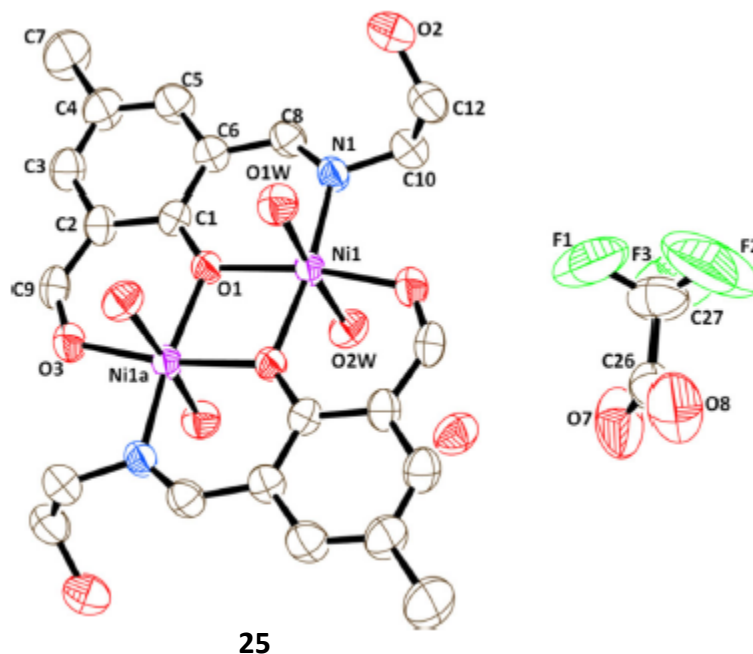
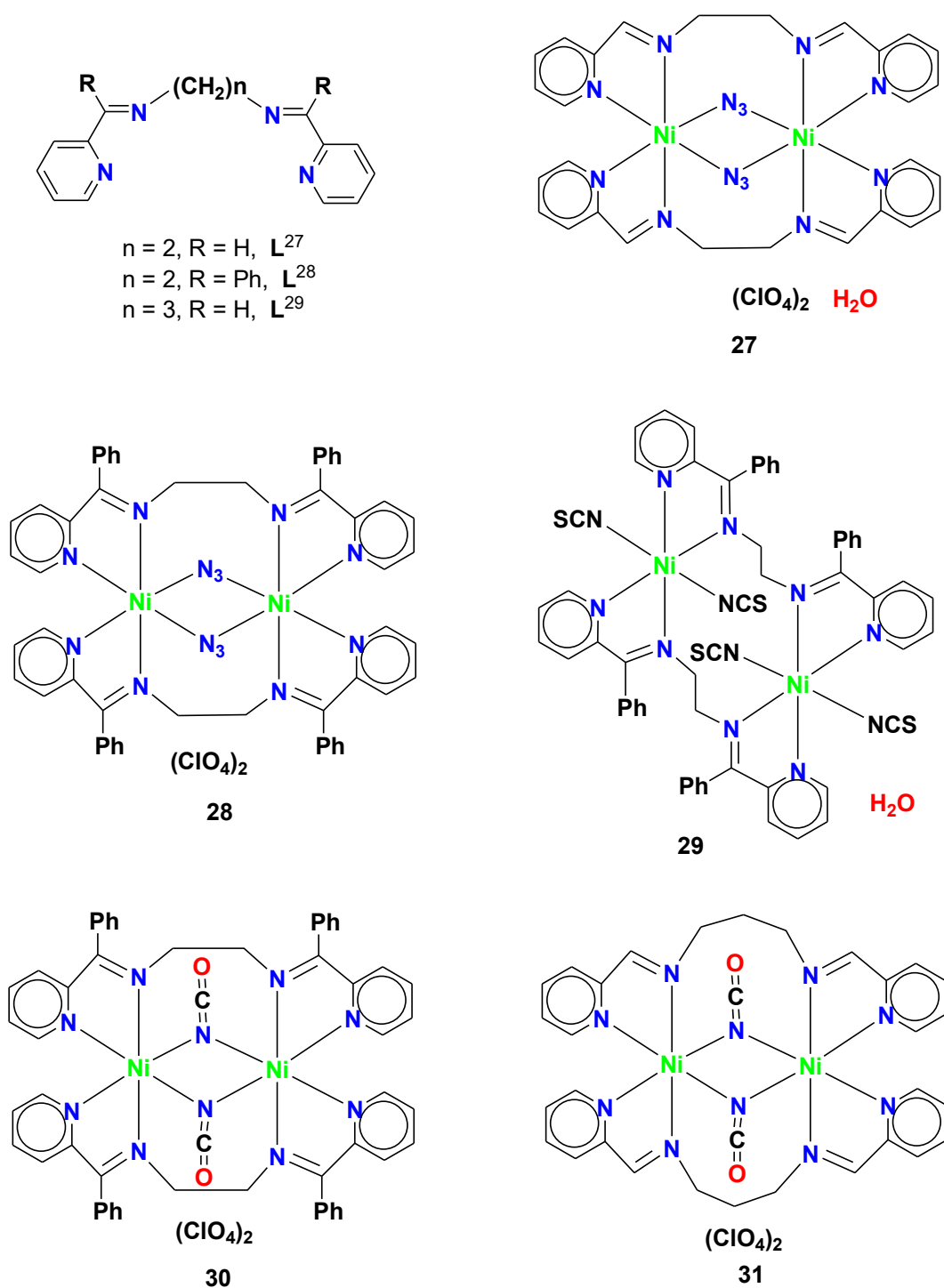


Figure 1.1: ORTEP diagram of the complex **25**

1.4.3. Dinuclear Ni(II) complexes with pyridine-2-aldehyde based Schiff base ligand:

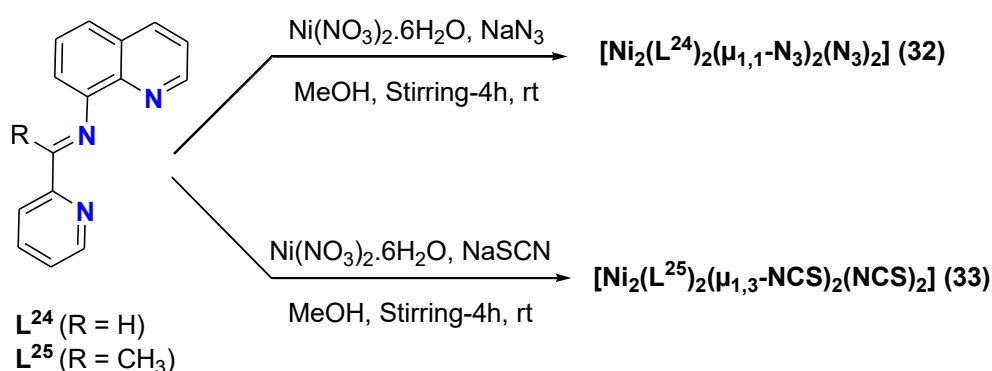
Chandra et al. [68] prepared a series of Ni(II) dinuclear complexes, $[\text{Ni}_2(\text{L}^{27})_2(\text{N}_3)_2](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$ (**27**), $[\text{Ni}_2(\text{L}^{28})_2(\text{N}_3)_2](\text{ClO}_4)_2$ (**28**), $[\text{Ni}_2(\text{L}^{28})_2(\text{NCS})_4]$ (**29**), $[\text{Ni}_2(\text{L}^{28})_2(\text{NCO})_2](\text{ClO}_4)_2$ (**30**), $[\text{Ni}_2(\text{L}^{29})_2(\text{NCO})_2](\text{ClO}_4)_2$ (**31**) using pyridine-2-aldehyde based Schiff base ligands L^{27} , L^{28} , and L^{29} in presence pseudohalide (N_3^- , SCN^- , and NCO^-) co-ligands (Scheme 1.24). Among all the complexes, Ni(II) atoms are joined by end-on (EO) pseudohalide bridge in **27**, **28**, **30**, and **31** where as in complex **29** there is no pseudohalide bridging but the Ni(II) atoms are bridged by the tetradentate ligand. Magnetic study explored that the pseudohalides bridged complexes showed ferromagnetic coupling interaction between the Ni(II) centres. They correlate their observation by density functional theory calculations.



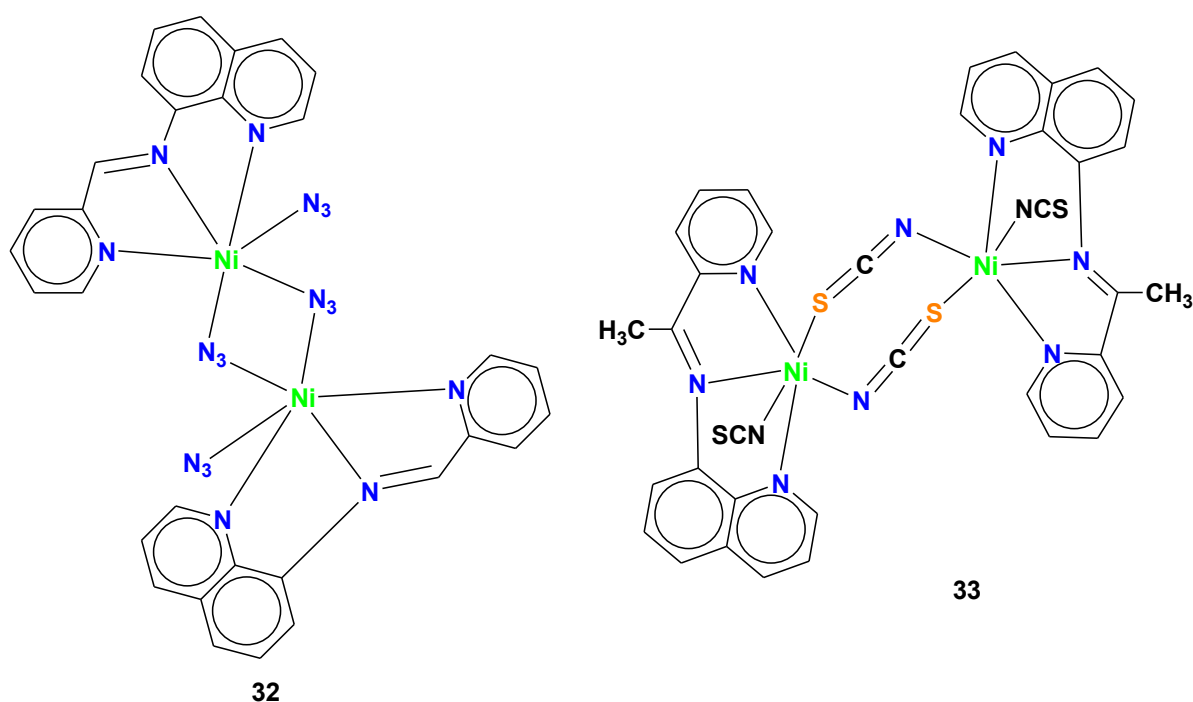
Scheme 1.24: Structure of the ligand L^{27} , L^{28} , and L^{29} and complexes **27-31**

Saha *et al.* [69] also reported the synthesis of two novel Ni(II) dinuclear complexes, $[Ni_2(L^{24})_2(\mu_{1,1}-N_3)_2(N_3)_2]$ (**32**) and $[Ni_2(L^{25})_2(\mu_{1,3}-NCS)_2(NCS)_2]$ (**33**) using aminoquinoline-

based Schiff base ligands (L^{24} and L^{25}) having tridentate N_3 -donor sites in presence of pseudohalides, N_3^- and SCN^- (Scheme 1.25 and Scheme 1.26). In both the complexes, Ni(II) ions attain an octahedral geometry. In complex **32**, two Ni(II) ions are joined by doubled end-on azide bridges where as in **33** the metal centres are connected by the end-to-end thiocyanato bridges. Both the complexes show a weak ferromagnetic coupling between the metal centres through pseudohalide bridges.

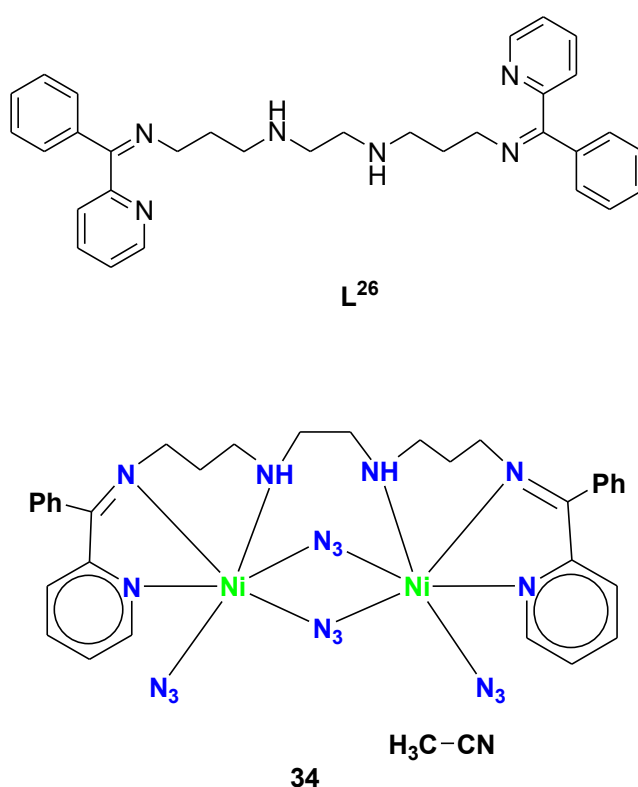


Scheme 1.25: Synthesis of the complex **32** and **33**



Scheme 1.26: Structure of the complex **32** and **33**

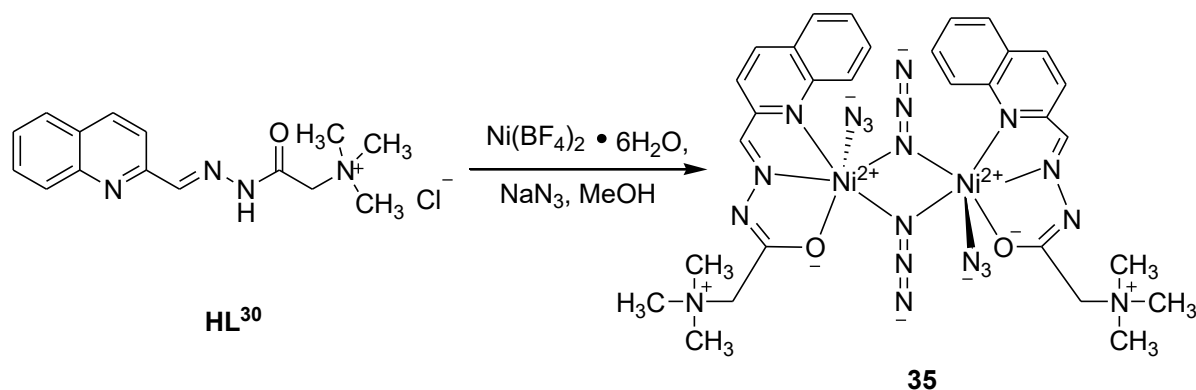
Sain *et al.* [70] afforded the complex $[\text{Ni}_2(\text{L}^{26})(\text{N}_3)_4]$ (**34**) when $\text{Ni}(\text{NO}_3)_2$ was subjected to react with the hexadentate Schiff base ligand L^{26} , obtained by condensation reaction between 2-benzoylpyridine and $\text{N,N}'$ -bis-(3-aminopropyl)ethylenediamine, in presence of NaN_3 (Scheme 1.27). Ni(II) centres in the complex experience a distorted octahedral geometry with NiN_6 coordination environments. The two Ni(II) ions are joined by doubled end-on azido bridges. Magnetic measurement revealed that the complex show the ferromagnetic magnetic coupling between the two Ni(II) centers.



Scheme 1.27: Structure of the ligand L^{26} and the complex **34**

Romanović *et al.* [71] reported the synthesis, magnetic studies with DFT calculation of dinuclear Ni(II) complexes having end-on azido bridge. When the ligand HL^{30} (prepared by condensation reaction between 2-quinolinecarboxaldehyde and trimethylammonium acetohydrazide chloride) was allowed to react with $\text{Ni}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$ and sodium azide (1: 1: 4 molar ratio) in methanol solvent, yielding a complex $[\text{Ni}_2(\text{L}^{30})_2(\mu_{1,1}-\text{N}_3)_2(\text{N}_3)_2]$ (**35**) (Scheme

1.28). Their DFT calculation and explanation about the ferromagnetic interaction between the Ni(II) centers (intra-dimer coupling) in the complex resembled with the experimental results.



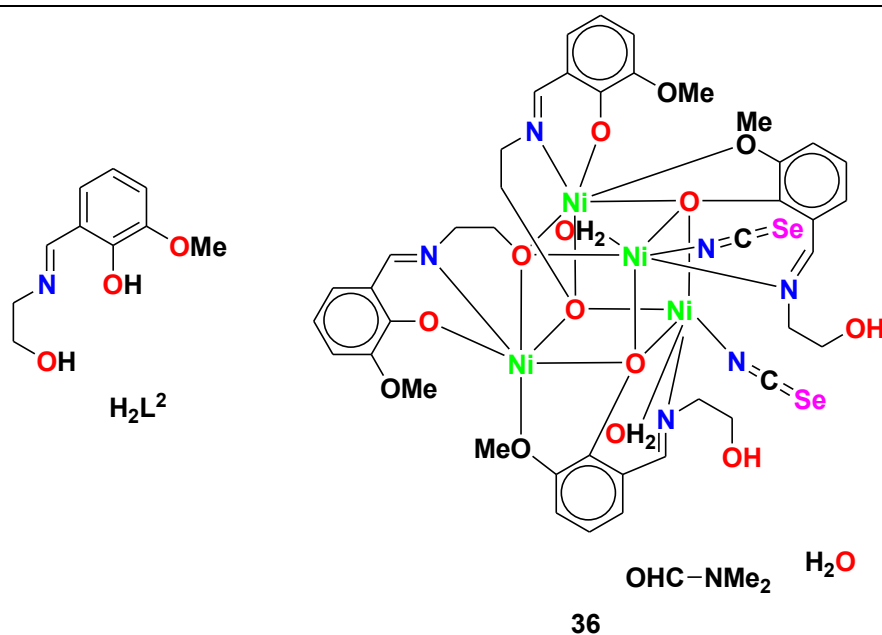
Scheme 1.28: Synthesis of the complex 35

1.5. Different polynuclear Ni(II) complexes:

1.5.1. Polynuclear Ni(II) complexes with monoformyl phenol based Schiff base ligand:

1.5.1.1. Polynuclear Ni(II) complexes with monoformyl phenol based Schiff base ligand derived from monoamine base:

Hazra *et al.* [53] reported the synthesis, structure and magnetism of a cubane type Ni(II) tetranuclear complex $[\text{Ni}_4(\text{L}^2)_2(\text{HL}^2)_2(\text{SeCN})_2(\text{H}_2\text{O})_2] \cdot \text{C}_3\text{H}_7\text{NO} \cdot 4\text{H}_2\text{O}$ (36) using a tetradentate Schiff base ligand, *N*-(2-hydroxyethyl)-3-methoxysalicylaldehyde (H_2L^2) (Scheme 1.29). Complex 36 attains an octahedral geometry around the Ni(II) centres with cubane type Ni_4O_4 core in which four Ni(II) atoms are joint together by two μ_3 -phenoxido and two μ_3 -alkoxido bridges. The said complex shows an overall weak ferromagnetic interaction.



Scheme 1.29: Structure of the ligand H_2L^2 and the complex **36**

Liu and his co-workers [55] also reported the synthesis of a Ni(II) tetranuclear complex with its magnetic studies. They prepared a tridentate ligand H_2L^2 by condensation between *o*-vanillin and 2-aminoethanol. These ligands were subjected to react with $NiCl_2$ in presence of thiocyanate to afford a tetranuclear complex $[Ni_2(HL^2)(L^2)(NCS)(MeOH)]_2(C_2H_5OH)$ (**37**) (Figure 1.2). In this complex four Ni(II) atoms are linked together by two μ_3 -phenoxido and two μ_3 -hydroxido bridges. Magnetic susceptibility measurement indicated that the complex shows ferromagnetic coupling.

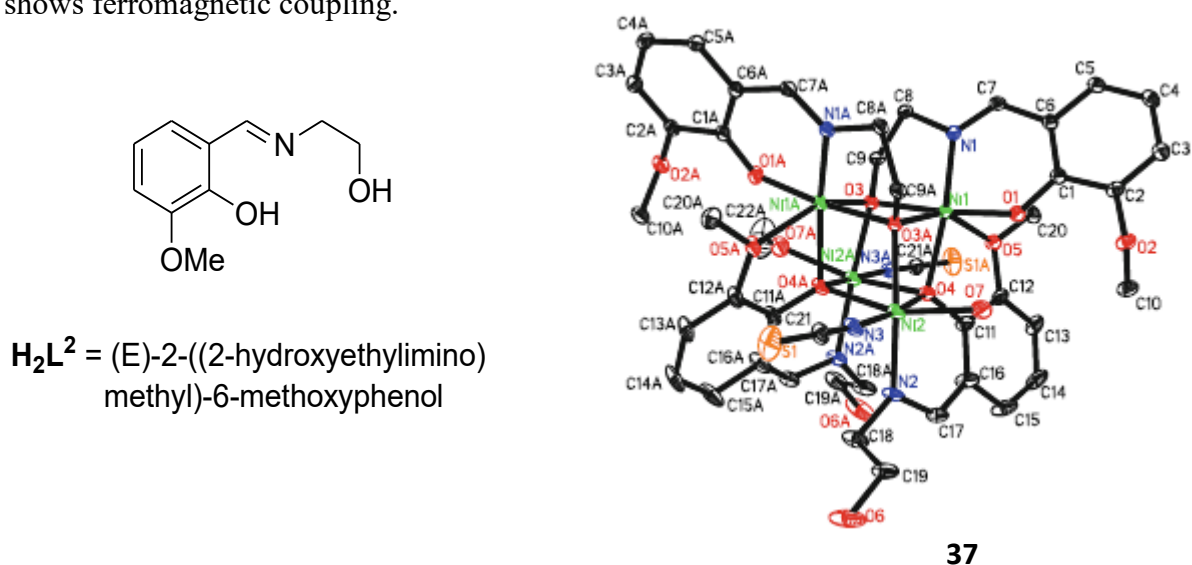
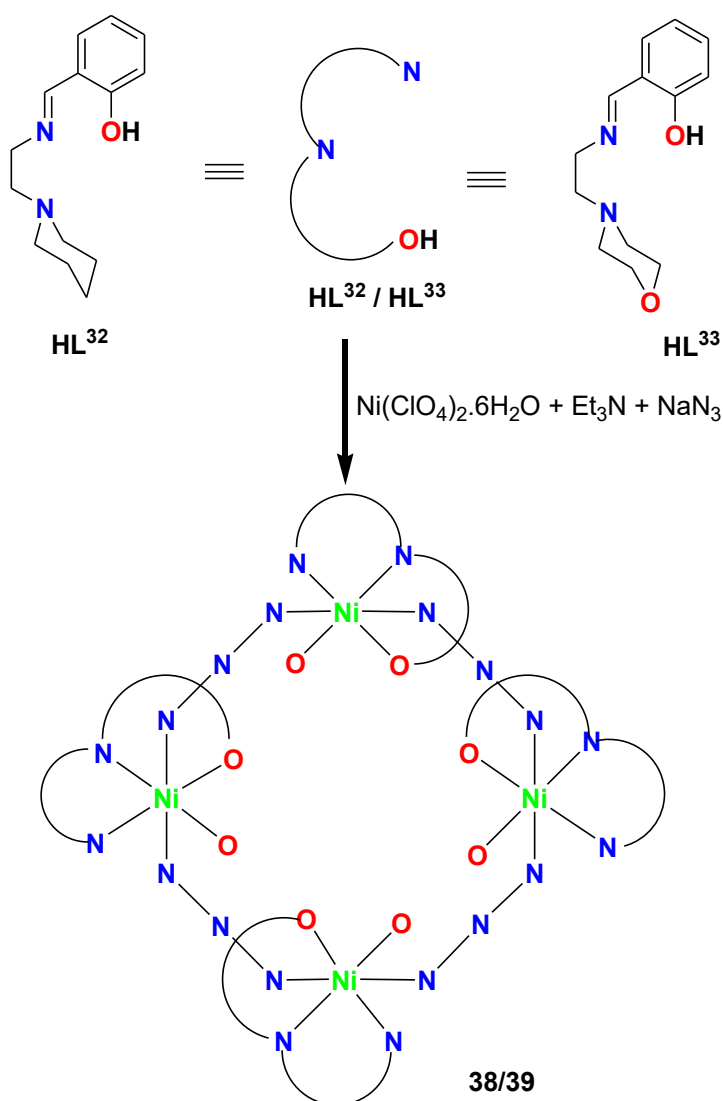


Figure 1.2: structure of the ligand H_2L^2 and ORTEP diagram of the complex **37**

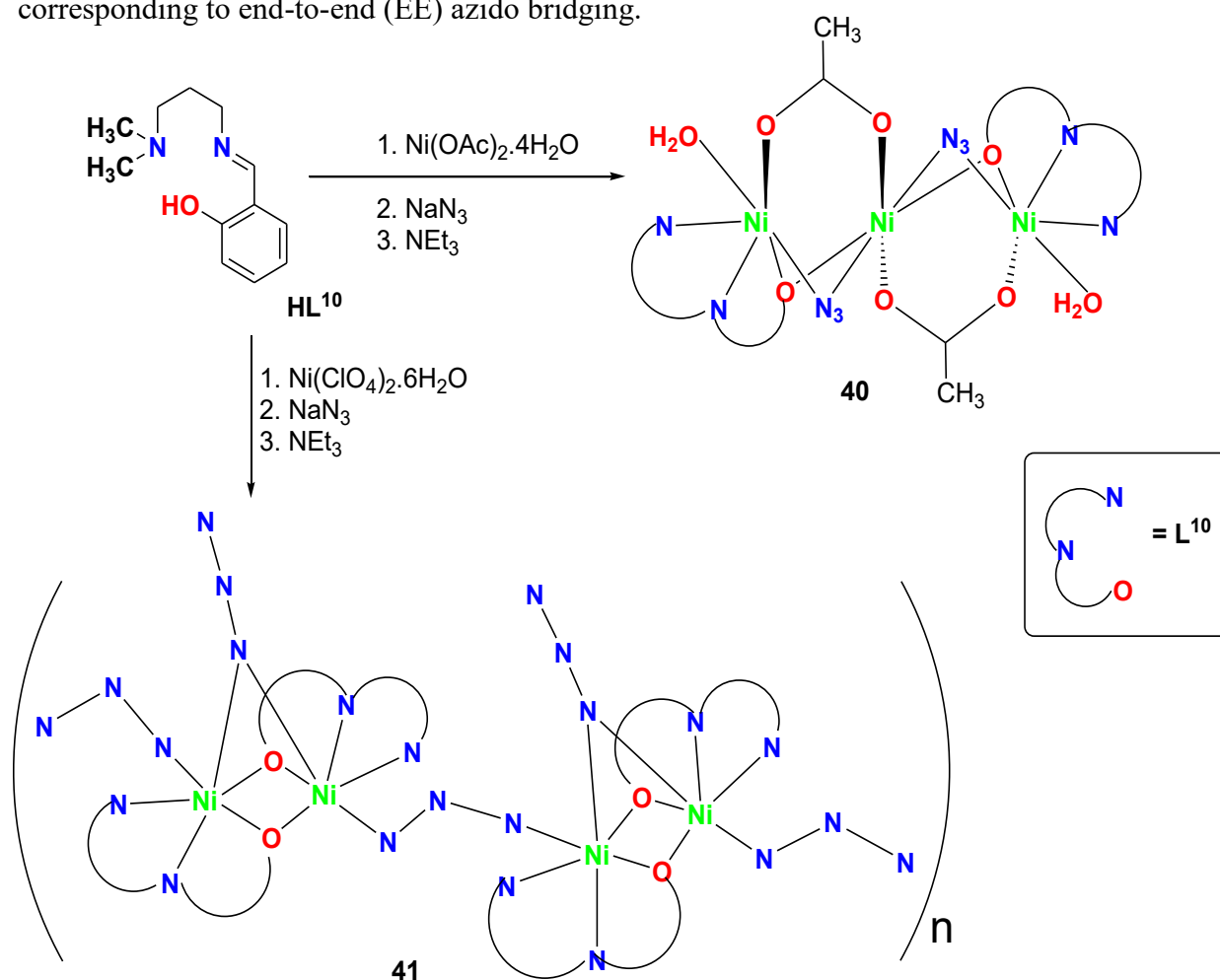
1.5.1.2. Polynuclear Ni(II) complexes with monoformyl phenol based Schiff base ligand derived from unsymmetric diamine base:

Mohanta *et al.* [52] reported end-to-end azido bridged tetra nuclear Ni(II) complexes with their structures and magnetic properties. In this context, they prepared two Schiff base ligand HL³² and HL³³ by condensation of salicylaldehyde with 1-(2-aminoethyl)-piperidine or 4-(2-aminoethyl)-morpholine, respectively. The two Ni(II) tetranuclear complexes having the formula $[\{\text{Ni}^{\text{II}}(\text{L}^{32})(\mu_{1,3}\text{-N}_3)(\text{H}_2\text{O})\}_4]$ (**38**) and $[\{\text{Ni}^{\text{II}}(\text{L}^{33})(\mu_{1,3}\text{-N}_3)(\text{H}_2\text{O})\}_4]$ (**39**) have end-to-end (μ -1,3) azide bridge between the Ni(II) centers (Scheme 1.30). Magnetic study revealed that complex **39** shows ferromagnetic interaction where as compound **38** exhibits antiferromagnetic interaction between the Ni(II) centre.



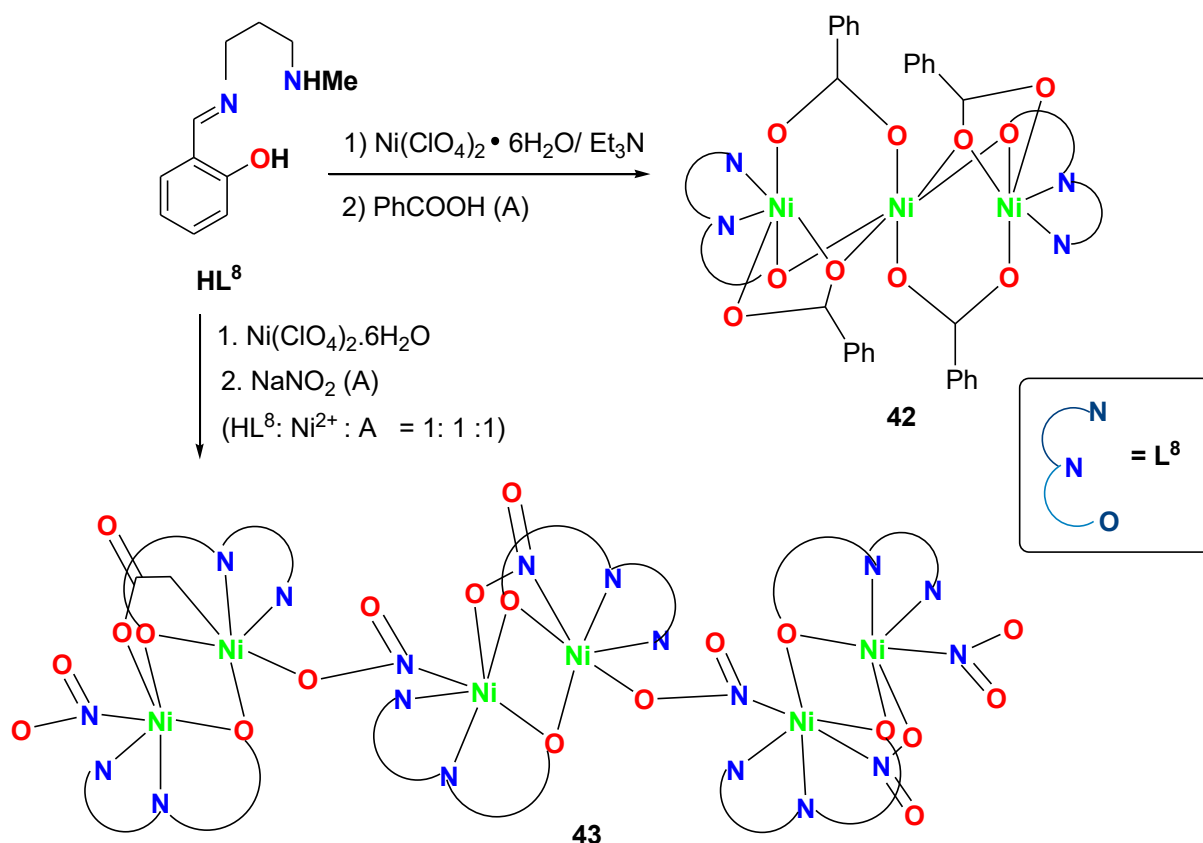
Scheme 1.30: Synthesis of the complex **38** and **39**

Ghosh *et al.* [72] prepared complexes $[\text{Ni}_3(\text{L}^{10})_2(\text{OAc})_2(\mu_{1,1}\text{-N}_3)_2(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$ (**40**) and $[\text{Ni}_2(\text{L}^{10})_2(\mu_{1,1}\text{-N}_3)(\mu_{1,3}\text{-N}_3)]_n$ (**41**) by reacting (2-[(3-dimethylaminopropylimino)-methyl]-phenol) (HL^{10}) with Ni(II) acetate (for **40**) or perchlorate (for **41**) in presence of sodium azide (Scheme 1.31). Complex **40** is a linear trinuclear complex of Ni(II) ion where two terminal Ni(II) ion and one central Ni(II) ion are connected through μ_2 -phenoxido, $\mu_{1,1}$ - azido and acetato bridges. Where as complex **41** is a zigzag chain of dimeric Ni_2 units. In this chain structure, two Ni(II) ions in the dimeric Ni_2 units are joined by two μ_2 -phenoxido and one $\mu_{1,1}$ - azido bridges and each dimeric Ni_2 units are connected to each other by $\mu_{1,3}$ - azido bridge to form the zigzag pattern. Complex **40** shows ferromagnetism whereas **41** show ferromagnetic behavior w.r.t the triply bridged Ni_2 unit and an antiferromagnetic behavior corresponding to end-to-end (EE) azido bridging.



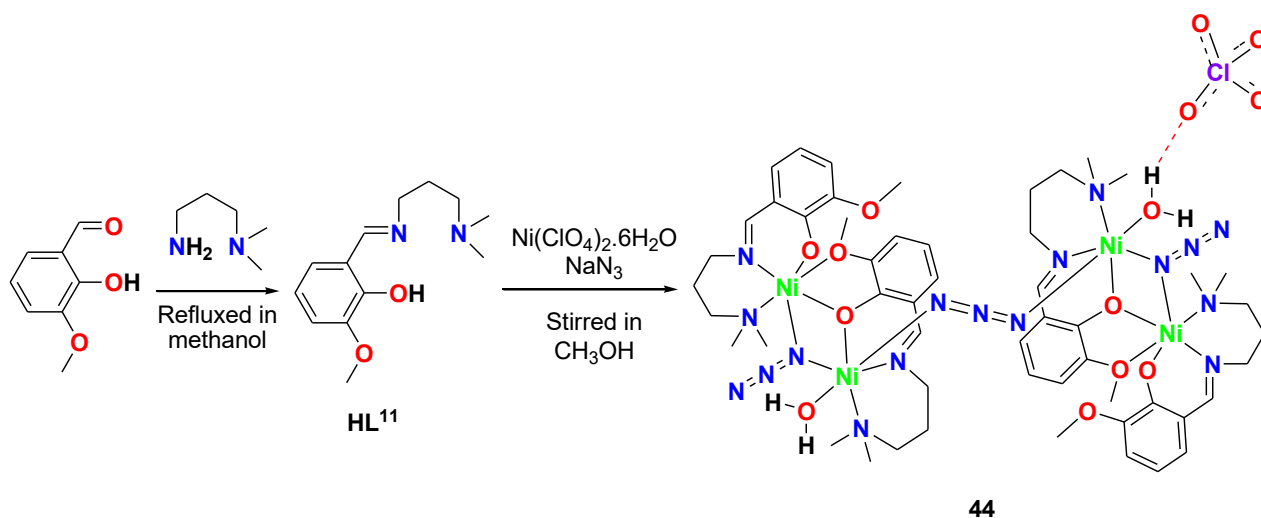
Scheme 1.31: Synthesis of the complex **40** and **41**

Recently the same group [61] mentioned above also reported the synthesis of trinuclear Ni(II) complex, $[\text{Ni}_3(\text{L}^8)_2(\text{O}_2\text{CPh})_4]$ (**42**), and a polynuclear complex, $[\text{Ni}_2(\text{L}^8)_2(\text{NO}_2)_2]_n$ (**43**) using a Schiff base ligand, HL^8 (2-[(3-Methylamino-propylimino)-methyl]-phenol) along with co-ligand NO_2^- or PhCOO^- (Scheme 1.32). Complex **42** has a linear trinuclear structure in which three Ni(II) centres are joint together by μ_2 -phenoxo and carboxylato bridges. Where as complex **43** form a one dimensional chain in which two Ni(II) ions in the dimeric Ni_2 units are joined by two μ_2 -phenoxido and a *cis*-(μ -nitrito-1 κ O:2 κ N) bridges and each dimeric Ni_2 units are connected to each other by *trans*-(μ -nitrito-1 κ O:2 κ N) bridge. Complex **42** experiences ferromagnetic coupling where as an alternating intra-chain antiferromagnetic interaction was observed in complex **43**.



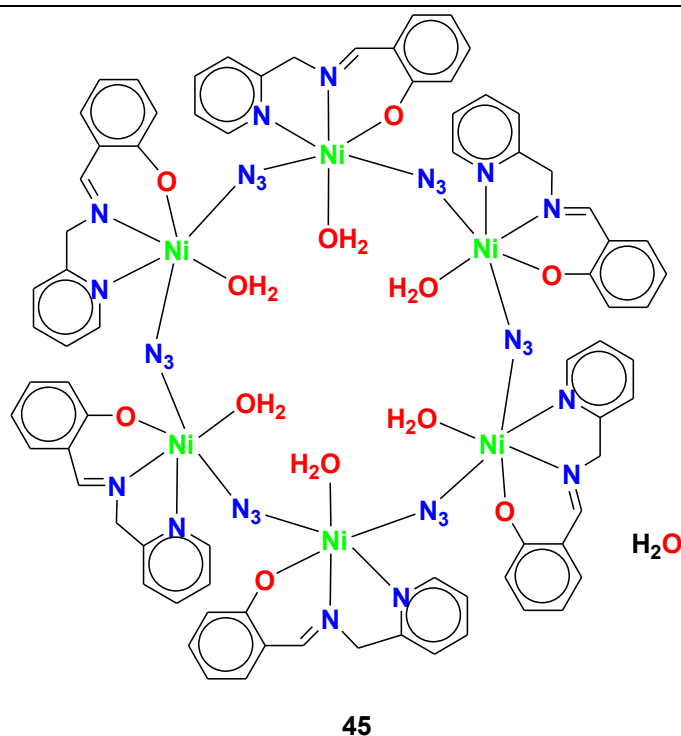
Scheme 1.32: Synthesis of the complex **42** and **43**

Chattopadhyay *et al.* [73] synthesized a tetranuclear Ni(II) complex of the formula $[\{\text{Ni}_2(\text{L}^{11})_2(\mu_{1,1}\text{-N}_3)(\text{H}_2\text{O})\}(\mu_{1,3}\text{-N}_3)\{\text{Ni}_2(\text{L}^{11})_2(\mu_{1,1}\text{-N}_3)(\text{H}_2\text{O})\}]\text{ClO}_4\cdot\text{CH}_3\text{OH}$ (**44**) in which two pseudo-dinuclear Ni_2 units were linked by a $\mu_{1,3}$ -azide bridge and the two elongated octahedral Ni(II) centres in each Ni_2 entities were connected through one $\mu_{1,1}$ -azido and one phenoxido bridge (Scheme 1.33). Magnetic studies showed that the complex exhibits a ferromagnetic interaction through both end-to-end (EE) and end-on (EO) azide bridging.



Scheme 1.33: Synthesis of the ligand HL^{11} and the complex **44**

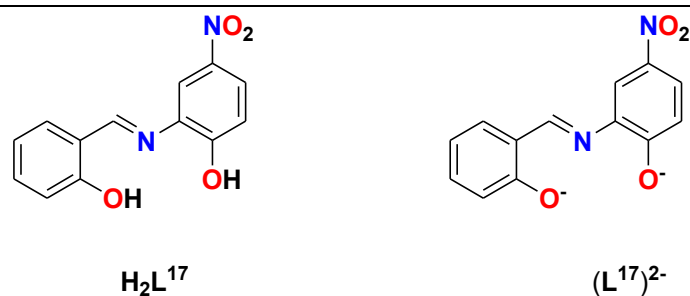
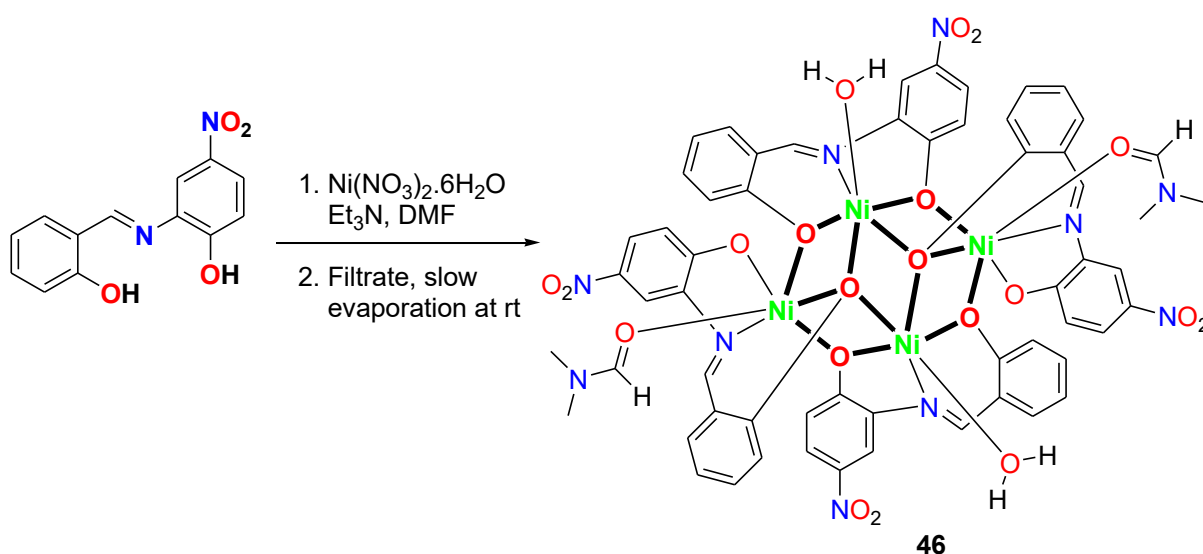
Sun *et al.* [74] reported a centrosymmetric hexanuclear wheel-shaped Ni(II) complex having the formula $[\text{Ni}(\text{L}^{13})(\mu_{1,1}\text{-N}_3)\text{H}_2\text{O}]_6\cdot\text{H}_2\text{O}$ (**45**) which was prepared by reaction of 2-[(pyridin-2-ylmethylimino)methyl] phenol (HL^{13}) and $\text{Ni}(\text{OAc})_2\cdot 4\text{H}_2\text{O}$ in presence of sodium azide (Scheme 1.34). The tridentate NNO donors Schiff base ligand (HL^{13}) was prepared from salicylaldehyde and 2-aminomethylpyridine. X-ray crystallography studies reveals that the complex is a perfect hexagon where six Ni(II) ions were linked through six $\mu_{1,1}$ -azido bridges to form the wheel-shaped structure. They also observed that the complex exhibits ferromagnetic behavior.



Scheme 1.34: Structure of the complex **45**

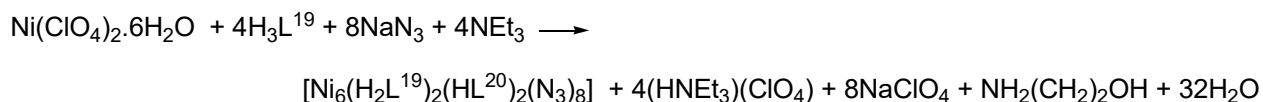
1.5.1.3. Polynuclear Ni(II) complexes with monoformyl phenol based Schiff base ligand derived from aminophenol:

Nayek *et al.* [64] prepared a new Schiff base ligand (H_2L^{17}) from Salicylaldehyde and 2-amino-4-nitrophenol (Scheme 1.35). By employing this Schiff base ligand they prepared a tetranuclear Ni(II) complex, $[Ni_4(L^{17})_4(DMF)_2(H_2O)_2].DMF$ (**46**) (Scheme 1.36). Single crystal X-ray diffraction study revealed that complex **46** has a defective dicubane structure in which Ni(II) ions were joined together by four μ_2 -phenoxo and two μ_3 -phenoxo bridged. The complex shows an antiferromagnetic coupling interaction.

Scheme 1.35: Neutral and deprotonated form of H_2L^{17} Scheme 1.36: Synthesis of the complex **46**

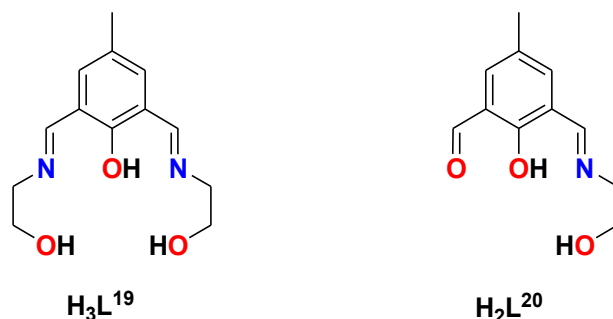
1.5.2. Polynuclear Ni(II) complexes with diformyl phenol based Schiff base ligand:

Ray and his co-workers [75] synthesized complex $[\text{Ni}_6(\text{H}_2\text{L}^{19})_2(\text{HL}^{20})_2(\text{N}_3)_8] \cdot 2\text{C}_2\text{H}_5\text{OH} \cdot 2\text{H}_2\text{O}$ (**47**) by the reaction given below.

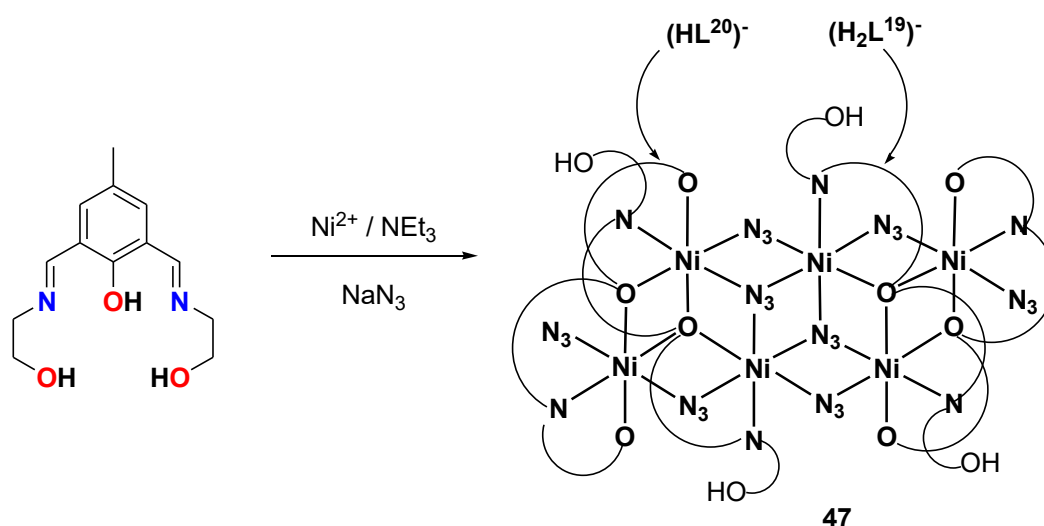


Complex **47** contains two $(\text{HL}^{20})^-$ ligand which was produced by partial hydrolysis of the ligand H_3L^{19} during course of the reaction (Scheme 1.37). The complex **47** is formed by four fused defective cubanes with $[\text{Ni}_6\text{O}_4\text{N}_6]$ core structure present in the Ni(II) centrosymmetric cluster (Scheme 1.38). In this complex, six azide ions bridged the Ni(II) ions in an end-on

bridging fashion in which four azide ions act as μ -bridge and two in μ_3 -bridges. Four bridging phenolate were also there [two μ , from $(H_2L^{19})^-$, and two μ_3 , from $(HL^{20})^-$]. It was further showed that the complex **47** was formed by dimerization of Ni_3^{II} fragments.



Scheme 1.37: structure of the ligand H_3L^{19} and H_2L^{20}



Scheme 1.38: Synthesis of the complex **47**

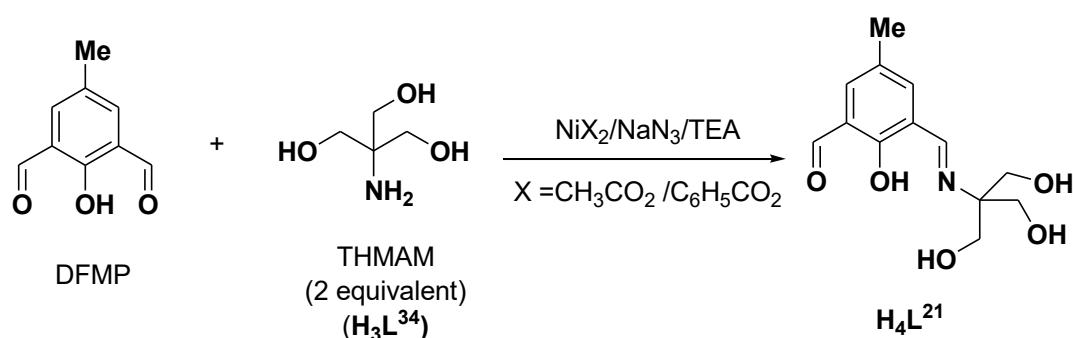
Tandon and his co-workers [76] synthesized the hexanuclear Ni(II) complexes

$[Ni_6(H_3L^{21})_2(HL^{34})_2(\mu-N_3)_4(CH_3CO_2)_2] \cdot 6C_3H_7NO \cdot C_2H_5OH$ (**48**) and

$[Ni_6(H_3L^{21})_2(HL^{34})_2(\mu-N_3)_4(C_6H_5CO_2)_2] \cdot 3C_3H_7NO \cdot 3H_2O \cdot CH_3OH$ (**49**). Where $(H_3L^{21})^-$ and $(HL^{34})^{2-}$ represent single and double deprotonated Schiff-base ligands originated from H_4L^{21}

and a tripodal ligand H_3L^{34} , respectively (Scheme 1.39). Complex **48** and **49** are very similar in structures where six Ni(II) ions are linked through two H_4L^{21} , two H_3L^{34} , four $\mu_{1,1}$ -azido bridges, and two $\mu-CH_3CO_2^-$ (in **48**) / $\mu-C_6H_5CO_2^-$ (in **49**) bridging ligands (Figure 1.3 and

Figure 1.4). In these two hexanuclear Ni(II) complexes, among the six Ni(II) ions, two terminal dinickel (Ni_2) units were linked to the central dinickel unit via four $\mu_{1,1}$ -azido and four μ_3 -methoxy bridges. Two Ni(II) ions in the terminal dinuclear (N_2) unit were bridged through one μ -phenolate group from $(\text{H}_3\text{L}^{21})^-$, one μ_3 -methoxy from $(\text{HL}^{34})^{2-}$ and one acetate (48)/benzoate (49) ion. Magnetic measurement explored that the ferromagnetic coupling interaction is observed between the Ni(II) ions in both 48 and 49.



Scheme 1.39: synthesis of the ligand H_4L^{21} from DFMP and H_3L^{34}

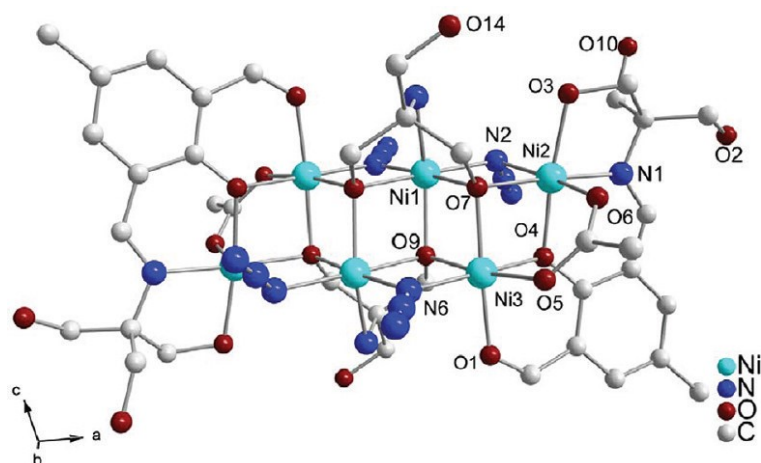


Figure 1.3: structure of the Complex 48

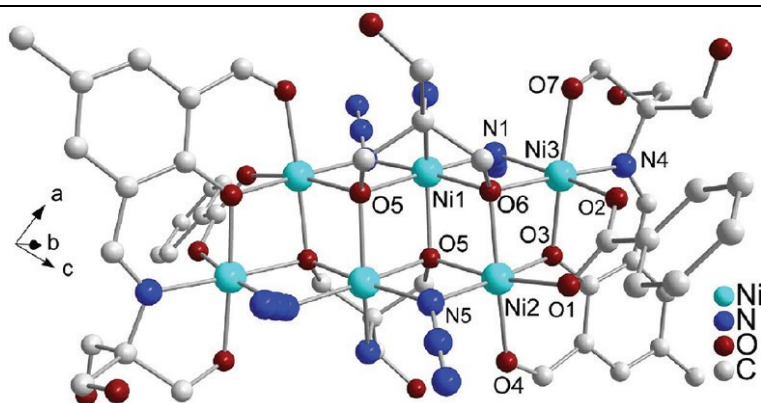


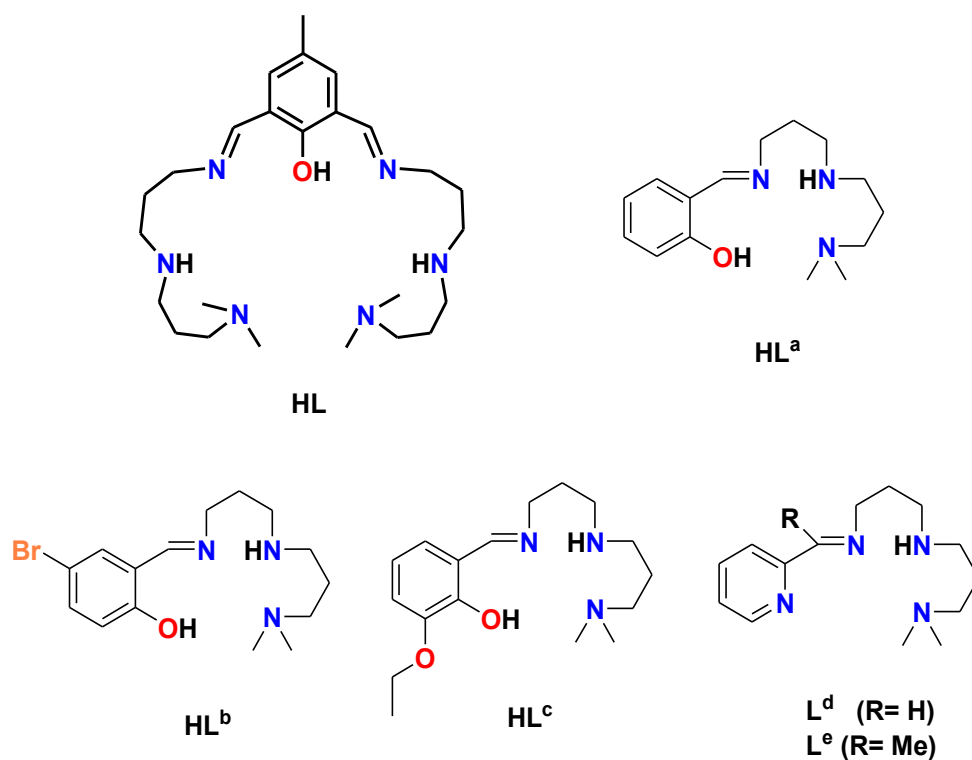
Figure 1.4: structure of the Complex 49

1.6 Aim of the Work:

The aim of this dissertation is bifocal. First, the design and synthesis of di and polynuclear Ni(II) complexes with various flexible ligands followed by the proper characterization of the prepared compounds by various techniques including X-ray crystallography. Secondly, the magnetic-structural correlation of the afforded materials want to achieve in order to understand the magnetic interaction among the metal centers.

Literature reports reveal that the structural and magnetic diversities of pseudohalido-bridged complexes are attributed to the diverse bonding modes of the bridging ligands and their orientation with respect to the paramagnetic centres. The major task in designing these compounds largely depends on the judicial choice of the blocking ligands and the stereochemical environment around the paramagnetic metal centres. Schiff-base ligands are extremely useful for the synthesis of such magnetically interesting compounds mainly because of their ease of synthesis and tremendous structural diversities. A large number of coordination compounds with Schiff base ligands derived from *N*-substituted diamine at one end and salicylaldehyde or pyridine-2-aldehyde have been developed with interesting magnetic properties. A triamine protected at one end, namely *N,N*-dimethyldipropylenetriamine, may also provide {N₄}- or {N₃O}- donor Schiff base ligands, when reacted with pyridine-2-aldehyde or salicylaldehyde, respectively, for the development

of coordination compounds. Moreover, the presence of bis(propylenic) linkers in this amine may allow the molecule to bend and rotate freely when binding to the metal centres so as to fulfil the coordinative requirements of the metal centres especially during the process of self-assembly. Surprisingly, only fewer report of structurally characterized complexes with the Schiff base derived from *N,N*-dimethyldipropylenetriamine is available in the literature. In this context, we intended to systematically develop the coordination chemistry of the transition metals derived from this triamine, with the goal of their applications in diverse fields including magnetic materials. Accordingly, in this present endeavour, we carried out the synthesis of tetradentate Schiff base ligands derived from *N,N*-dimethyldipropylenetriamine and salicylaldehyde/pyridine-2-aldehyde (Scheme 1.40). Moreover, binucleating Schiff base ligands derived from diformylphenol (DFMP) and *N,N*-dimethyldipropylenetriamine were employed to obtain high nuclearity clusters especially in the presene of azide bringing ligands.



Scheme 1.40: Schiff-base ligands employed for the synthesis of metal complexes in this
disertation

Efforts were made to prepare various ligands those differ in term of substitution at ligand arms with proper characterizations. Derivatives of salicylaldehyde could be one component for constructing such ligands. Synthesized di and polynuclear Ni(II) complexes of these ligands were characterized by IR spectroscopy and elemental analysis, and finally by X-ray diffraction study. After the structural catechization, the magnetic properties of these compounds were examined. Finally, the magneto-structural correlation provides us enough information to understand the basic magnetic phenomenon in these complexes which in turn enriched the field of molecular magnetism.

Hence, in the urge of the development of this field, our expertise encourages us to pursue in this field in order to design and synthesis of several dinuclear and polynuclear Ni(II) metal clusters with varieties of organic ligands mentioned above, which showed some interesting magnetic behavior. Furthermore, the magneto-structural correlations have been established from the experimental facts.

The outcome of this dissertation will be helpful for the further development of di and polynuclear paramagnetic transition metal complexes along with better understanding of single-molecule magnetism.

References:

- [1] (a) M. Albrecht, *Chem. Rev.* 2001, **101**, 3457. (b) B. Sarkar, M. S. Ray, Y. -Z. Li, Y. Song, A. Figuerola, E. Ruiz, J. Cirera, J. Cano, A. Ghosh, *Chem. Eur. J.* 2007, **13**, 9297. (c) P. Mukherjee, M. G. B. Drew, C. J. Gomez-García, A. Ghosh, *Inorg. Chem.* 2009, **48**, 4817. (d) C. Kachi-Terajima, R. Ishii, Y. Tojo, M. Fukuda, Y. Kitagawa, M. Asaoka, H. Miyasaka, *J. Phys. Chem. C* 2017, **121**, 12454. (e) A. Panja, N. C. Jana, S. Adak, P. Brandão, L. Dlhán, J. Titiš, R. Boča, *New J. Chem.* 2017, **41**, 3143.

- [2] (a) Q. Wang, J. Zhang, C. -F. Zhuang, Y. Tang, C. -Y. Su, *Inorg. Chem.* 2009, **48**, 287 and reference therein. (b) M. Zhao, C. Zhong, C. Stern, A. G. M. Barrett, B. M. Hoffman, *J. Am. Chem. Soc.* 2005, **127**, 9769. (c) S. Triki, F. Thétiot, F. Vandeveld, J. Sala-Pala, C. J. Gómez-García, *Inorg. Chem.* 2005, **44**, 4086. (d) W. Phonsri, C. G. Davies, G. N. L. Jameson, B. Moubaraki, J. S. Ward, P. E. Kruger, G. Chastanet, K. S. Murray, *Chem. Commun.* 2017, **53**, 1374.
- [3] (a) C. Maxim, F. Tuna, A. M. Madalan, N. Avarvari, M. Andruh, *Cryst. Growth Des.* 2012, **12**, 1654. (b) T. K. Michaelos, H. M. C. Lant, L. S. Sharninghausen, S. M. Craig, F. S. Menges, B. Q. Mercado, G. W. Brudvig, R. H. Crabtree, *ChemPlusChem* 2016, **81**, 1129.
- [4] (a) E. Fujita, B. S. Brunschwig, T. Ogata, S. Yanagida, *Coord. Chem. Rev.* 1994, **132**, 195. (b) T. Opstal, F. Verpoort, *Angew. Chem., Int. Ed.* 2003, **42**, 2876.
- [5] (a) M. Volpe, H. Hartnett, J. W. Leeland, K. Wills, M. Ogunshun, B. J. Duncombe, C. Wilson, A. J. Blake, J. McMaster, J. B. Love, *Inorg. Chem.* 2009, **48**, 5195. (b) P. Mahapatra, M. G. B. Drew, A. Ghosh, *Cryst. Growth Des.* 2017, **17**, 6809.
- [6] (a) H. Wang, D. Zhang, Z. -H. Ni, X. Li, L. Tian, J. Jiang, *Inorg. Chem.* 2009, **48**, 5946. (b) S. Khatua, S. H. Choi, J. Lee, K. Kim, Y. Do, D. G. Churchill, *Inorg. Chem.* 2009, **48**, 2993.
- [7] (a) X. -P. Yang, R. A. Jones, M. M. Oye, A. L. Holmes, W. -K. Wong, *Cryst. Growth Des.* 2006, **6**, 2122. (b) E. Guzman-Percastegui, J. G. Alvarado-Rodríguez, J. Cruz Borbolla, N. Andrade-Lopez, R. A. Vazquez-García, R. N. Nava-Galindo, T. Pandiyan, *Cryst. Growth Des.* 2014, **14**, 3742.
- [8] (a) K. C. Gupta, A. K. Sutar, *Coord. Chem. Rev.* 2008, **252**, 1420. (b) K. L. Gurunatha, T. K. Maji, *Inorg. Chem.* 2009, **48**, 10886.

- [9] (a) T. K. Maji, G. Mostafa, R. Matsuda, S. Kitagawa, *J. Am. Chem. Soc.* 2005, **127**, 17152. (b) D. Wang, S. -M. Li, J. -Q. Zheng, D. -Y. Kong, X. -J. Zheng, D. -C. Fang, L. -P. Jin, *Inorg. Chem.* 2017, **56**, 984. (c) R. Dey, R. Haldar, T. K. Maji, D. Ghoshal, *Cryst. Growth Des.* 2011, **11**, 3905.
- [10] Y. Garcia, V. Ksenofontov, P. Güthlich, *Hyperfine Interact.* 2002, **139-140**, 543.
- [11] N. S. Hush, A. T. Wong, G. B. Bacskay, J. R. Reimers, *J. Am. Chem. Soc.* 1990, **112**, 4192.
- [12] A. Aviram, *Int. J. Quantum Chem.* 1992, **42**, 1615.
- [13] O. Kahn, J. Kröber, C. Jay, *Adv. Mater.* 1992, **4**, 718.
- [14] A. J. Tasiopoulos, A. Vinslava, W. Wernsdorfer, K. A. Abboud, G. Christou, *Angew. Chem., Int. Ed.* 2004, **43**, 2117; (b) H. Miyasaka, R. Clerac, W. Wernsdorfer, L. Lecren, C. Bonhomme, K. Sugiura, M. Yamashita, *Angew. Chem., Int. Ed.* 2004, **43**, 2801
- [15] (a) J. Camarero, E. Coronado, *J. Mater. Chem.* 2009, **19**, 1687. (b) L. Bogani, W. Wernsdorfer, *Nat. Mater.* 2008, **7**, 179.
- [16] (a) R. Sessoli, D. Gatteschi, A. Caneschi, M. A. Novak, *Nature* 1993, **365**, 141. (b) R. Sessoli, H. L. Tsai, A. R. Schake, S. Y. Wang, J. B. Vincent, K. Folting, D. Gatteschi, G. Christou, D. N. Hendrickson, *J. Am. Chem. Soc.* 1993, **115**, 1804.
- [17] R. Bagai, G. Christou, *Chem. Soc. Rev.* 2009, **38**, 1011.
- [18] J. M. Clemente-Juan, E. Coronado, A. Forment-Aliaga, A. Gaita-Ariño, C. Giménez-Saiz, F. M. Romero, W. Wernsdorfer, R. Biagi, V. Corradini, *Inorg. Chem.* 2010, **49**, 386.
- [19] (a) G. A. Lawrance, *Introduction to Coordination Chemistry*, Wiley, 2009. (b) M. Satake, Y. Mido, *Coordination Chemistry*, Discovery Publishing House, 2011. (c) L. Tschugaeff *Berichte der deutschen chemischen Gesellschaft.* 1905, **38**, 2520.

-
- [20] A. Elias, B. D. Gupta, *Basic Organometallic Chemistry*, Universities Press, 2013.
- [21] T. J. Greenfield, A. E. Hoffman, N. Marino, A. G. Goos, F. Lloret, M. Julve, R. P. Doyle, *Inorg. Chem.* 2015, **54**, 6537.
- [22] (a) Z. Mazej, T. Gilewski, E. A. Goreshnik, Z. Jagličić, M. Derzsi, W. Grochala, *Inorg. Chem.* 2010, **49**, 7969. (b) D. Pinkowicz, H. Southerland, X. -Y. Wang, K. R. Dunbar, *J. Am. Chem. Soc.* 2014, **136**, 9922.
- [23] (a) E. -Q. Gao, Y. -F. Yue, S. -Q. Bai, Z. He, C. -H. Yan, *J. Am. Chem. Soc.* 2016, **138**, 1328. (b) M. S. E. Fallah, E. Rentschler, A. Caneschi, R. Sessoli, D. Gatteschi, *Angew. Chem., Int. Ed.* 1996, **35**, 1947.
- [24] (a) C. Masters, *Homogeneous Transition-Metal Catalysis: A Gentle Art*, Springer, 2011. (b) J. Adhikary, P. Chakraborty, S. Das, T. Chattopadhyay, A. Bauza, S. K. Chattopadhyay, B. Ghosh, F. A. Mautner, A. Frontera, D. Das, *Inorg. Chem.* 2013, **52**, 13442.
- [25] S. Brill, *Transition Metals in Biochemistry*, Springer, vol. 1977, **26**.
- [26] A. D. Burrows, *Science Progress.* 2002, **85**, 199.
- [27] H. Schiff, *Justus Liebigs Ann. Chem.* 1864, **131**, 118.
- [28] E. B. Middleton, *J. Am. Chem. Soc.* 1923, **45**, 2763.
- [29] (a) S. Yamada, *Coord. Chem. Rev.* 1999, **192**, 537. (b) M. Albrecht, *Chem. Rev.* 2001, **101**, 3457. (c) R. Ziessel, *Coord. Chem. Rev.* 2001, **216**, 195. (d) K. C. Gupta, A. K. Sutar, C. -C. Lin, *Coord. Chem. Rev.* 2009, **253**, 1926. (e) D. Zhang, H. Wang, Y. Chen, Z. -H. Ni, L. Tian, J. Jiang, *Inorg. Chem.* 2009, **48**, 11215.
- [30] E. C. Niederhoffer, J. H. Timmons, A. E. Martell, *Chem. Rev.* 1984, **84**, 137.
- [31] (a) E. Fujita, B. S. Brunshwig, T. Ogata, S. Yanagida, *Coord. Chem. Rev.* 1994, **132**, 195. (b) T. Opstal, F. Verpoort, *Angew. Chem. Int. Ed.* 2003, **42**, 2876.
-

- [32] (a) O. Khan, J. Galy, Y. Journax, J. Jaud, I. M. Badarau, *J. Am. Chem. Soc.* 1982, **104**, 2165. (b) J. -P. Costes, F. Dahan, A. Dupuis, *Inorg. Chem.* 2000, **39**, 165. (c) Q. Wang, J. Zhang, C. F. Zhuang, Y. Tang, C. Y. Su, *Inorg. Chem.* 2009, **48**, 287. (d) B. Sarkar, M. S. Ray, Y. -Z. Li, Y. Song, A. Figuerola, E. Ruiz, J. Cirera, J. Cano, A. Ghosh, *Chem. Eur. J.* 2007, **13**, 9297. (e) S. Chattopadhyay, M. G. B. Drew, C. Diaz, A. Ghosh, *Dalton Trans.* 2007, 2492.
- [33] J. Tisato, F. Refosco, F. Bandoli, *Coord. Chem. Rev.* 1994, **135**, 325.
- [34] S. S. Massoud, F. R. Louka, Y. K. Obaid, R. Vicente, J. Ribas, R. C. Fischerc, F. A. Mautner, *Dalton Trans.* 2013, **42**, 3968.
- [35] C. G. Pierpont, D. N. Hendrickson, D. M. Duggan, F. Wagner, E. K. Barefield, *Inorg. Chem.* 1975, **14**, 604.
- [36] (a) Charlot, M. F.; Kahn, O.; Chaillet, M.; Larrieu, C. *J. Am. Chem. Soc.* 1986, **108**, 2574. (b) A. Bencini, C. A. Ghilardi, S. Midollini, A. Orlandini, *Inorg. Chem.* 1989, **28**, 1958. (c) A. Escuer, R. Vicente, J. Ribas, M. S. El Fallah, X. Solans, M. FontBardía, *Inorg. Chem.* 1994, **33**, 1842.
- [37] A. Jeremies, S. Gruschinski, M. Meyer, V. Matulis, O. A. Ivashkevich, K. Kobalz, B. Kersting, *Inorg. Chem.* 2016, **55**, 4, 1843.
- [38] F. A. Mautner, M. Scherzer, C. Berger, R. C. Fischer, R. Vicente, S. S. Massoud, *Polyhedron* 2015, **85**, 20.
- [39] M. Monfort, J. Ribas and X. Solans, *Inorg. Chem.* 1994, **33**, 4271.
- [40] D. M. Duggan and D. N. Hendrickson, *Inorg. Chem.* 1974, **13**, 2929.
- [41] T. Rojo, R. Corte's, L. Lezama, M. I. Arriortua, K. Urtiaga, G. Villeneuve, *J. Chem. Soc., Dalton Trans.* 1991, 1779.
- [42] A. P. Ginsberg, R. C. Sherwood, R. W. Brookes, R. L. Martin, *J. Am. Chem. Soc.* 1971, **93**, 5927.

-
- [43] H. D. Bien, W. Gu, Q. Yu, S. P. Yan, D. Z. Liao, Z. H. Jiang, P. Cheng, *Polyhedron* 2005, **24**, 2002.
- [44] P. Bhowmik, S. Chattopadhyay, M. G. B. Drew, C. Diaz, A. Ghosh, *Polyhedron* 2010, **29**, 2637.
- [45] B. Larue, L. -T. Tran, D. Luneau, C. Reber, *Can. J. Chem.* 2003, **81**, 1168.
- [46] T. K. Maji, G. Mostafa, J. M. Clemente-Juan, J. Ribas, F. Lloret, K. -i. Okamoto, N. R. Chaudhuri, *Eur. J. Inorg. Chem.* 2003, 1005.
- [47] A. Escuer, R. Vicente, M. S. E. Fallah, X. Solans, M. FontBardia, *J. Chem. Soc., Dalton Trans.* 1996, 1013.
- [48] D. M. Duggan, D. N. Hendrickson, *Inorg. Chem.* 1974, **13**, 2056.
- [49] Z. Mahendrasinh, S. Ankita, S. B. Kumar, A. Escuer, E. Suresh, *Inorg. Chim. Acta* 2011, **375**, 333.
- [50] S. Choubey, K. Bhar, S. Chattopadhyay, A. Hazra, T. K. Maji, J. Ribas, B. K. Ghosh, *Dalton Trans.* 2012, **41**, 11551.
- [51] F. A. Mautner, M. Mikuriya, H. Ishida, H. Sakiyama, F. R. Louka, J. W. Humphrey, S. S. Massoud, *Inorganica Chimica Acta* 2009, **362**(11), 4073.
- [52] S. Sasmal, S. Mohanta *J. Chem. Sci.* 2012, **124** (6), 1353.
- [53] S. Hazra, R. Koner, P. Lemoine, E. C. Sañudo, S. Mohanta, *Eur. J. Inorg. Chem.* 2009, 3458.
- [54] A. Donmez, G. Oylumluoglu, M. B. Coban, C. Kocak, M. Aygun, H. Kara, *Journal of Molecular Structure* 2017, **1149**, 569.
- [55] Y. Zhang, X. M. Zhang, T. F. Liu, W. G. Xu, *Transition Met Chem.* 2010, **35**, 851.
- [56] S. Banerjee, M. G. B. Drew, C. Z. Lu, J. Tercero, C. Diaz, A. Ghosh, *Eur. J. Inorg. Chem.* 2005, 2376.
-

- [57] H. Bahron, S. S. Khaidir, A. M. Tajuddin, K. Ramasamy, B. M. Yamin, *Polyhedron* 2019, **161**, 84.
- [58] P. Mukherjee, M. G. B. Drew, C. J. G. Garcí'a, A. Ghosh, *Inorg. Chem.* 2009, **48**, 5848. [59] S. Naiya, M. G. B. Drew, C. Estarellas, A. Frontera, A. Ghosh, *Inorganica Chimica Acta*. 2010, **363**, 3904.
- [60] R. Biswas, S. Giri, S. Saha, A. Ghosh, *Eur. J. Inorg. Chem.* 2012, 2916.
- [61] K. Das, A. Datta, S. Nandi, S. B. Mane, S. Mondal, C. Massera, C. Sinha, C. H. Hung, T. Askun, P. Celikboyun, Z. Cantürk, E. Garribba, T. Akitsu, *Inorg. Chem. Front.* 2015, **2**, 749.
- [62] R. Sanyal, X. Zhang, P. Chakraborty, S. Giri, S. K. Chattopadhyay, C. Zhao, D. Das, *New J. Chem.* 2016, **40**, 7388.
- [63] F. Robert, B. Tinant, R. Clérac, P. L. Jacquemin, Y. Garcia, *Polyhedron* 2010, **29**, 2739.
- [64] R. Vinayak, A. Harinath, C. J. G. Garcí'a, T. K. Panda, S. Benmansour, H. P. Nayek, *ChemistrySelect*. 2016, **1**, 6532.
- [65] S. Saha, A. Sarkar, S. Das, T. K. Panda, K. Harms, H. P. Nayek, *ChemistrySelect*. 2017, **2**, 7865.
- [66] K. K. Abid, A. A. B. Omar, *Res Chem Intermed.* 2015, **41**, 1715.
- [67] M. Pait, A. Sarkar, E. Colacio, D. Ray, *Proc. Natl. Acad. Sci., India, Sect. A Phys. Sci.* 2014, **84**, 189.
- [68] M. Habib, T. K. Karmakar, G. Aromí', J. R. Arin~o, H. K. Fun, S. Chantrapromma, and S. K. Chandra, *Inorg. Chem.* 2008, **47**, 4109.
- [69] P. Ghorai, P. Brandão, S. Benmansour, C. J. G. García, A. Saha, *Polyhedron* **2020**, **188**, 114708.

-
- [70] S. Sain, S. Bid, A. Usman, H. K. Fun, G. Aromí, X. Solans, S. K. Chandra, *Inorganica Chimica Acta*. 2005, **358**, 3362.
- [71] M. Č. Romanovića, B. R. Čobeljića, A. Pevecb, I. Turelb, V. Spasojevićc, A. A. Tsaturyand, I. N. Shcherbakovd, K. K. Anđelkovića, M. Milenkoviće, D. Radanovićf, M. R. Milenković, *Polyhedron* 2017, **128**, 30.
- [72] R. Biswas, S. Mukherjee, P. Kar, A. Ghosh, *Inorg. Chem.* 2012, **51**, 15, 8150.
- [73] A. Bhattacharyya, M. Das, A. Bauza, S. Herrero, R. G. Prieto, A. Frontera, S. Chattopadhyay, *New J. Chem.* 2017, **41**, 13585.
- [74] B. Sun, X. Chen, Z. Li, L. Zhangb, Q. Zhao, *New J. Chem.* 2010, **34**, 190.
- [75] D. Mandal, V. Bertolasi, J. R. Ariño, G. Aromí, D. Ray, *Inorg. Chem.* 2008, **47**, 3465.
- [76] S. S. Tandon, S. D. Bunge, J. Sanchiz, L. K. Thompson, *Inorg. Chem.* 2012, **51**, 3270.

CHAPTER 2

CHAPTER 2

Structures and magnetism of mono- and di-nuclear Ni(II) complexes derived from {N₃O}-donor Schiff base ligand

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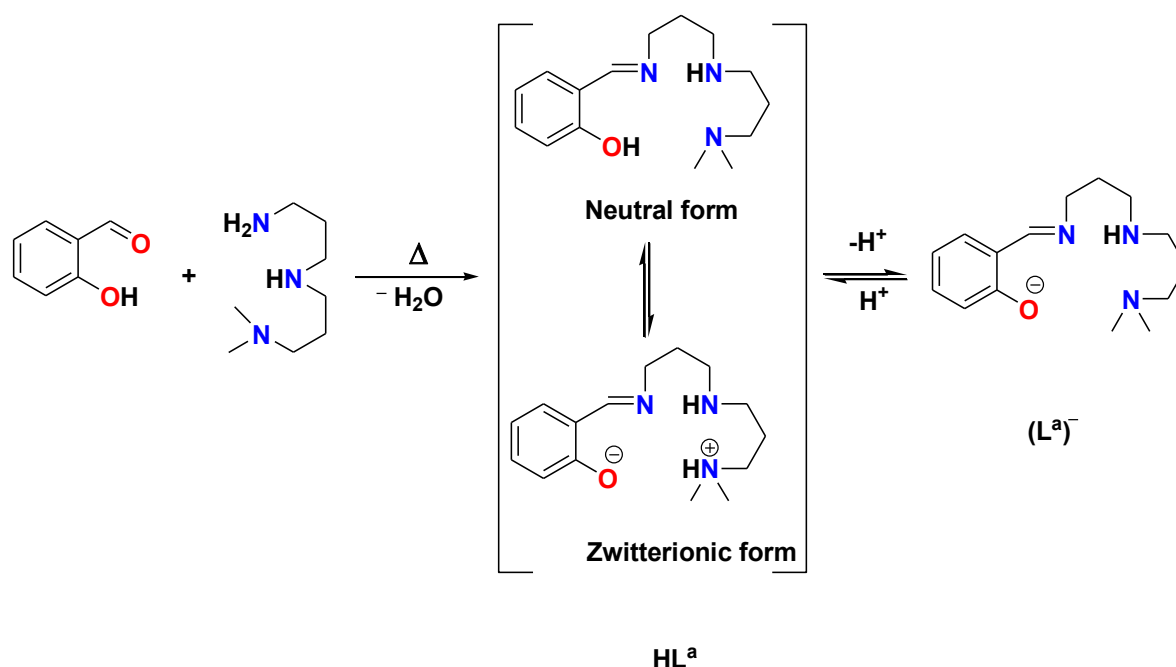
2.1. Introduction

The study of di- and polynuclear transition metal complexes bridged by pseudohalides is an attractive field of research because of their diverse magnetic properties [1–12]. Among the pseudohalides, azido bridged complexes have been studied extensively because of its versatile coordination modes, end-on ($\mu_{1,1}$) and end-to-end ($\mu_{1,3}$) modes being the most common ones, and its effective transmittance of the magnetic interaction between the paramagnetic ions [13–21]. In contrast, the heteroatomic pseudohalides, namely thiocyanate and cyanate, with polarizable π systems and two different donor atoms, which can coordinate the metal ions through either of the heteroatoms, or both, are less versatile than that of azide ion. Therefore, in contrast to the vast chemistry of azido bridged complexes, both structurally and magnetically important compounds with these pseudohalides have been less investigated. Last two decades witnessed rapid growth of azido-bridged Ni(II) systems, [22–44] and accordingly, the sophisticated magneto-structural correlations are available on these compounds to get insight into the fundamental aspects of the magnetic interactions [45,46]. These comprehensive data reveal that the most characteristic feature of the azido bridges is the relationship between coordination mode and magnetic behaviour. Generally, double $\mu_{1,3}$ -azido bridging leads to antiferromagnetic (AF) coupling, while $\mu_{1,1}$ coordination is associated with ferromagnetic (F) exchange between the Ni(II) centres with only exception where low angles of $\mu_{1,1}$ bridging azido ligands lead to the weak AF coupling [41]. Whereas, the double thiocyanato bridged Ni(II) complexes with $\mu_{1,3}$ bridging mode exhibit F interaction although weakly, [34,47–55] the mixed observations are made with $\mu_{1,3}$ bridged cyanato systems [49,56–59]. Reported dinuclear Ni(II) compounds with cyanato and thiocyanato with $\mu_{1,1}$ bridging mode are extremely scarce in the literature to establish the proper magneto-structural correlation, and thus further attention is required for the development of these systems. It is

worth noting that all three reported dinuclear systems with bis- $\mu_{1,1}$ bridged cyanato show weak F coupling, [40,60] while the magnetically characterized lonely known $\mu_{1,1}$ -thiocyanato bridged dinuclear Ni(II) complex exhibits antiferromagnetic interaction [61].

Literature reports reveal that the structural and magnetic diversities of pseudohalido bridged complexes are attributed to the diverse bonding modes of the bridging ligands and their orientation with respect to the paramagnetic centres. The major task in designing these compounds largely depends on the judicious choice of the blocking ligands and the stereochemical environment around the paramagnetic metal centres. Schiff-base ligands are extremely useful for the synthesis of such magnetically interesting compounds mainly because of their ease of synthesis and tremendous structural diversities. A large number of coordination compounds with Schiff base ligands derived from N-substituted diamine at one end and salicylaldehyde or pyridine-2-aldehyde have been developed with interesting magnetic properties [28,29,62–65]. A triamine protected at one end, namely *N,N*-dimethyldipropylenetriamine, may also provide {N₄}- or {N₃O}- donor Schiff base ligands, when reacts with pyridine-2-aldehyde or salicylaldehyde, respectively, for the development of coordination compounds. Moreover, the presence of bis(propylenic) linkers in this amine may allow the molecule to bend and rotate freely when binding to the metal centres so as to fulfil the coordinative requirements of the metal centres especially during the process of self-assembly. Surprisingly, only single report where structurally characterized Cu(II) complexes with the Schiff base derived from *N,N*-dimethyldipropylenetriamine is available in the literature [66]. In this context, we intended for the systematic development of coordination chemistry of the transition metals derived from this triamine, with the goal to their applications in diverse fields including biomimetic catalysis and magnetic materials. Accordingly, in this present endeavour, a tetradentate Schiff base HL^a (Scheme 2.1) derived from *N,N*-dimethyldipropylenetriamine and salicylaldehyde has been reacted with Ni(II) salts

both in the presence and absence of pseudohalides. Interestingly, we ended up with very diverse results of the isolation of some mono- and di-nuclear complexes of Ni(II) ions. Herewith, we report structures and magnetic properties of five new complexes, [Ni(HL^a)₂](ClO₄)₂ (**50**), [Ni(L^a)(sal)] (**51**), [Ni₂(L^a)₂(μ_{1,1}-N₃)₂] (**52**), [Ni₂(L^a)₂(μ_{1,1}-NCO)₂] (**53**) and [Ni₂(HL^a)₂(μ_{1,1}-NCS)₄].CH₃OH (**54**). Among them, **53** and **54** are extremely rare bis-μ_{1,1}-bridged Ni(II) compounds with bridging cyanato and thiocyanato groups, respectively. The most importantly, compound **54** is the first example of the ferromagnetically coupled bis-μ_{1,1}-thiocyanato bridged dinickel(II) complex.



Scheme 2.1: Schiff base HL^a employed in the present study

2.2. Experimental Section

2.2.1. Laboratory Techniques

2.2.1.1 Elemental Analysis (CHN)

The weight percentage of C (carbon), H (hydrogen) and N (nitrogen) in a prepared sample is examined by combusting the sample in presence of excess pure oxygen to obtain the mixture

of carbon dioxide, water and oxides of nitrogen. The produced gaseous mixture is then separated and determined the mass the percentage of carbon, hydrogen and nitrogen from carbon dioxide, water and oxides of nitrogen respectively. Elemental analyses (carbon, hydrogen and nitrogen) were carried out in a PerkinElmer 240C elemental analyser from Jadavpur University, kolkata.

2.2.1.2. Infra-red (IR) Spectroscopy

Infra-red (IR) spectroscopy is performed by passing radiation in the range of 400 – 4000 cm⁻¹ through a sample and measured the percentage of radiation absorbed at each wavelength. Absorption of radiation for a specific wavelength corresponds to the bond vibrations between the atoms present within the sample [67]. The infrared spectra of the prepared samples were recorded in the range of 400–4000 cm⁻¹ on a PerkinElmer Spectrum Two FTIR spectrophotometer using KBr pellets.

2.2.1.3. Single Crystal X-Ray Diffraction (SC-XRD)

Single crystal X-ray data of the prepared complexes were collected using a Bruker Kappa Apex-II CCD diffractometer equipped with fine focus sealed tube of monochromated Mo-K α radiation ($\lambda = 0.71073$ Å). The data were collected by scanning over the φ and ω directions and were averaged during refinement cycles. Data processing was performed using the Bruker APEX-II suite (v2.0-2) program. All available reflections to $2\theta_{\max}$ were harvested and corrected for Lorentz and polarization factors with Bruker SAINT plus. The multiscan absorption correction method was applied for data correction using the SADABS program [68]. The structures were solved by a combination of direct methods and refined by means of full matrix least-square technique based on F^2 using the SHELX-2013 suite [69]. All the non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms connected to carbon atoms were included in geometrically idealized positions with given thermal parameters related to those they are attached (1.5 times for methyl hydrogens and 1.2

times for others). While hydrogen atoms connected to nitrogen atoms were located on the difference Fourier map and isotropically treated with given thermal parameters equivalent to 1.2 times of the parent atoms. Drawings of the structures of the complexes were generated with the programs like MERCURY-3.8. Additional crystallographic data and refinement details for the complexes are given in the corresponding [Table 2.1](#).

2.2.1.4. SQUID Magnetometry

A SQUID magnetometer (MPMS-XL7, Quantum Design) has been used for magnetic data collection using the RSO mode of detection. The susceptibility taken at $B = 0.1$ T between $T = 2$ – 300 K was corrected for the underlying diamagnetism and converted to the effective magnetic moment. The magnetization was measured at two temperatures: $T = 2.0$ and $T = 4.6$ K at University of SS Cyril and Methodius, 91701 Trnava, Slovakia. For the SQUID analyses ($m = 21.11$ mg for cis isomer and $m = 10.00$ mg for trans isomer) the prepared crystalline samples were packed in a polyethylene bag, and for the VSM analyses ($m = 16.8$ mg for cis isomer and $m = 10.1$ mg for trans isomer). The samples were packed in a quartz capsule.

2.2.2 Chemicals Synthetic Techniques

2.2.2.1 Materials

Chemicals such as nickel(II) perchlorate hexahydrate (SRL India), Ni(II) acetate tetrahydrate (SRL India), *N,N*-dimethyldipropylenetriamine (Merck India) and salicylaldehyde (Hsal) (Merck India) were purchased from commercial sources and used as received. Solvents and some other chemicals were of reagent grade and used without further purification.

Caution! *Perchlorate and azide salts of metal complexes coordinated with organic ligands are potentially explosive. Only a small amount of material should be prepared, and it should be handled with great care.*

2.2.2.2. Synthesis of Schiff base ligand HL^a

The tetradentate {N₃O}-donor ligand (HL^a) was prepared by the Schiff base condensation method. Briefly, 1.0 mmol of N,N-dimethyldipropylenetriamine (159 mg) and 1.0 mmol of salicylaldehyde (122 mg) were combined in 20 mL of methanol. The resulting solution was heated to reflux for *ca.* 1 h, and allowed to cool at room temperature. The dark orange methanol solution of HL^a was subsequently used for the synthesis of the following complexes.

2.2.2.3 Synthesis of complex [Ni(HL^a)₂](ClO₄)₂ (50)

Ni(ClO₄)₂·6H₂O (366 mg, 1.0 mmol) and HL^a (2.0 mmol) were mixed in 30 mL of methanol with stirring. To the resulting green solution was added Et₃N (101 mg, 1.0 mmol) and the solution was heated to reflux for 30 min. The reaction mixture was then filtered and kept at room temperature. Analytically pure dark-green crystals suitable for X-ray diffraction were obtained from slow evaporation of the solution after couple of days, which was collected by filtration and washed with cold methanol/diethyl ether and air dried. Yield: 598 mg (77%). Anal. Calcd. for C₃₀H₄₂Cl₂N₆NiO₁₀: C 46.42%, H 5.45%, N 10.83 %. Found: C 46.61%, H 5.40%, N 10.67 %. FTIR (KBr, cm⁻¹): 1635 m (ν_{C=N}), 1076 s, 621s (ν_{Cl-O}).

2.2.2.4 Synthesis of complex [Ni(L^a)(sal)] (51)

Complex **51** was synthesized following the very similar procedure as described for **50**, but Ni(OAc)₂·4H₂O was used instead of Ni(ClO₄)₂·6H₂O. Colour: dark-green. Yield: 753 mg (85 %). Anal. Calcd. for C₂₂H₃₀N₃NiO₃: C 59.62%, H 6.82%, N 9.48 %. Found: C 59.84%, H 6.70%, N 9.37 %. FTIR (KBr, cm⁻¹): 1641 s (ν_{C=N} & ν_{C=O}).

2.2.2.5 Synthesis of [Ni₂(L^a)₂(μ_{1,1}-N₃)₂] (52)

Ni(NO₃)₂·6H₂O (582 mg, 2.0 mmol) and HL^a (2.0 mmol) were combined in 30 mL of methanol and stirred well for 15 min. Then, 10 mL methanol-water solution (9:1, v/v) of NaN₃ (130 mg, 2 mmol) was added to it and the solution mixture was allowed stirring for additional 10 min and filtered. Slow evaporation of the resulting green solution gave a dark-green crystalline compound containing X-ray diffraction quality plate like dark-green single crystals. Yield: 523 mg; 72%. Anal. Calcd. for C₃₀H₄₈N₁₂Ni₂O₂: C 49.62%, H 6.66%, N 23.15%. Found: C 49.84%, H 6.64%, 22.96 %. FTIR (KBr, cm⁻¹): 2052 vs (ν_{N₃⁻}); 1626 s (ν_{C=N}).

2.2.2.6. Synthesis of [Ni₂(L^a)₂(μ_{1,1}-NCO)₂] (53)

Complex **53** was synthesized adopting the identical procedure as described for **52**, except that NaNCO was used instead of NaN₃. Colour: Dark-green. Yield: 508 mg (70 %). Anal. Calcd. for C₃₂H₄₈N₈Ni₂O₄: C 52.93%, H 6.66%, N 15.43 %. Found: C 53.18%, H 6.50%, N 15.30 %. FTIR (KBr, cm⁻¹): 2173 vs (ν_{NCO⁻}); 1626 s (ν_{C=N}).

2.2.2.7. Synthesis of [Ni₂(HL^a)₂(μ_{1,1}-NCS)₄].CH₃OH (54)

Complex **54** was synthesized following the same methodology applied for the synthesis of **52**, but NH₄SCN was used in place of NaN₃. (Yield: 724 mg; 80%). Anal. Calcd. for C₃₅H₅₄N₁₀Ni₂O₃S₄: C 46.27%, H 5.99%, N 15.42 %. Colour: dark-green. Found: 46.50%, H 5.95%, N 15.35 %. FTIR (KBr, cm⁻¹): 2085 vs, 2003 vs (ν_{NCS⁻}); 1649 s (ν_{C=N}).

Table 2.1. Crystallographic data and structural refinement parameters of **50–54**

	50	51	52	53	54
Empirical formula	C ₃₀ H ₄₂ Cl ₂ N ₆ NiO ₁₀	C ₂₂ H ₃₀ N ₃ NiO ₃	C ₃₀ H ₄₈ N ₁₂ Ni ₂ O ₂	C ₃₂ H ₄₈ N ₈ Ni ₂ O ₄	C ₃₅ H ₅₀ N ₁₀ Ni ₂ O ₃ S ₄
Formula weight (g mol ⁻¹)	776.31	443.20	726.22	726.20	904.51
Temperature (K)	150(2)	150(2)	150(2)	150(2)	180(2)
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> (Å)	8.9692(4)	8.0642(2)	10.8264(6)	10.8271(7)	10.8625(3)
<i>b</i> (Å)	9.8140(4)	15.4540(4)	15.9223(8)	15.8847(10)	12.3213(3)
<i>c</i> (Å)	20.2915(7)	17.5161(6)	19.0138(11)	19.0150(13)	15.8254(4)
α (deg)	90.00	90	90.00	90.00	90.00
β (deg)	101.814(2)	101.7440(10)	90.451(2)	90.578(2)	104.3490(10)
γ (deg)	90.00	90	90.00	90.00	90.00
volume (Å ³)	1748.30(12)	2137.23(11)	3277.5(3)	3270.1(4)	2052.00(9)
<i>Z</i>	2	4	4	4	2
<i>D</i> _{calc} (g cm ⁻³)	1.477	1.377	1.472	1.475	1.464
μ (mm ⁻¹)	0.771	0.935	1.198	1.202	1.169
<i>F</i> (000)	814	940	1536	1536	948
θ Range (deg)	2.05–26.41	2.38–29.17	1.668–26.445	2.142–27.155	1.94–27.92
Reflections collected	35922	35679	30691	38986	24860
Independent reflections (<i>R</i> _{int})	3589(0.0416)	5749(0.0338)	6717(0.0571)	7233(0.0725)	4912(0.0474)
Observed reflections [<i>I</i> > 2 σ (<i>I</i>)]	2817	4789	4770	4734	3789
Data/restraints/parameters	2817/0/268	4789/1/268	4770/2/427	4734/0/427	3789/1/257
Goodness-of-fit on <i>F</i> ²	1.065	1.026	1.180	1.035	1.064
Final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0620, w <i>R</i> ₂ = 0.1569	<i>R</i> ₁ = 0.0312, w <i>R</i> ₂ = 0.0699	<i>R</i> ₁ = 0.0775, w <i>R</i> ₂ = 0.1799	<i>R</i> ₁ = 0.0669, w <i>R</i> ₂ = 0.1603	<i>R</i> ₁ = 0.0360, w <i>R</i> ₂ = 0.0774
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0799, w <i>R</i> ₂ = 0.1732	<i>R</i> ₁ = 0.0436, w <i>R</i> ₂ = 0.750	<i>R</i> ₁ = 0.1132, w <i>R</i> ₂ = 0.1988	<i>R</i> ₁ = 0.1143, w <i>R</i> ₂ = 0.1603	<i>R</i> ₁ = 0.0518, w <i>R</i> ₂ = 0.0849
Largest diff. peak/hole (e Å ⁻³)	0.735/–0.784	0.483/–0.245	1.512/–0.709	3.200/–0.883	0.603/–0.584

2.3. Results and Discussion

2.3.1 Syntheses and general characterizations

The condensation reaction of *N,N*-dimethyldipropylenetriamine with salicylaldehyde in a 1:1 molar ratio in methanol resulted Schiff base HL^a (Scheme 2.1). Reaction of this *in situ* generated Schiff base with Ni(ClO₄)₂·6H₂O and Ni(OAc)₂·4H₂O afforded dark-green crystalline compounds of [Ni(HL^a)₂](ClO₄)₂ (**50**) and [Ni(L^a)(sal)] (**51**), respectively. Synthesis of **50** and **51** is not sensitive to the stoichiometry of the reactants as both 1:1 and 1:2 molar ratios of metal salt and HL^a produced the same compounds. Among them, the later stoichiometry was adopted for better yields. Although we used triethylamine base for the synthesis of **50** and **51**, the deprotonated Schiff base L binds the metal centre as a tetradentate ligand in **51**, while the zwitterionic form of Schiff base is coordinated to metal centre in the tridentate fashion leaving the quaternary nitrogen free from coordination in **50**. The reaction of Schiff base HL^a with Ni(NO₃)₂·6H₂O and NaN₃ in aqueous methanol in a 1:1:1 molar ratio afforded a dark-green compound **52** of molecular formula [Ni₂(L^a)₂(μ_{1,1}-N₃)₂]. Similar reaction with NaNCO in aqueous methanol produced [Ni₂(L^a)₂(μ_{1,1}-NCO)₂] (**53**), which is an isomorphic compound to that of complex **52** presenting cyanato as the bridging ligand. But in an identical reaction condition if thiocyanate is used instead, the dinuclear compound [Ni₂(HL^a)₂(μ_{1,1}-NCS)₄].CH₃OH (**54**) was isolated, featuring analogues bridging as that found in azido (**52**) and cyanato (**53**) complexes. However, it is slightly different from other two compounds as the zwitterionic form of the Schiff base is coordinated to the metal centre in tridentate fashion instead of tetradentate anionic L^a bound to Ni(II) in **52** and **53**. It is important to note that addition of one equivalent of triethylamine eventually yielded identical product. Although some dissimilarity associated with mode of bonding of the Schiff base ligand to the metal centres are observed in these complexes, the remarkable structural resemblances are found in the bridging regions of these compounds, which is very

uncommon in pseudohalido bridged coordination chemistry in the presence of same organic blocking ligands.

2.3.2 IR Spectroscopy

IR spectroscopy is a useful tool to characterize counterion, bridging ligand, Schiff base ligand etc. Among five compounds, only **50** is an ionic compound, having ClO₄⁻ as a counter anion. The characteristic stretching and bending vibrations of ClO₄⁻ ions are observed at 1076 and 621 cm⁻¹, respectively, in the IR spectrum of **50**. The stretching vibrations of the azomethine (C=N) bond of the Schiff base are located in the range 1626–1649 cm⁻¹ in the IR spectra of **50** and **52–54**. However, the stretching vibration of azomethine bond together with the carbonyl group of salicylaldehyde was appeared at 1641 cm⁻¹ in **51**. The IR spectrum of **52** exhibits a strong and sharp band at 2052 cm⁻¹, characteristic to the asymmetric stretching vibration of the bridging azido ligand, which is similar to those, observed in analogous compounds [22–44]. The asymmetric stretching vibration of the bridging NCO⁻ ion for **53** is found at 2173 cm⁻¹ [40,60]. The IR spectrum of **54** consists of bifurcated bands at 2085 and 2003 cm⁻¹ corresponding to the asymmetric stretching vibrations of NCS⁻ ligands. The appearance of two strong peaks in the IR spectrum in **54** suggests the presence of both bridging and terminal thiocyanato ligands, consistent with the structural characterization of **54** (Figure 2.1). The higher frequency band is typical for bridging thiocyanato group whereas the lower frequency is assigned to an N-coordinated terminal thiocyanato ligand [70].

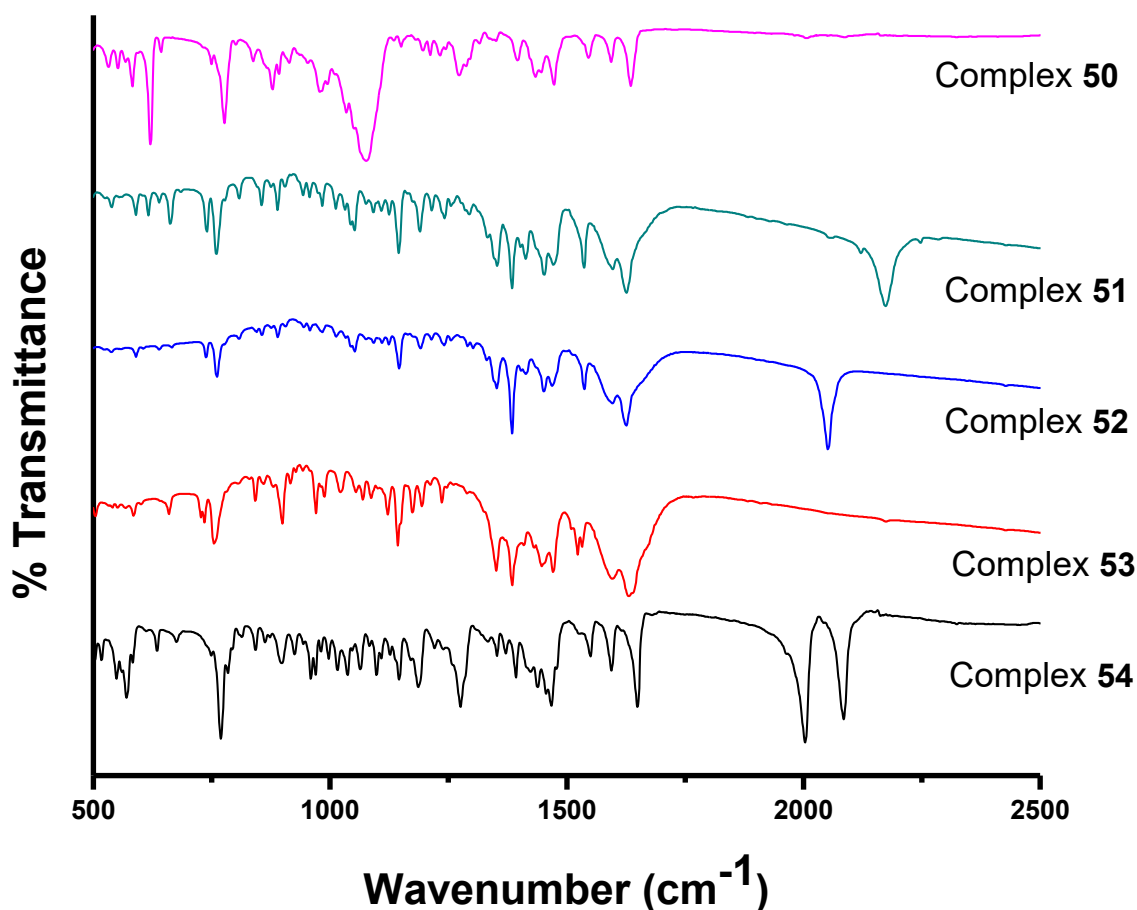


Figure 2.1: IR Spectroscopy of the complex 50-54

2.3.3. Description of crystal structures

The crystal structures of complexes **50–54** along with partial atom-numbering schemes are depicted in [Figures 2.2–2.6](#), respectively, and selected metric parameters in the metal coordination spheres are listed in [Table 2.1](#).

2.3.3.1. Mononuclear complexes **50** and **51**

Both **50** and **51** crystallize in the monoclinic space group $P2_1/c$. Neutral complex **51** crystallizes on a general position, while the complex cation of **50** crystallizes on an inversion centre together with a perchlorate counter ion on a general position. Two perchlorate ions per Ni in **50** requires protonation of the tertiary amine-N of the Schiff base ligands to balance

charge of the system i.e. the zwitterionic form of the Schiff base is bonded to the metal centre in **50**, while deprotonated Schiff base L^a binds the metal centre in **51**. The Ni(II) ion in both compounds is hexacoordinated, and the geometry around the metal centre can be best described as a distorted octahedral. The coordination sphere of Ni(II) in **50** is composed of {N₄O₂} donor set, while it is {N₃O₃} in **51**. Two zwitterionic Schiff base ligands connect the metal centre through phenolato-O, imine-N and secondary amine-N leaving protonated tertiary amine group free from coordination, and each of the zwitterionic ligands coordinates Ni(II) in the facial configuration in **50**. While only one deprotonated Schiff base binds the metal centre through all four donor sites including tertiary amine-N in **51**. The coordination sphere in **51** is completed by the coordination of deprotonated salicylaldehyde ligand using both phenolato-O and carbonyl-O. The imine, secondary amine and tertiary amine nitrogen atoms occupy one meridional position of hexacoordinate Ni(II) in **51**, while other meridional position is occupied by phenolato-O atom of the Schiff base together with two oxygen atoms from the deprotonated salicylaldehyde ligand. Ni–N distances of imine and secondary amine and Ni–O distances of phenolato group of the Schiff base ligand in **50** are found to be 2.049(5), 2.186(6) and 2.077(4) Å, respectively, which are comparable to bond distances observed in analogues Ni(II) complexes with similar coordination environments [28,29,62–65]. The imine bonds are somewhat shorter than the secondary amine nitrogen, which is along with line of their respective state of hybridization of coordinated nitrogen atoms. Similar observation is also made in **51** where the secondary amine nitrogen bond is found significantly longer than the imine nitrogen bond (Table 2.2). Furthermore, the significantly longer bond distance of tertiary amine over secondary amine group observed in the structure of **51** is probably due to the presence of two methyl substitutions at tertiary amine, which in turn increased the steric congestion around donor site, thereby leading to the weaker binding ability of the tertiary amine to the metal centre.

2.3.3.2 Dinuclear complexes 52–54

52 and **53** are isostructural and isomorphous compounds, and they crystallize in the monoclinic space group $P2_1/c$. The structures of **52** and **53** consist of neutral dimeric units of formulas $[\text{Ni}_2(\text{L}^{\text{a}})_2(\mu_{1,1}\text{-N}_3)_2]$ and $[\text{Ni}_2(\text{L}^{\text{a}})_2(\mu_{1,1}\text{-NCO})_2]$, respectively. In these complexes, each Ni(II) centre is hexacoordinated with a distorted octahedral geometry, being bonded with three N donor atoms and one phenolato-O atom of the deprotonated Schiff base ligand and two N atoms of the end-on bridging azido groups, which form the common edge within the dinuclear units, leading to edge-sharing bioctahedral structure. Likewise **51**, all the nitrogen atoms (imine, secondary amine and tertiary amine nitrogen atoms) of the triamine part of the deprotonated Schiff base coordinates Ni(II) in the meridional configuration, while the remaining meridional position is occupied by phenolato-O atom of the Schiff base together with two nitrogen atoms of bridging azido (in **52**) and cyanato (in **53**) ligands. Again, similar trend of bond lengths as found in compound **51** i.e. $\text{Ni-N}(\text{tertiary amine}) > \text{Ni-N}(\text{secondary amine}) > \text{Ni-N}(\text{imine})$, is observed in these complexes (Table 2.2). Although the absence of an inversion centre brings two different bridging angles in these complexes ($100.7(2)$ and $102.0(2)^\circ$ for **52**; $97.84(15)$ and $98.74(15)^\circ$ for **53**), the central NiN_2Ni rings are found eventually planar. The azido and cyanato ligands are nearly linear with N-N-N and N-C-O angles varying in the range $178.6(7)$ – $178.8(7)^\circ$ and $179.1(6)$ – $179.3(6)^\circ$, respectively. The slightly asymmetric double end-on azido bridge (with Ni-N bond distances of $2.121(5)/2.132(5)\text{\AA}$ and $2.227(5)/2.199(5)\text{\AA}$) separates the two Ni(II) ions by $3.357(5)\text{\AA}$, which are comparable to those of the previously reported analogous Ni(II) complexes [22–44]. Similar asymmetric double end-on cyanato bridging ($2.107(4)/2.115(4)\text{\AA}$ vs. $2.244(4)/2.280(4)\text{\AA}$) with $\text{Ni}\cdots\text{Ni}$ separation of $3.357(5)\text{\AA}$ is observed in **53**. Unlike azido bridging, the doubly end-on bridging NCO^- is extremely uncommon in Ni(II) coordination chemistry, and it is important to note that only three dinickel(II) compounds

with such bridging motif are reported in the literature [40,60]. However, in both compounds, the secondary amine hydrogen atom participates in an intramolecular hydrogen bonding to the phenoxido oxygen atom within the dimeric unit with donor-acceptor distances of 3.009 Å and 3.013 Å in **52** and **53**, respectively.

Compound **54** crystallizes in the monoclinic space group $P2_1/c$ and consists of a centrosymmetric dinuclear $[\text{Ni}_2(\text{HL}^{\text{a}})_2(\mu_{1,1}\text{-NCS})_4]$ unit and a disordered lattice methanol molecule. Ni(II) centres have a distorted octahedral structure with $\{\text{NiN}_6\}$ coordination environment, being bonded with two N donor atoms (one each of imine and secondary amine) and phenolato-O atom of the zwitterionic Schiff base, two N atoms of the $\mu_{1,1}$ -bridging thiocyanato groups, which form the common edge within the dinuclear unit, and a terminal thiocyanato ligand. Unlike **50**, the zwitterionic Schiff base connects the metal centre in the meridional configuration, while the remaining meridional position is occupied by thiocyanato ligands. Being centrosymmetric, the central $\{\text{NiN}_2\text{Ni}\}$ core is planar with bridging angle of $98.50(7)^\circ$ and Ni...Ni separation of 3.347(7)Å. Both, bridging and terminal thiocyanato groups are quasilinear, with N–C–S angles of $178.2(2)$ and $179.4(2)^\circ$, respectively. Compound **54** is very similar to that of **52** and **53** in that NCS^- ions feature analogues end-on bridging as that found in azido (**52**) and cyanato (**53**) complexes. However, the structural difference that found in these systems is mainly associated with diverse binding propensity of the ligand – tetradentate monoanionic Schiff base ligand binds Ni(II) in **52** and **53**, while the zwitterionic tridentate ligand binds the metal centre in **54** along with a terminal thiocyanato ligand to satisfy the coordination number six of Ni(II) centre as well as to balance the charge of the system. Likewise **52** and **53**, the secondary amine hydrogen atom is involved in an intradimer hydrogen bonding to the phenoxido oxygen atom within the dimeric unit with donor-accepter distance of 3.122 Å. Remarkably, the quaternary amine hydrogens participate in an intermolecular hydrogen bonding with phenolato-O atoms of the

Schiff bases from the adjacent dimeric units, resulting in the formation of 2D supramolecular structure in the *bc* plane (Figure 2.7). It is worth noting that end-to-end thiocyanato bridged dinickel(II) complexes are quite common in the literature [34,47–55]. In contrast, the end-on bridging dinickel(II) complexes are extremely scarce in the literature. In fact, only three of such structurally characterized complexes are available in the literature [61,71,72].

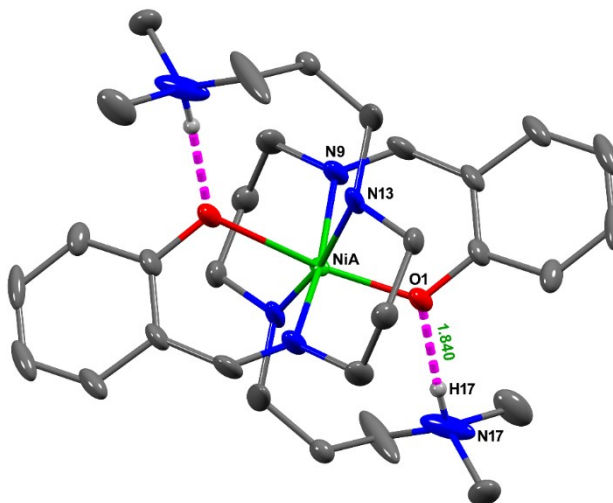


Figure 2.2: Crystal structure of **50** showing the atom numbering scheme. Ellipsoids are drawn at 30% probability level. H atoms are omitted for clarity. O–H...N bonding interactions are drawn as purple dashed lines.

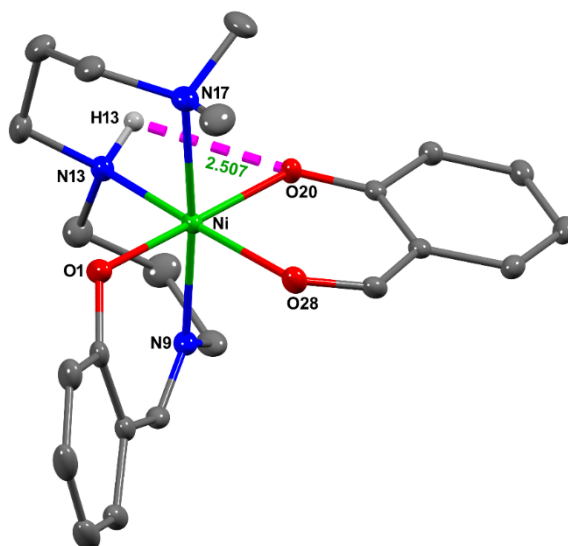


Figure 2.3: Crystal structure of **51** showing the atom numbering scheme. Ellipsoids are drawn at 30% probability level. O–H...N bonding interactions are drawn as purple dashed lines.

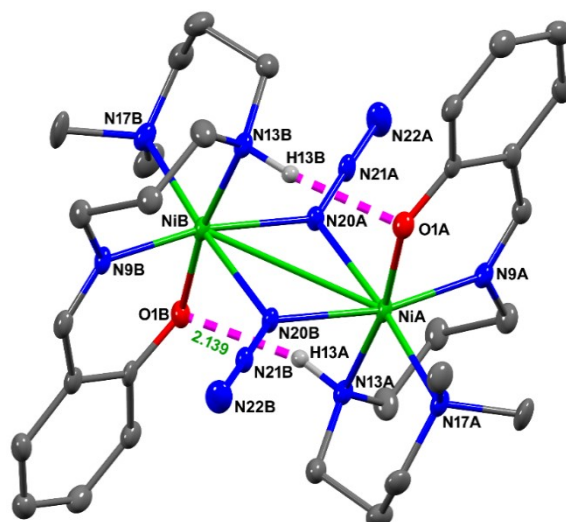


Figure 2.4: Crystal structure of **52** showing the atom numbering scheme. Ellipsoids are drawn at 50% probability level. O–H···N bonding interactions are drawn as purple dashed lines.

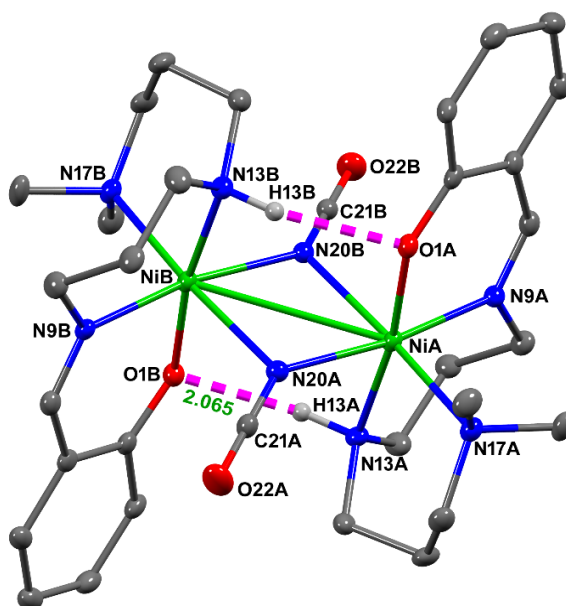


Figure 2.5: Crystal structure of **53** showing the atom numbering scheme. Ellipsoids are drawn at 30% probability level. O–H···N bonding interactions are drawn as purple dashed lines.

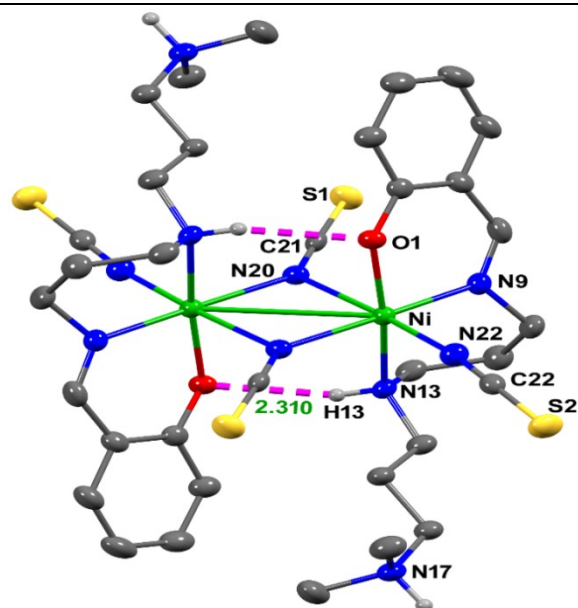


Figure 2.6: Crystal structure of **54** showing the atom numbering scheme. Ellipsoids are drawn at 30% probability level. O–H···N bonding interactions are drawn as purple dashed lines.

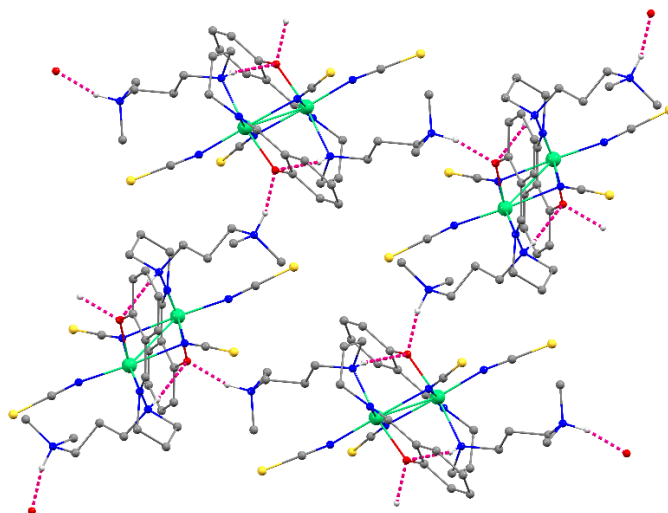


Figure 2.7: Hydrogen bonded supramolecular 2D sheet of **54** in the *bc* plane showing both inter- and intra-molecular hydrogen bonding interactions.

Table 2.2 Selected bond distances (Å) for **50–54**

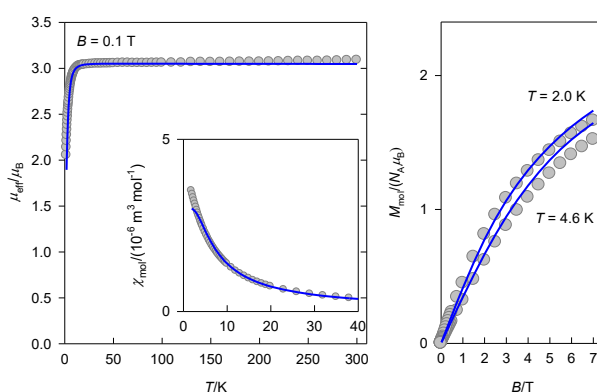
Bond	50	51	52	53	54
Ni(II)–N(imine)	2.052(3)	2.0507(13)	2.046(5) 2.053(5)	2.059(4) 2.057(4)	2.0298(17)
Ni(II)–N(secondary amine)	2.190(4)	2.1119(13)	2.128(5) 2.144(5)	2.154(4) 2.132(4)	2.1433(19)
Ni(II)–N(tertiary amine)	–	2.1979(13)	2.186(5) 2.198(5)	2.214(4) 2.205(4)	–
Ni(II)–O(phenolate)	2.075(3)	2.0284(10) 2.0078(10)	2.005(4) 2.014(4)	2.020(3) 2.006(3)	2.0570(15)
Ni(II)–N(pseudohalide)	–	–	2.121(5) 2.227(5) 2.132(5) 2.199(5)	2.107(4) 2.244(4) 2.115(4) 2.280(4)	2.1291(17) 2.2871(19)# 2.050(2)

Symmetry code: $-x, -y, -z$

2.3.4. Magnetic Studies

2.3.4.1. Mononuclear complexes

The effective magnetic moment for **50** adopts its room temperature value of $\mu_{\text{eff}} = 3.09 \mu_{\text{B}}$ and it stays constant down to 12 K when it drops down in an abrupt manner; at $T = 1.9$ K it is $\mu_{\text{eff}} = 2.05 \mu_{\text{B}}$ (Figure 2.8). This feature is typical for the zero-field splitting (zfs) of the $S = 1$ spin system with the axial zfs parameter $D > 0$ [73]. The magnetization per formula unit at $T = 2.0$ K and $B = 7.0$ T adopts a subnormal value of $M_1 = M_{\text{mol}}/N_{\text{A}}\mu_{\text{B}} = 1.66$ which also confirms a considerable zfs.

**Figure 2.8.** Magnetic data for **50**. Lines – fitted.

The magnetic data (molar magnetic susceptibility and molar magnetization) was fitted simultaneously by minimizing a joint functional $F = w \cdot R(\chi) + (1-w) \cdot R(M)$ with equal weights, $w = 0.5$. The spin Hamiltonian of the form

$$\hat{H}_k = D(\hat{S}_z^2 - \vec{S}^2/3)\hbar + g_x \hat{S}_x \hat{S}_x + g_y \hat{S}_y \hat{S}_y + g_z \hat{S}_z \hat{S}_z \quad (1)$$

yields the eigenvalues which enter the partition function and consequently the susceptibility and magnetization are reconstructed by using the apparatus of the statistical thermodynamics [74]. The fitting procedure gave the set of magnetic parameters as listed in Table 2.3; there is $D/hc = +7.2 \text{ cm}^{-1}$ and $g_z < g_x$ as predicted by the spin Hamiltonian theory [75].

The complex **51** displays temperature-independent effective magnetic moment $\mu_{\text{eff}} = 3.10 - 3.06 \mu_B$ between the room temperature and $T = 12 \text{ K}$; below this temperature its decrease is registered towards a limit of $\mu_{\text{eff}} = 2.63 \mu_B$ at $T = 1.9 \text{ K}$ (Figure 2.9). The magnetization data develops with the field differently when compared to **50**: there is a saturation of $M_1 = 2.0$ at $T = 2.0 \text{ K}$ and $B = 7.0 \text{ T}$. Both these features are characteristic for $D < 0$. Indeed, the fitting procedure confirmed $D/hc = -5.2 \text{ cm}^{-1}$ and $g_z > g_x$.

Table 2.3. Magnetic parameters for **50** through **54**.

System	J/hc / cm^{-1}	D/hc / cm^{-1}	g_z	g_x	χ_{TIM}^a	zj/hc / cm^{-1}	$R(\chi)$ /%	$R(M)$ /%	Ni-N-Ni /deg
50	-	+7.21	2.093	2.180	0	0	6.3	5.8	
51	-	-5.16	2.320	2.121	0	0	1.8	1.9	
52	+20.0	+5.12	2.376	-	0	- 0.060	1.3		100.7, 102.0
53	+13.7	+7.18	2.187	-	4.7		2.0	1.7	97.8, 98.7
54	+12.4	+6.87	2.118	-	10		4.3	2.1	98.5

^a χ_{TIM} in units of $10^{-6} \text{ m}^3 \text{ mol}^{-1}$. R – discrepancy factors of the fit.

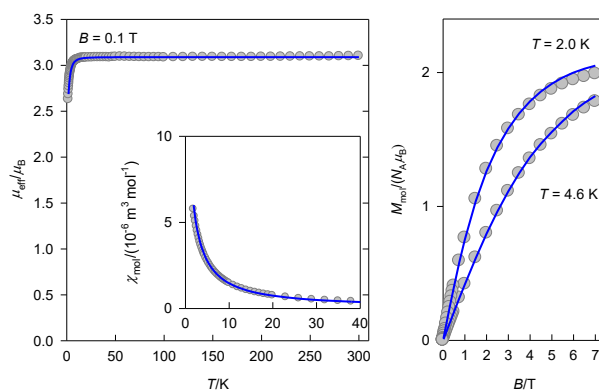


Figure 2.9. Magnetic data for **51**. Lines – fitted.

The difference in the sign of the D-parameter originates in the geometry of the chromophore {NiN₂N'O₂} for **50** and {NiN₃O₃} for **51**. The averaged bond lengths (Å) in **50** are $d(\text{Ni-N9}) = 2.052$, $d(\text{Ni-N13}) = 2.190$, and $d(\text{Ni-O1}) = 2.075$; the displacements from the averaged distances $\bar{d}(\text{Ni-N}) = 2.145$ and/or $\bar{d}(\text{Ni-O}) = 2.055$ are $\delta_i = (d_i - \bar{d}_i)$, i.e. $\delta(\text{Ni-N}) = -0.093$, $\delta(\text{Ni-N}') = 0.045$, and $\delta(\text{Ni-O}) = 0.020$ Å. Two similar displacements define equatorial plane of the bipyramid so that the chromophore behaves like a compressed bipyramid with the structural tetragonality parameter $D_{\text{str}} = \delta_z - (\delta_x + \delta_y)/2 = -12.55$ pm. However, the situation, is more complexed since the occupation number of the Ni site is only 0.5 and there are two NiA centres with the occupation numbers 0.25 and the distances $d(\text{NiA-O1}) = 1.887$ and 2.297 , $d(\text{NiA-N9}) = 1.998$ and 2.158 , and $d(\text{NiA-N13}) = 1.917$ Å.

In the complex **51** with the *mer*-{NiN₃O₃} chromophore all metal-ligand distances are different: $d(\text{Ni-O1}) = 2.0078$, $d(\text{Ni-O20}) = 2.0284$, $d(\text{Ni-O28}) = 2.1062$, $d(\text{Ni-N9}) = 2.0507$, $d(\text{Ni-N13}) = 2.1119$, and $d(\text{Ni-N17}) = 2.1979$ Å; the displacements are $\delta(\text{Ni-O1}) = -0.0472$, $\delta(\text{Ni-O20}) = -0.0266$, $\delta(\text{Ni-O28}) = 0.0512$, $\delta(\text{Ni-N9}) = -0.0943$, $\delta(\text{Ni-N13}) = -0.0331$, and $\delta(\text{Ni-N17}) = 0.0529$ Å. Thus it is difficult to simplify these data to a compressed or elongated tetragonal bipyramid in order to determine the structural tetragonality parameter D_{str} . However, this can be done by averaging *trans*-positioned distances: $\delta_1 = -0.0369$, $\delta_2 =$

0.00905, and $\delta_3 = -0.0207$. Now, the D_{str} parameter can be calculated in three ways using a constraint $E_{\text{str}} = (\delta_x - \delta_y)/2 < |D_{\text{str}}|/3$. Then $\delta_z = \delta_2$ and $\delta_{xy} = -0.0288$ gave $D_{\text{str}} = +3.785$, $E_{\text{str}} = 0.81$ pm, and $E/|D| = 0.21$.

It was found [76] that in a series of mononuclear Ni(II) complexes with the {NiA₄B₂} chromophore the structural tetragonality parameter D_{str} correlates with the magnetic anisotropy parameter D along a straight line with a positive slope. The original dataset has been enriched by some recent investigations [77-80]. The complexes **50** and **51**, however, do not match such a correlation probably owing to the problematic determination of D_{str} parameter.

2.3.4.2. Dinuclear complexes

The dinuclear complex **54** shows that the effective magnetic moment on cooling increases from its room temperature value $\mu_{\text{eff}} = 4.51 \mu_{\text{B}}$. (Figure 2.10). It passes through a maximum at $T = 8.7$ K and then drops down to $\mu_{\text{eff}} = 4.44 \mu_{\text{B}}$ at $T = 1.9$ K. The magnetization grows to $M_1 = 3.8$ at $T = 2.0$ K and $B = 7.0$ T. These data confirm a presence of the exchange interaction of a ferromagnetic nature ($J > 0$) and some zero-field splitting that operates at low temperature.

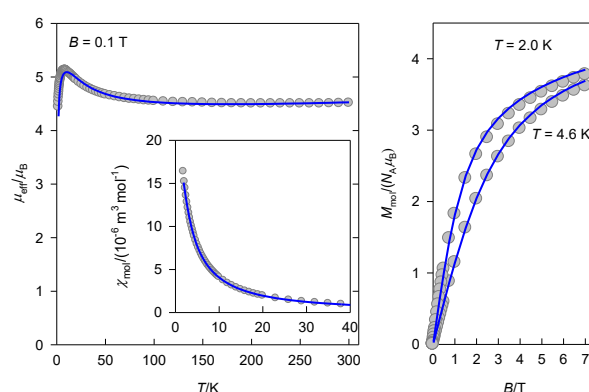


Figure 2.10. Magnetic data for **54**. Lines – fitted.

The magnetic data was fitted by using the spin Hamiltonian for a dinuclear system with the isotropic exchange and zfs

$$\hat{H}_k = -J(\vec{S}_A \cdot \vec{S}_B) \hbar \quad \overline{A=1} \quad \hbar \quad (2)$$

$$+ \sum_{A=1}^2 \mu_B B (g_{A,z} \hat{S}_{A,z} \cos \vartheta_k + g_{A,xy} \hat{S}_{A,x} \sin \vartheta_k) \hbar$$

Eventually the molecular field correction (*zj*) and temperature-independent magnetism χ_{TIM} can be applied

$$\chi = \chi^{\text{sh}} / [1 - (zj)\chi^{\text{sh}}] + \chi_{\text{TIM}} \quad (3)$$

In order to reduce the set of free parameters, isotropic Zeeman term has been considered ($g_z = g_x$). The final set of magnetic parameters is listed in [Table 2.3](#).

The positive exchange coupling constant can be rationalized by the bonding angle Ni-N-Ni = 98.50 deg that is close to the critical value when the ferromagnetic exchange prevails [81].

The {NiN₅O} chromophore is rather distorted with all metal-ligand distances being different.

The remaining two dinuclear complexes, **52** and **53**, display analogous magnetic functions to **54** ([Figures 2.11](#) and [2.12](#)) with the ferromagnetic exchange coupling and sizable zero-field splitting of the easy-plane character ($D > 0$).

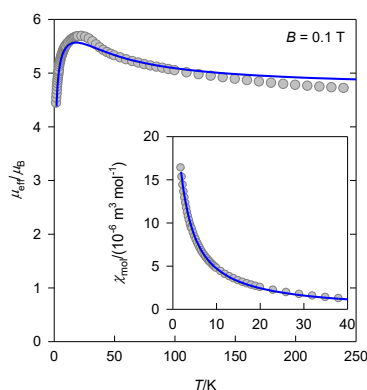


Figure 2.11. Magnetic data for **52**. Lines – fitted.

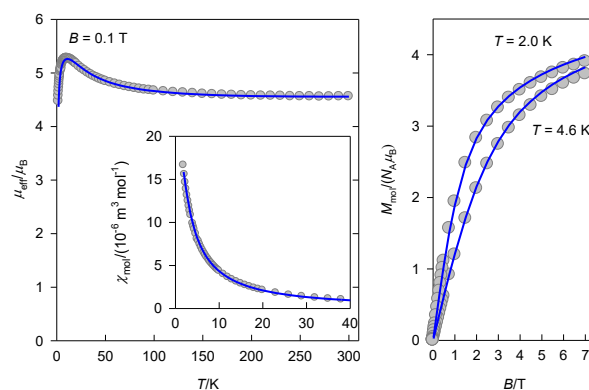


Figure 2.12. Magnetic data for **53**. Lines – fitted.

Among the several structural parameters that can affect the strength and sign of the exchange coupling constant (J) between the paramagnetic centers, the bridging angle is considered the most crucial factor in determining the net magnetic interaction. Theoretical studies by Ruiz *et al.* on doubly $\mu_{1,1}$ -azido bridged dinickel(II) complexes have revealed that the interaction predicted to be ferromagnetic on all values of Ni–N(N_3)–Ni angles (θ) ranging from 80° to 115° , with J increasing upon increasing this angle, reaching a maximum at around 104° and then decreases with increasing θ [45,46]. In fact, all the reported $\mu_{1,1}$ -azido bridged nickel(II) dimers exhibit ferromagnetic coupling [22–40,42–44] with only one exception where very low bridging angle of 90.4° propagates the AF interaction between Ni(II) centers [41]. The Ni–N–Ni angles of $100.7(2)^\circ$ and $102.0(2)^\circ$ found in **52** are very typical for this kind of systems, and thus the sign and magnitude of calculated J in **52** is reasonable. For bis($\mu_{1,1}$ -NCO) bridged Ni(II) dimers, the existing data are extremely scarce, and only three data set on such compounds are available in the literature where J values vary in the narrow range $+3.4$ to $+9.2 \text{ cm}^{-1}$ (Table 2.4) [40,60]. Similar ferromagnetic interaction is also observed in **53**, however, the magnetic coupling is found somewhat stronger in the present case. Although this dataset is too low to permit the proper magneto structural correlation, the similar trend that found in the theoretical prediction with doubly $\mu_{1,1}$ -azido bridged dinickel(II) systems, i.e. the J increasing with the increase of bridging angle, is observed in the cyanato bridged

systems. However, the reason for weaker coupling for cyanato bridged compounds compared to analogues azido systems can be understandable by means of theoretical calculations [40]. Interestingly, in the only previous example with doubly $\mu_{1,1}$ -thiocyanato bridged dinickel(II) complex, the magnetic coupling between the metal centers has found to be an antiferromagnetic with the J value of -13.2 cm^{-1} (Table 2.4) [61]. In contrast, the observed magnetic coupling is the ferromagnetic in nature in **54** with coupling constant of $+12.4 \text{ cm}^{-1}$. The Ni–N–Ni bridging angle found in that previously reported compound is 96.9° , while it is 98.50° in **54**. Careful inspection of the magneto-structural data of these doubly $\mu_{1,1}$ -pseudohalido bridged dinickel(II) systems reveals that, for azido bridged systems, [42] the smallest experimentally found bridging angle 90.4° leads to the very weak AF interaction (-1.77 cm^{-1}), while the next lowest angle of $95.5(3)/96.5(3)$ is responsible for significantly strong F interaction ($+31.62 \text{ cm}^{-1}$). Although the ferromagnetic coupling is predicted in the range of bridging angles 80 to 115° by theoretical means, the overestimation of J values cannot be ruled out especially at lower bridging angles. However, these experimental facts suggest that the bis($\mu_{1,1}$ -N₃) bridging groups could not be the universal ferromagnetic coupler in Ni(II) systems and the crossover angle for bis($\mu_{1,1}$ -azido) bridged dinickel(II) is closely located near about 91° . Similarly, the experimental facts indicate that the crossover angle is situated in-between 96.9° and 98.50° for thiocyanato system, and it might be just below 94° for cyanate bridging systems. It is interesting to note from these magneto-structural data that on moving from azido to cyanato to thiocyanato systems, the crossover angle is expected to move in higher values. More examples of doubly $\mu_{1,1}$ -NCO and $\mu_{1,1}$ -NCS bridged dinickel(II) systems and some data at lower $\mu_{1,1}$ -N₃ bridging angles along with sophisticated theoretical calculations are further required to reinforce the above conclusions.

Table 2.4. Selected structural and magnetic data of Ni(II) dimers with doubly end-on cyanato and thiocyanato bridges^a

Compounds	D/hc /cm ⁻¹	g	M–N–M (°)	J/hc /cm ⁻¹	Refs.
[Ni ₂ (L ²⁹) ₂ (μ _{1,1} -NCO) ₂](ClO ₄) ₂	+3.6	2.23	94.4(3), 95.8(4)	+3.4	40
[Ni ₂ (L ²⁸) ₂ (μ _{1,1} -NCO) ₂](ClO ₄) ₂	-12.32	2.21	95.33(13), 95.79(12)	+5.6	40
[Ni ₂ (terpy) ₂ (μ _{1,1} -NCO) ₂ (H ₂ O) ₂](PF ₆) ₂	+3.6	2.23	97.7(4)	+ 9.2	60
[Ni ₂ L ^a ₂ (μ _{1,1} -NCO) ₂] (53)	+7.18	2.187	97.84(15), 98.74(15)	+13.7	This work
[Ni ₂ (S-dept) ₂ (μ _{1,1} -NCS) ₂ (NCS) ₂]	-	2.142	96.9(8)	-13.2	61
[Ni ₂ (HL ^a) ₂ (μ _{1,1} -NCS) ₄]·CH ₃ OH (54)	+6.87	2.118	98.50(7)	+12.4	This work

^a terpy = terpyridine; L²⁹ = [N,N'-bis(2-pyridinylmethylene)]propane-1,3-diamine; L²⁸ = N,N'-bis(pyridin-2-yl)benzylidene]ethane-1,2-diamine; S-dept = N,N,N',N'-tetraethylpyridine-2,6-dithiocarboxamide.

2.4. Conclusions

We have synthesized some mono and dinuclear Ni(II) complexes with a new {N₃O} donor Schiff base ligand. X-ray structural analyses reveal the diverse coordination ability of the Schiff base in these compounds as both the zwitterionic form and the deprotonated ligand can bind the metal centre through tridentate and tetradentate fashions, respectively. The magnetic properties disclose some zero-field splitting for mononuclear complexes as expected for Ni(II) ion, and the exchange coupling of doubly end-on pseudohalido bridged complexes is found to be ferromagnetic in nature. Although a large number of bis(μ_{1,1}-N₃) bridged Ni(II) dimers are known, the analogues (μ_{1,1}-NCO) and (μ_{1,1}-NCS) bridged dinickel(II) complexes are extremely scarce in the literature and thus these compounds are important additions in the

family of such systems. Most remarkably, the thiocyanato compound is the first example of the ferromagnetically coupled system.

References

- [1] S. Accorsi, A. -L. Barra, A. Caneschi, G. Chastanet, A. Cornia, A. C. Fabretti, D. Gatteschi, C. Mortalò, E. Olivieri, F. Parenti, P. Rosa, R. Sessoli, L. Sorace, W. Wernsdorfer, L. Zobbi, *J. Am. Chem. Soc.* 2006, **128**, 4742.
- [2] A. Ferguson, J. Lawrence, A. Parkin, J. Sanchez-Benitez, K. V. Kamenev, E. K. Brechin, W. Wernsdorfer, S. Hill, M. Murrie, *Dalton Trans.* 2008, 6409.
- [3] J. M. Clemente-Juan, E. Coronado, A. Forment-Aliaga, A. Gaita-Arino, C. Gimenez-Saiz, F. M. Romero, W. Wernsdorfer, R. Biagi, V. Corradini, *Inorg. Chem.* 2010, **49**, 386.
- [4] H. -L. Sun, Z. -M. Wang, S. Gao, *Coord. Chem. Rev.* 2010, **254**, 1081.
- [5] M. Sarkar, R. Clerac, C. Mathoniere, N. G. R. Hearn, V. Bertolasi, D. Ray, *Inorg. Chem.* 2011, **50**, 3922.
- [6] M. Murugesu, M. Habrych, W. Wernsdorfer, K. A. Abboud, G. Christou, *J. Am. Chem. Soc.* 2004, **126**, 4766.
- [7] A. Bell, G. Aromí, S. J. Teat, W. Wernsdorfer, R. E. P. Winpenny, *Chem. Commun.* 2005, 2808.
- [8] S. Nayak, M. Evangelisti, A. K. Powell, J. Reedijk, *Chem. Eur. J.* 2010, **16**, 12865.
- [9] F. Meyer, S. Demeshko, G. Leibel, B. Kersting, E. Kaifer, H. Pritzkow, *Chem. Eur. J.* 2005, **11**, 1518.
- [10] G. Brunet, F. Habib, C. Cook, T. Pathmalingam, F. Loiseau, I. Korobkov, T. J. Burchell, A. M. Beauchemina, M. Murugesu, *Chem. Commun.* 2012, **48**, 1287.

- [11] J. Werner, M. Rams, Z. Tomkowicz, T. Runčevski, R. E. Dinnebier, S. Suckert, C. Näther, *Inorg. Chem.* 2015, **54**, 2893.
- [12] A. M. Ako, I. J. Hewitt, V. Mereacre, R. Clérac, W. Wernsdorfer, C. E. Anson, A. K. Powell, *Angew. Chem.* 2006, **118**, 5048.
- [13] J. Ribas, A. Escuer, M. Monfort, R. Vicente, R. Cortes, L. Lezama, T. Rojo, *Coord. Chem. Rev.* 1999, **193–195**, 1027.
- [14] A. Escuer, G. Aromí, *Eur. J. Inorg. Chem.* 2006, 4721.
- [15] Y. -F. Zeng, X. Hu, C. -F. Liu, X. -H. Bu, *Chem. Soc. Rev.* 2009, **38**, 469.
- [16] C. Adhikary, S. Koner, *Coord. Chem. Rev.* 2010, **254**, 2933.
- [17] X. -Y. Wang, Z. -M. Wang, S. Gao, *Chem. Commun.* 2008, 281.
- [18] S. Mukherjee, P. S. Mukherjee, *Acc. Chem. Res.* 2013, **46**, 2556.
- [19] T. C. Stamatatos, G. Christou, *Inorg. Chem.* 2009, **48**, 3308.
- [20] A. Escuer, J. Esteban, S. P. Perlepes, T. C. Stamatatos, *Coord. Chem. Rev.* 2014, **275**, 87.
- [21] P. Ghorai, A. Chakraborty, A. Panja, T. K. Mondal, A. Saha, *RSC Adv.* 2016, **6**, 36020.
- [22] S. Liang, Z. Liu, N. Liu, C. Liu, X. Di, J. Zhang, *J. Coord. Chem.* 2010, **63**, 3441.
- [23] S. S. Massoud, F. R. Louka, Y. K. Obaid, R. Vicente, J. Ribas, R. C. Fischerc, F. A. Mautner, *Dalton Trans.* 2013, **42**, 3968.
- [24] M. G. Barandika, R. Cortés, L. Lezama, M. K. Urtiaga, M. I. Arriortua, T. Rojo, *J. Chem. Soc., Dalton Trans.* 1999, 2971.
- [25] H. -D. Bian, W. Gu, Q. Yu, S. -P. Yan, D. -Z. Liao, Z. -H. Jiang, P. Cheng, *Polyhedron* 2005 **24**, 2002.
- [26] S. Sarkar, A. Mondal, A. Banerjee, D. Chopra, J. Ribas, K. K. Rajak, *Polyhedron* 2006, **25**, 2284.

- [27] S. Deoghoria, S. Sain, M. Soler, W. T. Wong, G. Christou, S. K. Bera, S. K. Chandra, *Polyhedron* 2003, **22**, 257.
- [28] P. Mukherjee, M. G. B. Drew, C. J. Gómez-García, A. Ghosh, *Inorg. Chem.* 2009, **48**, 5848.
- [29] S. K. Dey, N. Mondal, M. S. E. Fallah, R. Vicente, A. Escuer, X. Solans, M. Font-Bardía, T. Matsushita, V. Gramlich, S. Mitra, *Inorg. Chem.* 2004, **43**, 2427.
- [30] S. Sarkar, A. Mondal, M. S. E. Fallah, J. Ribas, D. Chopra, H. Stoeckli-Evans, K. K. Rajak, *Polyhedron* 2006, **25**, 25.
- [31] M. I. Arriortua, A. R. Cortes, L. Lezam, T. Rojo, X. Solans, M. Font-Bardia, *Inorg. Chim. Acta.* 1990, **174**, 263.
- [32] S. Nandi, D. Bannerjee, J. -S. Wu, T. -H. Lu, A. M. Z. Slawin, J. D. Woollins, J. Ribas, C. Sinha. *Eur. J. Inorg. Chem.* 2009, 3972.
- [33] A. Escuer, R. Vicente, M. S. E. Fallah, X. Solans, M. Font-Bardia, *Inorg. Chim. Acta.* 1996, **247**, 85.
- [34] R. Cortes, J. I. Ruiz de Larramendi, L. Lezama, T. Rojo, K. Urtiaga, M. I. Arriortua, J. Chem. Soc.; *Dalton Trans.* 1992, 2723.
- [35] S. Sain, S. Bid, A. Usman, H. -K. Fun, G. Aromic, X. Solans, S. K. Chandra, *Inorg. Chim. Acta.* 2005, **358**, 3362.
- [36] R. Vicente, A. Escuer, J. Ribas, M. S. E. Fallah, X. Solans, M. Font-Bardia, *Inorg. Chem.* 1993, **32**, 1920.
- [37] J. Ribas, M. Monfort, C. Diaz, C. Bastos, X. Solans, *Inorg. Chem.* 1994, **33**, 484.
- [38] X. -J. Lin, Z. Shen, Y. Song, H. -J. Xu, Y. -Z. Li, X. -Z. You, *Inorg. Chim. Acta.* 2005, **358**, 1963.
- [39] A. Escuer, R. Vicente, J. Ribas, X. Solans, *Inorg. Chem.* 1995, **34**, 1793.

- [40] M. Habib, T. K. Karmakar, G. Aromí, J. Ribas-Ariño, H. -K. Fun, S. Chantrapromma, S. K. Chandra, *Inorg. Chem.* 2008, **47**, 4109.
- [41] P. Chaudhuri, R. Wagner, S. Khanra, T. Weyhermüller, *Dalton Trans.* 2006, 4962.
- [42] A. Bhattacharyya, P. K. Bhaumik, M. Das, A. Bauzá, P. P. Jana, K. Harms, A. Frontera, S. Chattopadhyay, *Polyhedron* 2015, **101**, 257.
- [43] A. Solanki, M. Monfort, S. B. Kumar, *J. Mol. Struct.* 2013, **1050**, 197.
- [44] S. Sarkar, A. Datta, A. Mondal, D. Chopra, J. Ribas, K. K. Rajak, S. M. Sairam, S. K. Pati, *J. Phys. Chem. B*, 2006, **110**, 12.
- [45] E. Ruiz, J. Cano, S. Alvarez, P. Alemany, *J. Am. Chem. Soc.* 1998, **120**, 11122.
- [46] G. Manca, J. Cano, E. Ruiz, *Inorg. Chem.* 2009, **48**, 3139.
- [47] F. A. Mautner, M. Scherzer, C. Berger, R. C. Fischer, R. Vicente, S. S. Massoud, *Polyhedron* 2015, **85**, 20.
- [48] M. Monfort, J. Ribas, X. Solans, *Inorg. Chem.* 1994, **33**, 4271.
- [49] D. M. Duggan, D. N. Hendrickson, *Inorg. Chem.* 1974, **13**, 2929.
- [50] T. Rojo, R. Cortés, L. Lezama, M. I. Arriortua, K. Urtiaga, G. Villeneuve, *J. Chem. Soc., Dalton Trans.* 1991, 1779.
- [51] A. P. Ginsberg, R. C. Sherwood, R. W. Brookes, R. L. Martin, *J. Am. Chem. Soc.* 1971, **93**, 5927.
- [52] H. D. Bien, W. Gu, Q. Yu, S. P. Yan, D. Z. Liao, Z. H. Jiang, P. Cheng, *Polyhedron* 2005, **24**, 2002.
- [53] P. Bhowmik, S. Chattopadhyay, M. G. B. Drew, C. Diaz, A. Ghosh, *Polyhedron* 2010, **29**, 2637.
- [54] B. Larue, L. -T. Tran, D. Luneau, C. Reber, *Can. J. Chem.* 2003, **81**, 1168.
- [55] T. K. Maji, G. Mostafa, J. M. Clemente-Juan, J. Ribas, F. Lloret, K. -i. Okamoto, N. R. Chaudhuri, *Eur. J. Inorg. Chem.* 2003, 1005.

- [56] A. Escuer, R. Vicente, M. S. E. Fallah, X. Solans, M. Font-Bardia, *J. Chem. Soc., Dalton Trans.* 1996, 1013.
- [57] D. M. Duggan, D. N. Hendrickson, *Inorg. Chem.* 1974, **13**, 2056.
- [58] Z. Mahendrasinh, S. Ankita, S. B. Kumar, A. Escuer, E. Suresh, *Inorg. Chim. Acta.* 2011, **375**, 333.
- [59] S. Choubey, K. Bhar, S. Chattopadhyay, A. Hazra, T. K. Maji, J. Ribas, B. K. Ghosh, *Dalton Trans.* 2012, **41**, 11551.
- [60] M. I. Arriortua, R. Cortes, J. L. Mesa, L. Lezama, T. Rojo, G. Villeneuve, *Transition Met. Chem.* 1988, **13**, 371.
- [61] R. Kapoor, A. Kataria, A. Pathak, P. Venugopalan, G. Hundal, P. Kapoor, *Polyhedron* 2005, **24**, 1221.
- [62] S. Jana, B. K. Shaw, P. Bhowmik, K. Harms, M. G. B. Drew, S. Chattopadhyay, S. K. Saha, *Inorg. Chem.* 2014, **53**, 8723.
- [63] S. Sasmal, S. Hazra, P. Kundu, S. Majumder, N. Aliaga-Alcalde, E. Ruiz, S. Mohanta, *Inorg. Chem.* 2010, **49**, 9517.
- [64] S. Sasmal, S. Hazra, P. Kundu, S. Dutta, G. Rajaraman, E. Carolina Sañudo, S. Mohanta, *Inorg. Chem.* 2011, **50**, 7257.
- [65] S. Mukherjee, B. Gole, Y. Song, P. S. Mukherjee, *Inorg. Chem.* 2011, **50**, 3621.
- [66] A. Company, L. Gomez, R. Mas-Balleste, I. V. Korendovych, X. Ribas, A. Poater, T. Parella, X. Fontrodona, J. Benet-Buchholz, M. Sola, L. Que. Jr., E. V. Rybak-Akimova, M. Costas, *Inorg. Chem.* 2007, **46**, 4997.
- [67] A. K. Brisdon, *Inorganic Spectroscopic Methods*. Oxford: Oxford University Press, 1998.
- [68] G. M. Sheldrick, SADABS; University of Göttingen: Germany, 1996.
- [69] G. M. Sheldrick, *Acta Crystallogr., Sect. A: Found. Crystallogr.* 2008, **64**, 112.

-
- [70] J. Palion-Gazda, B. Machura, F. Lloret, M. Julve, *Cryst. Growth Des.* 2015, **15**, 2380.
- [71] P. A. Harding, K. Henrick, L. F. Lindoy, M. McPartlin, P. A. Tasker, *J. Chem. Soc., Chem. Commun.* 1983, 1300.
- [72] H. -W. Lin, *Acta Cryst.* 2008, E64, m295.
- [73] R. Boča, J. Titiš, in *Coordination Chemistry Research Progress*, Nova Science Publishers, New York, 2008, pp.247–304.
- [74] R. Boča, *Theoretical Foundations of Molecular Magnetism*, Elsevier, Amsterdam 1999.
- [75] R. Boča, *Struct. Bonding.* 2006, **1171**.
- [76] J. Titiš, R. Boča, *Inorg. Chem.* 2010, **49**, 3971.
- [77] A. Packová, J. Miklovič, J. Titiš, M. Koman, R. Boča, *Inorg. Chem. Commun.* 2013, **32**, 9.
- [78] J. Miklovič, A. Packová, P. Segl'a, J. Titiš, M. Koman, J. Moncol', R. Boča, V. Jorík, H. Krekuzska, D. Valigura, *Inorg. Chim. Acta.* 2015, **429**, 73.
- [79] J. Miklovič, P. Baran, R. Boča, *Nova Biotechnol. Chim.* 2016, **15**, 182.
- [80] N. Farkašová, J. Černák, L. R. Falvello, M. Orendáč, R. Boča, *Acta Cryst. C.* 2015, **71**, 252.
- [81] O. Kahn, *Molecular Magnetism*. VCH, Weinheim, 1993.
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CHAPTER 3

CHAPTER 3

Structural and magnetic resemblances in doubly chloro and pseudohalide bridged dinickel(II) complexes

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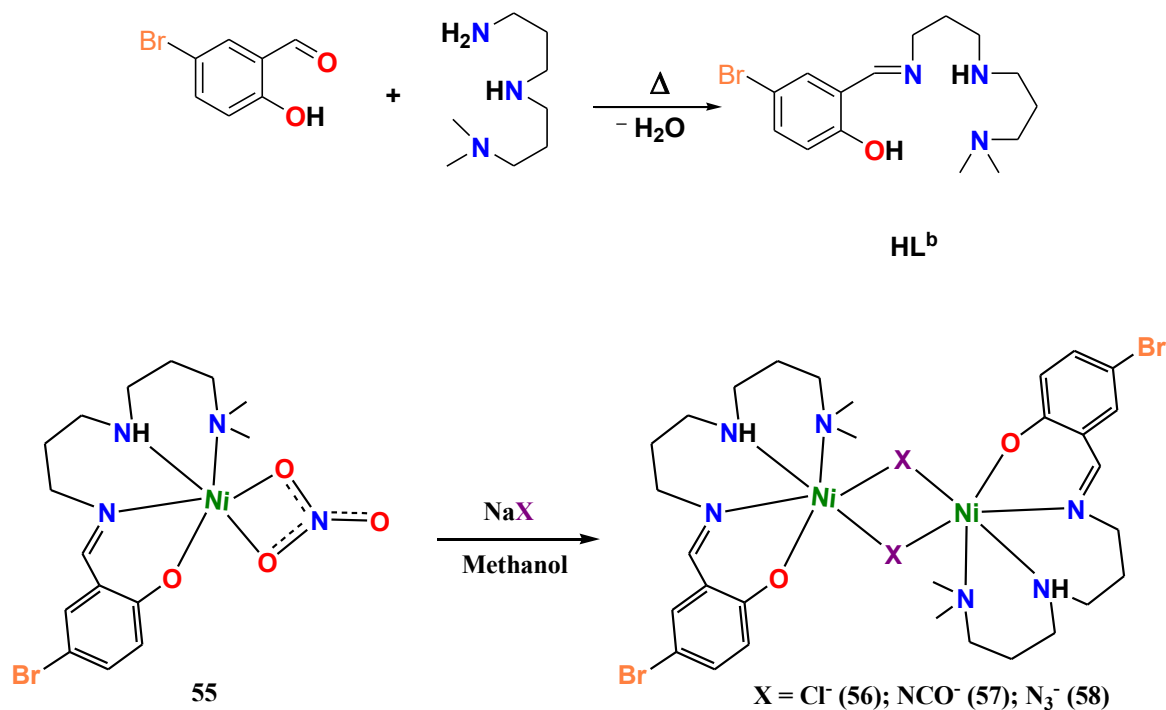
3.1. Introduction

Considerable attention has been directed towards the synthesis of di- and polynuclear transition metal complexes in recent years primarily because of their aesthetic structural diversity, relevance to the metalloenzymatic systems in biology [1–2] and fascinating magnetic properties [3–8]. In the field of molecular magnetism, Ni(II) ion is an automatic choice due to its large single-ion zero-field splitting, and as a consequence several di- and polynuclear Ni(II) complexes with interesting magnetic property have been developed [9–11]. The investigation of magnetic properties of binuclear Ni(II) complexes and correlating them with the structures are quite significant to gain insight into the fundamental aspects of the magnetic interactions as well as to integrate the derived ideas into the large clusters or extended systems to develop molecule-based magnetic materials with predictable magnetic properties. A common strategy to prepare such complexes is the utilization of a multidentate ligand along with judicious choice of a bridging ligand to transmit specific magnetic interactions between the paramagnetic metal centres [12]. The pseudohalide ligand particularly azide ion is the most attractive bridging ligand because of its diverse bridging modes, end-on ($\mu_{1,1}$) and end-to-end ($\mu_{1,3}$) modes being the most common ones, leading to the rich magnetic property in such compounds [12]. In contrast, the presence of two hetero-bridging atoms with polarizable π systems in other pseudohalides, namely thiocyanate and cyanate, which can coordinate the metal ions through either of the heteroatoms, or both, are less versatile than the azide ion. Therefore, in contrast to the vast coordination chemistry of azido bridged systems, [13–20] both structurally and magnetically interesting compounds with other pseudohalides are limited [21]. It is well known that halides and pseudohalides show great resemblances in several chemical and physical properties, but such similarity in coordination chemistry is quite limited, which is due to lack of coordinative versatility of one atom halide ion compared to polyatomic pseudohalides. If pseudohalides bind the metal

centre terminally or connect the metal centres through $\mu_{1,1}$ or $\mu_{1,1,1}$ bridging modes, then only it may have structural resemblance with halide analogues. Along with the rich coordination chemistry of azide bridged complexes, sophisticated experimental and theoretical magneto-structural correlations are available for azide complexes for better understanding the magnetic property of these systems, in which general tendency is that $\mu_{1,3}$ -azido bridge exerts antiferromagnetic (AF) coupling, while $\mu_{1,1}$ coordination mode propagates ferromagnetic (F) exchange between the metal centres [13–23]. Cyanate ion transmits magnetic interaction between the metal centres almost in similar way as that azide ion does but weakly and a scarcity of reports of such Ni(II) compounds is available in the literature to establish a sophisticated magneto-structural correlation for cyanato-bridged Ni(II) systems [19,21,24]. When Ni(II) is five-coordinate, the magnetic coupling observed between the metal ions is usually dominantly AF in nature, while in octahedral or pseudo-octahedral, the coupling is found generally ferromagnetic through chloro bridge [25,26]. It has been observed that the magnetic interaction may change from AF to F with small changes in structural geometry, bridging mode and associated parameters, etc. Developing magneto-structural correlations by only experimental means is a very challenging task because that requires structurally similar or identical complexes with all but one governing parameter being identical. Several di-azido and di-chloro bridged dinickel(II) complexes have been both structurally and magnetically characterized, however for a particular ligand system no such structural and magnetic resemblance has yet been established. Therefore, working on a particular ligand system with varied bridging chloride and pseudohalides may provide us significant information of their communicating ability in these systems.

We observed previously that the Schiff base ligand with N_3O donor sites derived from condensation of salicylaldehyde with *N,N*-dimethyldipropylenetriamine is capable to stabilize ferromagnetically coupled dinickel(II) complexes with azide and cyanate ions in $\mu_{1,1}$ bridging

fashion [21]. Therefore, we speculated that such organic ligands may be useful for the synthesis of ferromagnetically coupled dinickel(II) complexes with both bridging halides and pseudohalides with significant structural resemblance. Accordingly, in this present endeavour, a tetradentate Schiff base prepared from the condensation reaction of *N,N*-dimethyldipropylenetriamine and 5-bromosalicylaldehyde was reacted with nickel(II) nitrate in the presence of exogeneous chloride, azide and cyanate ions and finally ended up with the isolation of isomorphous compounds of dinickel(II) complexes with bridging chloride and pseudohalides (Scheme 3.1). Herein, we report crystal structures and magnetic property of four new complexes, $[\text{Ni}_2(\text{L}^b)_2(\text{NO}_3)_2] \cdot \text{CH}_3\text{OH}$ (**55**), $[\text{Ni}_2(\text{L}^b)_2(\mu\text{-Cl})_2]$ (**56**), $[\text{Ni}_2(\text{L}^b)_2(\mu_{1,1}\text{-NCO})_2]$ (**57**) and $[\text{Ni}_2(\text{L}^b)_2(\mu_{1,1}\text{-N}_3)_2]$ (**58**). All these dinickel(II) complexes show ferromagnetic coupling through bridging chloride and pseudohalides. Compound **57** is a precious addition to the only four known examples of this family, and unprecedented high degree of structural and magnetic resemblances of **56–58** is the major achievement of the present work.



Scheme 3.1. Schematic representation of the synthesised ligand and complexes.

3.2. Experimental Section

3.2.1. Laboratory Techniques

Laboratory techniques such as elemental analysis, infrared spectroscopy, UV-vis spectroscopy and single crystal X-ray Diffraction study are common as our previous work. The details about these techniques have been discussed in section 2.2.1 of chapter 2. In this case single-crystal X-ray diffraction data for the complex **55-58** were collected at Department of Chemistry, CICECO, University of Aveiro, 3810-193 Aveiro, Portugal.

Magnetic measurements of the crystalline compounds were performed using a commercial superconducting quantum interference device (SQUID) magnetometer. The direct current (dc) magnetic susceptibility was measured at 1.0 KOe from room temperature down to 2 K, while the magnetisation was measured at 2 K in external magnetic fields up to 50 kOe. The background coming from a weakly diamagnetic sample holder was found to be insignificant in comparison to the total signal measured and, so, its subtraction was omitted, but the diamagnetic contribution of the samples is taken into account in the calculations. Magnetic measurements were carried out at Institute of Low Temperature and Structure Research Polish Academy of Sciences ul. Okólna 2, 50-422 Wrocław, Poland

3.2.2. Chemicals Synthetic Techniques

3.2.2.1. Materials

N,N-dimethyldipropylenetriamine, Ni(II) nitrate hexahydrate, 5-bromosalicylaldehyde, sodium azide, sodium cyanate and sodium chloride were of reagent or analytical grade commercially available chemicals and were used as received. Solvents were of reagent grade and used without further purification.

Caution! *Metal-azide complexes with organic ligands are potentially explosive and a small amount of materials should be prepared at a time with great precaution.*

3.2.2.2. Synthesis of Schiff base ligand HL^b

The tetradentate N_3O donors ligand HL^b was prepared by the Schiff base condensation reaction (Scheme 3.1) of *N,N*-dimethyldipropylenetriamine (1.0 mmol, 159 mg) and 5-bromosalicylaldehyde (1.0 mmol, 201 mg) in 30 mL of methanol in refluxing condition for a period of about 1 h [27]. The resulting dark orange methanol solution of HL^b was allowed to cool at room temperature and was subsequently used for the synthesis of the complexes.

3.2.2.3. Synthesis of complex $[Ni_2(L^b)_2(NO_3)_2] \cdot CH_3OH$ (55)

$Ni(NO_3)_2 \cdot 6H_2O$ (582 mg, 2.0 mmol) and HL^b (2.0 mmol) were mixed in 30 ml of methanol, followed by addition of Et_3N (101 mg, 1.0 mmol). The resulting mixture was heated to reflux for about 1 h, leading to a dark green solution. It was then allowed to cool at room temperature and filtered to remove impurity if any and kept at ambient temperature for crystallization. Slow evaporation of the resulting green solution gave a dark-green crystalline compound containing X-ray diffraction quality blocked-shape dark-green single crystals after several days. Yield: 810 mg; 82%. Anal. Calcd. for $C_{16}H_{27}BrN_4NiO_5$: C 39.90%, H 5.51%, N 11.34%. Found: C 39.84%, H 5.60%, 11.16 %. FTIR (KBr, cm^{-1}): 1384 vs ($\nu_{nitrate}$); 1627 vs ($\nu_{C=N}$).

3.2.2.4. Synthesis of complex $[Ni_2(L^b)_2(\mu-Cl)_2]$ (56)

To a 20 ml methanol solution of complex **55** (494 mg, 1.0 mmol) 10 mL methanol-water solution (5:1, v/v) of NaCl (58 mg, 1 mmol) was added and the solution mixture was allowed to stir for about 20 min. The resulting dark green solution was filtered to remove impurity if any and left at ambient temperature for crystallization. Slow evaporation of the resulting green solution produced a dark-green crystalline compound containing blocked-shape dark-green single crystals suitable for X-ray diffraction study within a couple of days. Yield: 327

mg (75%). Anal. Calcd. for $C_{30}H_{46}Br_2Cl_2N_6Ni_2O_2$: C 41.38%, H 5.32%, N 9.65 %. Found: C 41.31%, H 5.40%, N 9.50 %. FTIR (KBr, cm^{-1}): 1627 m ($\nu_{C=N}$).

3.2.2.5. Synthesis of $[Ni_2(L^b)_2(\mu_{1,1}-NCO)_2]$ (**57**)

Complex **57** was synthesized adopting a very similar methodology as that applied for the synthesis of complex **56**, except the use of NaNCO instead of NaCl. Colour: Dark-green. Yield: 305 mg (69 %). Anal. Calcd. for $C_{32}H_{46}Br_2N_8Ni_2O_4$: C 43.48%, H 5.25%, N 12.68 %. Found: C 43.59%, H 5.30%, N 12.52 %. FTIR (KBr, cm^{-1}): 2176 vs (ν_{NCO^-}); 1625 s ($\nu_{C=N}$).

3.2.2.6. Synthesis of $[Ni_2(L^b)_2(\mu_{1,1}-N_3)_2]$ (**58**)

Complex **58** was synthesized following the same procedure as that employed for the synthesis of **56**, but NaN_3 was used in place of NaCl. (Yield: 336 mg; 76%). Anal. Calcd. for $C_{30}H_{46}Br_2N_{12}Ni_2O_2$: C 40.76%, H 5.24%, N 19.01 %. Colour: dark-green. Found: 40.85%, H 5.29%, N 18.82 %. FTIR (KBr, cm^{-1}): 2049 vs ($\nu_{N_3^-}$); 1623 s ($\nu_{C=N}$).

3.3. Results and Discussion

3.3.1. Syntheses and general characterizations

Schiff base ligand HL^b was synthesized following simple condensation reaction of *N,N*-dimethyldipropylenetriamine and 5-bromosalicylaldehyde in a 1:1 molar ratio in methanol. Subsequently, it was reacted with Ni(II) nitrate hexahydrate in methanol that resulted $[Ni_2(L^b)_2(NO_3)_2] \cdot CH_3OH$ (**55**). High degree of solubility of complex **55** in common organic solvents like alcohols and acetonitrile allowed us to use it as a precursor complex for the synthesis of other complexes. Accordingly, it was reacted with sodium salts of chloride, cyanate or azide, that afforded dark-green crystals of $[Ni_2(L^b)_2(\mu-Cl)_2]$ (**56**), $[Ni_2(L^b)_2(\mu_{1,1}-NCO)_2]$ (**57**) and $[Ni_2(L^b)_2(\mu_{1,1}-N_3)_2]$ (**58**), respectively, in high yields.

3.3.2. IR Spectroscopy

All the complexes were characterized by elemental analysis and IR spectroscopy and these data are given in the experimental section. All these complexes show a common feature of stretching vibration of the azomethine (C=N) bond of the Schiff base varying in the range 1623–1627 cm^{-1} . Additionally, the IR spectra of **57** and **58** exhibit strong and sharp bands at 2176 cm^{-1} and 2049 cm^{-1} , respectively, characteristic of the asymmetric stretching vibration of the bridging cyanate and azide ions, respectively, typical for end-on cyanate and azide bridged transition metal complexes.

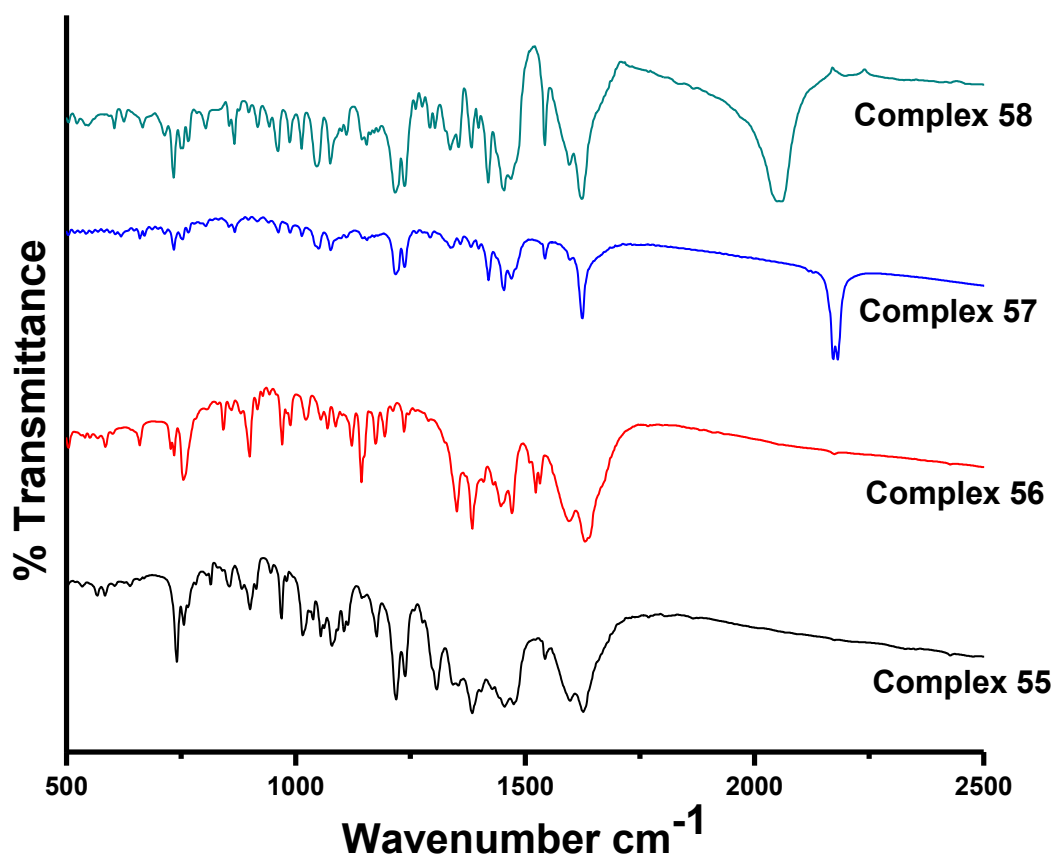


Figure 3.1: IR spectra of the complex 55-58

3.3.3. Description of crystal structures

Neutral complex $[\text{Ni}_2(\text{L}^b)_2(\text{NO}_3)_2] \cdot \text{CH}_3\text{OH}$ (**55**) crystallizes in the monoclinic space group $P2_1/n$. The details of the crystallographic data and structural refinement parameters are available in Table 3.1. The crystal structure of **55** with atom numbering scheme is depicted in Figure 3.2 and the selected bond parameters are given in Table 3.2. The Ni(II) ion in **55** is hexacoordinated with distorted octahedral geometry, being bonded with N_3O donor sites from the deprotonated Schiff base ligand together with a bidentate nitrate ion. The Ni–O distances of the coordinated nitrate are 2.141(1) and 2.247(2) Å, with their difference Δd being the metal centre as a bidentate fashion rather than anisobidentate one [27,28]. But significantly low bite angle of the nitrate ion of $58.90(5)^\circ$ is the main reason behind the significant distortion from the ideal octahedral geometry [29,30]. All the nitrogen atoms from the Schiff base ligand occupy one meridional position of Ni(II) centre in **55**, while three oxygen atoms, one from phenolate group of the Schiff base and two from bidentate nitrate ion, occupy other meridional position. The Ni–N distances of imine, secondary amine and tertiary amine and the Ni–O distance of phenolato-O of the Schiff base ligand in **55** are 2.052(2), 2.069(2), 2.1378(2) and 1.986(1) Å, respectively, which fall in line with reported Ni(II) complexes with similar coordination environments [13–20]. The structure of **55** in the solid state is mainly stabilized by hydrogen bonding interactions as displayed in Figure 3.3. The phenolate oxygen is connected with solvent methanol molecule through hydrogen bond of donor-acceptor distance of 2.866 Å, while the secondary amine group forms an intermolecular hydrogen bond with non-coordinated oxygen atom of the nitrate group from the neighbouring molecule with donor-acceptor distance of 3.059 Å, leading to a hydrogen bonded zig-zag chain running along the crystallographic b axis.

Complexes $[\text{Ni}_2(\text{L}^b)_2(\mu\text{-Cl})_2]$ (**56**), $[\text{Ni}_2(\text{L}^b)_2(\mu_{1,1}\text{-NCO})_2]$ (**57**) and $[\text{Ni}_2(\text{L}^b)_2(\mu_{1,1}\text{-N}_3)_2]$ (**58**) are isostructural and isomorphous compounds, and they crystallize in the monoclinic unit cell

with space group $P2_1/c$ (Table 3.1). These centro-symmetrical neutral complex molecules are formed by doubly bridged chloride or pseudohalide ions, and the structures of these compounds are depicted in Figure 3.4-3.6, respectively, and their important bond parameters are given in Table 3.2. The Ni(II) centres in these complexes are hexacoordinated with slightly distorted octahedral geometry in which, in addition to doubly bridging chloride or pseudohalide ions, the metal centres are bonded to three N donor atoms and one phenolato-O atom of the deprotonated Schiff base ligand. The bridging chloride or pseudohalide ions form the common edge within the dinuclear units, leading to edge-sharing bioctahedral structures (Figure 3.5). The Ni-(μ -Cl), Ni-N($\mu_{1,1}$ -NCO) and Ni-N($\mu_{1,1}$ -N₃) bond lengths of 2.467(1) and 2.507(1) Å, 2.202(2) and 2.225(2) Å, and 2.173(2) and 2.122(2) Å in complexes **56-58**, respectively, justify that the bridging region is slightly asymmetric, accounting slight distortion around Ni(II) ions in these systems. Unlike **55**, all the nitrogen atoms of the triamine part of the deprotonated Schiff base coordinate Ni(II) ion in the facial configuration, while the remaining facial position is occupied by phenolato-O atom of the Schiff base together with two bridging chloride ions in **56** and two nitrogen atoms of two bridging cyanate or azide ions in **57** and **58**, respectively.

Table 3.1. Crystallographic data and structural refinement parameters of 55–58

	55	56	57	58
Empirical formula	C ₁₆ H ₂₇ BrN ₄ NiO ₅	C ₃₀ H ₄₆ Br ₂ Cl ₂ N ₆ Ni ₂ O ₂	C ₃₂ H ₄₆ Br ₂ N ₈ Ni ₂ O ₄	C ₃₀ H ₄₆ Br ₂ N ₁₂ Ni ₂ O ₂
Formula weight (g mol ⁻¹)	494.03	870.87	884.01	884.03
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic
Space group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> (Å)	12.2994(6)	11.2323(2)	11.0315(6)	11.0594(6)
<i>b</i> (Å)	8.5918(5)	10.5474(2)	10.4411(5)	10.4447(5)
<i>c</i> (Å)	19.8818(10)	14.5752(2)	15.4241(8)	15.4302(8)
α (deg)	90	90	90	90
β (deg)	103.580(2)	96.641(1)	94.593(2)	94.321(2)
γ (deg)	90	90	90	90
volume (Å ³)	2042.25(19)	1715.16(5)	1770.86(16)	1777.31(16)
<i>Z</i>	4	2	2	2
<i>D</i> _{calc} (g cm ⁻³)	1.607	1.686	1.658	1.652
μ (mm ⁻¹)	2.940	3.621	3.368	3.355
<i>F</i> (000)	1016	888	904	904
θ Range (deg)	2.108–29.200	1.825–29.232	1.852–29.242	2.357–29.198
Reflections collected	43731	23739	20417	19058
Independent reflections (<i>R</i> _{int})	5509(0.0271)	4624 (0.0526)	4795 (0.380)	4794 (0.0417)
Observed reflections [<i>I</i> > 2 σ (<i>I</i>)]	4734	3394	3650	3486
Restraints/parameters	1/263	0/205	0/223	0/223
Goodness-of-fit on <i>F</i> ²	1.037	1.056	1.031	1.043
Final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0302, w <i>R</i> ₂ = 0.0770	<i>R</i> ₁ = 0.0330, w <i>R</i> ₂ = 0.0607	<i>R</i> ₁ = 0.0324, w <i>R</i> ₂ = 0.0711	<i>R</i> ₁ = 0.0363, w <i>R</i> ₂ = 0.0780
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0388, w <i>R</i> ₂ = 0.0817	<i>R</i> ₁ = 0.0580, w <i>R</i> ₂ = 0.0695	<i>R</i> ₁ = 0.0525, w <i>R</i> ₂ = 0.0791	<i>R</i> ₁ = 0.0622, w <i>R</i> ₂ = 0.0872
Largest diff. peak/hole (e Å ⁻³)	1.488/–1.029	0.545/–0.424	0.722/–0.346	0.788/–0.437

Table 3.2. Selected bond distances (Å) for **55–58**

Bond	55	56	57	58
Ni(II)–N(imine)	2.052(2)	2.060(2)	2.077(2)	2.069(2)
Ni(II)–N(secondary amine)	2.069(2)	2.125(2)	2.097(2)	2.094(2)
Ni(II)–N(tertiary amine)	2.138(2)	2.190(2)	2.120(2)	2.208(2)
Ni(II)–O(phenolate)	1.986(1)	2.011(2)	2.006(2)	2.006(2)
Ni(II)–X ^a	2.141(1) 2.247(2)	2.507(1) 2.467(1) ^b	2.225(2) 2.202(2) ^b	2.122(2) 2.173(2) ^b

^a X = O(nitrate) for **55**, Cl for **56**, N(azide) for **57** and N(cyanate) for **58**; ^b Symmetry code: –x, –y, –z

The different coordination modes of the triamine part of the ligand, meridional (in **55**) and facial (in **56–58**) justify the flexibility and adoptability of *N,N*-dimethyldipropylenetriamine in these systems, a key feature for being a good ligand in coordination chemistry. The Ni–N(imine), Ni–N(secondary amine) and Ni–N(tertiary amine) vary in the range 2.060(2)–2.077(2), 2.094(2)–2.125(2) and 2.120(2)–2.208(2) Å for **56–58**, respectively (Table 3.2), which are comparable to analogous complexes reported in the literature [21]. The centre of symmetry enforces the central Ni(μ-Cl)₂Ni (in **56**) and Ni(μ-N)₂Ni (in **57** and **58**) core structures to be perfectly planar. The bridging angles are 92.27(2), 98.47(2) and 101.99(1)° with metal-metal separations of 3.587(1), 3.274(1) and 3.338(1) Å for **56–58**, respectively, which are comparable to those reported earlier [13–26, 31–33]. Although handful examples of chloro and end-on azido bridged dinickel(II) complexes are known, complex **57** could be a precious addition in growing family of this type of complexes of totalling only five [19,21,24]. Being isomorphous compounds, they display similar types of noncovalent interaction, one of such notable interaction is the intramolecular hydrogen bonding interaction involving secondary amine of a Schiff base ligand and phenolate oxygen atom of

other Schiff base ligand in the dimeric unit with donor-acceptor distances in the range 2.992 to 3.180 Å.

It is interesting to note that all the structural parameters except at bridging region are almost identical in these complexes. The Ni–(μ -Cl) bond length in **56** is significantly longer than Ni–(μ -N) bond distances in bridging azide and cyanate ions in **57** and **58** as expected. Furthermore, the bridging angle in **57** is close to the orthogonality, while it is more obtuse in azide complex and an intermediate impression has been observed in the cyanate bridged one, resulting in a significant dissimilarity in bridging region. Remarkably, the system has overcome all these divergences and crystallized them with the identical crystallographic parameters, which is rarely achieved in coordination chemistry and for di-halide and di-pseudohalide bridged systems, it was not observed earlier.

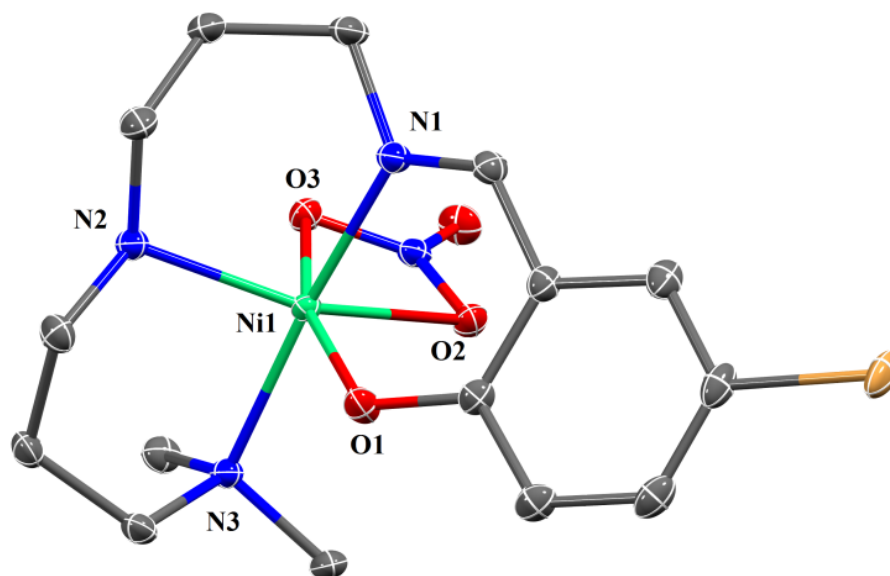


Figure 3.2: Crystal structure of **55** showing atom numbering scheme. The ellipsoids are drawn at 30% probability level and hydrogen atoms and solvent methanol have been omitted for clarity.

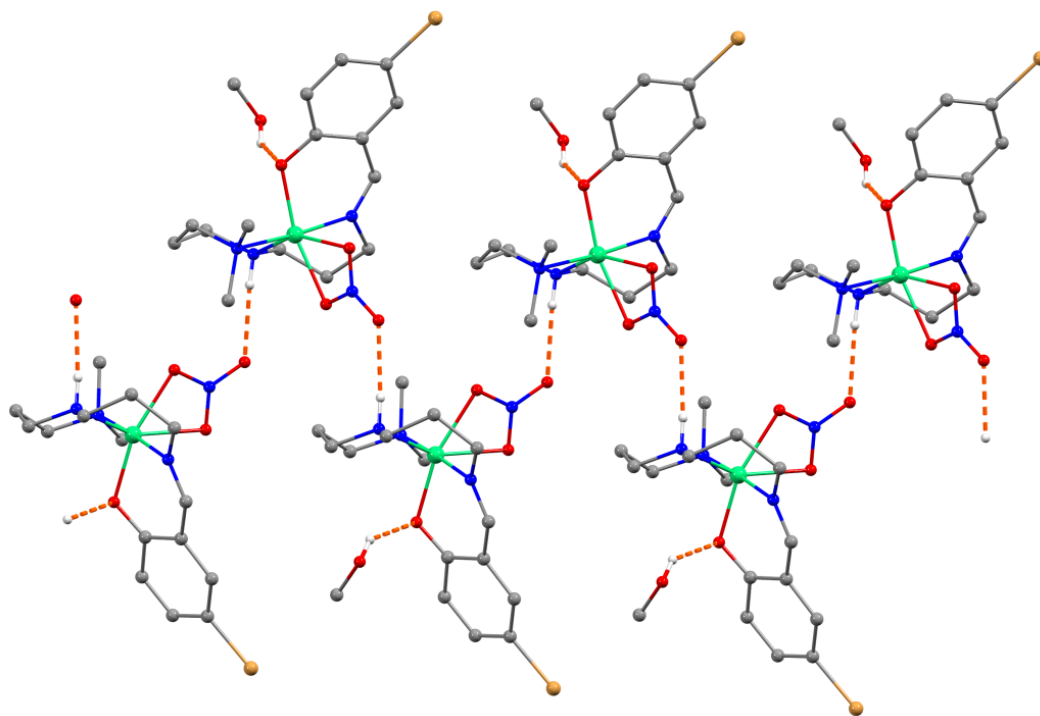


Figure 3.3: The crystal packing of **55** showing hydrogen bonded zig zag chain along the crystallographic *b* axis.

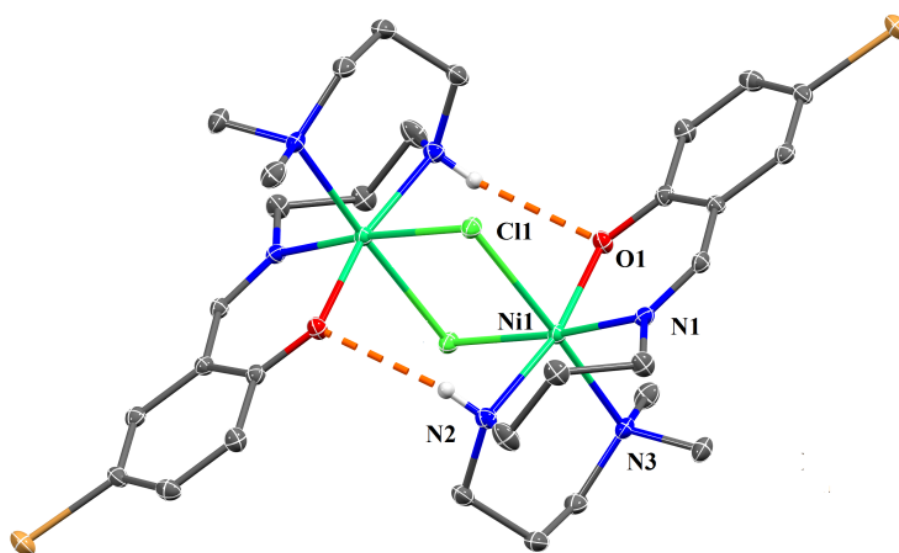


Figure 3.4: Crystal structure of **56** showing atom numbering scheme and intramolecular hydrogen bonds. The ellipsoids are drawn at 30% probability level.

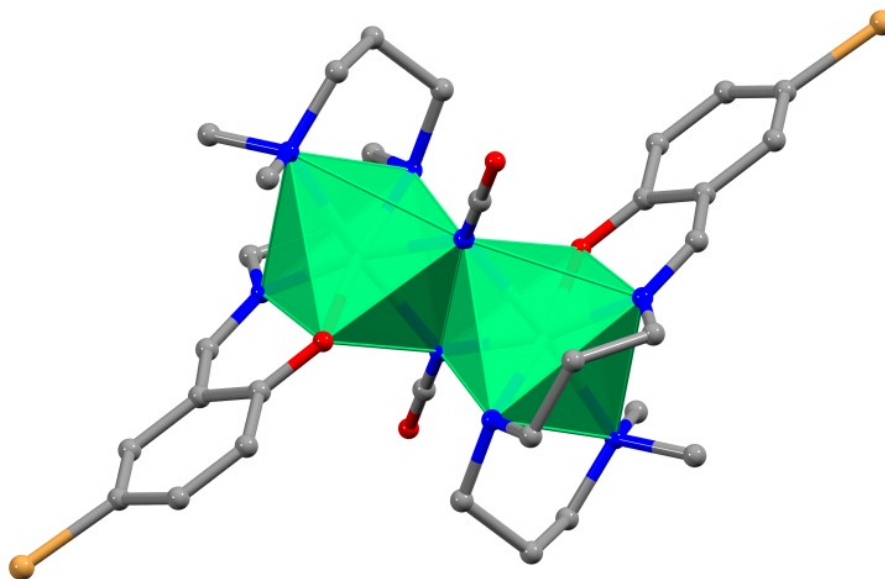


Figure 3.5: Crystal structure of **57** showing edge sharing bioctahedral structure and hydrogen atoms have been omitted for clarity.

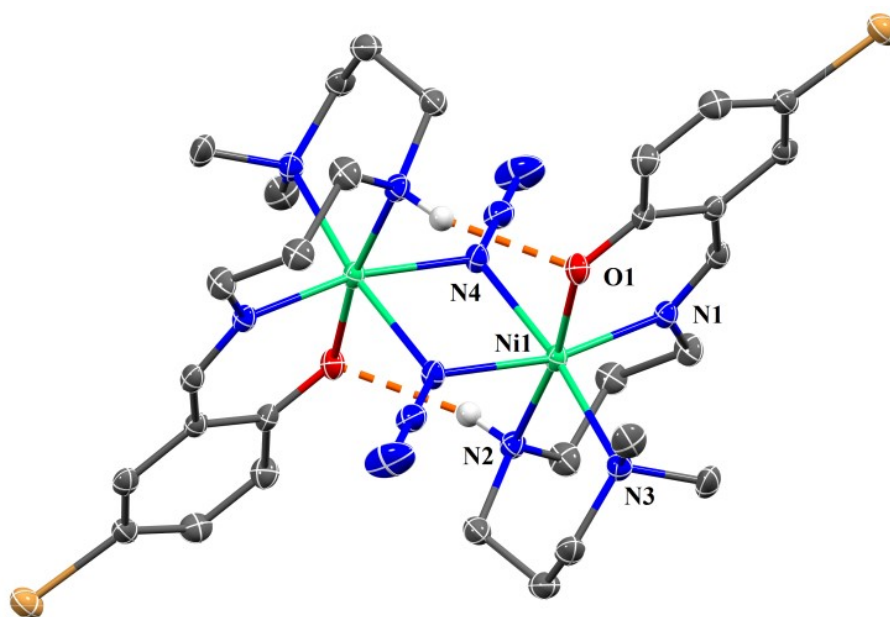


Figure 3.6: Crystal structure of **58** showing selected atom numbering scheme and intramolecular hydrogen bonding interaction. The ellipsoids are drawn at 30% probability level.

3.3.4. Magnetic properties

The direct current (dc) magnetic properties of dinuclear complexes **56–58** as χ_M and $\chi_M T$ product vs. T plots (χ_M being the molar magnetic susceptibility per dimer) under a constant magnetic field of 1.0 KOe in the temperature range 2–300 K and the molar magnetization as a function of applied dc magnetic field (M/μ_B f.u.⁻¹ vs. H) are shown in [Figure 3.7–3.9](#), respectively. The $\chi_M T$ product at room temperature for **56–58** is *ca.* 2.48, 2.51 and 2.80 emu mol⁻¹ K, respectively, which are slightly larger than that expected for two magnetically non-interacting Ni(II) ions with $S = 1$ (2.0 emu mol⁻¹ K), which is mainly due to unquenched orbital angular momentum of Ni(II) ions. The $\chi_M T$ increases continuously with decreasing temperature reaching a maximum of 3.57 emu mol⁻¹ K at 9.0 K for **56** and 3.47 emu mol⁻¹ K at 8.0 K for **57** and then $\chi_M T$ decreases sharply to attain a value *ca.* 2.69 emu mol⁻¹ K at 1.8 K. This feature is characteristic for an intramolecular ferromagnetic interaction between two Ni(II) ions with the influence of intermolecular interactions and/or zero-field splitting (ZFS) of ground state ($S = 2$), manifested at low temperature. Almost similar feature has been observed for **58** but without noticeable decrease of $\chi_M T$ value even at very low temperature, indicating dominant ferromagnetic exchange interaction between these spin carriers. The high-temperature χ_M^{-1} data obeys the Curie-Weiss law and the linear fitting of the same above 100 K yielded Weiss constant (θ_p) values of 13.3(3), 6.3(6) and 29(2) K for **56–58**, respectively, with reasonable Curie constant values, which further indicate that the magnetic interaction between Ni(II) ions is ferromagnetic in nature ([Figure 3.10–3.12](#)). A full-matrix diagonalization approach assuming isotropic exchange coupling Hamiltonian ($-2J\hat{S}_1\cdot\hat{S}_2$), Zeeman effect (g_{Ni} , average), axial zero-field splitting (D), and intermolecular interaction (zJ') was employed to analyse further the magnetic data using *PHI* program [34]. The simultaneous simulation of $\chi_M T$ and magnetisation data leads to good agreement between the calculated and observed data ([Figure 3.7–3.9](#)), and the best fittings afforded the following set

of parameters: $J = 6.84(10) \text{ cm}^{-1}$, $g_{\text{Ni}} = 2.21(0.1)$, $D = 5.51(2) \text{ cm}^{-1}$ and $zJ' = 0.003(4) \text{ cm}^{-1}$ for complex **56**; $J = 5.31(4) \text{ cm}^{-1}$, $g_{\text{Ni}} = 2.19(0.1)$, $D = 5.00(6) \text{ cm}^{-1}$ and $zJ' = 0.001(8) \text{ cm}^{-1}$ for complex **57** and $J = 18.8(7) \text{ cm}^{-1}$, $g_{\text{Ni}} = 2.27(0.3)$, $D = 3.31(14) \text{ cm}^{-1}$ and $zJ' = 0.038(1) \text{ cm}^{-1}$ for complex **58**.

As we have stated earlier that for a particular ligand system none of the previous report deals with the structural and magnetic studies involving doubly bridged halide and pseudohalide systems, so it is our privilege to analyse the magneto-structural data to gain insight into the magnetic properties in these systems. Although the ZFS parameter D and intermolecular coupling constant zJ' strongly interact with each other, thereby their overestimation cannot be ignored, yet the D values found in these complexes are comparable and fall in the region where it is clustered with several reported values even with same sign. However, these two parameters are poorly coupled with intramolecular exchange coupling constant J , leaving the exchange coupling constant J almost unaffected. The significantly stronger exchange interaction between two Ni(II) centres in **58** than other two complexes is well known, but the scenario is not so clear for chloro- and cyanato- bridged systems as their coexistence is one of the most scarcity in coordination chemistry. Our data provide us information that chloride ($J = 6.84(10) \text{ cm}^{-1}$) is better magnetic coupler than cyanate ion ($J = 5.31(4) \text{ cm}^{-1}$). If we look at the reported results, it is seen that J values (considering $\hat{H} = -2J\hat{S}_1\cdot\hat{S}_2$) vary from 1.91 to 36.3 cm^{-1} in doubly $\mu_{1,1}$ -azido-bridged dinickel(II) complexes, [13-20,32-34,35-46] while the ranges are 1.7 to 6.85 cm^{-1} [19,21,24] and 3.48 to 14.59 cm^{-1} [47-62] for doubly $\mu_{1,1}$ -cyanato-bridged and doubly μ -chloro-bridged analogues, respectively, and the trend of their average values is exactly replicated in the present study, that help us to conclude that $\mu_{1,1}$ -azido is superior magnetic exchanger among them, followed by μ -chloro and $\mu_{1,1}$ -cyanato.

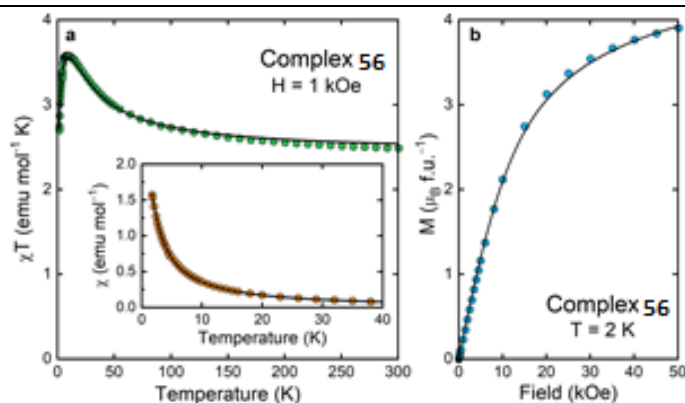


Figure 3.7: Magnetic data for **56**. (a) Thermal dependence of χ_M and $\chi_M T$ product measured at 1.0 kOe dc field. (b) Magnetisation data at 2K. Symbols and solid lines represent experimental and best fitted data.

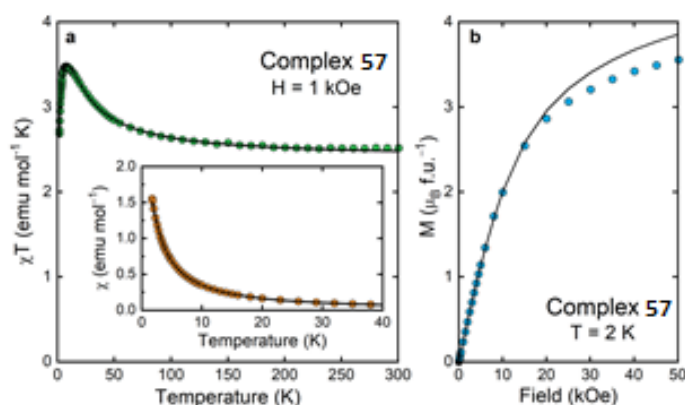


Figure 3.8: Magnetic data for **57**. (a) Thermal dependence of χ_M and $\chi_M T$ product measured at 1.0 kOe dc field. (b) Magnetisation data at 2K. Symbols and solid lines represent experimental and best fitted data.

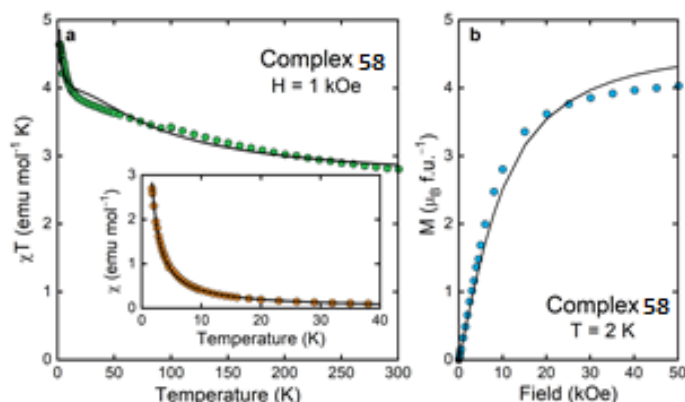


Figure 3.9: Magnetic data for **58**. (a) Thermal dependence of χ_M and $\chi_M T$ product measured at 1.0 kOe dc field. (b) Magnetisation data at 2K. Symbols and solid lines represent experimental and best fitted data.

It is well known that the sign and magnitude of the exchange coupling constant (J) between the paramagnetic centres is governed by several structural parameters. Among them,

the bridging angle plays the most crucial role in determining the overall magnetic interactions. Ruiz et al. theoretically established that doubly $\mu_{1,1}$ -azido bridged dinuclear Ni(II) complexes exhibit ferromagnetic interactions throughout the Ni–N–Ni angles (θ) ranging from 80° to 115° , with J values increasing as the angle increases, reaching a maximum approximately at 104° , and then decreases further with increasing θ [22,23]. In fact, all the reported $\mu_{1,1}$ -azido bridged dinickel(II) systems exhibit ferromagnetic coupling with only one exception where a very low bridging angle of 90.4° transmits AF interaction between Ni(II) centres [20]. The Ni–N–Ni angle found in **58** is $101.99(1)^\circ$, which falls within the range where strong ferromagnetic interaction prevail between two Ni(II) ions as suggested by the theoretical study, and therefore J value ($18.8(7) \text{ cm}^{-1}$) found in **58** is quite reasonable. However, although a large number of $\mu_{1,1}$ -azido bridged dinickel(II) systems are known, unlike theoretical prediction, the experimental data do not show clear relationship with Ni–N–Ni angles as a small variation of Ni–N–Ni angles in the narrow range *ca.* 98° – 103.9° , show a large variation of the J values from 1.91 to 43.9 cm^{-1} [13-20,32-34,35-46]. This is confirmed by the fact that the present bridging angle of $101.99(1)^\circ$ is very close to the value of 101.0° in $[\text{Ni}_2(\text{L}^{24})_2(\mu_{1,1}\text{-N}_3)_2(\text{N}_3)_2]$ (L^{24} = a tridentate quinoline-based ligand) [34] and 101.79° (average value) in $[\text{Ni}_2(\text{L}^{35})_2(\text{N}_3)_2(\mu_{1,1}\text{-N}_3)_2] \cdot \text{CH}_3\text{OH}$ (L^{35} = *N,N*-dimethyl-*N'*-(pyrid-2-ylmethyl)-ethylenediamine) [63], but show quite different J values of 6.1 and 1.91 cm^{-1} , respectively. In contrast, the magnetic interaction of the present complex is nicely agreed with other reported results that displayed very similar bridging angles of 101.6° in $[\text{Ni}_2(\text{terpy})_2(\text{N}_3)_2(\mu_{1,1}\text{-N}_3)_2] \cdot \text{H}_2\text{O}$ [14] and 101.4° (average value) in $[\text{Ni}_2(\text{L}^{26})_2(\text{N}_3)_2(\mu_{1,1}\text{-N}_3)_2]$ (L^{26} = a multidentate ligand) [41] with J values of 22.8 and 20.96 cm^{-1} , respectively. Notably, the present J value significantly differs from our previous result with similar ligand where salicylaldehyde was used instead of 5-bromosalicylaldehyde, in which average bridging angle and J value are 101.35° and 10 cm^{-1} , respectively [21] Slightly higher

bridging angle together with shorter average M–N($\mu_{1,1}$ -N₃) bond distance of 2.148 Å in **58** compared to 2.169 Å in the previous reported complex, could justify the stronger coupling constant value in the present complex.

In contrast to $\mu_{1,1}$ -N₃ bridged Ni(II) complexes, only four doubly $\mu_{1,1}$ -NCO bridged dinickel(II) complexes are known. The magnetic and crystallographic data of these five complexes are presented in Table 3.3, which shows that J values span in a narrow range 1.7 to 6.85 cm⁻¹ [19,21,24]. The sign and magnitude J value of 5.31(4) cm⁻¹ in **58** is again reasonable for such complexes. Interestingly, a general trend can be found in which J value increases with increasing in bridging angles, similar to theoretical prediction that has been done for azide analogues. As shown in Figure 3.13, the value found in our earlier report is slightly higher among this series, [21] that prompted us for further inspection of the structural parameters and it is seen that in the present case though the bond angle is slightly higher than the previous one, the average bond length in the bridging region found in reverse order, that may be the reason for such difference.

Previous studies on doubly chloro-bridged Ni(II) dimers showed that the magnetic interaction are predominantly ferromagnetic if the geometry of the metal centre is octahedral (Table 3.4), [26, 47–62] and the strength of the coupling varies from 3.48 to 14.59 cm⁻¹, with only one exception where AF interaction is operative between the metal centres with high degree of distortion of Ni(II) centres from the octahedral geometry [65]. Tamayo et al. have established that the strength of the ferromagnetic coupling become weaker with the increase of bridging angle from ideal value of 90° [26]. The value of bridging angle in **56** is 92.27(2)°, so it is in good agreement with the ferromagnetic interaction observed in **56**. However, the experimental data do not show clear relationship between the strength of the coupling and the

bridging angles, leaving an unsolved challenge which will require consideration of more than one structural parameter at once.

Table 3.3. Selected structural and magnetic data of doubly end-on cyanato bridged Ni(II) dimers (following $\hat{H} = -2J\hat{S}_1\cdot\hat{S}_2$ convention)^a

Compounds	J (cm ⁻¹)	D (cm ⁻¹)	g	M–N (Å)	M–N–M (°)	Refs.
[Ni ₂ (L ²⁹) ₂ (μ _{1,1} -NCO) ₂](ClO ₄) ₂	+1.7	+3.6	2.23	2.125, 2.090	94.4, 95.8	19
[Ni ₂ (L ²⁸) ₂ (μ _{1,1} -NCO) ₂](ClO ₄) ₂	+2.8	+3.6	2.23	2.099, 2.115	95.33, 95.79	19
[Ni ₂ (terpy) ₂ (μ _{1,1} -NCO) ₂ (H ₂ O) ₂](PF ₆) ₂	+ 4.59	–12.32	2.23	2.044, 2.195	97.7	24
[Ni ₂ (L ^a) ₂ (μ _{1,1} -NCO) ₂]	+6.85	+7.18	2.19	2.107, 2.244 2.115, 2.280	97.84, 98.74	21
[Ni ₂ (L ^b) ₂ (μ _{1,1} -NCO) ₂] (57)	+5.31	+5.00	2.19	2.225, 2.201	98.47	This work

^a terpy = terpyridine; L²⁹ = [N,N'-bis(2-pyridinylmethylene)]propane-1,3-diamine); L²⁸ = N,N'-bis(pyridin-2-yl)benzylidene]ethane-1,2-diamine; L^a = a tetradentate N₃O donor ligand

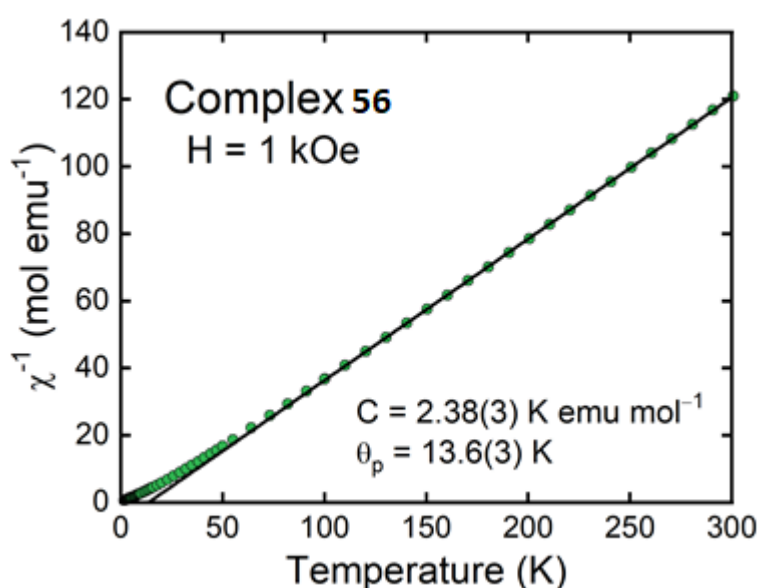


Figure 3.10: Curie-Weiss plot for complex **56** in the 100–300 K range.

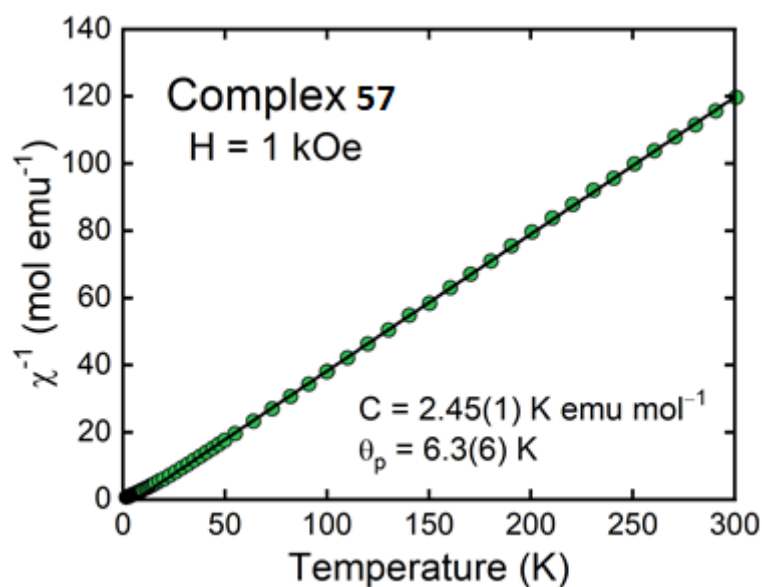


Figure 3.11: Curie-Weiss plot for complex **57** in the 100–300 K range.

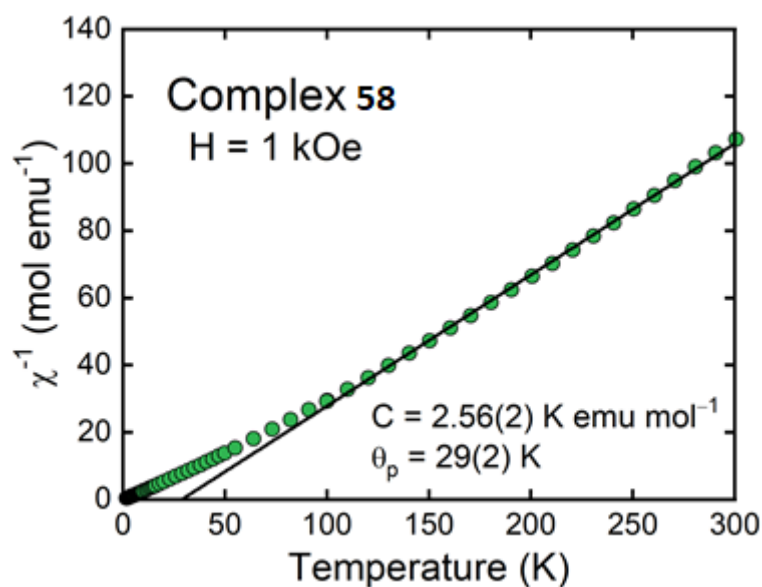


Figure 3.12: Curie-Weiss plot for complex **58** in the 100–300 K range.

Table 3.4. Selected structural and magnetic data of doubly end-on cyanato bridged Ni(II) dimers (following $\hat{H} = -2J\hat{S}_1\cdot\hat{S}_2$ convention)^b

Compounds	J (cm ⁻¹)	D (cm ⁻¹)	g	M–N (Å)	M–N–M (°)	Refs.
Ni ₂ Cl ₂ (TTF ⁺) ₂ [(I ₃) ₄ (I ₂) ₃ ·(H ₂ O) ₂ ·(C ₄ H ₈ O) ₃]	5.0	–16	2.26	2.365, 2.391	90.5, 91.8	48
[{Ni(ATsc)(MeOH)} ₂ (μ-Cl) ₂] ₂ Cl ₂	5.7	-	2.29	2.348, 2.396	91.5	49
[{Ni(ATHAc)(H ₂ O)} ₂ (μ-Cl) ₂] ₂ Cl ₂	6.6	-	2.30	2.327, 2.471	92.7	49
[{Ni(TPA)Cl} ₂] ₂ (ClO ₄) ₂ ·2HNEt ₃ ClO ₄	7.6	+ 0.51	2.07	2.365, 2.507	92.63	50
(C ₃ H ₆ N ₂ H ₆) ₂ [Ni ₂ Cl ₈ (H ₂ O) ₂]	8.13	–3.4	-	2.430, 2.459	95.05	51
[{Ni(eg) ₂ Cl} ₂] ₂ Cl ₂	9.0	-	-	2.383	93.03	52
[Ni ₂ (en) ₄ Cl ₂] ₂ Cl ₂	6.65	–3.6	2.21	2.461,	96.6	53
	4.83	–4.78	2.24	2.551		54
	10.5	+ 11.1	2.12			55
	3.48	+ 9.7	2.25			56
[{Ni(en) ₂ Cl} ₂] ₂ (ClO ₄) ₂	8.9	–4.2	2.18	2.461, 2.512	95.4	53
[{Ni(en) ₂ Cl} ₂] ₂ (Ph ₄ B) ₂	9.5	–7.7	2.16	2.403, 2.503	95.6	53,57
[{Ni(TPA)Cl} ₂] ₂ (ClO ₄) ₂ ·H ₂ O	14.59	–	2.02	2.363, 2.503	92.7	58
[Ni ₂ (bipy) ₂ (μ-Cl) ₂ Cl ₂ (H ₂ O) ₂]	8.4	+ 3.5	2.09	2.396, 2.405	91.56	59
[{Ni(L ³⁶) ₂ (μ-Cl) ₂](ClO ₄) ₂	9.95	+ 12	2.06	2.381, 2.535	93.52	26,60
[Ni ₂ (H ₃ L ³⁷) ₂ Cl ₂] ₂ Cl ₂	7.17	–7.5	2.35	2.433, 2.353	93.50	61
[Ni ₂ (H ₂ L ³⁸) ₂ Cl ₂] ₂ Cl ₂ ·4H ₂ O·2C ₄ H ₈ O ₂	7.6	-	2.12	2.393, 2.421	87.07	62
[Ni ₂ (L ³⁹) ₂ Cl ₂]	8.90	–7.52	-	2.416, 2.511	94.34	63
[Ni ₂ (L ^b) ₂ (μ-Cl) ₂] (56)	+6.84	+5.51	2.21	2.507, 2.467	92.27	This work

^b TTF = 4,5-bis(2pyridylmethylsulfanyl)-4',5'-ethylenedithiotetrathiafulvene; ATsc = 2-acetyl-2-thiazoline semicarbazone; ATHAc = 2-acetyl-2-thiazoline acetylhydrazone; TPA = tris-(2-pyridylmethyl)amine; eg = ethylene glycol; en = ethylenediamine; bipy = 2,2'-bipyridine; L³⁶ = 3,11-dithia-7,17-diazabicyclo[11.3.1]; heptadeca-1(17),13,15-triene; H₃L³⁷ = triethanolamine; H₂L³⁸ = bis((pyridin-2-yl)-1,2,4-triazol-3-yl)methane; L³⁹ = 1-(benzimidazolyl-2-methyl)-1,4,7-triazacyclononane

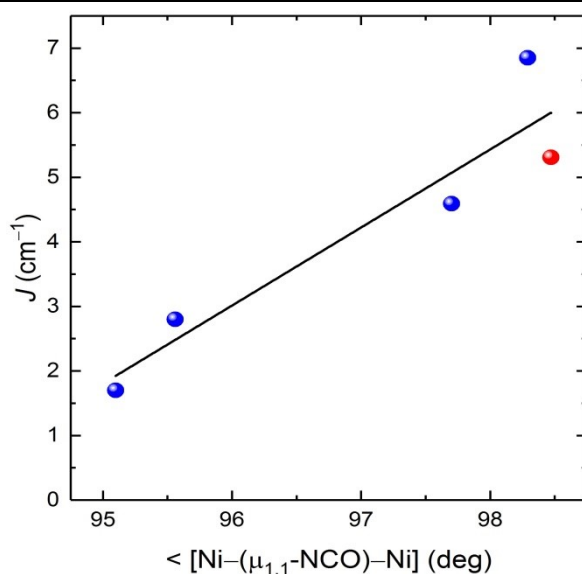


Figure 3.13: Magneto-structural correlation data showing dependence of J values with Ni- $\mu_{1,1}$ NCO-Ni bridging angles. The red symbol corresponds to the compound in this work.

3.4. Conclusions

Four new complexes, $[\text{Ni}_2(\text{L}^b)_2(\text{NO}_3)_2] \cdot \text{CH}_3\text{OH}$ (**55**), $[\text{Ni}_2(\text{L}^b)_2(\mu\text{-Cl})_2]$ (**56**), $[\text{Ni}_2(\text{L}^b)_2(\mu_{1,1}\text{-NCO})_2]$ (**57**) and $[\text{Ni}_2(\text{L}^b)_2(\mu_{1,1}\text{-N}_3)_2]$ (**58**) were synthesized from a tetradentate N_3O -donor Schiff base (HL^b), derived from the condensation reaction of N,N -dimethyldipropylenetriamine and 5-bromosalicylaldehyde. X-ray crystallography reveals that complexes **56–58** are isostructural and isomorphous dinickel(II) compounds with doubly bridging chloride and pseudohalides, and the nickel(II) centres are in octahedral coordination environments. Such structural coincidence in halide and pseudohalide bridged complexes for a particular ligand system is rare in coordination chemistry and is not seen earlier in doubly halide and pseudohalide bridged Ni(II) systems. All these three dinickel(II) complexes exhibit ferromagnetic interaction through bridging chloride or pseudohalides with ferromagnetic coupling constant J are 6.84(10), 5.31(4) and 18.8(7) cm^{-1} for **56–58**, respectively, suggesting that azide ion is superior magnetic coupler among them followed by chloride and cyanate ions, a replication of the average strength of exchange interactions

found in such complexes characterised magnetically. Most importantly, compound **57** is a precious addition to the only four known examples of this family, and unprecedented high degree of structural and magnetic resemblances of **56–58** is the major achievement of the present work.

References

- [1] S. W. Ragsdale, *J. Biol. Chem.* 2009, **284**, 18571.
- [2] M. A. Halcrow, G. Christou, *Chem. Rev.* 1994, **94**, 2421.
- [3] G. A. Craig, M. Murrie, *Chem. Soc. Rev.* 2015, **44**, 2135.
- [4] G. E. Kostakis, A. M. Ako, A. K. Powell, *Chem. Soc. Rev.* 2010, **39**, 2238.
- [5] M. Andruh, *Chem. Commun.* 2018, **54**, 3559.
- [6] S. Accorsi, A. -L. Barra, A. Caneschi, G. Chastanet, A. Cornia, A. C. Fabretti, D. Gatteschi, C. Mortalò, E. Olivieri, F. Parenti, P. Rosa, R. Sessoli, L. Sorace, W. Wernsdorfer, L. Zobbi, *J. Am. Chem. Soc.*, 2006, **128**, 4742.
- [7] H. -L. Sun, Z. -M. Wang, S. Gao, *Coord. Chem. Rev.* 2010, **254**, 1081.
- [8] M. Sarkar, R. Clérac, C. Mathonière, N. G. R. Hearn, V. Bertolasi, D. Ray, *Inorg. Chem.* 2011, **50**, 3922.
- [9] J. Ruiz, A. J. Mota, A. Rodríguez-Diéguez, I. Oyarzabal, J. M. Secob, E. Colacio, *Dalton Trans.* 2012, **41**, 14265.
- [10] L. Botana, J. Ruiz, A. J. Mota, A. Rodríguez-Diéguez, J. M. Seco, I. Oyarzabal, E. Colacio, *Dalton Trans.* 2014, **43**, 13509.
- [11] R. Boča, *Coord. Che. Rev.* 2004, **248**, 757.
- [12] A. Escuer, J. Esteban, S. P. Perlepes, T. C. Stamatatos, *Coord. Chem. Rev.* 2014, **275**, 87.

-
- [13] S. S. Massoud, F. R. Louka, Y. K. Obaid, R. Vicente, J. Ribas, R. C. Fischerc, F. A. Mautner, *Dalton Trans.* 2013, **42**, 3968.
- [14] M. G. Barandika, R. Cortés, L. Lezama, M. K. Urtiaga, M. I. Arriortua, T. Rojo, *J. Chem. Soc. Dalton Trans.*, 1999, 2971.
- [15] P. Mukherjee, M. G. B. Drew, C. J. Gómez-García, A. Ghosh, *Inorg. Chem.* 2009, **48**, 5848.
- [16] S. K. Dey, N. Mondal, M. S. E. Fallah, R. Vicente, A. Escuer, X. Solans, M. Font-Bardía, T. Matsushita, V. Gramlich, S. Mitra, *Inorg. Chem.* 2004, **43**, 2427.
- [17] S. Sarkar, A. Mondal, M. S. E. Fallah, J. Ribas, D. Chopra, H. Stoeckli-Evans, K. K. Rajak, *Polyhedron* 2006, **25**, 25.
- [18] S. Nandi, D. Bannerjee, J. -S. Wu, T. -H. Lu, A. M. Z. Slawin, J. D. Woollins, J. Ribas, C. Sinha. *Eur. J. Inorg. Chem.* 2009, 3972.
- [19] M. Habib, T. K. Karmakar, G. Aromí, J. Ribas-Ariño, H. -K. Fun, S. Chantrapromma, S. K. Chandra, *Inorg. Chem.* 2008, **47**, 4109.
- [20] P. Chaudhuri, R. Wagner, S. Khanra, T. Weyhermüller, *Dalton Trans.* 2006, 4962.
- [21] A. Panja, N. C. Jana, S. Adak, P. Brandão, L. Dlháň, J. Titiš, R. Boča, *New J. Chem.* 2017, **41**, 3143.
- [22] E. Ruiz, J. Cano, S. Alvarez, P. Alemany, *J. Am. Chem. Soc.* 1998, **120**, 11122.
- [23] G. Manca, J. Cano, E. Ruiz, *Inorg. Chem.* 2009, **48**, 3139.
- [24] M. I. Arriortua, R. Cortes, J. L. Mesa, L. Lezama, T. Rojo, G. Villeneuve, *Transition Met. Chem.* 1988, **13**, 371.
- [25] G. A. van Albada, J. J. A. Kolnaar, W. J. J. Smeets, Anthony L. Spek, J. Reedijk, *Eur. J. Inorg. Chem.* **1998**, 1337.
- [26] A. Tamayo, L. Escriche, C. Lodeiro, J. Ribas-Ariño, J. Ribas, B. Coveló, J. Casabó, *Inorg. Chem.* 2006, **45**, 7621.
-

-
- [27] N. C. Jana, M. Patra, P. Brandão, A. Panja, *Polyhedron* 2019, **164**, 23.
- [28] G. M. Sheldrick, SADABS, University of Göttingen, Germany, 1996.
- [29] G. M. Sheldrick, *Acta Crystallogr., Sect. A: Found. Crystallogr.* 2008, **64**, 112.
- [30] G. Parkin, *Chem. Rev.* 2004, **104**, 699.
- [31] A. Panja, T. Matsuo, S. Nagao, S. Hirota, *Inorg. Chem.* 2011, **50**, 11437.
- [32] A. Bhattacharyya, P. K. Bhaumik, M. Das, A. Bauzá, P. P. Jana, K. Harms, A. Frontera, S. Chattopadhyay, *Polyhedron* 2015, **101**, 257.
- [33] M. Č. Romanović, B. R. Čobeljić, A. Pevec, I. Turel, V. Spasojević, A. A. Tsaturyan, I. N. Shcherbakov, K. K. Anđelković, M. Milenković, D. Radanović, M. R. Milenković, *Polyhedron* 2017, **128**, 30.
- [34] P. Ghorai, P. Brandão, S. Benmansour, C. J. Gómez García, A. Saha, *Polyhedron* 2020, **188**, 114708.
- [35] N. F. Chilton, R. P. Anderson, L. D. Turner, A. Soncini, K. S. Murray, *J. Comput. Chem.* 2013, **34**, 1164.
- [36] P. P. Chakrabarty, S. Giri, D. Schollmeyer, H. Sakiyama, M. Mikuriya, A. Sarkar, S. Saha, *Polyhedron* 2015, **89**, 49.
- [37] H. -Z. Kou, S. Hishiya, O. Sato, *Inorg. Chim. Acta.* 2008, **361**, 2396.
- [38] S. Sarkar, A. Mondal, A. Banerjee, D. Chopra, J. Ribas, K. K. Rajak, *Polyhedron* 2006, **25**, 2284.
- [39] S. Sarkar, A. Datta, A. Mondal, D. Chopra, J. Ribas, K. K. Rajak, S. M. Sairam, S. K. Pati, *J. Phys. Chem. B* 2006, **110**, 12.
- [40] X. -J. Lin, Z. Shen, Y. Song, H. -J. Xu, Y. -Z. Li, X. -Z. You, *Inorg. Chim. Acta.* 2005, **358**, 1963.
- [41] S. Sain, S. Bid, A. Usman, H. -K. Fun, G. Aromic, X. Solans, S. K. Chandra, *Inorg. Chim. Acta.* 2005, **358**, 3362.
-

- [42] R. Cortes, J. I. Ruiz de Larramendi, L. Lezama, T. Rojo, K. Urtiaga, M. I. Arriortua, *J. Chem. Soc. Dalton Trans.* 1992, 2723.
- [43] R. Vicente, A. Escuer, J. Ribas, M. S. E. Fallah, X. Solans, M. Font-Bardia, *Inorg. Chem.* 1993, **32**, 1920.
- [44] J. Ribas, M. Monfort, C. Diaz, C. Bastos, X. Solans, *Inorg. Chem.* 1994, **33**, 484.
- [45] A. Escuer, R. Vicente, J. Ribas, X. Solans, *Inorg. Chem.* 1995, **34**, 1793.
- [46] A. Donmez, G. Oylumluoglu, M. B. Coban, C. Kocak, M. Aygun, H. Kara, *J. Mol. Struct.* 2017, **1149**, 569.
- [47] S. Liu, C. Ambrus, S. Dolder, A. Neels, S. Decurtins, *Inorg. Chem.* 2006, **45**, 9622.
- [48] E. Viñuelas-Zahínos, F. Luna-Giles, P. Torres-García, A. Bernalte-García, *Polyhedron* 2009, **28**, 1362.
- [49] B. Tong, S. -C. Chang, E. E. Carpenter, C. J. O'Connor, J. O. Lay Jr., R. E. Norman, *Inorg. Chim. Acta.* 2000, **300–302**, 855.
- [50] C. P. Landee, R. D. Willett, *Inorg. Chem.* 1981, **20**, 2521.
- [51] D. Knetsch, W. L. Groeneveld, *Inorg. Nucl. Chem. Lett.* 1976, **12**, 27.
- [52] Y. Journaux, O. Kahn, *J. Chem. Soc., Dalton Trans.* 1979, 1575.
- [53] R. Herchel, R. Boča, J. Krzystek, A. Ozarowski, M. Durán, J. van Slageren, *J. Am. Chem. Soc.* 2007, **129**, 10306.
- [54] A. P. Ginsberg, R. L. Martin, R. W. Brookes, R. C. Sherwood, *Inorg. Chem.* 1972, **11**, 2884.
- [55] K. O. Joung, C. J. O'Connor, E. Sinn, R. L. Carlin, *Inorg. Chem.* 1979, **18**, 804.
- [56] I. Bkouche-Waskman, Y. Journaux, O. Khan, *Transition Met. Chem.* 1981, **6**, 176.
- [57] Z. H. Zhang, X. H. Bu, Z. A. Zhu, Z. H. Jiang, Y. T. Chen, *Transition Met. Chem.* 1996, **21**, 235.

-
- [58] O. F. Ikotun, W. Ouellette, F. Lloret, M. Julve, R. P. Doyle, *Eur. J. Inorg. Chem.* 2007, 2083.
- [59] A. Tamayo, J. Casabó, L. Escriche, C. Lodeiro, B. Coveló, C. D. Brondino, R. Kivekäs, R. Sillampää, *Inorg. Chem.* 2006, **45**, 1140.
- [60] A. N. Gusev, V. F. Shul'gin, I. O. Ryush, M. Hasegawa, M. A. Kiskin, N. N. Efimov, K. A. Lyssenko, I. L. Eremenko, W. Linert, *Eur. J. Inorg. Chem.* 2017, 704.
- [61] A. -M. -C. Dumitriu, M. Cazacu, A. Bargan, S. Shova, C. Turta, *Polyhedron* 2013, **50**, 255.
- [62] Q. -X. Li, Q. -H. Luo, Y. -Z. Li, C. -Y. Duan, Q. -Y. Tu, *Inorg. Chim. Acta.* 2005, **358**, 504.
- [63] H. -D. Bian, W. Gu, Q. Yu, S. -P. Yan, D. -Z. Liao, Z. -H. Jiang, P. Cheng, *Polyhedron* 2005, **24**, 2002.
- [64] A. I. Gallego, O. Castillo, F. Zamora, S. Delgado, *RSC Adv.* 2013, **3**, 18406.
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CHAPTER 4

CHAPTER 4

Tuneable structures and magnetic property in pseudohalo-bridged dinuclear Ni(II) complexes derived from {N₄} and {N₃O} donor ligands

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4.1. Introduction

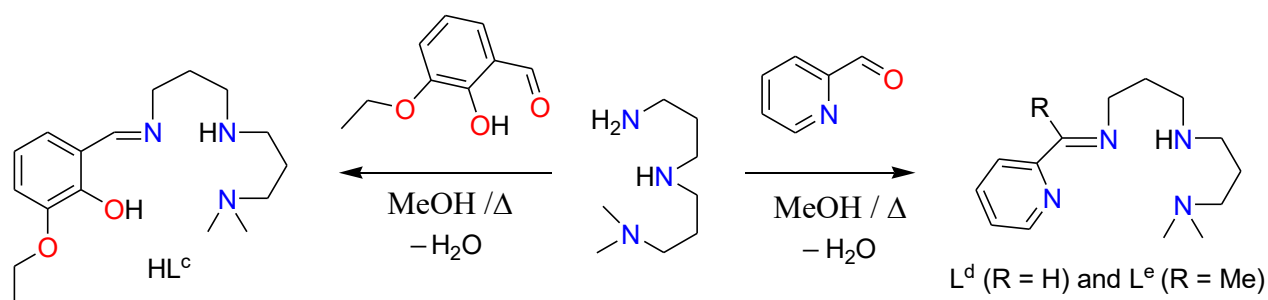
Synthesis of di- and poly-nuclear transition metal complexes with bridging pseudohalides is still attracting considerable research interest worldwide because of their structural diversities and rich magnetic properties [1–6]. In this context, the magnetochemistry of pseudohalo-bridged Ni(II) complexes have been extensively studied because of the presence of significant magnetic anisotropy in Ni(II) ions, arising from the second order spin-orbit coupling, in addition to the possible high spin ground states originating from the ferromagnetic coupling between the metal centres through the bridging pseudohalides [7–9]. Among all the pseudohalides, the azide anion is of special interest. It is well established that the azide ion with an end-on (EO, $\mu_{1,1}$) bridging mode provides ferromagnetic (F) interaction, while end-to-end (EE, $\mu_{1,3}$) azide usually transmits antiferromagnetic (AF) coupling between Ni(II) ions [10]. Besides the azide anion, the dicyanamide and cyanate ions are also frequently encountered in the molecular magnetic materials. The $\mu_{1,5}$ -dicyanamide (dca) bridges mediate mostly a very weak AF interaction between Ni(II) centres, while the $\mu_{1,3}$ -mode of dca transfers moderate AF interactions, leading to some long-range magnetic materials [11–15]. Cyanate ion, on the other hand, propagates magnetic interaction between Ni(II) centres in a similar fashion as that azide ion does but weakly and there is a scarcity of reports of such Ni(II) compounds in the literature [16–22]. In addition, unlike azide ion, an experimental magneto-structural correlation is yet to be established for cyanato-bridged Ni(II) systems [23,24].

Magnetically speaking for all these pseudohalides, the controllable specific bridging modes of them are of great value to dictate the desired magnetic properties of the resulting molecular compounds. A better understanding of the stereo-electronic factors governing the magnetic exchange interaction between metal ions through the bridging pseudohalides would enable us to design Ni(II) clusters with desired magnetic properties. However, the

coordination behaviour of these ions is mostly serendipitous and the predicted bridging modes have been achieved only in a few cases. In this regard, the organic ligands play crucial role in designing magnetically interesting Ni(II) cluster compounds as they may dictate the stereo-electronic structure at the metal centres and have a decisive influence on the bridging modes of the pseudohalides and thus the magnetic properties of the clusters [10]. Among all the organic ligands, Schiff-base ligands are quite useful for developing large numbers of Ni(II) clusters with diverse structural and magnetic properties, mainly because of the synthetic simplicity and tuneable stereo-electronic structures of these ligands by varying carbonyl and amine counterparts [25].

We are now developing coordination chemistry of 1st row transition metals with Schiff base ligands derived from a triamine protected at one end, namely *N,N*-dimethyldipropylenetriamine and salicylaldehyde or its derivatives for the interest in the fields of biomimetic catalysis and magnetic materials. We observed the diverse coordination adaptabilities of these ligands with varying denticity, which make these ligands as suitable synthons for further exploration of the coordination compounds with tuneable structures and properties [26,27]. As we know the charge of the ligands strongly influences the self-assembled neutralization processes, the ligands having same number of donor centres but different charges could end up with diverse structures especially in the presence of exogenous bridging ligands. Given the aforementioned consideration, three tetradentate Schiff base ligands HL^c, L^d and L^e (Scheme 4.1) were allowed to react with Ni(II) salts in the presence of different pseudohalide ions, resulting in a series of dinuclear Ni(II) complexes with diverse structures. Herein, the structures and magnetic properties of six new complexes [Ni₂(L^d)₂(μ_{1,3}-N₃)₂](ClO₄)₂ (**59**), [Ni₂(L^d)₂(μ_{1,3}-NCO)₂](ClO₄)₂ (**60**), [Ni₂(L^d)₂{μ_{1,5}-N(CN)₂}]₂(ClO₄)₂ (**61**), [Ni₂(L^e)₂(μ_{1,3}-N₃)₂](ClO₄)₂ (**62**), [Ni₂(L^e)₂(μ_{1,1}-N₃)₂].0.5MeCN (**63**) and

[Ni₂(L^c)₂(μ_{1,1}-NCO)₂].0.5MeCN (**64**) have been reported, with the magneto-structural relationship of these compounds been discussed.



Scheme 4.1: Synthesis of the Schiff base ligands

4.2. Experimental Section

4.2.1. Laboratory Techniques

Laboratory techniques such as elemental analysis, infrared and UV-vis spectroscopy and single crystal X-ray Diffraction study are similar as our previous work. The details about these techniques have been discussed in section 2.2.1 of chapter 2. Magnetic measurements were carried out at State Key Laboratory of Coordination Chemistry, Collaborative Innovation Centre of Advanced Microstructures, School of Chemistry and Chemical Engineering, Nanjing University, Nanjing, 210023, China. Details of the magnetic measurement procedure are available in the preceding chapter.

4.2.2. Chemicals and Synthetic techniques

4.2.2.1. Materials

All the chemicals such as Ni(II) perchlorate hexahydrate (MarK India), 3-ethoxysalicylaldehyde, pyridine-2-aldehyde, 2-acetylpyridine and *N,N*-

dimethyldipropylenetriamine were purchased from commercial sources and used without further purification. Solvents were of reagent grade and used as received.

Caution! Perchlorate and azide salts of metal complexes coordinated with organic ligands are potentially explosive. Only a small amount of material should be prepared, and it should be handled with great care.

4.2.2.2. Synthesis of the Schiff base ligands L¹, L² and HL³

The ligands were prepared adopting Schiff base condensation method [27]. When *N,N*-dimethyldipropylenetriamine was subjected to react with pyridine-2-aldehyde or 2-acetylpyridine or 3-ethoxysalicylaldehyde in methanol, tetradentate {N₄} or {N₃O} donor Schiff base ligands were produced. In a typical reaction, a mixture of 1.0 mmol of *N,N*-dimethyldipropylenetriamine (159 mg) and 1.0 mmol of pyridine-2-aldehyde (107 mg) in 20 mL methanol was taken in a round bottom flask and it was refluxed for ca. 1 h, and thereafter allowed to cool at room temperature. The deep orange methanol solution of L^d was subsequently used for the synthesis of complexes **59–61**. Using similar protocol, when condensation reaction was carried out using 2-acetylpyridine or 3-ethoxysalicylaldehyde instead of pyridine-2-aldehyde, it resulted ligands L^e and HL^c and subsequently used for the preparation of complexes **62–64**.

4.2.2.3. Synthesis of [Ni₂(L^d)₂(μ_{1,3}-N₃)₂](ClO₄)₂ (**59**)

Ni(ClO₄)₂·6H₂O (1.0 mmol, 366 mg) and Schiff base ligand L^d (1.0 mmol) were combined in 30 mL of methanol with stirring. To the reaction mixture NaN₃ (1.0 mmol, 65 mg) was added with continuous stirring and the resulting green solution was subjected to reflux for about 30 min. The reaction mixture was then filtered and kept at room temperature for crystallization. Crops of dark-green crystals, suitable for X-ray diffraction, were obtained from slow evaporation of the solution after a few days. Then the crystals were collected by filtration and

washed with cold methanol/diethyl ether and air dried to obtain analytically pure complex

59. Yield: 332 mg (74 %). Anal. Calcd. for $C_{28}H_{48}Cl_2N_{14}Ni_2O_8$: C 37.49 %, H 5.39 %, N 21.86 %. Found: C 37.74 %, H 5.60 %, N 21.67 %. Selected FTIR bands (cm^{-1}): 1075 s and 621 s (ClO_4^-); 1599 m (pyridyl); 1651 w (azomethine); 2080 s (azide).

4.2.2.4. Synthesis of $[Ni_2(L^d)_2(\mu_{1,3}-NCO)_2](ClO_4)_2$ (**60**)

Complex **60** was prepared following a similar procedure as described for **59**, but $NaNCO$ was used instead of NaN_3 . Colour: dark-green. Yield: 305 mg (68 %). Anal. Calcd. for $C_{30}H_{48}Cl_2N_{10}Ni_2O_{10}$: C 40.17 %, H 5.39 %, N 15.61 %. Found: C 40.34 %, H 5.58 %, N 15.37 %. Selected FTIR bands (cm^{-1}): 1076 s and 621 s (ClO_4^-); 1601 m (pyridyl); 1653 w (azomethine); 2222 s (cyanate).

4.2.2.5. Synthesis of $[Ni_2(L^d)_2\{\mu_{1,5}-N(CN)_2\}_2](ClO_4)_2$ (**61**)

Complex **61** was prepared following the same synthetic methodology applied for **59**, but $NaN(CN)_2$ was added instead of NaN_3 . Colour: dark-green. Yield: 364 mg (77 %). Anal. Calcd. for $C_{32}H_{48}Cl_2N_{14}Ni_2O_8$: C 40.67 %, H 5.12 %, N 20.75 %. Found: C 40.54 %, H 5.28 %, N 20.57 %. Selected FTIR bands (cm^{-1}): 1069 s and 621 s (ClO_4^-); 1600 m (pyridyl); 1646 w (azomethine); 2195 s, 2246 m, 2303 m (dicyanamide).

4.2.2.6. Synthesis of $[Ni_2(L^e)_2(\mu_{1,3}-N_3)_2](ClO_4)_2$ (**62**)

Complex **62** was synthesised following an identical procedure as described for **59**, but ligand L^e was used in place of L^d . Colour: dark-green. Yield: 305 mg (68 %). Anal. Calcd. for $C_{30}H_{52}Cl_2N_{14}Ni_2O_8$: C 38.95 %, H 5.67 %, N 21.20 %. Found: C 40.04 %, H 5.58 %, N 21.07 %. Selected FTIR bands (cm^{-1}): 1080 s and 620 s (ClO_4^-); 1598 m (pyridyl); 1631 w (azomethine); 2073 s (azide).

4.2.2.7. Synthesis of [Ni₂(L^c)₂(μ_{1,1}-N₃)₂]*·*0.5MeCN (**63**)

A mixture of Ni(ClO₄)₂·6H₂O and Schiff base ligand HL^c in methanol/acetonitrile (1:1, v/v) was used to prepare complex **63** adopting a very similar procedure as described for **59** and in the presence of Et₃N (1.0 mmol). Colour: dark-green. Yield: 338 mg (81 %). Anal. Calcd. for C₇₀H₁₁₄N₂₅Ni₄O₈: C 50.39 %, H 6.89 %, N 20.99 %. Found: C 50.52 %, H 6.99 %, N 20.71 %. Selected FTIR bands (cm⁻¹): 1619 s (azomethine); 2052 s (azide).

4.2.2.8. Synthesis of [Ni₂(L^c)₂(μ_{1,1}-NCO)₂]*·*0.5MeCN (**64**)

Complex **64** was prepared following the same methodology applied for the synthesis of **63**, but NaNCO was used in place of NaN₃. Colour: dark-green. Yield: 292 mg (70 %). Anal. Calcd. for C₇₄H₁₁₄N₁₇Ni₄O₁₂: C 53.27 %, H 6.89 %, N 14.27 %. Found: C 53.44 %, H 6.99 %, N 14.11 %. Selected FTIR bands (cm⁻¹): 1619 s (azomethine); 2171 s (cyanate).

4.3. Results and discussion

4.3.1. Syntheses and general characterization

The tetradentate {N₄}-donor ligand L^d (or L^e) was prepared by adopting a traditional Schiff base condensation method in which *N,N*-dimethyldipropylenetriamine was allowed to react with pyridine-2-aldehyde (or 2-acetylpyridine) in a 1:1 molar ratio in methanol. Similarly, the tetradentate {N₃O}-donor ligand (HL^c) was synthesised when condensation reaction was carried out using 3-ethoxysalicylaldehyde (Scheme 4.1). Six new dark-green binuclear crystalline complexes [Ni₂(L^d)₂(μ_{1,3}-N₃)₂](ClO₄)₂ (**59**), [Ni₂(L^d)₂(μ_{1,3}-NCO)₂](ClO₄)₂ (**60**), [Ni₂(L^d)₂{μ_{1,5}-N(CN)₂}]₂(ClO₄)₂ (**61**), [Ni₂(L^c)₂(μ_{1,3}-N₃)₂](ClO₄)₂ (**62**), [Ni₂(L^c)₂(μ_{1,1}-N₃)₂]*·*0.5MeCN (**63**) and [Ni₂(L^c)₂(μ_{1,1}-NCO)₂]*·*0.5MeCN (**64**) were readily obtained through one-pot reaction of Ni(ClO₄)₂·6H₂O, Schiff base ligand and pseudohalide salts in a 1:1:1 molar ratio in methanol (or a mixture of methanol and acetonitrile). Additionally,

triethylamine was used to deprotonate ligand HL^c for the synthesis of **63** and **64**. One important observation was that ligands L^d and L^c afforded double EE pseudohalo-bridged dinickel(II) complexes, while ligand HL^c resulted double EO azido (or cyanato) bridged dinickel(II) complexes. Therefore, the present study discloses that replacing pyridyl group by phenolic moiety the different bridging modes of pseudohalides may be achieved.

4.3.2. IR Spectroscopy

The IR spectra of complexes **59**, **62** and **63** display a very strong absorption band in the region 2052–2080 cm⁻¹ which is due to the asymmetric stretching frequency, $\nu(\text{N}_3^-)$, of the coordinated azido groups. The observed $\nu(\text{N}_3^-)$ frequencies for the complexes are consistent with those observed in other related end-to-end or end-on azido bridged dinickel(II) complexes [10]. The asymmetric stretching vibrations of end-to-end or end-on NCO⁻ for complexes **60** and **64** are found in the range 2171–2222 cm⁻¹, [16–22] while the asymmetric and symmetric stretching vibrations of dicyanamide ions in **61** are observed in the range 2195–2303 cm⁻¹ [11–15]. The IR spectra of **59–62** also display two strong bands; one broad band at around 1076 cm⁻¹ and a sharp band at 621 cm⁻¹, which can be assigned to the stretching and bending vibrations of perchlorate counterions. The broadening of the stretching band may be attributed to the involvement of perchlorate ions in hydrogen bonding interaction in the solid state. In addition, the IR spectra of all the complexes consist of common bands in the region 1619–1653 cm⁻¹, which are attributable to the $\nu(\text{C}=\text{N})$ stretching frequency of the azomethine bond of the Schiff base ligands in **63** and **64**. The additional bands at around 1600 cm⁻¹ for complexes **59–62** are attributed to the pyridyl groups.

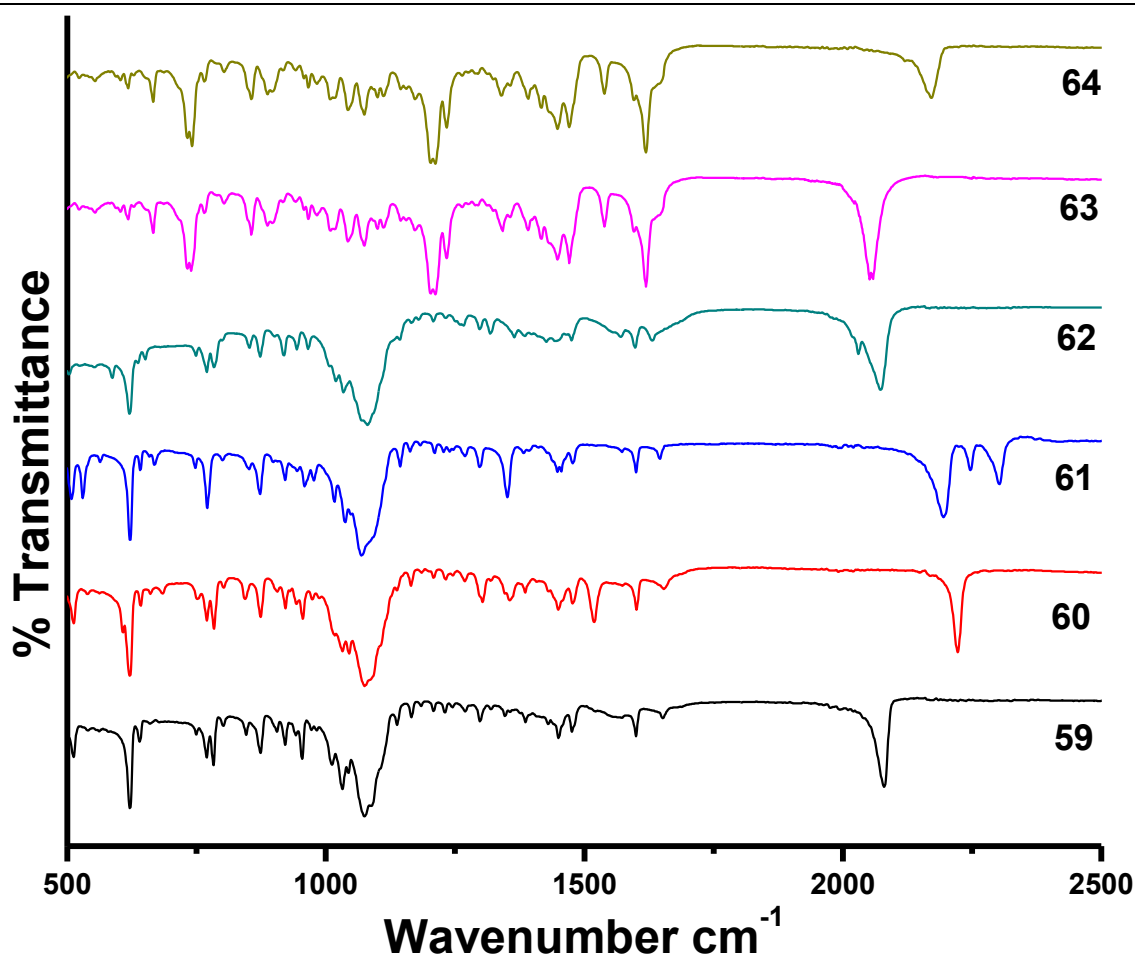


Figure 4.1: IR spectra of the complex 59-64

4.3.3. Description of crystal structures

$[Ni_2(L^d)_2(\mu_{1,3}-N_3)_2](ClO_4)_2$ (**59**) and $[Ni_2(L^d)_2(\mu_{1,3}-NCO)_2](ClO_4)_2$ (**60**) are isostructural and isomorphous compounds and both crystallized in the monoclinic space group $P2_1/n$ (Figure 4.2 and 4.3) (Table 4.1). Crystallographic data and refinement details for the complexes are given in Table 4.1. The centrosymmetric dimeric complex cations of **59** and **60** are constructed with doubly EE bridged pseudohalides (N_3^- and NCO^-), and the Ni(II) ions in these complexes are hexacoordinated with a distorted octahedral geometry. The coordination sites of Ni(II) ions in **59** are fulfilled by $\{N_6\}$ donor set whereas it is $\{N_5O\}$ in **60**. Each Ni(II) centre in **59** or **60** is bonded with four nitrogen donor atoms of the Schiff base ligand and two nitrogen donor atoms from one each of centro-symmetrically related EE bridging

azide ions in **59** and one oxygen atom and one nitrogen atom from two centro-symmetrically related EE bridging cyanato groups in **60**. In both complexes, three N-atoms (imine, secondary amine and tertiary amine N-atoms) from the triamine part of the Schiff base ligand facially coordinate the Ni(II) centre. The Ni–N bond distances of pyridine, imine, secondary amine and tertiary amine of the Schiff base ligand vary in the range 2.072(3) to 2.135(3) Å in **59**, which are comparable to the literature reported values in closely related Ni(II) complexes [17,26]. The bridging region is slightly asymmetric as can be seen from the Ni–N bond distances of 2.120(3) and 2.185(3) Å of the bridging azide ions. Similar bond lengths are observed in **60** (see Table 4.2), but the bridging region is more asymmetric as reflected from the different Ni–N (2.045(3) Å) and Ni–O (2.217(2) Å) bond distances of bridging cyanato ligands, which should be due to the presence of hetero bridging atoms (oxygen and nitrogen atoms) in cyanate ion in **60**. The EE pseudohalide bridges are almost linear with an angle N7–N6–N5 of 177.2(3)° for azide ions in **59** and an angle N5–C15–O1 of 176.3(5)° for cyanate ligands in **60**. The N6–N5–Ni angle of 133.5(2)° differs considerably from N6–N7–Ni1a of 116.7(2)° in **59** and the Ni1...Ni1a separation is 5.203 Å (symmetry code: a = 2–x, –y, –z). While in **60**, the C15–N5–Ni1b bond angle of 152.0(4)° differs significantly from C15–O1–Ni1 of 111.6(3)° with the Ni1...Ni1b separation of 5.326 Å (symmetry code: b = 1–x, 1–y, z). These values are consistent with the structural results obtained for other EE azido- and cyanato-bridged Ni(II) complexes [19–21,28–36]. The two bridging pseudohalides in both **59** and **60** lie in the same plane and two Ni(II) centres deviate slightly out of that plane in either sides, leading to a chair-like arrangement of the eight-membered {Ni(μ_{1,3}-N₃/NCO)₂Ni} core. The dihedral angle (δ) between the plane defined by two pseudohalide ions and the N–Ni–N (in **59**) or N–Ni–O (in **60**) are 34.51° and 17.74°, respectively. Further inspection of the crystal structures discloses that two edges of Ni(II) polyhedra are connected by EE bridging pseudohalides (see Figure 4.3). Moreover, in both **59** and **60**, the secondary amine hydrogen

atom of the Schiff base ligand participates in hydrogen bonding interaction with the oxygen atom of the perchlorate counter ion with the N...O distances are 3.164(4) and 3.162(4) Å in **59** and **60**, respectively. The crystal packing is further stabilised by the C–H... π interaction involving C–H proton of pyridyl group and π electrons of the pseudohalide ligands as shown in Figure 4.2 and 4.3 for **59** and **60**, respectively. It is worth noting that, unlike the azido bridged compounds, [28–36] the doubly EE cyanato-bridged dimeric Ni(II) complexes are rare with only a limited examples reported in the literature [19–21].

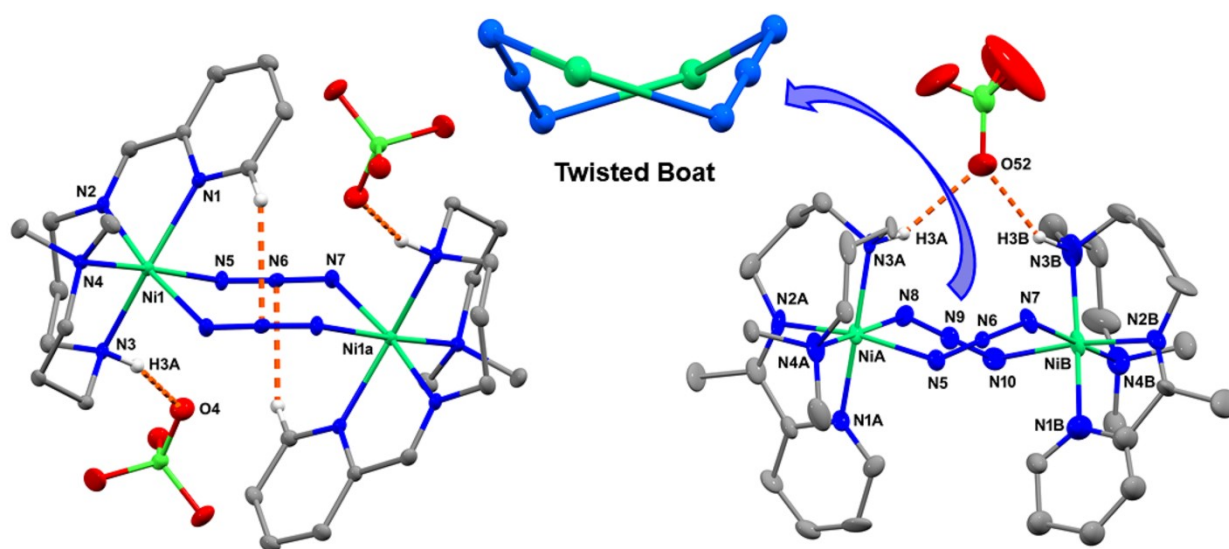


Figure 4.2: Crystal structures of **59** (left) and a partial set of **62** (right) showing selected atom numbering scheme. Ellipsoids are drawn at the 30% probability level. The weak interactions are displayed as dashed lines.

CHAPTER 4

Table 4.1 Crystallographic data and structural refinement parameters of **59–64**

	59	60	61	62	63	64
Empirical formula	$C_{28}H_{48}Cl_2N_{14}Ni_2O_8$	$C_{30}H_{48}Cl_2N_{10}Ni_2O_{10}$	$C_{32}H_{48}Cl_2N_{14}Ni_2O_8$	$C_{60}H_{104}Cl_{14}N_{38}Ni_4O_{16}$	$C_{70}H_{114}N_{25}Ni_4O_8$	$C_{74}H_{114}N_{17}Ni_4O_{12}$
Formula weight (g mol ⁻¹)	897.12	897.10	945.16	1850.35	1668.70	1668.66
Crystal system	Monoclinic	Monoclinic	Monoclinic	Orthorhombic	Triclinic	Triclinic
Space group	$P2_1/n$	$P2_1/n$	$P2_1/n$	$Fdd2$	$P\bar{1}$	$P\bar{1}$
a (Å)	8.2434(4)	8.3729(9)	8.1790(6)	26.3729(18)	15.0146(11)	15.0212(11)
b (Å)	13.7798(7)	13.6040(14)	27.2301(18)	43.882(4)	15.3326(10)	15.3518(12)
c (Å)	16.7261(8)	16.8216(19)	9.5177(7)	20.6839(16)	18.7906(14)	18.7416(14)
α (deg)	90	90	90	90	106.124(2)	106.273(3)
β (deg)	96.059(3)	94.390(4)	100.369(3)	90	106.924(2)	106.932(3)
γ (deg)	90	90	90	90	91.258(2)	91.228(3)
Volume (Å ³)	1889.34(16)	1910.4(4)	2085.1(3)	23937(3)	3950.7(5)	3943.8(5)
Z	4	4	2	12	2	2
D_{calc} (g cm ⁻³)	1.577	1.560	1.505	1.540	1.403	1.405
μ (mm ⁻¹)	1.205	1.193	1.096	1.144	1.008	1.010
F(000)	936	936	984	11616	1770	1770
θ range (deg)	1.919–27.174	1.927–27.138	1.496–29.193	1.334–25.832	2.079–29.195	2.236–27.984
Reflections collected	16252	15382	27011	38367	190619	166025
Independent reflections	4197 (0.0692)	4222 (0.0644)	5580 (0.0453)	11119 (0.0791)	21354 (0.0440)	15319 (0.0489)
Observed reflections	2927	2773	4182	7773	17043	12961
[I > 2 σ (I)]						
Restraints/parameters	1/249	1/249	0/267	1/710	0/993	0/989
Goodness-of-fit on F ²	1.016	1.029	1.059	1.019	1.031	1.036
Final R indices	$R_1=0.0452$	$R_1=0.0501$	$R_1=0.0368$	$R_1=0.0953$	$R_1=0.0329$	$R_1=0.0307$
[I > 2 σ (I)]	$wR_2=0.0912$	$wR_2=0.1035$	$wR_2=0.0746$	$wR_2=0.2343$	$wR_2=0.0753$	$wR_2=0.0680$
R indices (all data)	$R_1=0.0789$	$R_1=0.0930$	$R_1=0.0580$	$R_1=0.1370$	$R_1=0.0506$	$R_1=0.0421$
	$wR_2=0.1053$	$wR_2=0.1184$	$wR_2=0.0824$	$wR_2=0.2666$	$wR_2=0.0833$	$wR_2=0.0732$
Largest diff. peak/hole (e Å ⁻³)	0.908/–0.414	1.313/–0.566	0.472/–0.442	1.683/–0.848	1.000/–0.604	0.948/–0.531

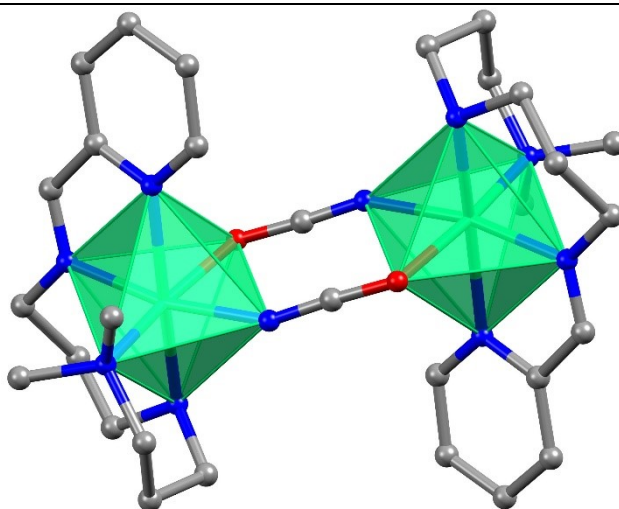


Figure 4.3: Crystal structure of complex **60** along with local coordination geometry of Ni(II) ions.

Table 4.2 Selected bond distances (Å) for **59–64**

Bond	59	60	61	62#	63#	64#
Ni(II)–N(pyridine)	2.125(3)	2.124(3)	2.1331(17)	2.059(13)	-	-
Ni(II)–N(imine)	2.072(3)	2.067(3)	2.0704(17)	2.065(12)	2.0610(17)	2.0474(15)
Ni(II)–N(secondary amine)	2.102(3)	2.100(3)	2.0891(17)	2.054(14)	2.1098(17)	2.1303(14)
Ni(II)–N(tertiary amine)	2.135(3)	2.1116(3)	2.1662(15)	2.166(13)	2.2163(17)	2.1949(15)
Ni(II)–O(phenolate)	-	-	-	-	2.0077(13)	2.0226(12)
Ni(II)–O(pseudohalide)	-	2.217(2)	-	-	-	-
Ni(II)–N(pseudohalide)	2.120(3)	2.045(3) ^b	2.1380(16)	2.156(12)	2.1139(17)	2.1194(14)
	2.185(3) ^a		2.0692(16) ^c	2.206(13) ^d	2.2550(16) ^e	2.2048(14) ^e

Symmetry codes: a = 2–x, –y, –z; b = 1–x, 1–y, –z; c = 1–x, –y, 1–z; d = –x, –y, z; e = 1–x, –y, –z and # denotes that the bond parameters of one of the crystallographically independent molecules are presented.

$[\text{Ni}_2(\text{L}^{\text{d}})_2\{\mu_{1,5}\text{-N}(\text{CN})_2\}_2](\text{ClO}_4)_2$ (**61**) crystallised in the monoclinic space group $P2_1/n$ where the asymmetric unit contains half of the dinuclear complex cation on an inversion centre and a perchlorate counter ion on a general position to balance the charge. The structure of complex **61** (Figure 4.4) is very similar to that of the structures of **59** and **60**, but the central $\{\text{Ni}(\mu_{1,5}\text{-N}(\text{CN})_2)_2\text{Ni}\}$ core in **61** is somewhat different from $\{\text{Ni}(\mu_{1,3}\text{-N}_3)_2\text{Ni}\}$ in **59** or

$\{\text{Ni}(\mu_{1,3}\text{-NCO})_2\text{Ni}\}$ in **60**. The Ni...Ni separation (7.346 Å) through the five-atom dicyanamide bridges is significantly larger in **61** than that found in three-atom bridged pseudohalides in **59** and **60** as expected. The coordinating fashion of the Schiff base ligand to the metal centre is exactly the same as that found in **59** and **60**. The Ni(II) ion in **61** is therefore again hexacoordinated in a distorted octahedral geometry with all four N donor atoms of the Schiff base ligand together with two N donor atoms from two symmetry related end-to-end bridging dicyanamide groups at cis positions (Table 4.2). Two N–C–N bond angles of bridging dicyanamide group are $174.3(2)^\circ$ (N5–C15–N6) and $175.0(2)^\circ$ (N7–C16–N6), while C16–N6–C15 angle is $118.91(17)^\circ$, which are typical for $\mu_{1,5}$ -dicyanamide bridges [11–15]. Like in **59** and **60**, the secondary amine hydrogen atom of the Schiff base ligand in **61** is hydrogen bonded with the oxygen atom of the perchlorate counter ion with N...O bond distance of 3.223(2) Å. The solid-state packing is further stabilised by the C–H... π interaction involving C–H proton of pyridyl group and π electrons of the bridging dicyanamide as shown in Figure 4.4.

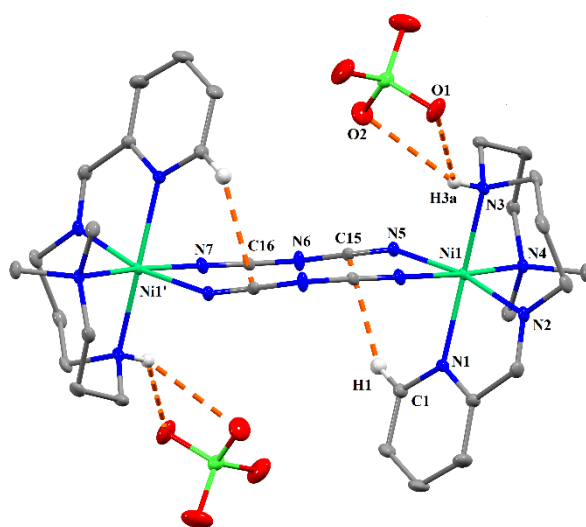


Figure 4.4: Crystal structure of complex **61** with selected atom numbering scheme. Ellipsoids are drawn at the 30% probability level. The non-covalent interactions are shown as dashed lines.

Crystallographic study reveals that similar to complex **59**, [Ni₂(L^c)₂(μ_{1,3}-N₃)₂](ClO₄)₂ (**62**) is also comprised with doubly μ_{1,3}-azido-bridged dinickel(II) cations and two ClO₄⁻ ions (Figure 4.2 and Table 4.2). But complex **62** crystallised in the orthorhombic *Fdd2* space group in which the asymmetric unit contains two crystallographically distinguishable complex cations, one residing on a general position and other one on the two-fold axis. Each Ni(II) ion is again six-coordinated, being bonded with four nitrogen atoms of ligand L² and two nitrogen atoms from two bridging azide ions in cis positions. However, the essential differences in these structures originate from the presence of different symmetry elements i.e. inversion centre in **59** and two-fold rotation axis in **60**. That brings different hydrogen bonding patterns in these structures as shown in Figure 4.2. Secondary amine groups connected to Ni(II) centres in **59** are placed in opposite sides of central {Ni(μ_{1,3}-N₃)₂Ni} core and thereby interact with different perchlorate ions through hydrogen bonds, while they reside at the same side, leading to a cooperative hydrogen bonding interaction with a perchlorate ion in **62** (Figure 4.2). Remarkably, the {Ni(μ_{1,3}-N₃)₂Ni} core structure is quite different in two cases as it adopts a chair-like arrangement in **59** where both azide ions lie on a same plane, while the two azide bridges are non-coplanar and cross linked the Ni(II) ions with a twisted boat type arrangement of {Ni(μ_{1,3}-N₃)₂Ni} core in **62**. The intramolecular Ni...Ni separations in two crystallographically independent dimeric units are 5.257(3) and 5.271(3) Å, whereas the closest intermolecular separation between the Ni(II) centres is 8.672(3) Å. It is noteworthy that the two bridging azides with cross-linked and non-coplanar (μ_{1,3}-N₃)₂ structure is unusual, as the planarity is a common feature of dinickel(II) complexes with double μ_{1,3}-N₃ bridges [28–36], and for dinickel(II) system only four such compounds are both structurally and magnetically characterized [37–40]. The Ni–(μ_{1,3}-N₃)–Ni (Ni–N...N–Ni) torsion angles (τ) are 68.67, 71.00 and 76.95°, which are close to that found in similar systems [37–40].

Compounds $[\text{Ni}_2(\text{L}^\circ)_2(\mu_{1,1}\text{-N}_3)_2] \cdot 0.5\text{MeCN}$ (**63**) and $[\text{Ni}_2(\text{L}^\circ)_2(\mu_{1,1}\text{-NCO})_2] \cdot 0.5\text{MeCN}$ (**64**) are isostructural and isomorphous (Figure 4.5 and 4.6), and they crystallised in the triclinic space group $P\bar{1}$ in which four crystallographically independent neutral complex molecules sit on inversion centres together with an acetonitrile molecule on a general position. In both complexes, the Ni(II) centres are hexacoordinated with a distorted octahedral structure. The coordination numbers of the Ni(II) ion are satisfied by three N donor atoms and one phenolate-O atom of the deprotonated Schiff base ligand and two N-atoms from either the EO bridging azide ions (in **63**) or cyanate ions (in **64**). These cis disposed pseudohalide ions share the common edges, leading to the edged-sharing bioctahedral structures (see Figure 4.5). Like **59–62**, three N-atoms (imine, secondary amine and tertiary amine N-atoms) of the deprotonated Schiff base ligand facially coordinate the Ni(II) centres in **63** and **64**. The Ni–N bond distances in **63** and **64** are comparable to that observed in **59–62** (Table 4.2) and the related complexes reported in the literature [16–18, 41–61]. The central $\{\text{NiN}_2\text{Ni}\}$ cores are planar in both complexes as dictated by the centre of symmetry with the Ni–N–Ni bridging angles spanning in the range $100.74(6)$ – $102.06(5)^\circ$ and $97.51(8)$ – $98.50(7)^\circ$ in **63** and **64**, respectively. The azide and cyanate ions are nearly linear with N–N–N and N–C–O bond angles of $178.55(18)^\circ$ and $179.3(2)^\circ$, respectively. The doubly EO pseudohalide bridges in both compounds are slightly asymmetric with the Ni–N bond distances of 2.114(2) and 2.255(2) Å in **63** and 2.119(2) and 2.205(1) Å in **64**. The average separation of the metal centres in the dimeric units is 3.377 Å in **63** and 3.284 Å in **64**. The secondary amine hydrogen atom involves in hydrogen bonding interaction with the phenoxido oxygen atom within the dimeric unit with average N...O distances of 3.033 Å and 3.002 Å in **63** and **64**, respectively, to provide the solid-state stability of these compounds. Additional stability in the solid-state is gained by the π – π interaction involving π -electrons of acetonitrile molecule and the aromatic ring of the Schiff base ligand (not shown). It is worth noting that, unlike

azido bridging [41–61], the doubly EO cyanato-bridged dimeric Ni(II) complexes are scarce, and only few dinuclear Ni(II) compounds with such a bridging motif are available in the literature [16–18, 62].

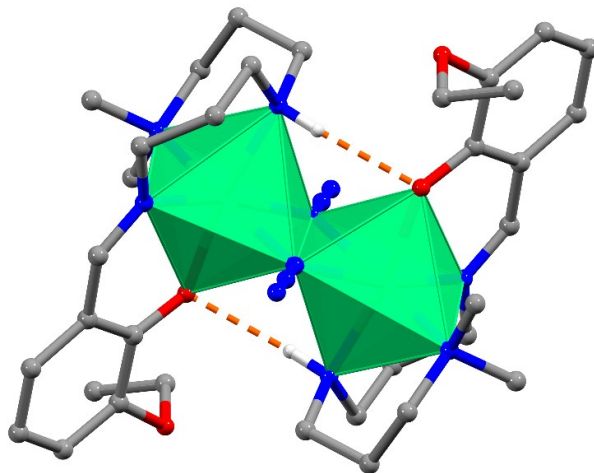


Figure 4.5: Crystal structure of complex **63** along with local coordination geometry of Ni(II) ions.

From the structural studies, it is clear that just by fine tuning of the organic ligands, diverse bridging modes of pseudohalides can be achieved. For example, an additional methyl group in L^e ligand brings the crossed linked and nonplanar double EE azido-bridged Ni(II) dimer in **62**, while EE bridging azides are planar in complex **59**. The central $\{Ni(\mu_{1,3}-N_3)_2Ni\}$ core structures in two cases are also significantly different as it is a chair like arrangement in **59** while a twisted boat like arrangement is observed in **62** (Figure 4.2). Further inspection of the crystal structures reveals that although the connectivity of both L^d and deprotonated HL^c ligands to the metal centres are similar, leaving two cis positions of the metal centre for bridging azides, the bridging modes of azide ions are different in these systems i.e. EE ($\mu_{1,3}$) in **59** and EO ($\mu_{1,1}$) in **63**. It is reasonable to point out that the hydrogen bonding interaction between phenolate-O as an acceptor and secondary amine as a donor from either of the organic ligands in the dimeric unit could overcome the increased steric crowding in the system when azides bridge the metal centres in an EO fashion. In absence of the hydrogen

bond acceptor ability of the pyridyl group in **59**, the azide ions prefer to bridge the metal centres in an EE fashion to minimize the steric repulsion in the system.

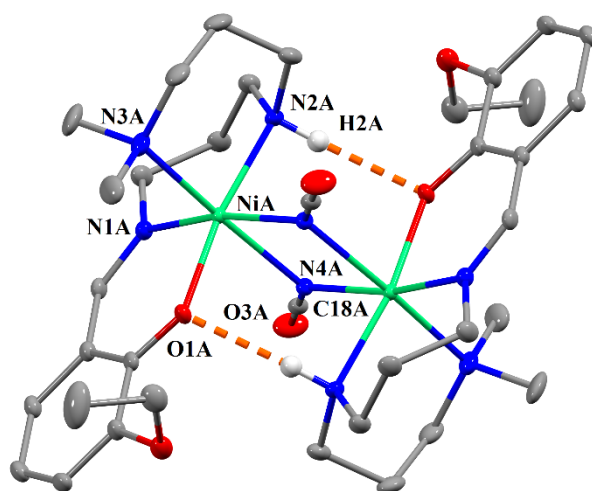


Figure 4.6: Crystal structure of complex **64** with selected atom numbering scheme. Ellipsoids are drawn at the 30% probability level. The non-covalent interactions are shown as dashed lines.

4.3.4. Magnetic studies

The temperature dependence of the magnetic properties of complexes **59** and **60** as χ_M and $\chi_M T$ product vs. T plots (χ_M being the molar magnetic susceptibility per dimer) under a constant magnetic field of 1.0 kOe are displayed in [Figure 4.7 and 4.8](#), respectively. At room temperature the $\chi_M T$ values of 2.20 and 2.25 cm³ mol⁻¹ K for **59** and **60**, respectively, are slightly higher than the calculated value of 2.0 cm³ mol⁻¹ K for two isolated Ni(II) ions with $S = 1$ and $g = 2$, which is due to the spin-orbit coupling of Ni(II) ion at room temperature. The $\chi_M T$ values decrease continuously from room temperature and tends to zero at 2 K for both cases. This magnetic behaviour is typical for an intramolecular antiferromagnetic interaction between two Ni(II) ions. The Curie–Weiss analysis ([Figure 4.9 and 4.10](#)) of the magnetic susceptibility data above 100 K with negative Weiss values (–15.01 and –7.36 K, respectively) as well as the presence of distinct maxima in χ_M vs. T plots in **59** and **60** agrees well with the antiferromagnetic interaction between the metal centres. The isothermal

magnetisation of **59** and **60** as depicted in Figure 4.11 and 4.12, respectively, justify the diamagnetic ground state at low temperature, and therefore zero-field splitting (ZFS) does not have much influence in the magnetic property of these systems. A full-matrix diagonalization approach assuming an isotropic spin exchange Hamiltonian ($-2J\hat{S}_1\cdot\hat{S}_2$), Zeeman interaction (g_{Ni} , average), and intermolecular interaction (zJ') was further employed to analyse the magnetic data using *PHI* program [63]. The best fittings afforded the following set of parameters: $J = -6.95(1) \text{ cm}^{-1}$, $g_{\text{Ni}} = 2.13(1)$, and $zJ' = 0.39(10) \text{ cm}^{-1}$ for complex **59** and $J = -2.71(2) \text{ cm}^{-1}$, $g_{\text{Ni}} = 2.17(1)$ and $zJ' = -0.48(6) \text{ cm}^{-1}$ for complex **60**.

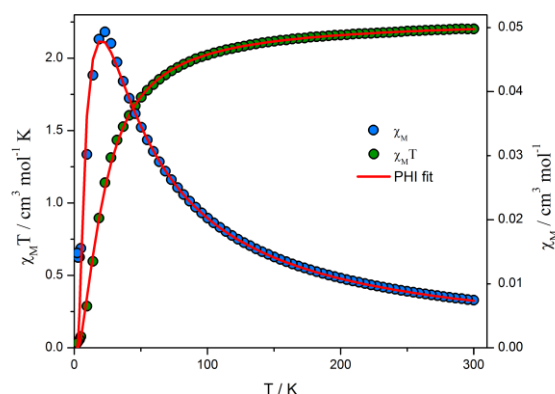


Figure 4.7: Plots of χ_M and $\chi_M T$ vs. T for complex **59**. Symbols and solid lines represent experimental data and the best theoretical fits, respectively.

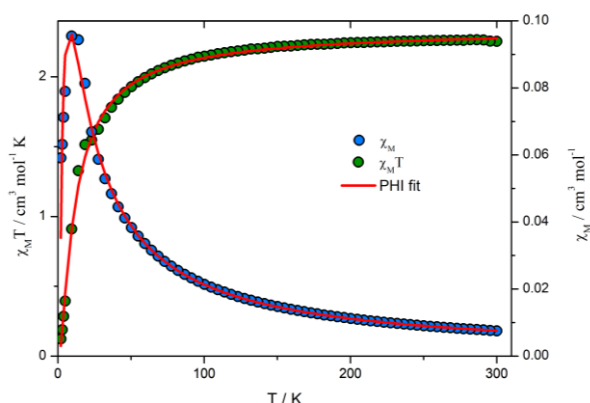


Figure 4.8: Plots of χ_M and $\chi_M T$ vs. T for complex **60**. Symbols and solid lines represent experimental data and the best theoretical fits, respectively.

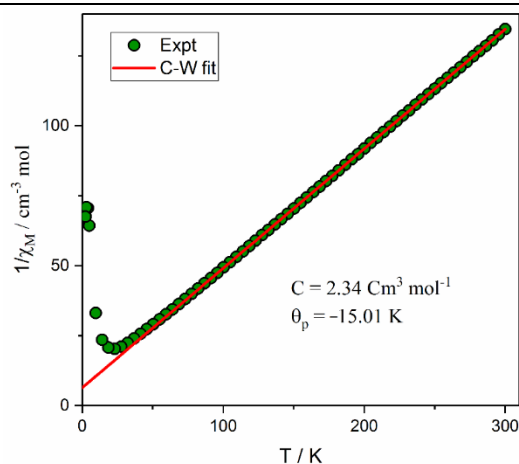


Figure 4.9: Curie-Weiss plot for complex **59** in the 100–300 K range.

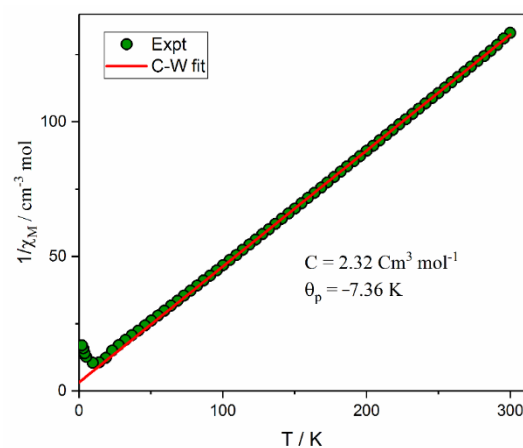


Figure 4.10: Curie-Weiss plot for complex **60** in the 100–300 K range.

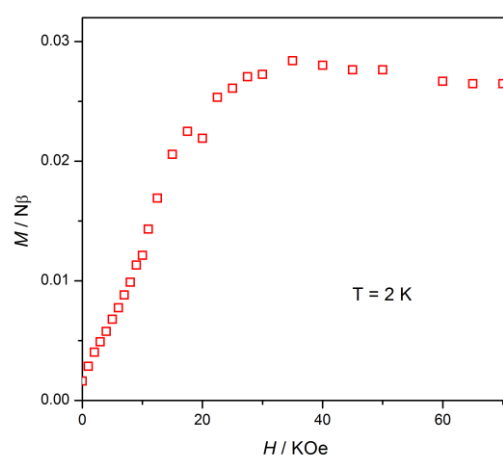


Figure 4.11: Isothermal magnetization of **59** at 2 K in the applied dc field 0–70 KOe.

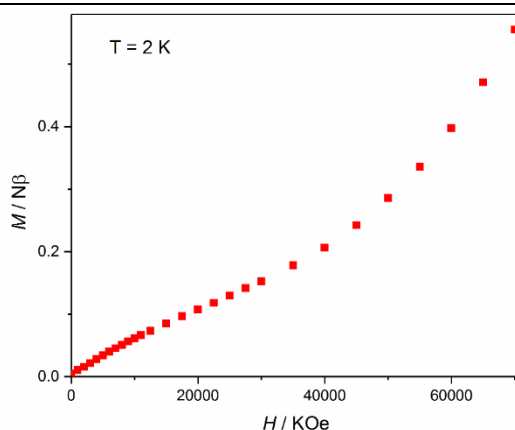


Figure 4.12: Isothermal magnetization of **60** at 2 K in the applied dc field 0–70 KOe.

The $\chi_M T$ versus T plot per dimeric unit of **61** is shown in Figure 4.13. At room temperature the $\chi_M T$ value of $2.24 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ is again usual for two isolated Ni(II) ions. The $\chi_M T$ values remain almost constant down to 60 K and thereafter gradually decreases with lowering the temperature to attain a minimum value of $1.51 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ at 2 K. This magnetic behaviour is characteristic for a very weak antiferromagnetically coupled Ni(II) ions through $\mu_{1,5}\text{-N}(\text{CN})_2$ -bridges [11–15]. In addition, the isothermal field dependent magnetization data measured at 2 and 5 K were also depicted in Figure 4.13, showing regular paramagnetic behaviour. The magnetic data were fitted simultaneously using *PHI* program, assuming isotropic exchange Hamiltonian ($-2J\hat{S}_1\cdot\hat{S}_2$), Zeeman interaction (g_{Ni}) and axial zero-field splitting (D), and neglecting intermolecular interaction (zJ'). The best-fitting offers $J = -0.15 (14) \text{ cm}^{-1}$, $g_{\text{Ni}} = 2.13(1)$ and $D = 2.64(5) \text{ cm}^{-1}$ for **61**. The negligibly small exchange interaction is consistent with the intramolecular Ni $\cdots$ Ni separation of 7.346 Å through the bridging dicyanamide ligands. In fact, the analysis of the magnetic data, considering only the presence of single ion anisotropy and ignoring the exchange interaction, resulted identical fitting with the best fit parameters $g_{\text{Ni}} = 2.12(1)$ and $D = 2.97(2) \text{ cm}^{-1}$.

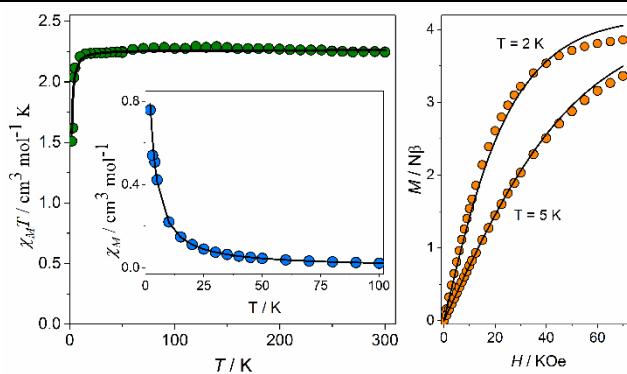


Figure 4.13: Magnetic data for **61**. Thermal dependence of χ_M and $\chi_M T$ product measured at 1.0 kOe dc field (left) and magnetisation data at different temperatures (right). Symbols and solid lines represent experimental and best fitted data, respectively.

The magnetic property per dimeric unit of **62** as χ_M and $\chi_M T$ product vs. T plots and the molar magnetization as a function of applied dc magnetic field ($M / N\beta$ vs. H) are displayed in Figure 4.14. The $\chi_M T$ product at room temperature for **62**, *ca.* $2.34 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$, is again typical for two magnetically isolated Ni(II) ions. Upon cooling, the $\chi_M T$ product increases continuously to a maximum of $3.18 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ at 19 K and thereafter decreases sharply to a value of $2.35 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ at 2 K. This behaviour is characteristic for an intramolecular ferromagnetic exchange between two Ni(II) ions together with the influence of an intermolecular interaction and/or zero-field splitting (ZFS) of the ground state ($S = 2$), manifested at low temperature. The Curie–Weiss plot (Figure 4.15) of the magnetic susceptibility data above 100 K with positive Weiss value (12.92 K) further supports the ferromagnetic coupling between the metal centres. Analysis of the magnetic data applying isotropic exchange Hamiltonian ($-2J\hat{S}_1\cdot\hat{S}_2$), Zeeman effect (g_{Ni} , average), axial zero-field splitting (D), and intermolecular interaction (zJ') yielded the following set of best fit parameters: $J = 13.21(1) \text{ cm}^{-1}$, $g_{\text{Ni}} = 2.09(1)$, $D = 7.20(1) \text{ cm}^{-1}$ and $zJ' = -0.011(8) \text{ cm}^{-1}$ for complex **62**.

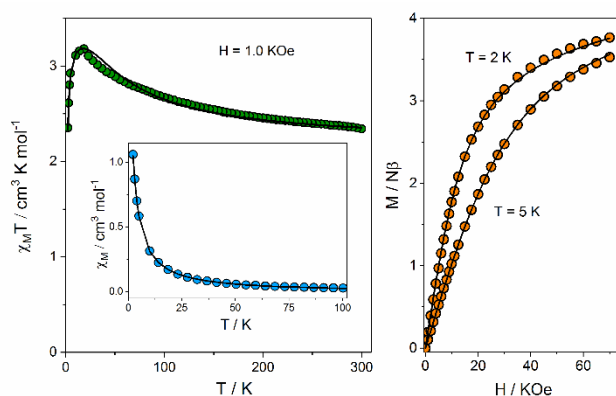


Figure 4.14: Magnetic data for **62**. Thermal dependence of χ_M and $\chi_M T$ product measured at 1.0 kOe dc field (left) and Magnetisation data at different temperatures (right). Symbols and solid lines represent experimental and best fitted data, respectively.

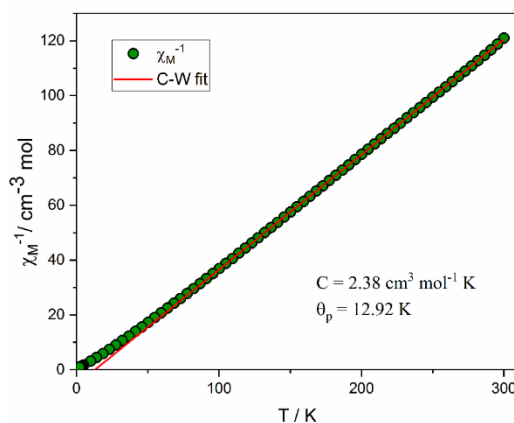


Figure 4.15: Curie-Weiss plot for complex **62** in the 100–300 K range.

The χ_M and $\chi_M T$ product vs. T plots per dimeric units of **63** and **64** and the molar magnetization as a function of applied dc magnetic field ($M / N\beta$ vs. H) are shown in [Figure 4.16](#) and [4.17](#), respectively. The $\chi_M T$ product at room temperature for **63** and **64** is *ca.* 2.89 and 2.63 cm³ mol⁻¹ K, respectively, which are slightly higher than calculated for two magnetically non-interacting Ni(II) ions. The $\chi_M T$ product increases continuously with decreasing temperature reaching a maximum of 3.57 cm³ mol⁻¹ K at 50 K for **63** and 3.22 cm³ mol⁻¹ K at 15 K for **64** and then $\chi_M T$ decreases sharply to attain a value *ca.* 1.38 and 1.69 cm³ mol⁻¹ K at 2 K for **63** and **64**, respectively. This feature is again typical for an intramolecular ferromagnetic exchange between two Ni(II) ions with the influence of

intermolecular interactions and/or zero-field splitting (ZFS) of ground state ($S = 2$), particularly at low temperature. The Curie–Weiss analysis (Figure 4.18 and 4.19) of the magnetic susceptibility data above 100 K are also consistent with ferromagnetic interaction. Analysis of the magnetic data considering isotropic spin exchange Hamiltonian ($-2J\hat{S}_1\cdot\hat{S}_2$), Zeeman effect (g_{Ni} , average), axial zero-field splitting (D), and intermolecular interaction (zJ') afforded the following set of best fit parameters: $J = 28.79(2) \text{ cm}^{-1}$, $g_{\text{Ni}} = 2.23(1)$, $D = 14.23(2) \text{ cm}^{-1}$ and $zJ' = -0.085(4) \text{ cm}^{-1}$ for complex **63** and $J = 3.70(2) \text{ cm}^{-1}$, $g_{\text{Ni}} = 2.28(1)$, $D = 8.05(4) \text{ cm}^{-1}$ and $zJ' = -0.067(2) \text{ cm}^{-1}$ for complex **64**.

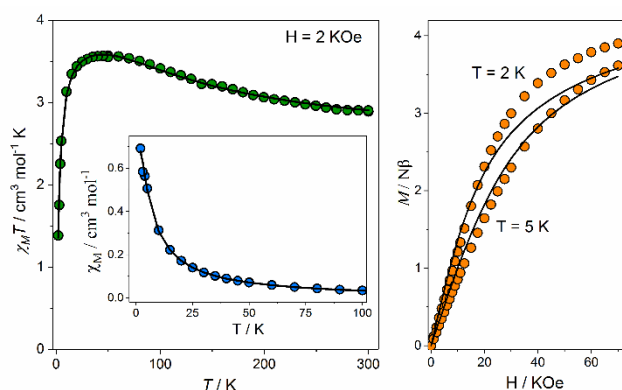


Figure 4.16: Magnetic data for **63**. Thermal dependence of χ_M and $\chi_M T$ product measured at 1.0 kOe dc field (left) and Magnetisation data at different temperatures (right). Symbols and solid lines represent experimental and best fitted data, respectively.

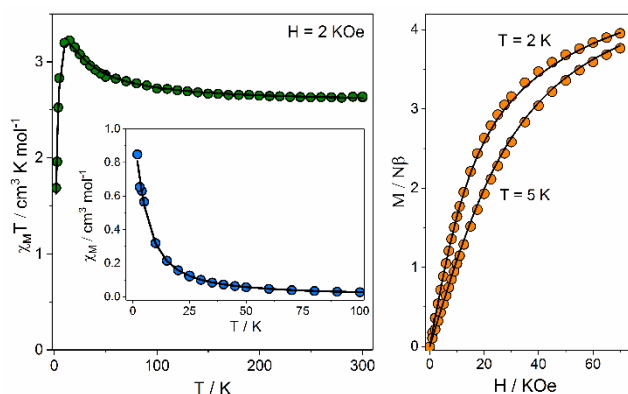


Figure 4.17: Magnetic data for **64**. Thermal dependence of χ_M and $\chi_M T$ product measured at 1.0 kOe dc field (left) and Magnetisation data at different temperatures (right). Symbols and solid lines represent experimental and best fitted data, respectively.

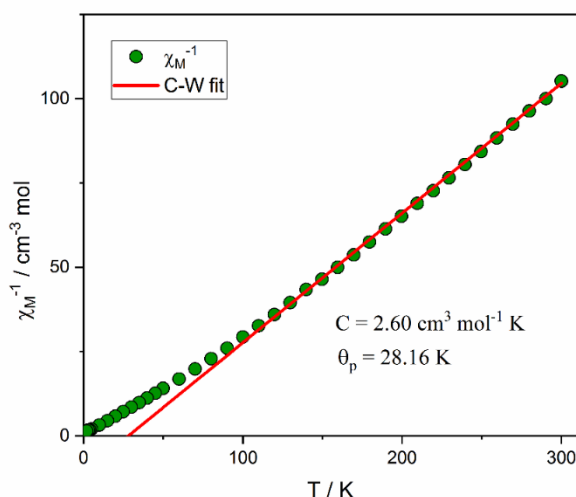


Figure 4.18: Curie-Weiss plot for complex **63** in the 100–300 K range.

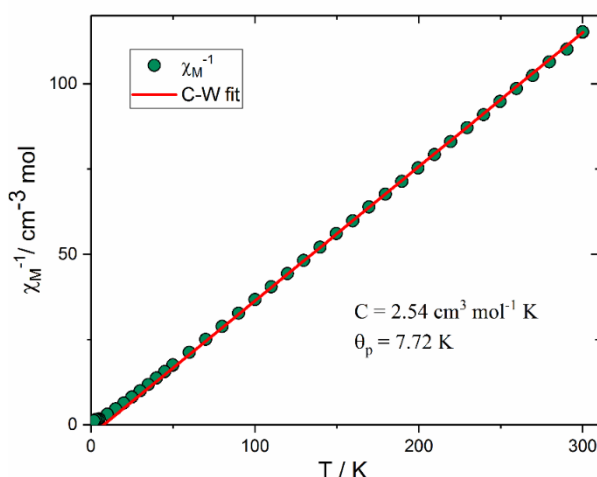


Figure 4.19: Curie-Weiss plot for complex **64** in the 100–300 K range.

The handful examples of double EE azido-bridged dinickel(II) complexes with [Ni₂(μ_{1,3}-N₃)₂]²⁺ core structures and planar bridging azides are known in which azide ions propagate AF interaction between the Ni(II) ions [28–36]. The main factor that determines the magnitude of J value in such systems is the dihedral angle (δ) between the planes defined by the six azide-N atoms and the N–Ni–N plane: the more planar the structure (δ is close to 0°) the more antiferromagnetic the interaction and hence higher $|J|$ value, whereas the Ni–N(azide) distance and other structural parameters are less important [24]. In complex **59**, the dihedral angle δ of 34.51° should account for the relatively small J value of -6.95 cm^{-1} ,

which is agreed well with the magneto-structural data available in these systems [28–36]. Unlike azido-bridged analogues, the examples of double EE cyanato-bridged dinickel(II) complexes are limited (Table 4.3) [19–21]. It was also well predicted that cyanate ions transmit similar magnetic interaction between the metal centres but weakly, and the comparatively lower J values found for cyanato bridges as a consequence of the lower spin density on the N and O atoms [19]. The relatively high δ value of 17.74° is responsible for the loss of overlap derived of the lower planarity of the bridging region and as a consequence the lowest J value of $-2.71(2) \text{ cm}^{-1}$ for **60** perfectly lies on the line of J values reported until now.

Table 4.3 Selected structural and magnetic data of doubly EE cyanato bridged Ni(II) dimers (following $\hat{H} = -2J\hat{S}_1\cdot\hat{S}_2$ convention)^a. Angles are given in degree.

Compounds	$J (\text{cm}^{-1})$	g	$\angle\text{Ni-O-C}$	$\angle\text{Ni-N-C}$	Dihedral angle (δ) ^b	Refs.
$[\text{Ni}(\text{L}^{40})(\text{NCO})]_2(\text{BF}_4)_2$	-5.35	2.30	122.0	150.1	4.8	19
$[\text{Ni}(\text{tren})(\text{NCO})]_2(\text{BF}_4)_2$	-4.4	2.28	117.1	155.0	9.1	20
$[\text{Ni}(\text{L}^{41})(\text{NCO})]_2(\text{PF}_6)_2$	-3.1	2.16	110.9/111.4	147.9/152.0	18.6/20.8	21
60	-2.71	2.17	111.6(3)	152.0(4)	17.74	This work

^a L^{40} = DL-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane, tren = 2,2',2''-tri-aminotriethylamine; L^{41} = N,N-bis(3,5-dimethylpyrazol-1-ylmethyl)aminomethylpyridine.

Although the general formula of $[\text{Ni}_2(\text{L}^e)_2(\mu_{1,3}\text{-N}_3)_2](\text{ClO}_4)_2$ (**62**) is identical with $[\text{Ni}_2(\text{L}^d)_2(\mu_{1,3}\text{-N}_3)_2](\text{ClO}_4)_2$ (**59**), the magnetic property of these compounds are significantly different. Unlike in **59**, the interaction between the Ni(II) centres in **62** is ferromagnetic in nature though double EE bridges. The difference of the magnetic properties arises essentially from the different connectivity in the bridging region. In **62**, two bridging EE azides are not planar and crosslinked, and in such cases the nature of the magnetic interaction may be either F or AF, mainly depending on two structural parameters in the bridging region such as the

Ni–N–N bond angles and the Ni– $\mu_{1,3}$ -N₃–Ni (Ni–N $\cdots$ N–Ni) torsion angle [64]. Maximum coupling was expected for a Ni–N–N angle of 108° and decreases when the Ni–N–N angle increases and the exchange interactions would be ferromagnetic if the angle exceeds 155°. Similarly, for a fixed Ni–N–N angle AF coupling is expected to be maximum for a Ni–N $\cdots$ N–Ni torsion angle of 180° (or 0°) and decreases when Ni–N $\cdots$ N–Ni torsion angle deviates from linearity and the interaction would be ferromagnetic if the torsion angle approaches to 90° [64]. In general, the Ni–N–N angle does not exceed 155° and it is found that if the Ni–N–N angle exceeds 120° and the Ni–N $\cdots$ N–Ni torsion angle approaches to 90° a ferromagnetic coupling between the metal centres is observed. The average Ni–N–N angle of 124.54° and the average Ni–N $\cdots$ N–Ni torsion angle of 72.21° is nicely agreed with the overall ferromagnetic interaction in complex **62**. It is interesting to note that only four structurally and magnetically characterised crosslinked double EE azido-bridged systems are known in which only in two cases Ni–N $\cdots$ N–Ni torsion angle was close to 90°, leading to a ferromagnetically coupled system (Table 4.4) [37,38], and thus compound **62** is a valuable addition to this series with perfect agreement of the magneto-structural data.

Table 4.4 Selected structural and magnetic data of doubly crosslinked EE azido-bridged Ni(II) dimers (following $\hat{H} = -2J\hat{S}_1\cdot\hat{S}_2$ convention)^b. Angles are given in degree.

Compounds	J (cm ⁻¹)	D (cm ⁻¹)	g	Ni–N–N	Torsion angle (τ)	Refs.
$\{[Ni(L^{42})N_3]_2(ClO_4)_2(CH_3OH)_2\}$	+ 8.45	6.0	2.28	117.14–18.83	78.80	39
$[Ni_2(L^{43})_2(\mu_{1,3}-N_3)_2](ClO_4)_2$	+ 7.13	–	2.18	117.8–127.7	69.2	40
$[Ni(L^{44})_2(\mu_{1,3}-N_3)]_2(ClO_4)_2\cdot 8CH_3OH$	– 29	10	2.1	130.0	46.7	41
$[(L^{45})_2Ni_2(N_3)_2(\mu_{1,3}-N_3)_2]$	– 36.4	0 (fixed)	2.04	124.5–128.2	34.28	42
62	+ 13.21	7.20	2.09	123.7–127.1	68.67–76.95	This work

^b L^{42} = N,N'-bis-(3,5-dipiperidin-1-yl)-[2,4,6]triazin-1-yl-pyridin-2-ylmethylethane-1,2-diamine; L^{43} = N,N',N''-tris(4-methoxybenzyl)tris(2-aminoethyl)amine; L^{44} = 2,6-dimethyl-2,3-bis(2-pyridyl)quinoxaline; L^{45} = 1,4,7-trimethyl-1,4,7-triazacyclononane

Table 4.5. Selected structural and magnetic data of doubly end-on cyanato bridged Ni(II) dimers (following $\hat{H} = -2J\hat{S}_1\cdot\hat{S}_2$ convention)^c

Compounds	J (cm ⁻¹)	D (cm ⁻¹)	g	M–N (Å)	M–N–M (°)	Refs.
[Ni ₂ (L ²⁹) ₂ (μ _{1,1} -NCO) ₂](ClO ₄) ₂	+1.7	+3.6	2.23	2.125, 2.090	94.4, 95.8	16
[Ni ₂ (L ²⁸) ₂ (μ _{1,1} -NCO) ₂](ClO ₄) ₂	+2.8	+3.6	2.23	2.099, 2.115	95.33, 95.79	16
[Ni ₂ (terpy) ₂ (μ _{1,1} -NCO) ₂ (H ₂ O) ₂](PF ₆) ₂	+ 4.59	–12.32	2.23	2.044, 2.195	97.7	18
[Ni ₂ (L ^a) ₂ (μ _{1,1} -NCO) ₂]	+6.85	+7.18	2.19	2.107, 2.244 2.115, 2.280	97.84, 98.74	17
[Ni ₂ (L ⁴⁶) ₂ (μ _{1,1} -NCO) ₂]	+5.31	+5.00	2.19	2.225, 2.201	98.47	64
64	+3.70	+8.05	2.28	2.119, 2.205	97.51, 98.50	This work

^c L²⁹ = [N,N'-bis(2-pyridinylmethylene)]propane-1,3-diamine; L²⁸ = N,N'-bis(pyridin-2-yl)benzylidene]ethane-1,2-diamine; terpy = terpyridine; L^a and L⁴⁶ = tetradentate $\{N_3O\}$ and N_4 donor ligands respectively

Unlike **59** and **62**, in complex **63**, two Ni(II) ions are bridged by double EO bridging azides, and working with such system Ruiz et al. theoretically predicted the ferromagnetic interaction on all ranges of Ni–N(μ_{1,1}-N₃)–Ni angles, with J increasing upon increasing the bridging angle, reaching a maximum at 104° approximately [23]. In fact, all the reported μ_{1,1}-azido bridged Ni(II) dimers exhibit ferromagnetic interaction with only one exception where a very low bridging angle of 90.41° transmits AF interaction between Ni(II) centres [47]. The average Ni–N–Ni angle found in **63** is 101.39°, which falls within the range where strong ferromagnetic interaction prevail between two Ni(II) ions, and therefore J value of 28.79(2) cm⁻¹ found in **63** is quite reasonable. However, unlike theoretical prediction, the

experimental data do not show clear relationship with Ni–N–Ni angles as a small variation of Ni–N–Ni angles in a narrow range *ca.* 98°–103.9°, show a large variation of the J values from 1.91 to 43.9 cm⁻¹ [41–61], leaving an unsolved challenge which will require consideration of more than one structural parameter at once. In contrast to $\mu_{1,1}$ -N₃ bridged Ni(II) complexes, only five doubly $\mu_{1,1}$ -NCO bridged dinickel(II) complexes are known [16–18,62] The magnetic and crystallographic data of these complexes are presented in Table 5, which shows that J values span in a narrow range of 1.7 to 6.85 cm⁻¹. The sign and magnitude of J value of 3.70(2) cm⁻¹ in **64** is again reasonable for such complexes in which a general tendency is that J value increases with increasing bridging angles, similar to the theoretical prediction carried out for azide analogues [23]

4.4. Conclusion

We have synthesized and characterized six novel dinuclear Ni(II) complexes with the different bridging modes of pseudohalides. The pyridyl containing neutral ligands favours EE bridged complexes **59**, **60** and **62**, while phenolate containing anionic ligand stabilizes the EO bridged compounds **63** and **64**. Their magnetic properties were discussed based on their structures. For the isostructural and isomorphous compounds **59** and **60** with EE bridging pseudohalides, an intramolecular antiferromagnetic interaction is observed, and the doubly EE cyanato-bridged dimeric Ni(II) complexes are scarce in the literature. The magnetic behaviour of compound **61** is characteristic for a weak antiferromagnetically coupled Ni(II) ions through $\mu_{1,5}$ -N(CN)₂-bridges. For complex **62**, an additional methyl group in L^e ligand brings the crossed and nonplanar double EE azido-bridges, which transfers ferromagnetic coupling between the metal centres. Unlike **59**, **60** and **62**, Ni(II) centres of both complexes **63** and **64** are linked by the doubly EO bridging modes. Apparently, complex **63** represents the strong ferromagnetic interaction through the bridging azides as the average Ni–N–Ni angle (101.39°) falls within the range where strong ferromagnetic interaction prevails. Also,

complex **64** expressing the positive *J* value is rational according to the theoretical prediction. Overall, there still exists an unsolved challenge to synthesize and study the rare linked motifs of Ni(II) dimer to perfect the discipline.

References

- [1] G. A. Craig, M. Murrie, *Chem. Soc. Rev.* 2015, **44**, 2135.
- [2] G. E. Kostakis, A. M. Ako, A. K. Powell, *Chem. Soc. Rev.* 2010, 39, 2238.
- [3] M. Andruh, *Chem. Commun.* 2018, **54**, 3559.
- [4] S. Accorsi, A.-L. Barra, A. Caneschi, G. Chastanet, A. Cornia, A. C. Fabretti, D. Gatteschi, C. Mortalò, E. Olivieri, F. Parenti, P. Rosa, R. Sessoli, L. Sorace, W. Wernsdorfer, L. Zobbi, *J. Am. Chem. Soc.* 2006, **128**, 4742.
- [5] X.-Y. Wang, Z.-M. Wang, S. Gao, *Chem. Commun.* 2008, 281.
- [6] M. Sarkar, R. Clérac, C. Mathonière, N. G. R. Hearn, V. Bertolasi, D. Ray, *Inorg. Chem.* 2011, **50**, 3922.
- [7] J. Ruiz, A. J. Mota, A. Rodríguez-Diéguez, I. Oyarzabal, J. M. Secob, E. Colacio, *Dalton Trans.* 2012, **41**, 14265.
- [8] L. Botana, J. Ruiz, A. J. Mota, A. Rodríguez-Diéguez, J. M. Seco, I. Oyarzabal, E. Colacio, *Dalton Trans.* 2014, **43**, 13509.
- [9] (a) R. Boča, *Coord. Chem. Rev.* 2004, **248**, 757. (b) J. Miklovič, D. Valigura, R. Boča, J. Titiš, *Dalton Trans.* 2015, **44**, 12484.
- [10] A. Escuer, J. Esteban, S. P. Perlepes, T. C. Stamatatos, *Coord. Chem. Rev.* 2014, **275**, 87.
- [11] R. Biswas, C. Diaz, A. Ghosh, *Polyhedron* 2013, **56**, 172.
- [12] D. Ghoshal, H. Bialas, A. Escuer, M. Font-Bardía, T. K. Maji, J. Ribas, X. Solans, R. Vicente, E. Zangrando, N. R. Chaudhuri, *Eur. J. Inorg. Chem.* 2003, 3929.

- [13] F. A. Mautner, M. Mikuriya, H. Ishida, H. Sakiyama, F. R. Louka, J. W. Humphrey, S. S. Massoud, *Inorg. Chim. Acta.* 2009, **362**, 4073.
- [14] K. Ma, Q. Shi, M. Hu, X. Cai, S. Huang, *Inorg. Chim. Acta.* 2009, **362**, 4926.
- [15] R. Boca, M. Boca, M. Gembocký, L. Jäger, C. Wagner, H. Fuess, *Polyhedron* 2004, **23**, 2337.
- [16] M. Habib, T. K. Karmakar, G. Aromí, J. Ribas-Ariño, H. -K. Fun, S. Chantrapromma, S. K. Chandra, *Inorg. Chem.* 2008, **47**, 4109.
- [17] A. Panja, N.C. Jana, S. Adak, P. Brandão, L. Dlháň, J. Titiš, R. Boča, *New J. Chem.* 2017, **41**, 3143.
- [18] M. I. Arriortua, R. Cortes, J. L. Mesa, L. Lezama, T. Rojo, G. Villeneuve, *Transition Met. Chem.* 1988, **13**, 371.
- [19] A. Escuer, R. Vicente, M.S.E. Fallah, X. Solans, M. Font-Bardia, *J. Chem. Soc., Dalton Trans.* 1996, 1013.
- [20] (a) D. M. Duggan, D. N. Hendrickson, *Inorg. Chem.* 1974, **13**, 2056. (b) D. M. Duggan and D. N. Hendrickson, *Inorg. Chem.* 1974, **13**, 2929.
- [21] Z. Mahendrasinh, S. Ankita, S. B. Kumar, A. Escuer, E. Suresh, *Inorg. Chim. Acta.* 2011, **375**, 333.
- [22] Z. Serna, N. De la Pinta, M. K. Urtiaga, L. Lezama, G. Madariaga, J. M. Clemente-Juan, E. Coronado, R. Cortés, *Inorg. Chem.* 2010, **49**, 11541.
- [23] E. Ruiz, J. Cano, S. Alvarez, P. Alemany, *J. Am. Chem. Soc.* 1998, **120**, 11122.
- [24] F. F. de Biani, E. Ruiz, J. Cano, J. J. Novoa, S. Alvarez, *Inorg. Chem.* 2000, **39**, 3221.
- [25] P. S. Perlepe, L. Cunha-Silva, K. J. Gagnon, S. J. Teat, C. Lampropoulos, A. Escuer, T. C. Stamatatos, *Inorg. Chem.* 2016, **55**, 3, 1270.
- [26] A. Panja, S. Adak, P. Brandão, L. Dlháň, R. Boča, *Eur. J. Inorg. Chem.* **2020**, 2362.
- [27] A. Panja, N. C. Jana, P. Brandão, *Mol. Catal.* **2018**, 449, 49.

- [28] Z. Mahendrasinh, S. B. Kumar, E. Suresh, J. Ribas, *Transition Met. Chem.* 2010, **35**, 757.
- [29] S. S. Massoud, F. A. Mautner, R. Vicente, A. A. Gallo, E. Ducasse, *Eur. J. Inorg. Chem.* 2007, 1091.
- [30] M. Monfort, I. Resino, J. Ribas, X. Solans, M. Font-Bardia, H. Stoeckli-Evans, *New J. Chem.* 2002, **26**, 1601.
- [31] A. Escuer, R. Vicente, M. S. E. Fallah, X. Solans, M. Font-Bardia, *Inorg. Chim. Acta.* 1998, 278, 43.
- [32] J. Ribas, M. Monfort, B. K. Ghosh, R. Cortés, X. Solans, M. Font-Bardia, *Inorg. Chem.* 1996, **35**, 864.
- [33] J. Ribas, M. Monfort, C. Diaz, C. Bastos, X. Solans, *Inorg. Chem.* 1993, **32**, 3557.
- [34] C. G. Pierpont, D. N. Hendrickson, D. M. Duggna, F. Wagner, E. K. Barefield, *Inorg. Chem.* 1975, **14**, 604.
- [35] P. Chaudhuri, M. Guttman, D. Ventur, K. Wieghardt, B. Nuber, J. Weiss, *J. Chem. Soc., Chem. Commun.* 1985, 1618.
- [36] A. Escuer, I. Castro, F. Mautner, M. S. E. Fallah, R. Vicente, *Inorg. Chem.* 1997, **36**, 4633.
- [37] I. I. Ebralidze, G. Leitus, L. J. W. Shimon, R. Neumann, *Inorg. Chim. Acta.* 2009, **362**, 4760.
- [38] X. -T. Liu, Q. -L. Liu, *J. Mol. Struct.* 2008, 889, 160.
- [39] C. -Y. Liao, H. -H. Wei, S. -C. Cheng, S. Mohanta, *Tamkang Journal of Science and Engineering* 2002, **5**, 201.
- [40] P. Chaudhuri, T. Weyhermiller, E. Bill, K. Wieghardt, *Inorg. Chim. Acta.* 1996, 252, 195.

- [41] S. S. Massoud, F. R. Louka, Y. K. Obaid, R. Vicente, J. Ribas, R. C. Fischerc, F. A. Mautner, *Dalton Trans.* 2013, **42**, 3968.
- [42] M. G. Barandika, R. Cortés, L. Lezama, M. K. Urtiaga, M. I. Arriortua, T. Rojo, *J. Chem. Soc., Dalton Trans.* 1999, 2971.
- [43] P. Mukherjee, M. G. B. Drew, C. J. Gómez-García, A. Ghosh, *Inorg. Chem.* 2009, **48**, 5848.
- [44] S. K. Dey, N. Mondal, M. S. E. Fallah, R. Vicente, A. Escuer, X. Solans, M. Font-Bardía, T. Matsushita, V. Gramlich, S. Mitra, *Inorg. Chem.* 2004, **43**, 2427.
- [45] S. Sarkar, A. Mondal, M. S. E. Fallah, J. Ribas, D. Chopra, H. Stoeckli-Evans, K. K. Rajak, *Polyhedron* 2006, **25**, 25.
- [46] S. Nandi, D. Bannerjee, J. -S. Wu, T. -H. Lu, A. M. Z. Slawin, J. D. Woollins, J. Ribas, C. Sinha. *Eur. J. Inorg. Chem.* 2009, 3972.
- [47] P. Chaudhuri, R. Wagner, S. Khanra, T. Weyhermüller, *Dalton Trans.* 2006, 4962.
- [48] A. Bhattacharyya, P. k. Bhaumik, M. Das, A. Bauzá, P. P. Jana, K. Harms, A. Frontera, S. Chattopadhyay, *Polyhedron* 2015, **101**, 257.
- [49] M. Č. Romanović, B. R. Čobeljić, A. Pevec, I. Turel, V. Spasojević, A. A. Tsaturyan, I. N. Shcherbakov, K. K. Anđelković, M. Milenković, D. Radanović, M. R. Milenković, *Polyhedron* 2017, **128**, 30.
- [50] P. Ghorai, P. Brandão, S. Benmansour, C. J. Gómez García, A. Saha. *Polyhedron* 2020, **188**, 114708.
- [51] P. P. Chakrabarty, S. Giri, D. Schollmeyer, H. Sakiyama, M. Mikuriya, A. Sarkar, S. Saha, *Polyhedron* 2015, **89**, 49.
- [52] H. -Z. Kou, S. Hishiya, O. Sato, *Inorg. Chim. Acta.* 2008, **361**, 2396.
- [53] S. Sarkar, A. Mondal, A. Banerjee, D. Chopra, J. Ribas, K. K. Rajak, *Polyhedron* 2006, **25**, 2284.

- [54] S. Sarkar, A. Datta, A. Mondal, D. Chopra, J. Ribas, K. K. Rajak, S. M. Sairam, S. K. Pati, *J. Phys. Chem. B* 2006, **110**, 12.
- [55] X. -J. Lin, Z. Shen, Y. Song, H. -J. Xu, Y. -Z. Li, X. -Z. You, *Inorg. Chim. Acta.* 2005 **358**, 1963.
- [56] S. Sain, S. Bid, A. Usman, H. -K. Fun, G. Aromic, X. Solans, S. K. Chandra, *Inorg. Chim. Acta.* 2005, **358**, 3362.
- [57] R. Cortes, J. I. Ruiz de Larramendi, L. Lezama, T. Rojo, K. Urtiaga, M. I. Arriortua, *J. Chem. Soc. Dalton Trans.* 1992, 2723.
- [58] R. Vicente, A. Escuer, J. Ribas, M. S. E. Fallah, X. Solans, M. Font-Bardia, *Inorg. Chem.* 1993, **32**, 1920.
- [59] J. Ribas, M. Monfort, C. Diaz, C. Bastos, X. Solans, *Inorg. Chem.* 1994, **33**, 484.
- [60] A. Escuer, R. Vicente, J. Ribas, X. Solans, *Inorg. Chem.* 1995, **34**, 1793.
- [61] A. Donmez, G. Oylumluoglu, M. B. Coban, C. Kocak, M. Aygun, H. Kara, *J. Mol. Struct.* 2017, **1149**, 569.
- [62] M. Patra, P. Brandão, A. P. Pikul, S. Adak, A. Panja, *ChemistrySelect.* 2020, **5**, 12924.
- [63] N. F. Chilton, R. P. Anderson, L. D. Turner, A. Soncini, K. S. Murray, *J. Comput. Chem.* 2013, **34**, 1164.
- [64] A. Escuer, R. Vicente, J. Ribas, M. S. E. Fallah, X. Solans, M. Font-Bardia, *Inorg. Chem.* 1994, **33**, 1842.

CHAPTER 5

CHAPTER 5

A novel triple aqua, phenoxo and carboxylato bridged dinickel(II) complex and its magnetic and comparative biomimetic catalytic studies with analogous dinickel(II) complexes

List of Section

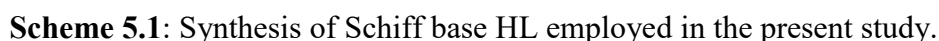
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5.1. Introduction

The synthesis and structural studies of transition metal complexes with a variety of bridging ligands have been still attracting considerable research interest worldwide mainly because of their relevance in biological systems, catalysis, and molecular magnetism [1–3]. Literature has witnessed vast development of coordination chemistry of the compartmental ligands which consist of two symmetrical or asymmetricalpendent arms at 2- and 6- positions of phenolic group. These ligands are capable to bind simultaneously two homo- or hetero-metallic transition metal ions, leading to phenoxo-bridged dinuclear complexes [4–7]. In some cases, the presence of additional bridges such as hydroxide, carboxylate and pseudohalide ions maylead to doubly or triply bridgeddinuclear metal complexes in which two metal ions are placed inclose proximity of 2.9–4.0 Å [8–15]. In many of these compounds, the metal centres are coordinatively unsaturated and/or the metal ions are weakly bonded to the ligands, which made this class of compounds as attractive candidates for the biomimetic studies and consequently they have been extensively employed in structural and functional modelling of various metalloenzymes, like catechol oxidase [10,11], catalase [12], urease [13], purple acid phosphatases [14] phosphoesterases and DNA nucleases [15] to gain insight into the mechanistic aspect of the metalloenzymes. In addition to the modelling structures and functions of the active sites of metalloenzymes, these compounds could provide a large number of ferro-/antiferro-magnetically coupled discrete dinuclear metal complexes that help to gain insight into the fundamental aspects of the pairwise exchange interactions, knowledge of which at least assess qualitatively the magnetic coupling in high nuclearity systems for the betterment of the field of molecular magnetism [16]

We have been using the N/O-donor Schiff bases derived from *N,N*-dimethyldipropylenetriamine for quite some time for the synthesis of transition metal complexes with intriguing magnetic properties [17,18] and biomimetic catalysis, modelling

the function of phenoxazinone synthase [19-21]. The diverse coordination ability of this triamine further prompted us to explore coordination ability of the ligands derived from this triamine. We have also recently explored the coordination chemistry of Schiff base ligand (HL, Scheme 5.1), resulted from the condensation of 2,6-diformyl-4-methylphenol and *N,N*-dimethyldipropylenetriamine with Ni(II) salts in presence of azide ions in different stoichiometries, that exhibited diverse magnetic properties ranging from antiferro- to ferromagnetic interactions [22]. Although the phenoxazinone synthase is a multicopper oxidase that catalyses the oxidative coupling of two substituted *o*-aminophenols to the phenoxazinone chromophore through the catalytic activation of dioxygen in the final stage of the biosynthesis of a naturally occurring antitumor drug actinomycin D [23] used clinically for the treatment of various cancers [24-26] several other transition metal (mostly manganese and cobalt) complexes were proved to be excellent functional models of this metalloenzyme [10]. Ni(II) complexes on the other hand extensively studied for biomimetic catalysis of other oxidase metalloenzymes like catechol oxidase, but phenoxazinone synthase ability of this metal complexes has yet to be explored [10]. Therefore, in the present endeavour, three dinickel(II) complexes, $[\text{Ni}_2(\mu\text{-L})(\mu\text{-OH})](\text{ClO}_4)_2$ (**65**), $[\text{Ni}_2(\mu\text{-H}_2\text{L})(\mu\text{-OH})(\text{NCS})_3](\text{NCS})$ (**66**), $[\text{Ni}_2(\mu\text{-HL})(\mu\text{-OBz})(\mu\text{-H}_2\text{O})(\text{OBz})](\text{ClO}_4)_2 \cdot 2.5\text{H}_2\text{O}$ (**67**) (where HOBz = benzoic acid) have been synthesised using compartmental Schiff base ligand HL. The crystal structures, magnetic property and biomimetic catalytic activity modelling the function of phenoxazinone synthase of these complexes were further investigated and discussed. Interestingly, complex **67**, consisting of a triple aqua, phenoxo and carboxylato bridges, is a unique example in dinickel(II) chemistry.



5.2.1.1. UV-Vis Spectroscopy

Light in the wavelength range of 200–800 nm have been used for the prepared samples dissolved in various solvents. The Beer-Lambert law, **Eq. 5.1** (where A is absorbance, c is concentration of the sample and l is the path length of the sample) have been used to calculate the molar extinction coefficient (ϵ), the magnitude of which determines the types of transition occurring [27].

UV-vis spectra were recorded on an Agilent Carry-60 diode array UV-vis spectrophotometer (Agilent 8453) at room temperature with cuvette of 1-cm path-length.

$$A = \epsilon cl \quad \text{Eq. 5.1}$$

5.2.1.2. EPR Spectroscopy

The X-band EPR spectra were measured in methanol using a JEOL JES-FA 200 instrument at liquid nitrogen temperature (77 K).

5.2.1.3. Kinetics of the Phenoxazinone Synthase Activity

The phenoxazinone synthase like activity of **65–67** was examined UV-vis spectrophotometrically using *o*-aminophenol (OAPH) as a model substrate. Kinetic experiments for the formation of 2-aminophenoxazin-3-one were carried out by monitoring increase of the spectral band ~435 nm ($\epsilon = 9095 \text{ M}^{-1} \text{ cm}^{-1}$) [28] as a function of time in air-saturated methanol at ambient temperature (25 °C). Detailed kinetic studies were performed to gain into the reaction kinetics for the catalytic oxidation of OAPH and for this purpose a varying amount of the substrates (5×10^{-4} to 1×10^{-2} M) were allowed to react with a fixed complex concentration (5×10^{-5} M), maintaining the pseudo-first-order reaction condition. The rates of the reactions were calculated adopting initial rate method. Kinetic parameters K_M , $V_{\max}$, and k_{cat} , were determined by applying Michaelis-Menten equation. The turnover

number (k_{cat} value) was obtained by dividing the V_{max} values by the concentration of the complex used.

5.2.1.4. Mass Spectrometry

Electrospray ionization mass spectrometry (ESI-MS positive) was carried out in a MicromassQ-tof-Micro Quadrupole mass spectrometer.

5.2.2. Chemicals and Synthetic techniques

5.2.2.1. Materials

2,6-diformyl-4-methylphenol (DFMP) was prepared following a literature reported method [29] and *N,N*-dimethyldipropylenetriamine was purchased from Aldrich. All other chemicals (metal salts and solvents) were analytical or reagent grade and used as received.

Warning! Perchlorate salts of metal complexes with organic ligands are potentially explosive. Only small quantities of the compounds should be prepared, and these should be handled with great care.

5.2.2.2. Synthesis of Schiff base ligand HL

The Schiff base was prepared by the condensation of *N,N*-dimethyldipropylenetriamine and 2,6-diformyl-4-methylphenol in methanol as reported earlier [22].

5.2.2.3. Synthesis of $[Ni_2(\mu-L)(\mu-OH)](ClO_4)_2$ (65)

$Ni(ClO_4)_2 \cdot 6H_2O$ (0.366 g, 1.0 mmol), HL (0.5 mmol) and triethylamine (0.5 mmol) were mixed together in a 30 mL of methanol and were allowed to reflux for about 1 h. After cooling, the reaction mixture was filtered and the clear deep-green solution was kept at room temperature for slow evaporation. Dark-green single crystals suitable for X-ray analysis were obtained from the filtrate after a few days. The crystals were collected by filtration and washed with methanol/ether and air dried. Yield: 0.339 g, 87 %. Anal. calcd. for $C_{25}H_{46}Cl_2N_6Ni_2O_{10}$: C 38.55 %, H 5.95 %, N 10.79 %. Found: C 38.34 %, H 6.04 %, 10.66 %. Selected FTIR bands (cm^{-1}): 625 s, 1088-1116 vs (νClO_4^-); 1635 s ($\nu C=N$).

5.2.2.4. Synthesis of $[Ni_2(\mu-H_2L)(\mu-OH)(NCS)_3](NCS)$ (66)

$Ni(NO_3)_2 \cdot 6H_2O$ (0.290 g, 1.0 mmol), the Schiff base ligand (0.5 mmol) and triethylamine (0.5 mmol) were combined in 30 mL of methanol. The resulting green solution was allowed to reflux for ca. 1 h. Thereafter, a solution of sodium thiocyanate (2.0 mmol, 0.162 g) dissolved in minimum amount of methanol was added to the resulting green solution drop wise over a period of 5 min with constant stirring. The reaction mixture (bright dark-green) was stirred under reflux for ca. 30 min, and it was filtered to remove if any minute quantity of precipitate. The clear dark-green filtrate was kept undisturbed at ambient temperature that afforded dark green crystals of **66** within a week, appropriate for single crystal X-ray diffraction measurements. The crystals were collected by filtration and washed with methanol/ether and air dried. Yield: 0.327 g, 78 %. Anal. calcd. for $C_{29}H_{48}N_{10}Ni_2O_2S_4$: C 42.77 %, H 5.94 %, N 17.20 %. Found: C 42.64 %, H 6.01 %, 17.01 %. Selected FTIR bands (cm^{-1}): 1634 s, 1644 s ($\nu C=N$); 2068 vs, 2092 vs (νNCS^-).

5.2.2.5. Synthesis of $[Ni_2(\mu-HL)(\mu-OBz)(\mu-H_2O)(OBz)](ClO_4)_2 \cdot 2.5H_2O$ (67**)**

$Ni(ClO_4)_2 \cdot 6H_2O$ (0.366 g, 1.0 mmol), the Schiffbase ligand (0.5 mmol) and triethylamine (0.5 mmol) were combined in 30 mL of methanol. The resulting green solution was allowed to reflux for ca. 1 h. Thereafter, a methanolic solution of benzoic acid (0.122 g, 1.0 mM) and triethylamine (1.0 mmol) was added with stirring, and it was further allowed to stir for another 30 min. The resulting dark-green reaction mixture was filtered and left at room temperature for crystallisation. The green crystalline single crystals were separated out from the solution within a couple of days with quality suitable for X-ray single crystal diffraction. The crystals were then filtered and washed with methanol/ether and air dried. Yield: 0.395 g, 74 %. Anal. calcd. for $C_{39}H_{63}Cl_2N_6Ni_2O_{16.5}$: C 43.85 %, H 5.94 %, N 7.87 %. Found: C 43.99 %, H 6.01 %, N 7.71 %. Selected FTIR bands (cm^{-1}): 623 m, 1094 vs (νClO_4^-); 1601–1645 s ($\nu C=N$ & νCOO^-).

5.3. Results and discussion**5.3.1. Synthesis and general characterizations**

The reaction of a methanolic solution of the compartmental Schiff base ligand (HL) with $Ni(ClO_4)_2 \cdot 6H_2O$ in a 1:2 molar ratio in methanol afforded $[Ni_2(\mu-L)(\mu-OH)](ClO_4)_2$ (**65**). The corresponding reaction with $Ni(ClO_4)_2 \cdot 6H_2O$ in the presence of benzoic acid in a 1:2:1 molar ratio resulted $[Ni_2(\mu-HL)(\mu-OBz)(\mu-H_2O)(OBz)](ClO_4)_2 \cdot 2.5H_2O$ (**67**). Similar reaction with $Ni(NO_3)_2 \cdot 6H_2O$ in presence of NaSCN in a 1:2:2 molar ratio in refluxing methanol solution produced $[Ni_2(\mu-H_2L)(\mu-OH)(NCS)_3](NCS)$ (**66**). An equimolar amount of triethylamine was added for deprotonation of the Schiff base ligand in all cases and also for benzoic acid in **67**. These complexes were obtained in high yield in which phenolic group of the ligand is deprotonated that bridges two metal ions, leading to dinickel(II) complexes. X-ray quality

single crystals of **65–67** were obtained by slow evaporation of the reaction mixtures. The isolated complexes were characterized by elemental microanalyses, IR and UV-vis spectroscopies (Figure 5.1 and 5.2, respectively) and single crystal X-ray diffraction study and these complexes are fairly soluble in common organic solvents like methanol, acetonitrile and DMF.

5.3.2. IR Spectroscopy

The IR spectra of the complexes (Figure 5.1) display some common features such as a band due to a N–H stretching vibration in the range $3244\text{--}3278\text{ cm}^{-1}$, the O–H stretching vibration at $3444\text{--}3465\text{ cm}^{-1}$ of bridging hydroxide and/or water of crystallisations (in **67**), and the azomethine (C=N) bonds of the Schiff base in the range $1601\text{--}1645\text{ cm}^{-1}$. However, the azomethine and carboxylate bands are hardly distinguishable in **67**. Additionally, the IR spectra of **65** and **67** display the stretching vibration of ClO_4^- ion as a split band over the range $1088\text{--}1116\text{ cm}^{-1}$. The splitting of the $\nu(\text{Cl--O})$ band is attributed to the result of involvement of the counter ClO_4^- ions in H-bonding interactions in the solid state. Moreover, the bending vibration of ClO_4^- ion is observed at $623\text{--}625\text{ cm}^{-1}$ in the IR spectra of these complexes [18,21]. The IR spectrum of **66** also displays a bifurcated band at 2068 and 2092 cm^{-1} , characteristic for the asymmetric stretching vibrations of NCS^- ion. The appearance of two strong peaks in the IR spectrum in **66** is consistent with the presence of both coordinated and non-coordinated NCS^- ion, as evidenced by the structural characterization [21,30].

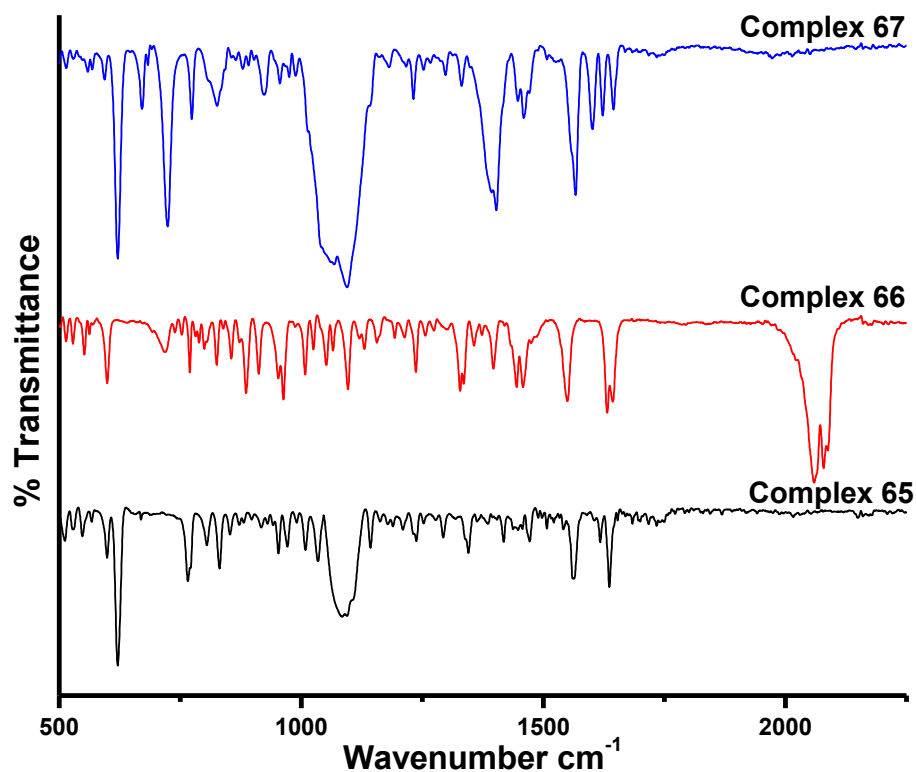


Figure 5.1: IR spectra of complexes 65–67.

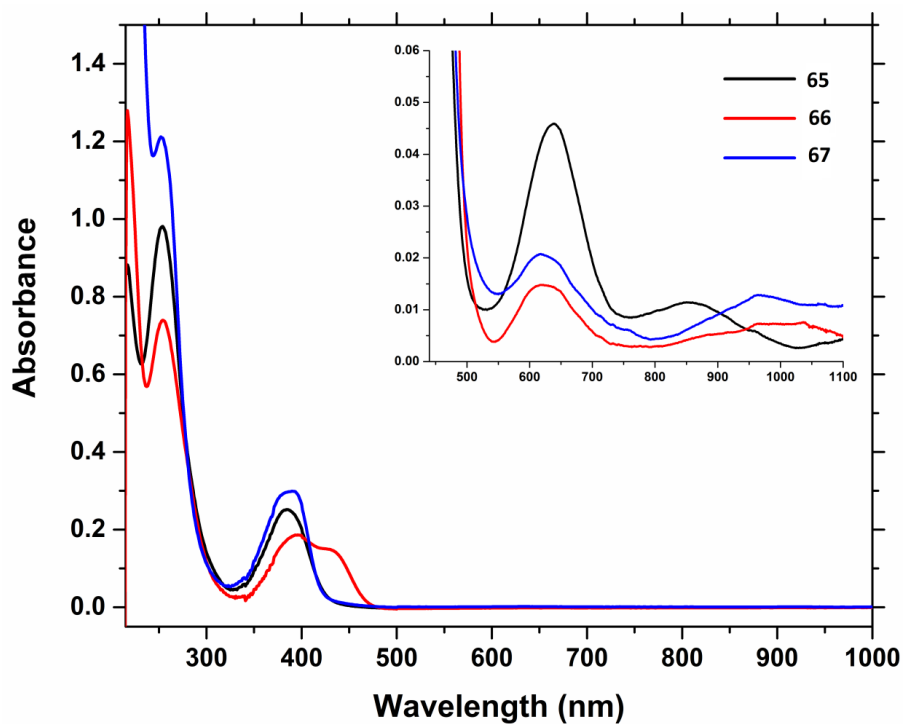


Figure 5.2: UV-Vis Spectra of the complexes 65–67 at $[\text{complex}] = 5 \times 10^{-5} (\text{M})$ whereas the inset spectra were recorded at $[\text{complex}] = 1 \times 10^{-3} (\text{M})$.

5.3.3. Description of crystal structures

Crystal structures of all the complexes were determined by single crystal X-ray diffraction study. Whereas the details of the data collection and structural refinement for the complexes are assembled in Table 5.1, the selected bond distances and angles can be found in Table 5.2 and Table 5.3, respectively. Complex **65** crystallized in the monoclinic $P2_1/n$ space group and the crystal structure consists of a dinuclear $[\text{Ni}_2(\mu\text{-L})(\mu\text{-OH})]^{2+}$ cation and two ClO_4^- anions (Figure 5.3). Within the dimeric unit, Ni(II) ions are bridged by the phenoxo group of the Schiff base ligand together with the exogenous hydroxo ligand with the Ni–Ni distance of 3.154 Å and the phenoxo and hydroxo bridging angles of 101.77(6) and 106.32(7)°, respectively. Both Ni(II) centres exhibit a NiN_3O_2 coordination sphere which is made up with the bridging phenoxo and hydroxo oxygen atoms and three nitrogen atoms from the triamine part of the ligand. The coordination polyhedra around the metal centres is best described as a distorted square pyramidal as indicated by the structural parameter τ (square pyramid, $\tau = 0$; trigonal bipyramid, $\tau = 1$; $\tau = (\alpha - \beta)/60^\circ$, where α and β are the two largest angles around the central atom) values of 0.05 and 0.15 [31]. The Ni(II) centres are displaced out of the least square planes constructed by exogenous hydroxo group and phenoxo oxygen atom and imine and secondary amine nitrogen atoms from the Schiff base ligand towards the apically coordinated tertiary amine nitrogen atom with deviation of 0.357 Å. The bond distances around the metal coordination spheres are usual for Ni(II) complexes (see Table 5.2) [13,32–46]. Both perchlorate counter anions form moderate to strong hydrogen bonding interactions, one of them with the secondary amine group ($\text{N5}\cdots\text{O4}$, 3.147(3) Å) only and other one with both the secondary amine group ($\text{N2}\cdots\text{O7}$, 2.995(3) Å) and bridging hydroxo group ($\text{O2}\cdots\text{O9}$, 3.148(2) Å) as shown in Figure 5.3 and 5.4. The closest separation between the Ni(II) centres within the neighbouring dimeric unit is 8.551 Å.

Table 5.1 Crystal details and structure refinement parameters of complexes **65–67**.

	65	66	67
Empirical formula	C ₂₅ H ₄₆ Cl ₂ N ₆ Ni ₂ O ₁₀	C ₂₉ H ₄₈ N ₁₀ Ni ₂ O ₂ S ₄	C ₃₉ H ₆₃ Cl ₂ N ₆ Ni ₂ O _{16.5}
Formula weight (g mol ⁻¹)	779.00	814.43	1068.27
Crystal system	monoclinic	triclinic	triclinic
Space group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$
<i>a</i> (Å)	18.1138(11)	9.2680(4)	12.8331(12)
<i>b</i> (Å)	9.9392(6)	11.2105(4)	14.2244(13)
<i>c</i> (Å)	19.5105(10)	18.8811(7)	15.4895(15)
α (deg)	90.00	87.895(2)	63.296(3)
β (deg)	108.764(2)	78.990(2)	72.834(3)
γ (deg)	90.00	77.785(2)	77.698(3)
volume (Å ³)	3325.9(3)	1882.01(13)	2402.7(4)
<i>Z</i>	4	2	2
<i>D</i> _{calc} (g cm ⁻³)	1.556	1.437	1.477
μ (mm ⁻¹)	1.354	0.5701.264	0.969
<i>F</i> (000)	1632	856	1122
θ range (deg)	2.205–29.196	1.099–29.196	2.494–26.459
Reflections collected	113948	96578	38722
Independent reflections (<i>R</i> _{int})	8997 (0.0469)	10151 (0.0363)	9821 (0.0361)
Observed reflections [<i>I</i> >2 σ (<i>I</i>)]	7329	8735	8027
Restraints/parameters	1/445	0/459	3/636
Goodness-of-fit on <i>F</i> ²	1.042	1.040	1.031
Final <i>R</i> indices [<i>I</i> >2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0325, <i>wR</i> ₂ = 0.0735	<i>R</i> ₁ = 0.0248, <i>wR</i> ₂ = 0.0587	<i>R</i> ₁ = 0.0328, <i>wR</i> ₂ = 0.0756
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0476, <i>wR</i> ₂ = 0.0801	<i>R</i> ₁ = 0.0326, <i>wR</i> ₂ = 0.0623	<i>R</i> ₁ = 0.0463, <i>wR</i> ₂ = 0.0826
Largest diff. peak/hole (e Å ⁻³)	1.079/–0.738	0.391/–0.357	0.551/–0.594

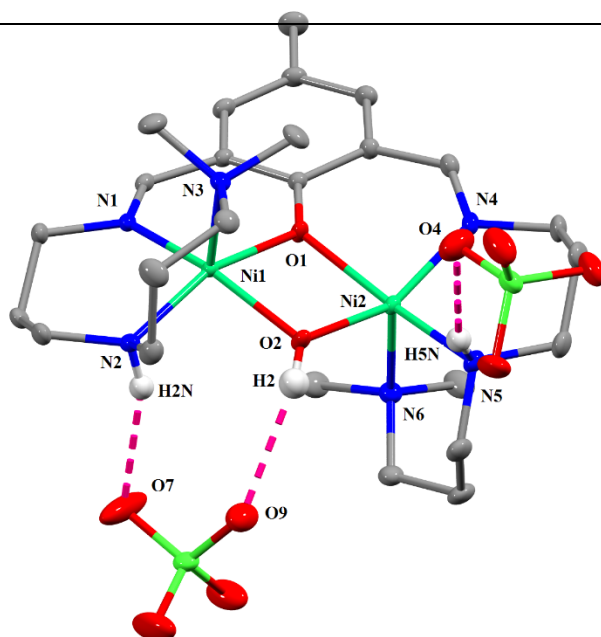


Figure 5.3: Crystal structure of **65** displaying selected atom labelling scheme and hydrogen bonding interactions. Ellipsoids are drawn at 30% probability level and most of the hydrogen atoms are omitted for clarity.

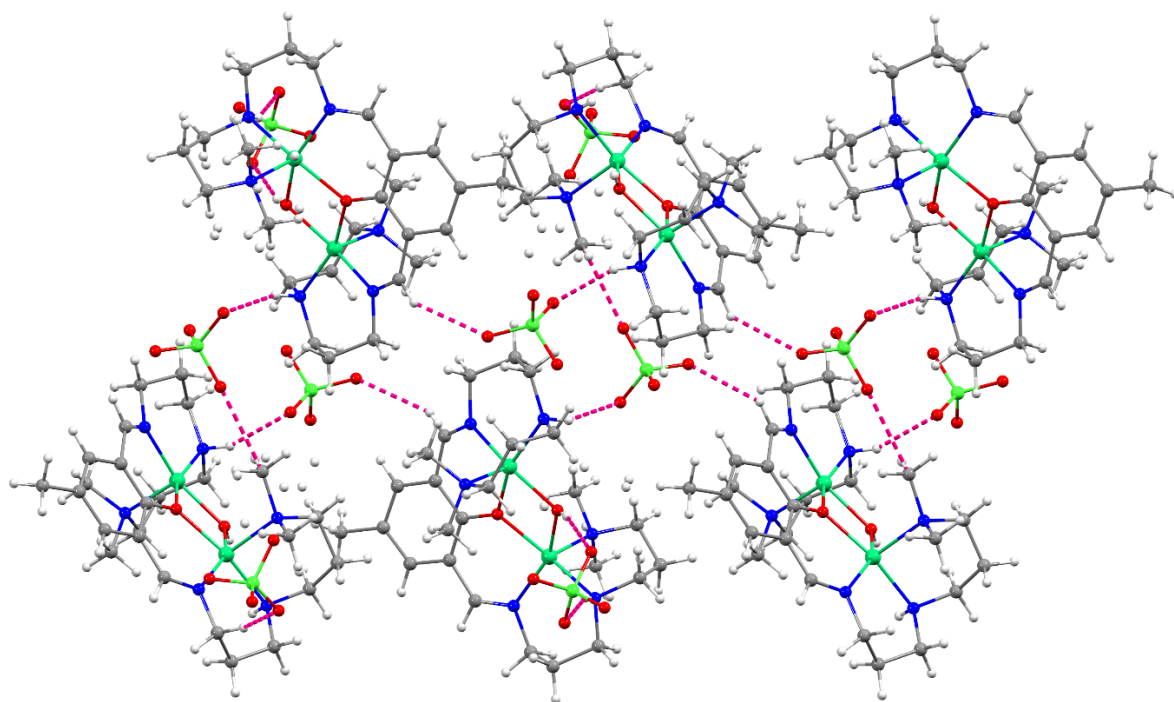


Figure 5.4: The crystal packing of complex **65** displaying different hydrogen bonding interactions.

Table 5.2 Selected bond distances (Å) for complexes **65–67**.

Bond	65	66	67
Ni1–O1	2.0313(12)	2.0829(9)	2.0407(14)
Ni1–O2	1.9674(14)	2.0484(9)	2.1691(15)
Ni1–O3	-	-	1.9998(14)
Ni1–O5	-	-	2.0783(14)
Ni1–N1	2.0305(15)	2.0370(11)	2.0460(17)
Ni1–N2	2.0780(16)	2.1301(11)	2.1108(18)
Ni1–N3	2.0809(16)	-	-
Ni1–N7	-	2.0628(12)	-
Ni1–N8	-	2.1327(12)	-
Ni2–O1	2.0333(13)	2.0188(9)	2.0222(14)
Ni2–O2	1.9733(14)	2.0257(9)	2.2546(15)
Ni2–O4	-	-	2.0682(14)
Ni2–N4	2.0349(16)	2.0124(11)	2.0641(18)
Ni2–N5	2.0605(16)	2.0570(11)	2.0993(18)
Ni2–N6	2.0810(16)	-	2.1620(18)
Ni2–N9	-	2.0129(12)	-

Table 5.3 Selected bond angles (°) for complexes **65–67**.

Bond Angles	65	66	67
Ni1–O1–Ni2	101.77(6)	100.30(4)	104.72(6)
Ni1–O2–Ni2	106.32(7)	101.25(4)	93.30(6)
O2–Ni1–N1	152.58(6)	166.87(4)	164.45(6)
O2–Ni1–O1	76.02(5)	78.19(4)	77.60(6)
N1–Ni1–O1	89.36(6)	88.69(4)	86.93(6)
O2–Ni1–N2	91.31(6)	97.73(4)	99.62(6)
N1–Ni1–N2	96.44(6)	95.37(4)	95.71(7)
O1–Ni1–N2	161.53(6)	172.59(4)	175.29(6)

Complex **66** crystallized in the triclinic *P*space group and the crystal structure (Figure 5.5) consists of a dinuclear $[\text{Ni}_2(\mu\text{-H}_2\text{L})(\mu\text{-OH})(\text{NCS})_3]^+$ cation and a thiocyanate anion. Like **65**, within the dinuclear unit, Ni(II) ions are bridged by the phenoxo group together with the exogeneous hydroxo ligand with the Ni–Ni distance of 3.149 Å and the phenoxo and hydroxo bridging angles of 100.30(4) and 101.25(4)°, respectively, but two metal centres are in different coordination environments i.e. NiN_4O_2 coordination sphere for Ni1 ion and NiN_3O_2 coordination sphere for Ni2 centre. In addition to the bridging hydroxo and phenoxo groups, the coordination sphere around Ni1 is fulfilled by two N-bound trans disposed thiocyanate ions and imine and secondary amine nitrogen atoms from one arm of the Schiff base, while the coordination sphere of Ni2 is satisfied by one terminal N-bound thiocyanate ion and imine and secondary amine nitrogen atoms from other arm of the Schiff base ligand with usual bond distances (Table 5.2) [13,32-46]. The coordination polyhedron around the Ni1 centre is best described as a distorted octahedron as reflected by the significant deviation of *cisoid* (78.19(4)–96.62(4)°) and *transoid* (166.87(4)–174.46(5)°) angles from the ideal values, while the geometry around Ni2 centre is close to the square pyramidal, being the structural parameter τ value of 0.27 [31]. Unlike **65**, the tertiary amine groups in **66** are protonated and thus involve in H-bonding interaction as depicted in Figure 5.5 in which one protonated tertiary amine is connected with oxygen atom of bridging hydroxide through an intramolecular hydrogen bond with $\text{N3}\cdots\text{O2}$ distance of 2.585(2) Å, while other protonated tertiary amine group establishes an intermolecular hydrogen bond with nitrogen atom of non-coordinated thiocyanate ion with $\text{N6}\cdots\text{N10}$ distance of 2.824(2) Å. S atom of the non-coordinated thiocyanate ion further involves in bifurcated hydrogen bonding with the bridging O–H ($\text{O2}\cdots\text{S4} = 3.414(1)$ Å) and secondary amine N–H protons ($\text{N5}\cdots\text{S4} = 3.5773(12)$ Å) from the neighbouring complex cation, leading to the formation of a supramolecular hydrogen bonded dimer of dimers as depicted in Figure 5.5 and 5.6. The

closest separation between the Ni(II) centres within the neighbouring dimeric units is 9.268 Å, which is slightly higher than that found in **65**.

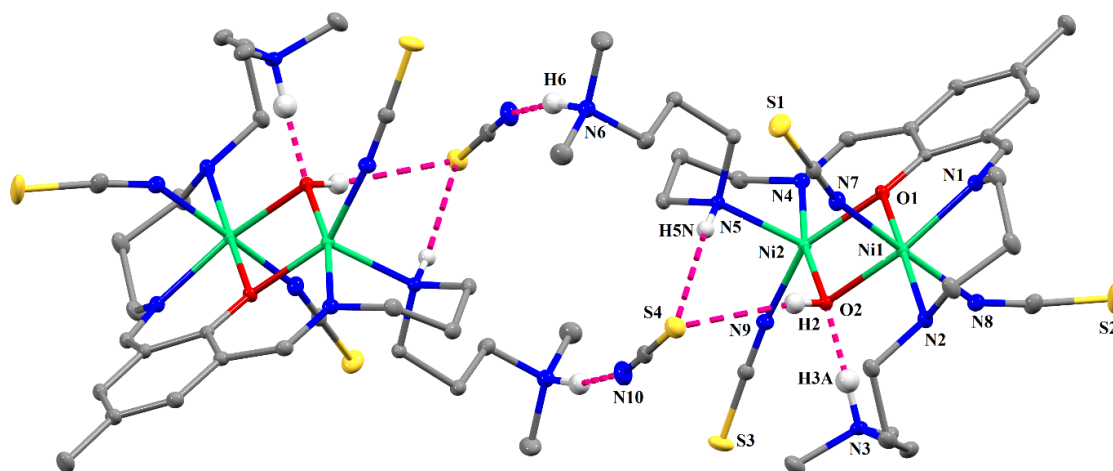


Figure 5.5: Crystal structure of **66** showing atom numbering scheme and hydrogen bonding interactions. Ellipsoids are drawn at 30% probability level and most of the hydrogen atoms are omitted for clarity.

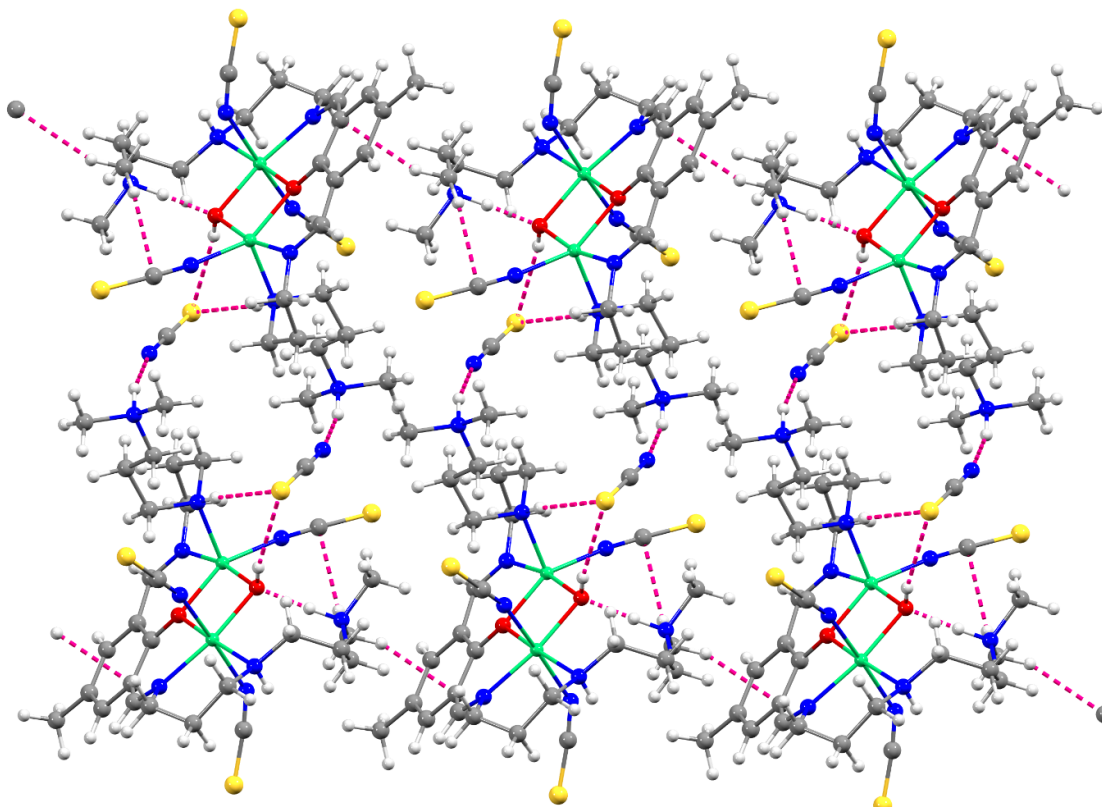


Figure 5.6: The crystal packing of complex **66** displaying different weak non-covalent interactions.

Complex **67** crystallized in the triclinic *P*space group and the crystal structure (Figure 5.7) consists of a dinuclear $[\text{Ni}_2(\mu\text{-HL})(\mu\text{-OBz})(\mu\text{-H}_2\text{O})(\text{OBz})]^{2+}$ cation and two ClO_4^- anions and few water of crystallisations. In this dimeric entity, both Ni(II) centres are in an octahedral environment being triply bridged by aphenoxo group of the Schiff base ligand and a benzoate ion in *syn-syn* configuration and an aqua ligand with the Ni–Ni separation in the dimeric unit of 3.217 Å and the phenoxo and aqua bridging angles of 104.72(6) and 93.30(6)°, respectively. The remaining coordination sites are fulfilled by three nitrogen atoms from one triamine arm in Ni2 centre, while imine and secondary amine nitrogen atoms from other arm of the Schiff base and one oxygen atom of the monodentate benzoate ion fulfil the coordination sites around Ni1 centre. The non-coordinated oxygen atom of the monodentate benzoate ion in turn is involved in strong hydrogen bonding interaction with the bridging aqua ligand ($\text{O2}\cdots\text{O6}$, 2.545(2) Å) as depicted in Figure 5.7, thereby stabilising the triply-bridged structure. Therefore, in the present case, the zwitterionic form of the Schiff base ligand is coordinated to the metal centres in which the phenolic group is deprotonated and is bridged by the two metal centres leaving one of the tertiary amine group protonated. This protonated tertiary amine group participates in strong hydrogen bonding interaction with one of the water of crystallisations ($\text{N3}\cdots\text{O15}$, 2.676(3)Å). Furthermore, the solid state structure of complex **67** is stabilised by a complex network of moderate to strong hydrogen bonding interactions with the involvements of perchlorate counter anions, lattice water molecules and secondary amine groups of the Schiff base ligands with donor acceptor distances varied in the range 2.545(2)–3.245(3) Å (Figure 5.8). Although it is a triply bridged system, the Ni–Ni separation in the dimeric unit of 3.217 Å is slightly longer than that found in **65** and **66**, while the closest separation within the neighbouring dimeric unit is found to be 7.956 Å.

Structural studies reveal a diverse coordination ability of the Schiff base ligand HL in the present systems as the monoanionic L^- form of the ligand is bonded to the metal centres in

65, while monocationic H_2L^+ and the zwitterionic form of the ligand coordinate the metal centres in **66** and **67**, respectively. Another notable observation is the geometrical differences around the metal centres in these complexes as it is a five coordinated and square pyramidal structure for both Ni(II) centres in **65**, while one Ni(II) ion is in square pyramidal geometry and other one in octahedral geometry in **66** and both the metal centres are in octahedral geometry in **67**. However, the most remarkable structural feature is a unique bridging pattern found in complex **67**. Literature reports reveal that the aqua bridged dinickel(II) complexes are not much abundant and it is generally been a part of a triplebridged system in which it is mostly associated with either double phenoxo bridges [32-38] or double carboxylato bridges [39-45]. Further observation is that when it is associated with di(phenoxo) bridges, the bridging aqua angle is less than 90° and when it is coupled with two *syn-syn* carboxylate bridges, the bridging aqua angles are quite large and it is always greater than 100° . In the present system (complex **67**) an intermediate aqua bridging angle of $93.30(6)^\circ$ was observed as it is associated with one phenoxo and one *syn-syn* carboxylate bridge. The structure of **67** is very close to a dinickel(II) complexes where the bridging phenoxo is replaced by alkoxo group [46]. With all sorts of notable dissimilarities, all these complexes are constructed with an edge-sharing bi-polyhedral structures in which two bridging phenoxo and hydroxo groups form the common edge in **65** and **66**, while it is formed by the bridging phenoxo and aqua ligands in **67** (see Figure 5.9) and both the bridging atoms occupy the equatorial positions of the metal centres irrespective of their geometries. The *syn-syn* carboxylate bridge occupies the apical positions of two adjacent bioctahedral structures in **67**.

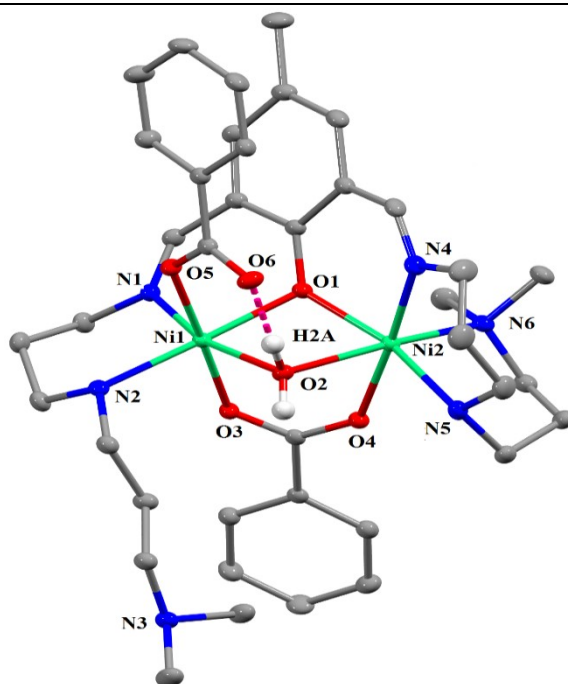


Figure 5.7: Crystal structure of complex cation of **67** displaying selected atom labelling scheme and hydrogen bonding interaction. Ellipsoids are drawn at 30% probability level and most of the hydrogen atoms are omitted for clarity.

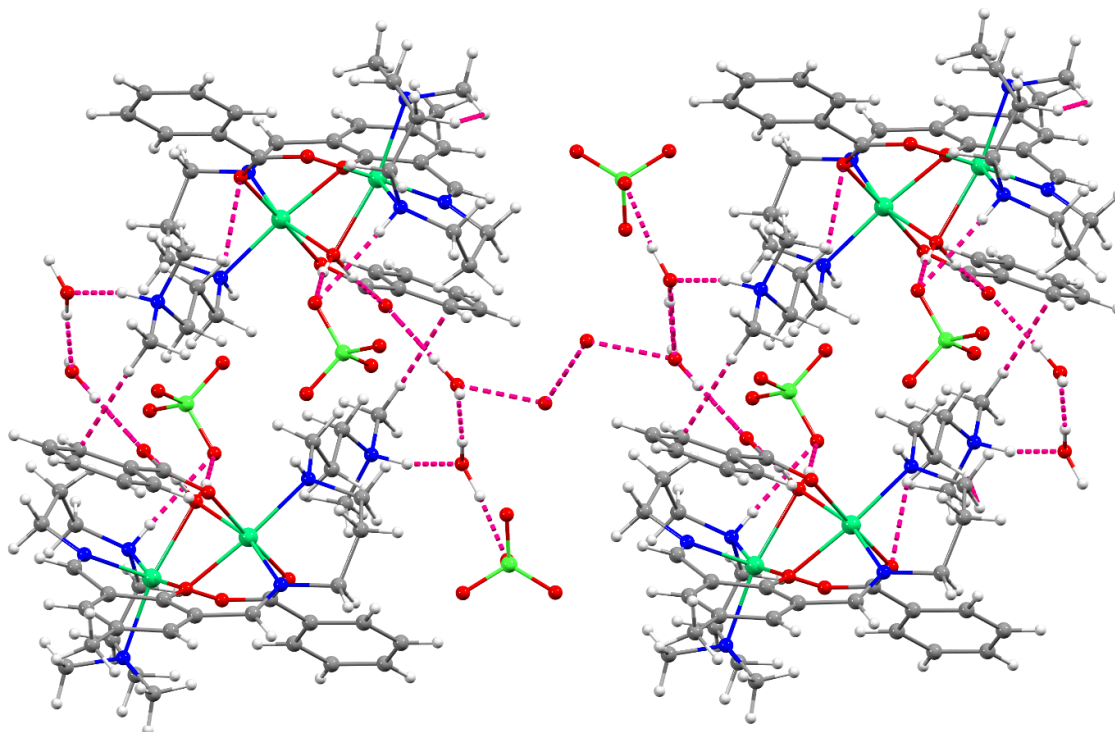


Figure 5.8: The crystal packing of complex **67** displaying different hydrogen bonding interactions.

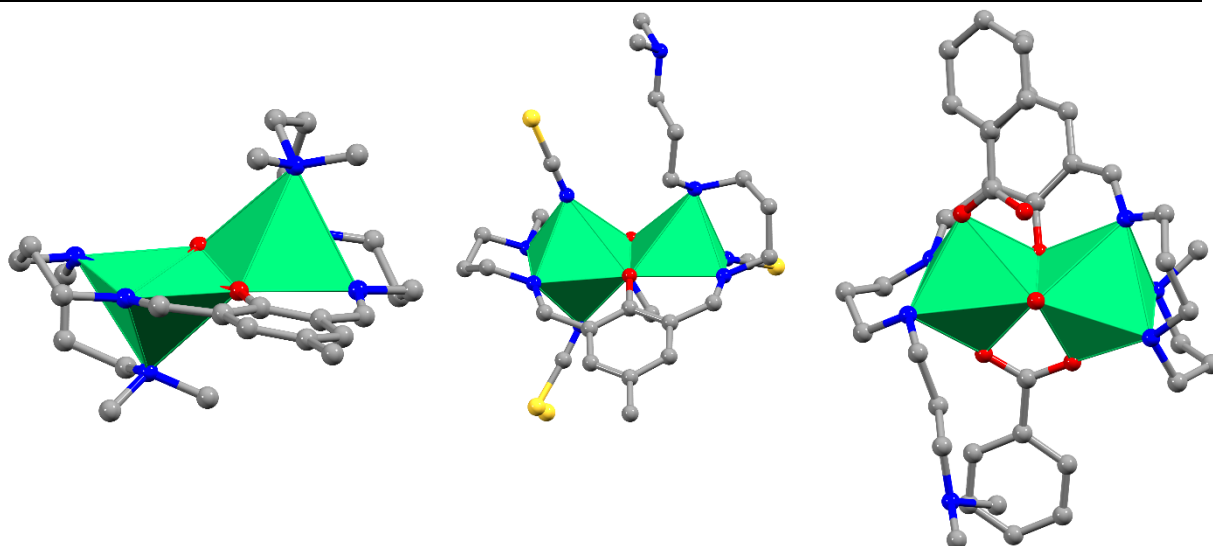


Figure 5.9: Crystal structures of **65–67** showing edge sharing bi-polyhedral structures and hydrogen atoms have been omitted for clarity.

5.3.4. Magnetic properties

The DC magnetic susceptibility was measured on polycrystalline samples of **65–67** in the temperature range 300 – 2 K in a constant applied magnetic field of 2 kOe. The temperature dependent susceptibility per mole χ and χT products are displayed in Figure 5.10. As can be seen from the figure, the susceptibility values increase with decreasing temperature from room temperature and reaching a maximum at approximately 130 K for **65**, 45 K for **66** and 11 K for **67** and decrease thereafter, which is a clear indication of antiferromagnetic interaction between the Ni(II) ions in the dimeric units. At room temperature, the χT values of 2.4 emu K/mol for **66** and **67** are slightly higher than the calculated value of 2.0 emu K/mol for two non interacting Ni(II) ions with $S = 1$ and $g = 2$, which is due to orbital contribution of Ni(II) ion at room temperature. However, χT value of 1.8 emu K/mol for **65** is slightly lower than the theoretical value, indicating that antiferromagnetic coupling between two Ni(II) centres is operative even at room temperature. The isotropic Heisenberg model $H = -JS_1 \cdot S_2$, where S_1 and S_2 are equal to 1, and J is an interaction parameter, can be applied to

describe the temperature dependent magnetic susceptibility of these systems using the following equation [47],

$$\chi = \frac{g^2 N_A \mu_B^2}{k_B T} \frac{2(e^x + 5e^{3x})}{1 + 3e^x + 5e^{3x}} (1 - \rho) + \frac{4g^2 N_A \mu_B^2}{3k_B T} \rho \quad (\text{Eq. 5.2})$$

where $x = J/k_B T$ and other symbols acquire their usual meaning. The second term accounts for a small amount of noncoupled magnetic moments and ρ is a molar fraction of these noncoupled species. The best fit to experimental data was obtained (full green line in Figure 5.10) with $J/k_B = -143$ K, $g = 2.3$ and $\rho = 1$ % for **65**, $J/k_B = -42$ K, $g = 2.3$ and $\rho = 0$ % for **66**, and $J/k_B = -12$ K, $g = 2.2$ and $\rho = 5$ % for **67**.

As already described in the structural section, complexes **65** and **66** are dinickel(II) systems with phenoxo and hydroxo bridges. Experimental and theoretical magneto-structural correlations reveal that the major factor controlling the exchange coupling in double phenoxo/alkoxo/hydroxo bridged $\text{Ni}(\mu\text{-O})_2\text{Ni}$ complexes is the bridging Ni–O–Ni angle in which a ferromagnetic coupling is expected when the Ni–O–Ni angle is close to 90° [48]. As the Ni–O–Ni angle deviates from 90° , the ferromagnetic coupling decreases and above the critical Ni–O–Ni angle of $\sim 98^\circ$, the coupling becomes antiferromagnetic and the strength of coupling constant increases with increasing the angles. The phenoxo and hydroxo bridging angles in **66** of $100.30(4)$ and $101.25(4)^\circ$, respectively, are significantly larger than the critical angle and thus the antiferromagnetic coupling between the Ni(II) centres is quite reasonable. The same angles ($101.77(6)$ and $106.32(7)^\circ$ respectively) in **65** are even larger than that found in **66**, consistent with the J/k_B of -143 K in **65**. Furthermore, the geometry of both the metal centres in **65** is square pyramidal, while it is octahedral or square pyramidal for either of the metal ions in **66**. Thus, the average bridging Ni–O distances for equatorially coordinated bridging atoms in **65** (range $1.9674(14)$ – $2.0333(13)$ Å) is somewhat shorter than that of **66** (range $2.0188(9)$ – $2.0829(9)$ Å), which is expected to increase effective overlap in

the super-exchange pathway executed through bridged atoms in **65**, leading to stronger antiferromagnetic coupling in **65** over **66**. The connectivity of two Ni(II) centres in **67** is significantly different from **65** and **66** as it is a triply bridged system, comprising with a *syn-syn* carboxylate, a phenoxo and an aqua bridge. The *syn-syn* carboxylate bridge generally propagates antiferromagnetic interaction between two metal centres [49]. When it is coupled with an aqua bridge and the aqua bridging angle being larger than 100° , the Ni(II) ions experience stronger antiferromagnetic interaction due to the complementary effect of these bridging ligands. Similarly, almost all the aqua and phenoxo triply bridged systems transmit weak to moderate ferromagnetic interactions as in these systems all the bridging angle fall well below the critical angle. In the present case, the antiferromagnetic coupling is expected as usual through *syn-syn* carboxylate bridge and also through the phenoxo bridge as the phenoxo bridging angle is $104.72(6)^\circ$. However, the bridging aqua angle of $93.30(6)^\circ$ being significantly lower than that of the critical angle likely transmits the ferromagnetic interaction between the metal ions. Therefore, the counter complimentary effect of the aqua bridge is responsible for overall weaker antiferromagnetic coupling in **67** [46].

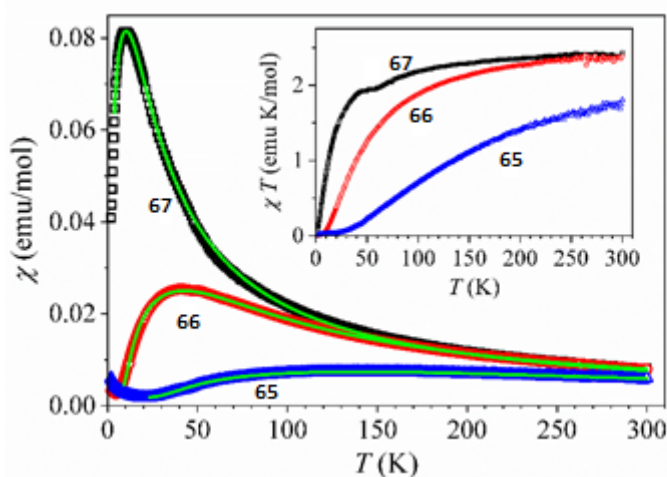


Figure 5.10: Temperature dependent molar magnetic susceptibility of **65–67**. Full green lines are fits with equation (1) and parameters shown in Table 5.4. Inset shows the χT vs. T plots.

Table 5.4 Magnetic parameters for **65**–**67**.

	χ^T (emu K/mol)	$\mu_{eff} = \sqrt{8 \chi^T / 2}$ (μ_B per Ni ion)	J (K)	g	ρ (%)
65	1.8	2.7	− 143	2.3	1
66	2.4	3.1	− 42	2.3	0
67	2.4	3.1	− 12	2.2	5

5.3.5. Catalytic oxidation of *o*-aminophenol

Phenoxazinone synthase like activity of all the complexes were examined using *o*-aminophenol (OAPH) as a model substrate. The progress of catalytic reaction of a mixture of OAPH (0.02 mM) and the complexes ($5.0 \times 10^{-5} \text{ M}$ or 1.0×10^{-4}) in dioxygen saturated methanol is monitored UV-vis spectrophotometrically at ambient temperature (25 °C). The time dependent spectral profiles as depicted in Figure 5.11 disclose the gradual development of spectral band atca. 435 nm, indicating catalytic formation of phenoxazinone chromophore. Detailed kinetic study was further carried out to gain insight into the catalytic efficiency in these complexes and for that all the complexes ($5.0 \times 10^{-5} \text{ M}$) were allowed to react with excess OAPH, maintaining the pseudo-first-order condition, and the initial rates of the reactions were extracted. The plots of initial rates against the concentrations of the substrate (Figure 5.12) follow a rate saturation kinetics which can be modelled with Michaelis-Menten kinetics to extract the parameters $V_{\max}$, K_M , and K_{cat} and these values can be found in Table 5.5.

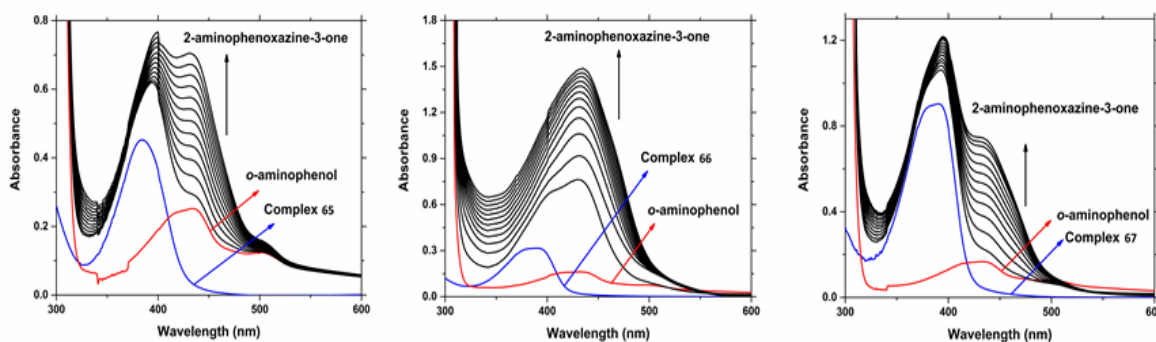


Figure 5.11: Time-dependent spectral profile for the oxidation of OAPH ($1 \times 10^{-2} \text{ M}$) in air-saturated methanol in presence of catalytic amount of complexes **65**–**67** ($5 \times 10^{-5} \text{ M}$).

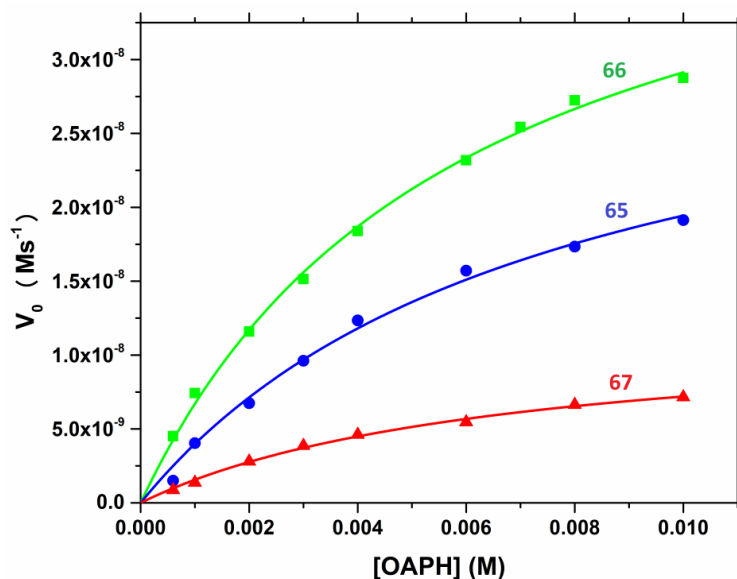


Figure 5.12: Michaelis–Menten plot for the oxidation of OAPH in dioxygen-saturated methanol catalysed by complexes **65–67** at room temperature. Symbols and solid lines represent the experimental and simulated profiles, respectively.

Table 5.5 Kinetic parameters of phenoxazinone synthase like activity for **65–67**.

Catalyst	$V_{\max}$ (Ms^{-1})	K_M (M)	k_{cat} (h^{-1})
65	$(3.41 \pm 0.24) \times 10^{-8}$	$(7.57 \pm 0.99) \times 10^{-3}$	12.30
66	$(4.64 \pm 0.15) \times 10^{-8}$	$(5.92 \pm 0.38) \times 10^{-3}$	16.70
67	$(1.19 \pm 0.06) \times 10^{-8}$	$(6.68 \pm 0.61) \times 10^{-3}$	4.32

5.3.6. Reaction mechanism and comparative catalytic activity

Structural studies on metalloenzymes and several efficient functional models disclose that the available vacant sites or labile positions for substrates binding are prerequisite for the efficient catalytic activity [10,11,50]. In complexes **65** and **66**, the metal centres are either coordinatively unsaturated and/or bonded with substitutionally labile thiocyanate ions that favour the coordination of OAPH to the metal centres, leading to efficient catalytic conversion of the substrate to the product 2-aminophenoxazin-3-one. The observed rate saturation kinetics further support the complex-substrate adduct formation in these systems.

But in complex **67**, only one Ni(II) centre (Ni1) is bonded with a monodentate benzoate ion which is strongly connected with the bridging aqua ligand through an intramolecular hydrogen bond and thereby formation of a complex-substrate adduct by replacement of the monodentate benzoate ion in **67** is not much favourable, leading to a weaker conversion of the substrate to the product.

Further information regarding the formation of a complex-substrate intermediate and the course of the reaction can be obtained from the mass spectral study, and for that the mass spectra of one of the most reactive complexes (complex **66**) itself and in presence of excess amount of OAPH (20 equivalents) were recorded and are displayed in [Figure 5.13 and 5.14](#), respectively. The peaks at $m/z = 651.22, 664.20, 677.17, 701.49$ and 736.17 are the dinickel(II) species of compositions $[\text{Ni}_2(\text{L})(\text{NCS})(\text{MeOH})]^+$, $[\text{NaNi}_2(\text{L})(\text{OH})(\text{MeO})(\text{MeOH})]^+$, $[\text{Ni}_2(\text{L})(\text{NCS})_2]^+$ or $[\text{NaNi}_2(\text{L})(\text{NCS})(\text{OH})(\text{OH}_2)]^+$, $[\text{NaNi}_2(\text{HL})(\text{NCS})_2]^+$ and $[\text{NaNi}_2(\text{HL})(\text{NCS})(\text{OH})(\text{OH}_2)]^+$, respectively, which are well supported by their isotopic distribution patterns. A mononuclear Ni-species is also found at $m/z = 562.27$ which is matched with a monocationic species of composition $[\text{Ni}(\text{HL})(\text{NCS})_2]^+$. Interestingly, when mass spectra were recorded in presence of excess OAPH, the most of peaks found in complex itself were disappeared. The new major peaks are again well assignable and these are either the substrate, product or intermediate related species. The peak at $m/z = 213.06$ is consistent with a protonated species of the product 2-aminophenoxazin-3-one (calculated $m/z = 213.07$). The peak at $m/z = 215.08$ is quite interesting as it matched with a protonated species of an important reactive intermediate II-B (calculated $m/z = 215.09$) generated in the course of oxidative coupling of *o*-aminophenol at the penultimate step of the formation of 2-aminophenoxazin-3-one as drawn in [Scheme 5.2](#). The peaks at $m/z = 950.96, 964.95, 982.99$ and 1028.00 are most important peaks as their peak-to-peak separation of unity and isotopic distribution patterns are matched with complex-substrate intermediate

species of compositions $[\text{NaNi}_2(\text{L})(\text{OH})(\text{OAP})_2(\text{NCS})_2(\text{H}_2\text{O})]^+$, $[\text{NaNi}_2(\text{L})(\text{OH})(\text{OAP})_2(\text{NCS})_2(\text{MeOH})]^+$, $[\text{NaNi}_2(\text{L})(\text{OH})(\text{OAP})_2(\text{NCS})_2(\text{H}_2\text{O})(\text{MeOH})]^+$ and $[\text{Na}_2\text{Ni}_2(\text{L})(\text{OH})(\text{OAP})_2(\text{NCS})_2(\text{H}_2\text{O})_4]^+$, respectively. The peak at $m/z = 514.50$ is a dicationic species as suggested by the peak-to-peak separation of 0.5 and therefore this dicationic species is a conjugate acid of the monocationic species found at $m/z = 1028.00$.

So, the mass spectrometry together with the rate saturation kinetics disclose that the catalytic cycle starts with the coordination of the substrates to the metal centres as depicted in [Scheme 5.2](#). In the complex-substrate adduct two thiocyanate ions and two OAPH molecules are bonded to the metal centres as suggested by the mass spectrometry where all the complex-substrate intermediate species are characterised with this composition. Thereafter, an intramolecular electron transfer occurs from the substrate to the complex. In order to better understand the electron transfer process, we have carried out the X-band EPR spectra at 77 K of complex **66** both in presence and absence of the substrate. As usual, the compound itself is found EPR silent. But when an excess OAPH (20 equivalents) was added to the complex, an isotropic signal at $g = 2.008$ appeared that indicates the generation of an organic free radical during the course of this reaction ([Figure 5.15](#)). Therefore, the EPR study excludes the possible involvement of the redox participation of the metal centre electron transfer process, leaving the ligand centre base reduction to the formation of imine radical anion intermediate with concomitant oxidation of OAPH to OAP radical. The present results are consistent with most of the previously reported Ni(II) complexes with Schiff base ligands, showing catechol oxidase like activity where the Schiff base undergoes one electron reduction during the catalytic cycle [51]. The slightly higher reactivity of **66** over **65** could be due to the overall positive charge of the ligand (H_2L^+) in **66** compared to the negative charge of ligand (L^-) in **65**, favouring the reduction of imine bond towards the formation of imine radical anion intermediate in **66**. The OAP radical is thereafter converted to *o*-benzoquinonemonoamine

(BQMI) in many ways, including the disproportionation of the OAP radical itself and finally produces 2-aminophenoxazin-3-one through the multiple steps as shown in [Scheme 5.2](#).

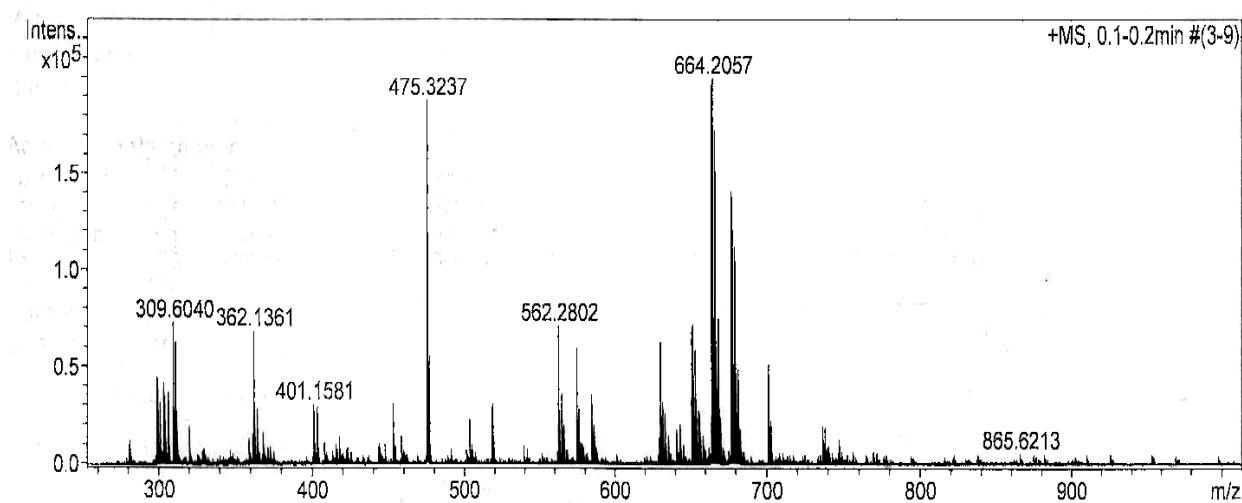


Figure 5.13: Electrospray ionization mass spectrum (ESI-MS positive) of **66**.

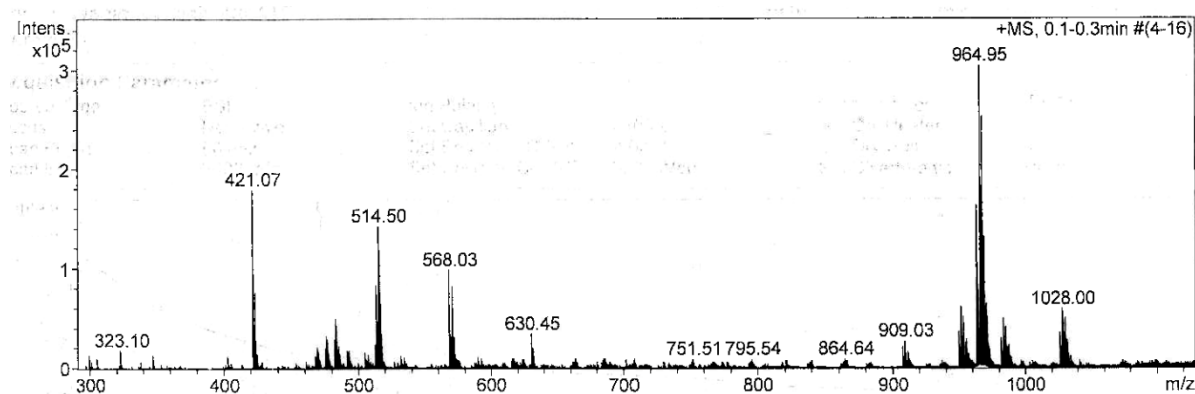


Figure 5.14: Electrospray ionization mass spectrum (ESI-MS positive) of a 1:50 mixture of **66** and OAPH in methanol recorded after 10 min of mixing.

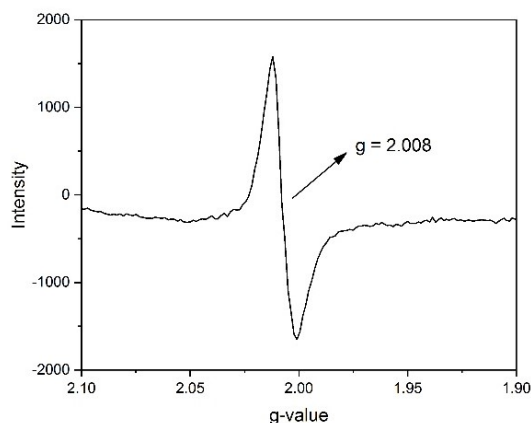
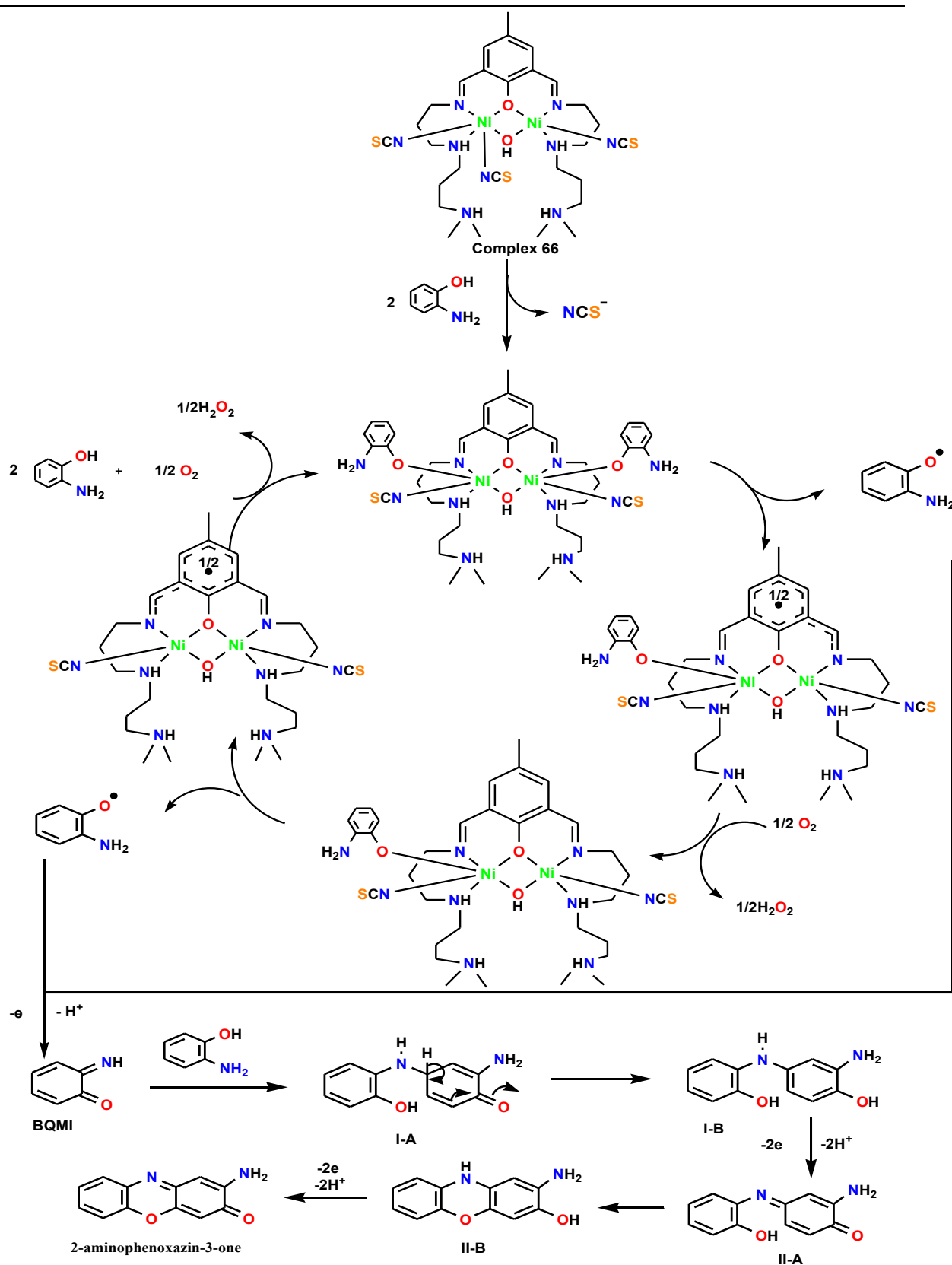


Figure 5.15: X-band EPR spectrum of complex **66** in presence of excess OAPH.



Scheme 5.2: The most probable mechanistic pathway for the catalytic oxidation of the substrate in aerobic condition.

5.4. Conclusion

In conclusion, three dinickel(II) complexes, namely $[\text{Ni}_2(\mu\text{-L})(\mu\text{-OH})](\text{ClO}_4)_2$ (**65**), $[\text{Ni}_2(\mu\text{-H}_2\text{L})(\mu\text{-OH})(\text{NCS})_3](\text{NCS})$ (**66**) and $[\text{Ni}_2(\mu\text{-HL})(\mu\text{-OBz})(\mu\text{-H}_2\text{O})(\text{OBz})](\text{ClO}_4)_2 \cdot 2.5\text{H}_2\text{O}$ (**67**) (where HOBz = benzoic acid), have been synthesized with an end-off compartmental ligand (HL) derived from the Schiff base condensation of 2,6-diформyl-4-methylphenol and *N,N*-dimethyldipropylenetriamine in methanol. X-ray crystallography reveals that both **65** and **66** are phenoxo and hydroxo bridged compounds, while complex **67** is a unique tripleaqua, phenoxo and carboxylato bridged dinickel(II) complex. Although the similar bridging pattern that found in **67** is known in the literature, the combination of aqua, carboxylate and phenoxo bridges could be a new addition in dinickel(II) coordination chemistry. The synthesized complexes display a weak to moderate antiferromagnetic coupling between the Ni(II) centres within the dimeric units with *J* values spanning in the range –12 to –143 K and a magneto-structural correlation has been performed to gain insight in the exchange pathway. All these complexes exhibit moderate catalytic activity relevant to the phenoxazinone synthase and the extent of catalytic reactivity has been further explored where the substitutionally labile sites and/or vacant sites at the metal centres are responsible for the higher reactivity in **65** and **66**. The mass spectrometry further supports the complex-substrate adduct formation and the EPR spectroscopy indicates possible involvement of the ligand-centre based reduction in the catalytic cycle and thereby altogether disclose the mechanistic insight in the catalytic activity. Although the numbers of examples of Ni(II)-based efficient models for other metallo-oxidases such as catechol oxidase are available, the present modelling of the Ni(II) complexes for phenoxazinone synthase activity could be an important addition to the biorelevant catalytic activity.

References

- [1] (a) S. Ciurli, In *Metal Ions in Life Sciences*, ed. A. Sigel, H. Sigel, R. K. O. Sigel, JohnWiley & Sons, Chichester, 2007, **2**, 241. (b) A. L. Noffke, A. Habtemariam, A. M. Pizarro, P. J. Sadler, *Chem. Commun.* 2012, **48**, 5219. (c) J. X. Liang, H. J. Zhong, G. Yang, K. Vellaisamy, D. L. Ma, C. H. Leung, *J. Inorg. Biochem.* 2017, **177**, 276. (d) M. Odachowski, C. Marschner, B. Blom, *Eur. J. Med.* 2020, **204**, 112613.
- [2] (a) G. Ambrosi, M. Formica, V. Fusi, L. Giorgi, Ma. Micheloni, *Coord. Chem. Rev.* 2008, **252**, 1121. (b) H. Suo, G. A. Solan, Y. Ma, W. -H. Sun, *Coord. Chem. Rev.* 2018, **372**, 101. (c) P. Sun, D. Yang, Y. Li, B. Wang, J. Qu, *Dalton Trans.* 2020, **49**, 2151. (d) A. R. Jeong, J. W. Shin, J. H. Jeong, K. H. Bok, C. Kim, D. Jeong, J. Cho, S. Hayami, K. S. Min, *Chem.–Eur. J.* 2017, **23**, 3023.
- [3] (a) J. A. DeGayner, I. -R. Jeon, T. D. Harris, *Chem.Sci.* 2015, **6**, 6639. (b) S. Sasmal, S. Roy, L. Carrella, A. Jana, E. Rentschler, S. Mohanta, *Eur. J. Inorg. Chem.* 2015, **4**, 680. (c) X. Ma, E. A. Suturina, M. Rouzières, M. Platunov, F. Wilhelm, A. Rogalev, R. Clérac, P. Dechambenoit, *J. Am. Chem. Soc.* 2019, **141**, 7721. (d) M. D.Santana, G. García, M. Julve, F. Lloret, J. Pérez, M. Liu, F. Sanz, J. Cano, G. López, *Inorg. Chem.* 2004, **43**, 2132.
- [4] S. S. Massoud, M. Spell, C. Ledet, T. Junk, R. Herchel, R. C. Fischer, Z. Travnick, F. A. Mautner, *DaltonTrans.* 2015, **44**, 2110.
- [5] G. Ambrosi, M. Formica, V. Fusi, L. Giorgi, M. Micheloni, *Coord. Chem. Rev.* 2008, **252**, 1121.
- [6] (a) S. Svane, F. Kryuchkov, C. J. Lennarston, C. K. McKenzie, F. Kjeldsen, *Angew. Chem., Int. Ed.* 2012, **51**, 3216. (b) R. K. Edgal, A. D. Bond, C. J. Mckenzie, *DaltonTrans.* 2009, 3833. (c) R. K. Edgal, F. B. Larsen, A. D. Bond, C. J. Mckenzie, *Inorg. Chim. Acta.* 2005, **358**, 376.
-

- [7] (a) A. Boisen, A. Hazell, C. J. McKenzie, *Chem. Commun.* 2001, 2136 (b) P. Dalgaard, A. Hazell, C. J. McKenzie, B. Moubaraki, K. S. Murray, *Polyhedron* 2000, **19**, 1909. (c) H. Adams, D. Bradshaw, D. E. Fenton, *Inorg. Chim. Acta.* 2002, **332**, 195.
- [8] F. R. Xavier, A. Neves, A. Casellato, R. A. Peralta, A. J. Bortoluzzi, B. Szpoganicz, P. C. Severino, H. Terenzi, Z. Tomkowicz, S. Ostrovsky, W. Haase, A. Ozarowski, J. Krzystek, J. Telser, G. Schenk, L. R. Gahan, *Inorg. Chem.* 2009, **48**, 7905.
- [9] F. Michel, P. Torelli, St. F. Thomas, C. Duboc, C. Philouze, S. Belle, E. Hamman, S. Saint-Aman, J. L. Pierre, *Angew. Chem., Int. Ed.* 2005, **44**, 438.
- [10] S. K. Dey, A. Mukherjee, *Coord. Chem. Rev.* 2016, **310**, 80.
- [11] (a) S. J. Smith, C. J. Noble, R. C. Palmer, G. R. Hanson, G. Schenk, L. R. Gahan, M. J. Riley, *J. Biol. Inorg. Chem.* 2008, **13**, 499. (b) T. P. Camargo, F. F. Maia, C. Chaves, B. de Souza, A. J. Bortoluzzi, N. Castilho, N. T. Bortolotto, H. Terenzi, E. E. Castellano, W. Haase, Z. Tomkowicz, R. A. Peralta, A. Neves, *J. Inorg. Biochem.* 2015, **146**, 77. (c) K. S. Banu, T. Chattopadhyay, A. Banerjee, S. Bhattacharya, E. Suresh, M. Nethaji, E. Zangrando, D. Das, *Inorg. Chem.* 2008, **47**, 7083.
- [12] (a) R. L. Lomoth, P. Huang, J. Zheng, L. Sun, L. Hammarström, B. Akermark, S. Styring, *Eur. J. Inorg. Chem.* 2002, 5965. (b) Y. Gultneh, Y. T. Tesema, T. B. Yisgedu, R. J. Butcher, G. Wang, G. T. Yee, *Inorg. Chem.* 2006, **45**, 3023.
- [13] (a) H. Carlsson, M. Haukka, A. Bousseksou, J. -M. Latour, E. Nordlander, *Inorg. Chem.* 2004, **43**, 26, 8252. (b) F. Meyer, *Prog. Inorg. Chem.* 2009, **56**, 487. (c) T. Koga, H. Furutachi, T. Nakamura, N. Fukita, M. Ohba, K. Takahashi, H. Ōkawa, *Inorg. Chem.* 1998, **37**, 989.
- [14] (a) C. Pathak, S. K. Gupta, M. K. Gangwar, A. P. Prakasham, P. Ghosh, *ACS Omega* 2017, **2**, 8, 4737. (b) X. Zhou, X. -P. Zhang, W. Li, D. L. Phillips, Z. Ke, C. Zhao, *Inorg. Chem.* 2020, **59**, 17, 12065. (c) P. V. Bernhardt, S. Bosch, P. Comba, L. R.

- Gahan, G. R. Hanson, V. Mereacre, C. J. Noble, A. K. Powell, G. Schenk, H. Wadepohl, *Inorg. Chem.* 2015, **54**, 15, 7249.
- [15] (a) T. P. Camargo, A. Neves, R. A. Peralta, C. Chaves, E. C. P. Maia, E. H. Lizarazo-Jaimes, D. A. Gomes, T. Bortolotto, D. R. Norberto, H. Terenzi, D. L. Tierney, G. Schenk, *Inorg. Chem.* 2018, **57**, 1, 187. (b) S. K. Barman, T. Mondal, D. Koley, F. Lloretand R. Mukherjee, *Dalton Trans.* 2017, **46**, 4038.
- [16] (a) M. Jarenmark, M. Haukka, S. Demeshko, F. Tuczek, L. Zuppiroli, F. Meyer, E. Nordlander, *Inorg. Chem.* 2011, **50**, 9, 3866. (b) S. S. Massoud, C. C. Ledet, T. Junk, S. Bosch, P. Comba, R. Herchel, J. Hošek, Z. Trávníček, R. C. Fischerd, F. A. Mautner, *Dalton Trans.* 2016, **45**, 12933.
- [17] M. Patra, P. Brandão, A. P. Pikul, S. Adak, A. Panja, *ChemistrySelect.* 2020, **5**, 12924.
- [18] A. Panja, N. C. Jana, S. Adak, P. Brandão, L. Dlhán, J. Titiš, R.Boča, *New J. Chem.* 2017, **41**, 3143.
- [19] N. C. Jana, P. Brandão, A. Frontera, A. Panja, *Dalton Trans.* 2020, **49**, 14216.
- [20] A. Panja, N. C. Jana, P. Brandão, *Molecular Catalysis* 2018, **449**, 49.
- [21] A. Panja, N. C. Jana, P. Brandão, *New J. Chem.* 2017, **41**, 9784.
- [22] A. Panja, S. Adak, P. Brandão, L. Dlhán, R. Boča, *Eur. J. Inorg. Chem.* 2020, 2362.
- [23] C. E. Barry, P. G. Nayar, T. P. Begley, *J. Am. Chem. Soc.* 1988, **110**, 3333.
- [24] Z. Farhane, F. Bonnier, H. J. Byrne, *J. Biophotonics* 2018, **11**, 1.
- [25] X. Mu, L. Song, Q. Li, R. Yin, X. Zhao, D. Wang, *Int. J. Gynecol. Obstet.* 2018, **143**, 225.
- [26] J. Koshibu-Koizumi, M. Akazawa, T. Iwamoto, M. Takasaki, F. Mizuno, R. Kobayashi, A. Abe, A. Tomoda, M. Hamatake, R. Ishida, *J. Cancer Res. Clin. Oncol.* 2002, **128**, 363.

- [27] A. K. Brisdon, *Inorganic Spectroscopic Methods*. Oxford: Oxford University Press, (1998).
- [28] A. C. Sousa, M. C. Oliveira, L. O. Martins, M. P. Robalo, *Green Chem.* 2014, **16**, 4127.
- [29] C. N. Verani, E. Rentschler, T. Weyhermüller, E. Bill, P. Chaudhuri, *J. Chem. Soc., Dalton Trans.* 2000, 251.
- [30] M. Shyamal, T. K. Mandal, A. Panja, A. Saha, *RSC Adv.* 2014, **4**, 53520.
- [31] A. W. Addison, T. N. Rao, J. Reedijk, J. V. Rijn, G. C. Verschoor, *J. Chem. Soc., Dalton Trans.* 1984, 1349.
- [32] R. Modak, Y. Sikdar, S. Mandal, S. Chatterjee, A. Bieńko, J. Mroziński, S. Goswami, *Inorg. Chim. Acta.* 2014, **416**, 122.
- [33] L. Rodríguez, E. Labisbal, A. Sousa-Pedrares, J. A. García-Vázquez, J. Romero, M. L. Durán, J. A. Real, A. Sousa, *Inorg. Chem.* 2006, **45**, 7903.
- [34] R. Biswas, P. Kar, Y. Song, A. Ghosh, *Dalton Trans.* 2011, **40**, 5324.
- [35] R. Biswas, S. Giri, S. K. Saha, A. Ghosh, *Eur. J. Inorg. Chem.* 2012, 2916.
- [36] R. Biswas, C. Diaz, A. Bauzá, M. Barceló-Oliver, A. Frontera, A. Ghosh, *Dalton Trans.* 2014, **43**, 6455.
- [37] R. Biswas, C. Diaz, A. Ghosh, *Polyhedron* 2013, **56**, 172.
- [38] S. Banerjee, M. G. B. Drew, C. -Z. Lu, J. Tercero, C. Diaz, A. Ghosh, *Eur. J. Inorg. Chem.* 2005, 2376.
- [39] A. A. Nikiforov, E. N. Dubrov, D. O. Blinou, V. V. Gurzhiy, A. A. Selyutin, I. N. Klykin, A. P. Zhdanov, A. E. Minkovich, N. S. Panina, A. V. Eremin, *Polyhedron* 2021, **195**, 114971.
- [40] B. -H. Ye, I. D. Williams, X. -Y. Li, *J. Inorg. Biochem.* 2002, **92**, 128.
- [41] A. Karmakar, K. Deka, R. J. Sarma, J. B. Baruah, *Inorg. Chem. Commun.* 2006, **9**, 836.
- [42] A. Karmakar, R. J. Sarma, J. B. Baruah, *Eur. J. Inorg. Chem.* 2006, 4673.

- [43] K. Müller, M. Korb, C. Koo, R. Klingeler, D. Miesel, A. Hildebrandt, T. Rüffer, H. Lang, *Polyhedron* 2017, **138**, 185.
- [44] J. P. S. Walsh, S. Sproules, N. F. Chilton, A. -L. Barra, G. A. Timco, D. Collison, E. J. L. McInnes, R. E. P. Winpenny, *Inorg. Chem.* 2014, **53**, 8464.
- [45] J. Overgaard, J. P. S. Walsh, V. R. Hathwar, M. R. V. Jørgensen, C. Hoffman, J. A. Platts, R. Piltz, R. E. P. Winpenny, *Inorg. Chem.* 2014, **53**, 11531.
- [46] D. Volkmer, B. Hommerich, K. Griesar, W. Haase, B. Krebs, *Inorg. Chem.* 1996, **35**, 3792.
- [47] O. Kahn, *Molecular Magnetism*, VCH Publishers: New York, 1993, 211.
- [48] (a) M. P. Palacios, A. J. Mota, J. E. Perea-Buceta, F. J. White, E. K. Brechin, E. Colacio, *Inorg. Chem.* 2010, **49**, 10156. (b) J. Ruiz, A. J. Mota, A. Rodríguez-Diéguez, I. Oyarzabal, J. M. Secob, E. Colacio, *Dalton Trans.* 2012, **41**, 14265.
- [49] (a) C. Ruiz-Pérez, J. Sanchiz, M. H. Molina, F. Lloret, M. Julve, *Inorg. Chem.* 2000, **39**, 1363. (b) A. R. Fortea, P. Alemany, S. Alvarez, E. Ruiz, *Chem. Eur. J.* 2001, **7**, 627.
- [50] A. Panja, M. Shyamal, A. Saha and T. K. Mandal, *Dalton Trans.* 2014, **43**, 5443.
- [51] (a) M. Mondal, P. M. Guha, S. Giri, A. Ghosh, *J. Mol. Catal. Chem. A* 2016, **424**, 54. (b) T. Chakraborty, S. Mukherjee, S. Dasgupta, B. Biswas, D. Das, *Dalton Trans.* 2019, **48**, 2772. (c) S. Dasgupta, J. Adhikary, S. Giri, A. Bauza, A. Frontera, D. Das, *Dalton Trans.* 2017, **46**, 5888. (d) T. Ghosh, J. Adhikary, P. Chakraborty, P. K. Sukul, M. S. Jana, T. K. Mondal, E. Zangrando, D. Das, *Dalton Trans.* 2014, **43**, 841.

CHAPTER 6

CHAPTER 6

Syntheses, structures and magnetic properties of ferromagnetically / antiferromagnetically coupled penta- and hexa-nuclear azido-bridged nickel(II) coordination clusters

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6.1. Introduction

Last few decades witnessed rapid development of polynuclear coordination clusters with spin-coupled paramagnetic transition metal ions not only because of understanding of their fundamental magnetic phenomena but also for their potential applications as single-molecule magnets (SMMs) [1–9] and single-chain magnets (SCMs) [10–14], and in magnetic refrigeration and quantum computing and nanotechnological devices [15,16]. A rational approach to synthesize discrete exchange-coupled transition metal clusters depends on the synthetic strategy that involves the use of transition metal ions, multidentate blocking ligands in conjunction with the flexidentate bridging ligands to propagate specific magnetic interactions between the metal centers. In majority, the doubly or triply bridging anions like N_3^- , NCS^- , $\text{N}(\text{CN})_2^-$, CN^- , $\text{C}_2\text{H}_3\text{O}_2^-$, $\text{C}_6\text{H}_5\text{O}^-$ and OH^- are used for the construction of magnetically interesting coordination clusters [17]. The sign and magnitude of the magnetic exchange interactions between the metal centers in coordination clusters depend on a number of factors; the most important of these are the type of bridging ligands and bridge angles. Among all, azido and hydroxo (phenoxido and alkoxido) bridges are the most versatile mediators of magnetic exchange interactions between paramagnetic ions due to their diverse coordination ability [18]. In most of the reported complexes, azido bridges propagate antiferromagnetic (end-to-end, $\mu_{1,3}$ bridges) or ferromagnetic interactions (end-on, $\mu_{1,1}$ bridges) depending upon the nature of the bridges [19].

New ligands could provide us the opportunity to attain new structural types and spin topologies. Schiff-base ligands have been extensively used as blocking ligands in developing magnetically interesting compounds mainly because of their synthetic simplicity and tremendous structural diversities. The choice of ligands is always a major issue in the development of new synthetic routes to produce such type of coordination clusters [20].

Phenol-based dinucleating Schiff base ligands are needed to be special mentioned as they are capable to bind simultaneously two metal ions [21], leading to the formation of M_2L type complexes in absence of any bridging ligand. Introduction of secondary bridging units, such as HO^- and N_3^- , may result in assembly of the transition metal coordination clusters from two or more M_2L units [22]. Such clusters display a variety of topologies, such as, tetrahedron [23], cubane [24], open dicubane [25], fused defective open dicubane [26], pentanuclear vertex-shared double cubane [27], and stepped cubane [28]. We recently initiated a project towards development of coordination chemistry with Schiff bases derived from a triamine, *N,N*-dimethyldipropylenetriamine, in which the diverse coordination adaptabilities of the triamine part of the ligands were observed [29]. We speculated that the dinucleating Schiff base ligands derived from this triamine would provide enough flexibility to self-assembly of the transition metal ions when react with additional bridging ligands to afford high nuclearity transition metal clusters. With this aim, a new dinucleating Schiff base ligand HL as shown in Scheme 5.1 was allowed to react with Ni(II) salts in presence of azide ions to yield two pentanuclear and one hexanuclear Ni(II) coordination compounds, $[Ni_5(H_2L)_2(\mu_{1,1}-N_3)_4(N_3)_2(\mu_3-OH)_2(H_2O)_2](NO_3)_4 \cdot 6H_2O$ (**68**), $[Ni_5(L)_2(\mu_{1,3}-OAc)_2(\mu_{1,1}-N_3)_4(\mu_3-OH)_2] \cdot 12H_2O \cdot 2CH_3OH$ (**69**) and $[Ni_6(H_2L)_2(\mu_{1,1}-N_3)_4(\mu_{1,3}-N_3)_2(N_3)_4(\mu_3-OH)_2(H_2O)_2](ClO_4)_2 \cdot 4H_2O$ (**70**). The crystal structures and magnetic properties of the complexes were further investigated and discussed.

6.2. Experimental Section

6.2.1. Laboratory Techniques

Laboratory techniques such as elemental analysis (CHN), infrared spectroscopy (IR), UV-visible spectroscopy and single crystal X-ray Diffraction study are similar as our previous

work. The details about these techniques have been discussed in section 2.2.1 of chapter 2. Single crystal X-ray Diffraction study was performed at Department of Chemistry, CICECO-Aveiro Institute of Materials, University of Aveiro, 3810-193 Aveiro, Portugal. Magneto chemistry was carried out at Department of Chemistry, Faculty of Natural Sciences, University of SS Cyril and Methodius, 917 01 Trnava, Slovakia. Samples of the nominal mass about 20 mg have been encapsulated into gelatine made containers and inserted into the SQUID magnetometer (MPMS-XL7, Quantum Design). At the external field $B_0 = 0.1$ T the magnetic data was taken between $T = 1.9 - 300$ K and raw magnetic moment of the specimen has been converted to the molar magnetic susceptibility, and displayed as the effective magnetic moment μ_{eff}/μ_B vs T . The measured magnetic susceptibility was not corrected for the underlying diamagnetic susceptibility because of high uncertainties and/or non-existence of the constitutive Pascal constants in the present cases. The field scan between $B = 0$ and 7 T at low temperature ($T_0 = 2.0$ or 4.6 K) enables evaluating the molar magnetization that is expressed per formula unit and bohr magneton, $M_1 = M_{\text{mol}}/N_A\mu_B$ vs B .

6.2.2. Chemicals and Synthetic techniques

6.2.2.1. Materials

2,6-diformyl-4-methylphenol (DFMP) was prepared according to literature reported method [30], and *N,N*-dimethyldipropylenetriamine was purchased from Aldrich. All other chemicals (metal salts and solvents) were analytical or reagent grade and used without further purification.

Caution! *Azido complexes of metal ions consisting of organic ligands are potentially explosive. Only small quantities of the complexes should be prepared, and these should be handled with great care.*

6.2.2.2. Synthesis of Schiff base ligand HL

The ligand (HL) used in the present work was prepared by single step Schiff base condensation method. Briefly, 1.0 mmol of *N,N*-dimethyldipropylenetriamine (159 mg) and 0.5 mmol of 2,6-diformyl-4-methylphenol (DFMP) (82 mg) were mixed in 20 mL of methanol. The resulting solution was heated to reflux for ca. 1 h, and allowed to cool at room temperature. The dark orange methanol solution of HL was subsequently used for the synthesis of the following complexes.

6.2.2.3. Synthesis of complex $[Ni_5(H_2L)_2(\mu_{1,1}-N_3)_4(N_3)_2(\mu_3-OH)_2(H_2O)_2](NO_3)_4 \cdot 6H_2O$ (68)

$Ni(NO_3)_2 \cdot 6H_2O$ (0.145 g, 0.50 mmol), dissolved in 20 mL of methanol was added to a 20 mL methanol solution of the Schiff-base ligand (0.25 mmol) dropwise with stirring, resulting in a green solution. A solution of sodium azide (NaN_3) (1.0 mmol, 0.065 g) dissolved in minimum amount of methanol was added to the resulting green solution dropwise over a period of 5 min with constant stirring. The reaction mixture (bright dark-green) was stirred under reflux for ca. 30 min, and it was filtered to remove if any minute quantity of precipitate. The filtrate was kept undisturbed at ambient temperature that afforded dark green crystals of **68** suitable for X-ray diffraction within couple of days. The crystals of **68** were collected by filtration and washed with methanol/ether and air dried. Yield: 0.31 g, 43.8%. Anal. calcd. for $C_{50}H_{112}N_{34}Ni_5O_{24}$: C 32.21%, H 6.06%, N 25.56%. Found: C 32.34%, H 6.04%, N 24.46%. Selected FTIR bands (KBr, cm^{-1}): 1384 s ($\bar{\nu}NO_3^-$); 1627 s, 1643 s ($\bar{\nu}C=N$); 2051 s, 2070 s ($\bar{\nu}N_3^-$).

6.2.2.4. Synthesis of complex $[Ni_5(L)_2(\mu_{1,3}-OAc)_2(\mu_{1,1}-N_3)_4(\mu_3-OH)_2] \cdot 12H_2O \cdot 2CH_3OH$ (69)

Compound **69** was synthesised following an identical procedure as that described for **69** except the use of $Ni(CH_3CO_2)_2 \cdot 4H_2O$ in place of $Ni(NO_3)_2 \cdot 6H_2O$. Yield: 0.67 g, 43.8%. Anal. calcd. for $C_{56}H_{130}N_{24}Ni_5O_{22}$: C 37.44%, H 7.09%, N 19.07%. Found: C 37.52%, H

7.14%, 18.96%. Selected FTIR bands (KBr, cm^{-1}): 1634 s, 1644 s ($\bar{\nu}\text{C}=\text{N}$ & ($\bar{\nu}\text{OAc}^-$); 2061 s ($\bar{\nu}\text{N}_3^-$).

6.2.2.5. Synthesis of complex $[\text{Ni}_6(\text{H}_2\text{L})_2(\mu_{1,1}\text{-N}_3)_4(\mu_{1,3}\text{-N}_3)_2(\text{N}_3)_4(\mu_3\text{-OH})_2(\text{H}_2\text{O})_2](\text{ClO}_4)_2 \cdot 4\text{H}_2\text{O}$ (**70**)

$\text{Ni}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (0.549 g, 1.5 mmol), and HL (0.5 mmol) were mixed together in a 30 mL of methanol and were allowed to reflux for about 30 min. To the resulting green solution 5 mL methanol-water (4:1. v/v) solution of NaN_3 (0.185 mg, 3 mmol) was added with stirring for a period of 5 min and the solution mixture was heated to reflux for about 30 min and filtered. The filtrate was kept undisturbed at ambient temperature that afforded **70** containing X-ray diffraction quality dark-green single crystals. They were collected by filtration and washed with methanol/ether and air dried. Yield: 0.67 g, 43.8%. Anal. calcd. for $\text{C}_{50}\text{H}_{104}\text{Cl}_2\text{N}_{42}\text{Ni}_6\text{O}_{18}$: C 35.40%, H 6.29%, N 28.60%. Found: C 35.52%, H 6.14%, N 28.55%. Selected FTIR bands (KBr, cm^{-1}): 623 s, 1120 s ($\bar{\nu}\text{ClO}_4^-$); 1636 s ($\bar{\nu}\text{C}=\text{N}$); 2053 s, 2072 ($\bar{\nu}\text{N}_3^-$).

6.3. Results and Discussion

6.3.1. Syntheses and and general charaterizations

In the search for ligands that can induce new structural features and capable of synthesizing high nuclearity clusters, a Schiff base ligand (HL) with a high degree of conformational flexibility was prepared *in situ* by the reaction of 2,6-diformyl-4-methylphenol (DFMP) and *N,N*-dimethyldipropylenetriamine in 1:2 molar ratio in methanol under refluxing condition (Scheme 5.1). This *in situ* generated Schiff base ligand was thereafter allowed to react with different Ni(II) salts and sodium azide in varied stoichiometry and in presence of triethylamine base to obtain diverse high nuclearity Ni(II) clusters. One-pot four-component reaction of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ with HL and NaN_3 in MeOH in the presence of triethylamine

base in 2:1:4 stoichiometry afforded a green solution which gave crystalline compound $[\text{Ni}_5(\text{H}_2\text{L})_2(\mu_{1,1}\text{-N}_3)_4(\text{N}_3)_2(\mu_3\text{-OH})_2(\text{H}_2\text{O})_2](\text{NO}_3)_4 \cdot 6\text{H}_2\text{O}$ (**68**). Similar reaction when carried out using $\text{Ni}(\text{CH}_3\text{CO}_2)_2 \cdot 4\text{H}_2\text{O}$ instead of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $[\text{Ni}_5(\text{L})_2(\mu_{1,3}\text{-OAc})_2(\mu_{1,1}\text{-N}_3)_4(\mu_3\text{-OH})_2] \cdot 12\text{H}_2\text{O} \cdot 2\text{CH}_3\text{OH}$ (**69**) was isolated in crystalline form. Although the structures of both **68** and **69** are very similar, the distinct role of counter ions is noticed. The weaker coordinating nitrate ions involve in balancing the charge of the complex cation in **68**, while better coordinating acetato ligand bridges Ni(II) centers in **69**, leading to the formation of an electroneutral complex. The stoichiometric ratio of the reactants also played crucial role in the complex formation, such as when the similar reaction is carried out using $\text{Ni}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$, HL and NaN_3 in MeOH in the presence of triethylamine base in 3:1:6 molar ratio, it resulted only isolable product $[\text{Ni}_6(\text{H}_2\text{L})_2(\mu_{1,1}\text{-N}_3)_4(\mu_{1,3}\text{-N}_3)_2(\text{N}_3)_4(\mu_3\text{-OH})_2(\text{H}_2\text{O})_2](\text{ClO}_4)_2 \cdot 4\text{H}_2\text{O}$ (**70**) in reasonable yield. The presence of counterion in the crystal structure of **70** suggests that, in addition to the stoichiometry of the reactants, use of perchlorate salt seems to have significant role in the formation this complex.

6.3.2. IR Spectroscopy

Compound **69** is an electroneutral complex, while both **68** and **70** are ionic compounds having NO_3^- and ClO_4^- as counter anions, respectively, to balance the charge of complex cations. The characteristic stretching band of nitrate ion at 1384 cm^{-1} in the IR spectrum of **68** is consistent with the above fact. Similarly, the stretching and bending vibrations of ClO_4^- ion at 1076 and 621 cm^{-1} , respectively, in the IR spectrum of **70**, ensure the presence of ClO_4^- ions in the crystal lattices [31]. The stretching vibrations of the azomethine ($\text{C}=\text{N}$) bonds of the Schiff base are located in the range $1627\text{--}1643\text{ cm}^{-1}$ in the IR spectra of **68** and **70**. However, the stretching vibration of the azomethine bond together with the acetate ion is appeared at 1644 cm^{-1} in **69**. The IR spectrum of **68** exhibits a bifurcated strong and sharp

band at 2051 and 2070 cm^{-1} , characteristic of the asymmetric stretching vibration of the azido ligands. The bifurcation of the band is indicative of the presence of at least two different kinds of azido ligands, consistent with the structural characterization of **68**. Similar bifurcation of the asymmetric stretching vibration of the azido ligands at 2053 and 2072 cm^{-1} was also observed in the IR spectrum of complex **70** (Figure 6.1). Unlike **68** and **70**, the IR spectrum of complex **69** is composed of a single strong and sharp asymmetric stretching vibration of the azido ligands at 2061 cm^{-1} , indicating the presence of only one type of azido ligand in this complex.

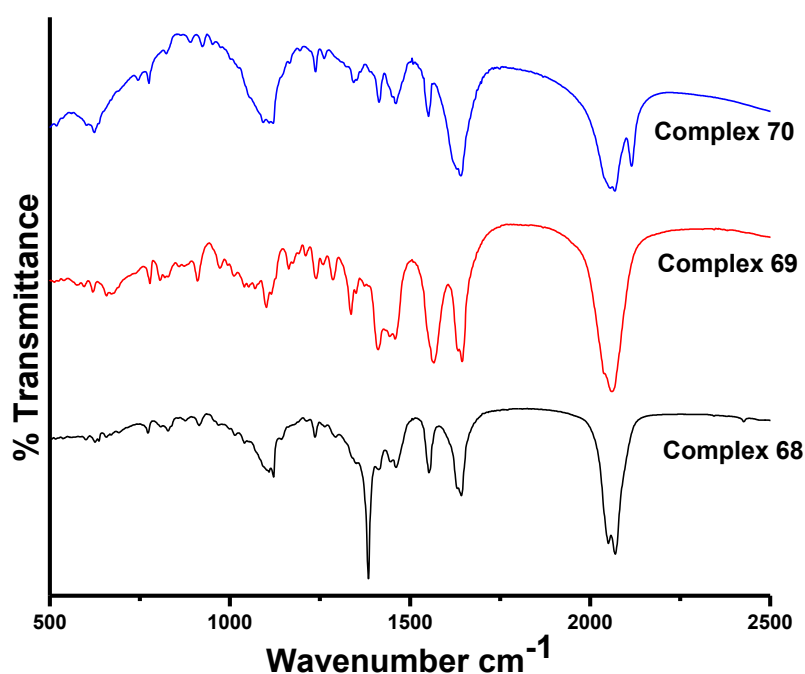


Figure 6.1: IR spectra of the complex **68-70**

6.3.3. Description of crystal structures

The solid-state molecular structures of compounds **68-70** were established by single-crystal X-ray diffraction analyses and the perspective views the crystal structures of complexes **68-70** along with partial atom numbering scheme are displayed in Figure 6.2-6.4, respectively. Selected bond distances and bond angles around the metal coordination spheres

in **68-70** are given in Table 6.1, Table 6.2 and Table 6.3, respectively. X-ray diffraction study reveals that compound **68** crystallizes in the monoclinic space group $P2_1/c$, while complex **69** crystallizes in the triclinic space group $P\bar{1}$. Important crystallographic data and refinement details for the complexes are given in Table 6.4. As the structures of both **68** and **69** are very similar, only the structure of the representative compound **68** has been described in detail. The asymmetric unit of **68** is comprised with a trinuclear Ni(II) cationic part, two nitrate ions and three lattice water molecules in which all atoms are in full occupancy except Ni1 that resides on an inversion center with half occupancy. The symmetry operation through a crystallographic inversion center produces a full set of the centrosymmetric compound $[\text{Ni}_5(\text{H}_2\text{L})_2(\mu_{1,1}\text{-N}_3)_4(\text{N}_3)_2(\mu_3\text{-OH})_2(\text{H}_2\text{O})_2](\text{NO}_3)_4 \cdot 6\text{H}_2\text{O}$ (**68**). Structural analysis discloses that the complex cation is composed of five Ni^{II} ions held together by two doubly bridging phenoxido groups ($\mu\text{-O}2$ and its symmetry equivalent) from Schiff base ligands, two triply bridging hydroxido groups ($\mu_3\text{-O}1$ and its symmetry equivalent), four end-on (EO) doubly bridging N_3^- ions (N7, N10 and their symmetry equivalents). Peripheral ligation is provided by eight nitrogen atoms from two Schiff base ligand H_2L (N1, N2, N4 and N5 and their symmetry equivalents), two azido ligands (N13 and its symmetry equivalent) and aqua ligands (O3 and its symmetry equivalent). Four non-coordinating NO_3^- ions are present in the molecular structures along with six lattice water molecules. Therefore, the protonation of the tertiary amine-N atoms of the Schiff base ligands is required to balance the charge of the system.

The core topology of five Ni^{II} atoms can be best described as a symmetric bowtie in which two reverse triangles ($\text{Ni}1\text{-Ni}2\text{-Ni}3$ and $\text{Ni}1\text{-Ni}2'\text{-Ni}3'$) share a common vertex Ni1 [32-34]. All Ni^{II} centers reside on a same plane which is because of the presence of a crystallographic inversion center located at middle Ni1 atom. Each triangle is best described as nearly isosceles with $\text{Ni}\cdots\text{Ni}$ separations of 3.159 and 3.165 Å and 3.233 Å. Each of the

four end-on doubly bridging N_3^- bridges the central Ni(II) ion and one peripheral Ni(II) ion in asymmetric fashion, while triply bridging $\mu_3\text{-HO}^-$ groups almost symmetrically links the central Ni(II) atom with the two peripheral metal ions on either side of the complex cation (See Table 6.1 and Figure 6.2). The two peripheral metal ions are further connected by the doubly bridging phenoxido groups from the Schiff base ligands. Therefore, the formation of Ni_5 -cluster can be viewed as an aggregation of two dinuclear $[\text{Ni}_2(\mu\text{-H}_2\text{L})(\text{N}_3)(\text{H}_2\text{O})]$ fragments with an additional Ni(II) ion from $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ salt supported by the exogenous azido and hydroxido bridges. Further inspection of the crystal structure reveals that the three-dimensional arrangement of the $[\text{Ni}_5(\mu\text{-N}_3)_4(\mu\text{-OH})_2(\mu\text{-O-phenoxaido})_2]$ core has the shape of a defective vertex-shared (Ni1) dicubane where one vertex is missing from each cubane. The bond angles in the defective dicubane vary in the range 79.46 to 102.44° . In addition to the bridging atoms in $[\text{Ni}_5(\mu\text{-N}_3)_4(\mu\text{-OH})_2(\mu\text{-O-phenoxaido})_2]$ core structure, Ni2 and Ni3 centers are further bonded with two N-donor atoms from either arm of the Schiff base along with a terminal azido and an aqua ligands, respectively. Same thing is also applicable for their symmetry equivalents. Overall, the coordination environments of Ni1 and Ni2 are comprised with N_4O_2 donor sets, while it is N_3O_3 for Ni3 center. Thus, all of the Ni(II) atoms are six-coordinated with slightly distorted octahedral geometry in which the Ni–O and Ni–N bond distances span in the range $2.025(3)$ to $2.160(3)$ Å (see Table 6.1).

The structure of $[\text{Ni}_5(\text{L})_2(\mu_{1,3}\text{-OAc})_2(\mu_{1,1}\text{-N}_3)_4(\mu_3\text{-OH})_2] \cdot 12\text{H}_2\text{O} \cdot 2\text{CH}_3\text{OH}$ (**69**) is very similar to that of **68**, with the essential differences being the replacement of the terminal azido and aqua ligands bonded to Ni2 and Ni3, respectively, by the bridging acetato group. The Ni2...Ni3 distance in **69** is found somewhat shorter (2.975 Å) than that in **68** (3.159 Å) because of the presence of this additional bridging acetato ligand. As a further consequence, the phenoxido- and hydroxido- bridging angles are also reduced significantly (92.92° and 93.98° , respectively) in comparison to 100.31° and 98.91° , respectively, that found in **68**.

Moreover, the neutral complex molecule crystallizes with twelve water and two disordered methanol molecules in the crystal lattices in **69**. The electroneutrality of the complex molecule ensures that the non-coordinated tertiary amine-N atoms are not protonated in **69** but they remain protonated in **68** that resulted different hydrogen bonding patterns in the solid-state structures of these compounds. Whereas the tertiary amine nitrogen atoms in the Schiff base ligand are protonated in **68**, thereby participating in strong hydrogen bonding interaction with the oxygen atoms of the nitrate counter ions with N...O distances of 2.802 and 2.885 Å. The tertiary amine nitrogen in **69** is on the other hand not protonated, which is involved in strong hydrogen bonding interactions as an acceptor with the lattice water molecules with N...O distances of 2.748 and 2.851 Å. Additionally, a large numbers of solvent molecules present in the crystal lattices stabilize the solid-state structures of **68** and **69** by the participation of moderate to strong hydrogen bonding interactions as shown in Figure 6.5 and 6.6, respectively.

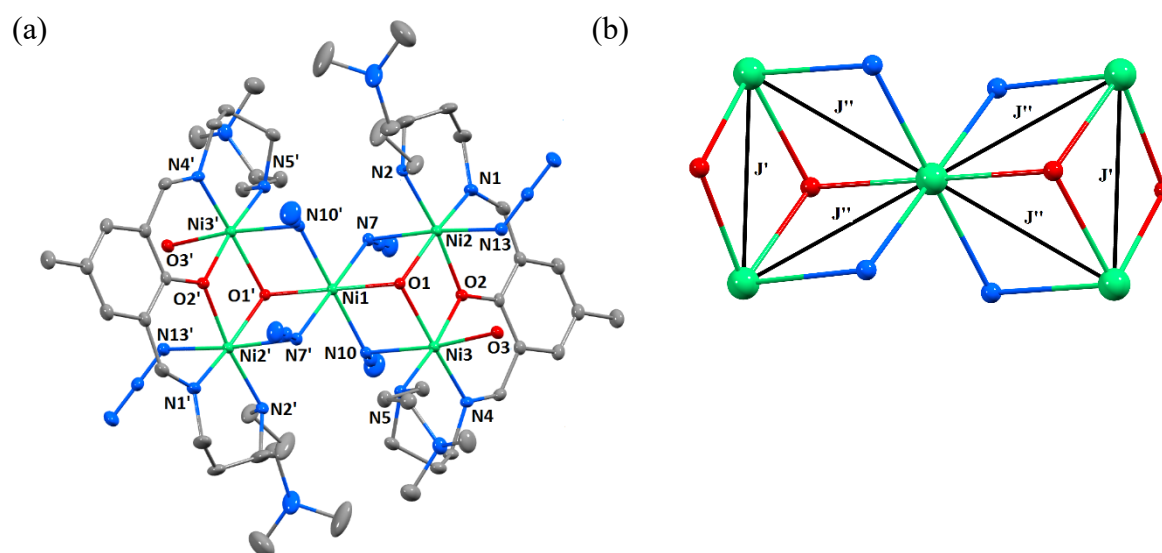
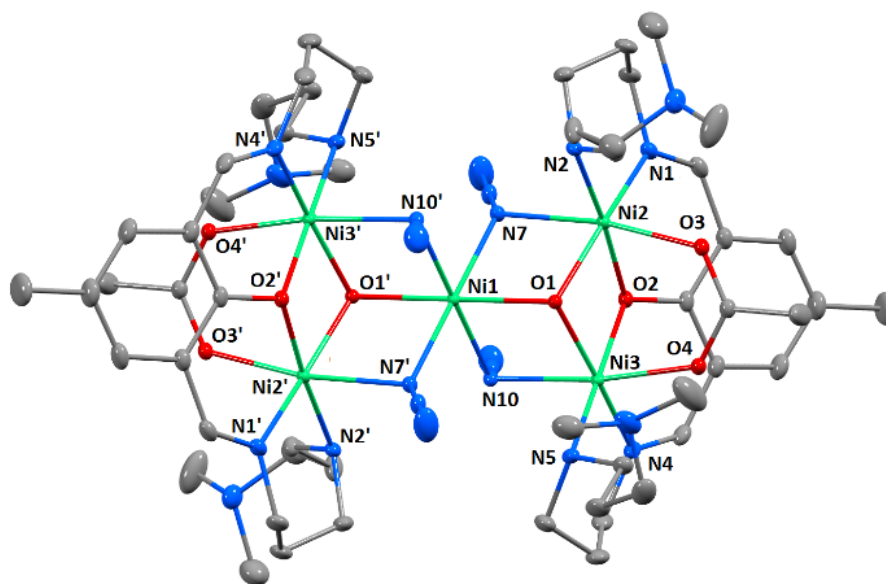
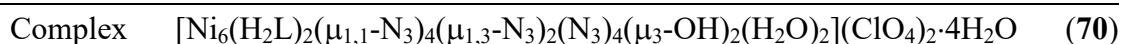


Figure 6.2: (a) Crystal structure of **68** with partial atom numbering scheme. Primed and unprimed atoms are related by the crystallographic inversion center. Ellipsoids are drawn at the 30% probability level. H atoms, NO₃⁻ ions and solvent molecules are omitted for clarity. (b) Skeletal representation of the Ni₅ core structure displaying magnetic coupling scheme.

Table 6.1 Selected bond Distances (Å) and Angles (deg) for complex **68**.

Distances			
Ni1–O1	2.062(2)	Ni1–N10	2.126(3)
Ni1–N7	2.160(3)	Ni2–N1	2.037(4)
Ni2–O2	2.063(3)	Ni2–O1	2.086(3)
Ni2–N2	2.117(3)	Ni2–N13	2.120(3)
Ni3–N4	2.025(3)	Ni3–O2	2.051(3)
Ni3–O1	2.071(2)	Ni3–O3	2.095(3)
Ni3–N5	2.106(3)	Ni3–N10	2.160(3)
Angles			
O1–Ni1–N10	82.88(10)	O1–Ni1–N7	81.59(11)
N10–Ni1–N7	87.54(12)	O2–Ni2–O1	79.46(10)
N1–Ni2–N2	96.59(14)	O1–Ni2–N7	79.97(10)
O2–Ni3–O1	80.11(10)	O1–Ni3–N10	81.84(10)
N4–Ni3–N5	97.25(13)	O2–Ni3–N10	91.70(11)
Ni1–O1–Ni2	102.44(11)	Ni1–N7–Ni2	95.60(12)
Ni1–O1–Ni3	99.95(10)	Ni1–N10–Ni3	95.19(12)
Ni3–O1–Ni2	98.90(11)	Ni3–O2–Ni2	100.31(11)

**Figure 6.3:** Crystal structure of **69** with partial atom numbering scheme. Primed and unprimed atoms are related by the crystallographic inversion center. Ellipsoids are drawn at the 30% probability level. H atoms and solvent molecules are omitted for clarity.



crystallizes in the monoclinic space group $P2_1/n$ in which the crystallographic asymmetric unit is built up by a trinuclear Ni(II) fragment with triangular arrangements of the metal centers with Ni...Ni separations of 3.155, 3.190 and 3.213 Å, one perchlorate ion and two lattice water molecules. The symmetry operation through an inversion center generates the full set of **70** in which Ni1 atom and its symmetry equivalent Ni1' center are connected by doubly bridging end-to-end azido ($\mu_{1,3}\text{-N}_3$) ligands and the inversion center is located at the midpoint of the central $[\text{Ni}_2(\mu_{1,3}\text{-N}_3)_2]$ core, made up with Ni1, Ni1' and doubly bridging end-to-end azido ligands. Interestingly, the core structure of the Ni(II) triangle in **70** is identical as that found in **68** where triply bridging hydroxido group ($\mu_3\text{-O1}$) connects the metal centers in association with a doubly bridging phenoxido group ($\mu\text{-O2}$) to connect the peripheral metal centers and four end-on (EO) doubly bridging N_3^- ions to connect Ni1 either with Ni2 or Ni3. Metric parameters inside the triangular unit in **70** are very similar to those found in **68** without significant differences (see Table 6.3). Now if we consider all the bridging phenoxido-O, hydroxido-O and azido-N atoms together with three Ni centers, it results a defective cubane with a missing vertex, identical to that found in **68**. Whereas in **68**, a defective dicubane is formed by sharing a vertex (Ni1) of symmetry related two defective cubanes, the two defective cubes on the other hand in **70** are connected to each other by Ni1 and its symmetry equivalent Ni1' through doubly $\mu_{1,3}\text{-N}_3^-$ bridges with Ni1...Ni1' distance of 5.174 Å. In addition to bridging donor atoms constituting the core structure, Ni1 center is bonded with a terminal azido ligand, while Ni2 and Ni3 are bonded with two nitrogen donor atoms from either arm of the Schiff base ligands and a terminal azido ligand to Ni2 and an aqua ligand to Ni3 atom. Overall, the coordination environments around the metal centers are N_5O , N_4O_2 and N_3O_3 for Ni1, Ni2 and Ni3 atoms, respectively. Thus, all of the Ni(II) atoms are six-coordinated with slightly distorted octahedral geometry in which the Ni–O and Ni–N

bond distances are comparable to that found in **68** and **69** and to the reported compounds having closely related structures [32-34].

Table 6.2 Selected bond Distances (Å) and Angles (deg) for complex **69**.

Distances			
Ni1–O1	2.0141(16)	Ni1–N10	2.149(2)
Ni1–N7	2.173(2)	Ni2–N1	2.027(2)
Ni2–O2	2.0557(17)	Ni25–O1	2.0480(17)
Ni2–N2	2.112(2)	Ni2–N7	2.155(2)
Ni3–N4	2.023(2)	Ni3–O2	2.0478(17)
Ni3–O1	2.0399(17)	Ni2–O3	2.0935(17)
Ni3–N5	2.0791(17)	Ni3–N5	2.099(2)
Ni3–O10	2.183(2)		
Angles			
Ni1–O1–Ni2	104.35(8)	Ni1–N7–Ni2	95.71(8)
Ni1–O1–Ni3	102.45(7)	Ni1–N10–Ni3	93.70(8)
Ni3–O1–Ni2	93.37(7)	Ni3–O2–Ni2	92.92(7)

Table 6.3 Selected bond Distances (Å) and Angles (deg) for complex **70**.

Distances			
Ni2–N1	2.009(3)	Ni2–O1	2.061(3)
Ni2–O2	2.074(3)	Ni2–N13	2.108(4)
Ni2–N2	2.150(4)	Ni2–N7	2.219(3)
Ni3–N4	2.036(4)	Ni3–O2	2.057(3)
Ni3–O1	2.092(3)	Ni3–O3	2.113(3)
Ni3–N10	2.117(3)	Ni3–N5	2.127(3)
Ni1–N16	2.066(4)	Ni1–O1	2.068(3)
Ni1–N10	2.068(3)	Ni1–N19	2.096(4)
Ni1–N21	2.097(3)	Ni1–N7	2.145(3)
Angles			
Ni2–O1–Ni3	100.37(11)	Ni2–O1–Ni1	102.20(12)
Ni3–O2–Ni2	101.13(11)	Ni1–O1–Ni3	98.64(12)
Ni1–N10–Ni3	97.81(13)	Ni1–N7–Ni2	94.81(12)

A large number of pentanuclear Ni(II) coordination clusters with different topological structures, such as linear, cross-like, trigonal bipyramidal-like, ring-like, bowtie-like and pentagonal-like motifs, are reported in the literature [31]. Among them bowtie/twisted bowtie is the most popular motif in Ni₅ coordination chemistry. Notably, only seven azido-bridged Ni₅ clusters have been structurally characterized with bowtie/twisted bowtie topology [32]. Interestingly, the present core structure is unique in that, although several azido-bound Ni-clusters have been reported in the literature, the core found in **68** has not been observed either in discrete Ni₅-clusters or as a recognizable sub-fragment of high-nuclearity Ni(II)-clusters [27,34]. Therefore, complexes **68** and **69** are important addition to the growing family of Ni₅-cluster with bowtie-like topology. The hexanuclear azido-based Ni(II) clusters reported in the literature mostly belong to a motif featuring four fused defective cubanes [28,35]. Some cyclic or hexagonal topological displacements were also observed in Ni₆ clusters [36]. However, the topology found in **70** is closely related to a Ni₆-cluster reported recently where two Ni₃ triangles are connected by a singly μ -1,5-bridged dicyanamide ion [37]. The solid-state structure of **70** is stabilized by means of strong hydrogen bonding interactions. As the tertiary amine-N atoms of the Schiff base ligand are protonated to balance the charge of the system, they participate in strong hydrogen bonding interactions as hydrogen bond acceptors. Interestingly, one tertiary amine-N atom forms the intramolecular hydrogen bond with a coordinated azido ligand with N...N distance of 2.951 Å, while other tertiary amine-N atom from other arm of the Schiff base constitutes the intermolecular hydrogen bond with a lattice water molecule (N...O, 2.740 Å), which simultaneously participates in the hydrogen bonding interactions with a perchlorate counter ion (O...O, 2.904 Å) and an coordinated azido ligand (O...N, 2.666 Å) from the neighboring complex cation. Several other hydrogen bonding interactions as shown in Figure 6.7 are responsible for overall stability of **70** in the solid-state.

Table 6.4 Crystallographic data and structural refinement parameters of **68–70**

	68	69	70
Empirical formula	C ₅₀ H ₁₁₂ N ₃₄ Ni ₅ O ₂₄	C ₅₅ H ₁₂₄ N ₂₄ Ni ₅ O ₂₂	C ₅₀ H ₁₀₄ Cl ₂ N ₄₂ Ni ₆ O ₁₈
Formula weight (g mol ⁻¹)	1867.28	1767.32	2004.91
Crystal system	Monoclinic	Triclinic	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i> (Å)	12.6955(7)	11.9859(9)	14.0521(2)
<i>b</i> (Å)	22.6202(14)	12.9619(9)	15.2166(3)
<i>c</i> (Å)	14.2401(9)	15.3454(12)	20.1598(4)
α (deg)	90.00	93.929(3)	90.00
β (deg)	97.044(2)	97.194(3)	106.750(1)
γ (deg)	90.00	116.601(3)	90.00
volume (Å ³)	4058.5(4)	2094.0(3)	4127.78(13)
<i>Z</i>	2	1	2
<i>D</i> _{calc} (g cm ⁻³)	1.528	1.402	1.613
μ (mm ⁻¹)	1.229	1.182	1.493
<i>F</i> (000)	1964	938	2088
θ Range (deg)	2.220–29.203	2.074–27.171	1.576–26.442
Reflections collected	94041	35912	25465
Independent reflections (<i>R</i> _{int})	10969 (0.0723)	9252 (0.0286)	8432 (0.0343)
Observed reflections [<i>I</i> > 2 σ (<i>I</i>)]	7414	7815	6155
Restraints/parameters	7/612	44/542	3/599
Goodness-of-fit on <i>F</i> ²	1.069	1.051	1.034
Final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0524, w <i>R</i> ₂ = 0.1474	<i>R</i> ₁ = 0.0390, w <i>R</i> ₂ = 0.1116	<i>R</i> ₁ = 0.0478, w <i>R</i> ₂ = 0.1237
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0975, w <i>R</i> ₂ = 0.1808	<i>R</i> ₁ = 0.0488, w <i>R</i> ₂ = 0.1181	<i>R</i> ₁ = 0.0722, w <i>R</i> ₂ = 0.1397
Largest diff. peak/hole (e Å ⁻³)	0.884/–1.060	1.524/–0.950	1.119/–0.691

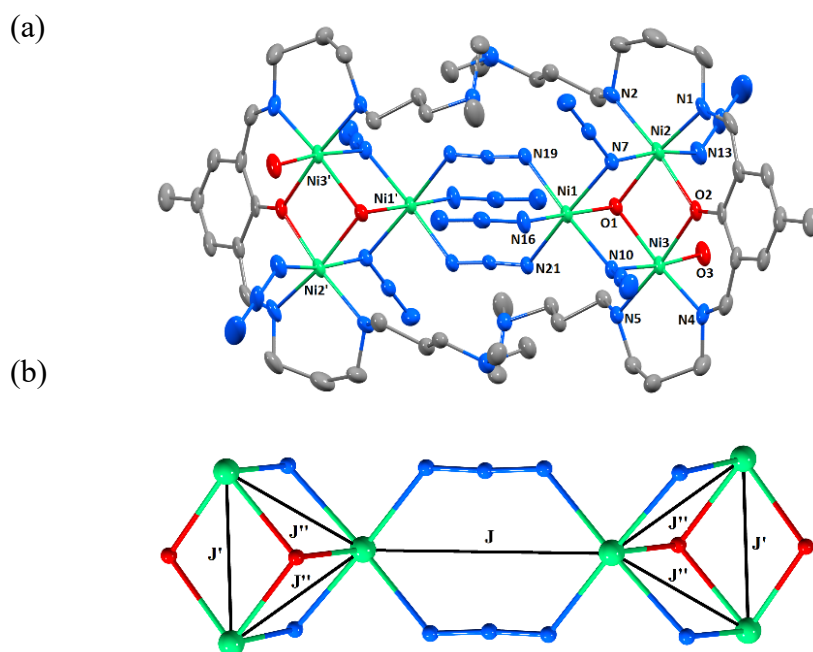


Figure 6.4 (a) Crystal structure of **70** with partial atom numbering scheme. Primed and unprimed atoms are related to the crystallographic inversion center. Ellipsoids are drawn at the 30% probability level. H atoms, ClO_4^- ions and solvent molecules are omitted for clarity. (b) Skeletal representation of core structure displaying magnetic coupling scheme.

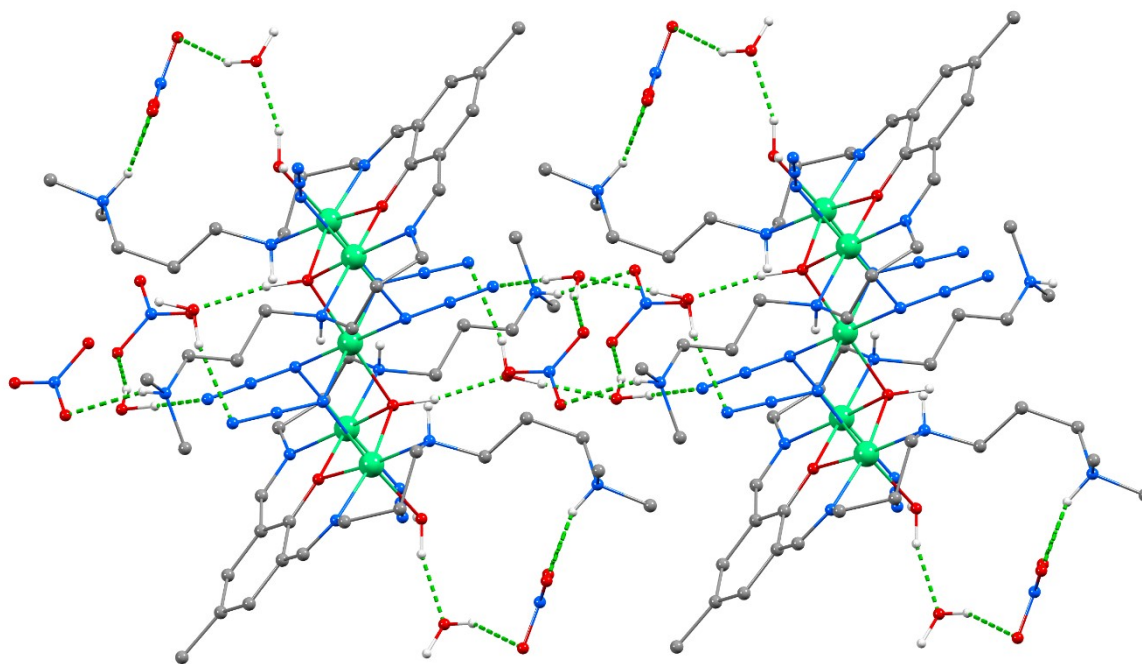


Figure 6.5 A part of the solid-state packing of **68** showing hydrogen bonding interactions.

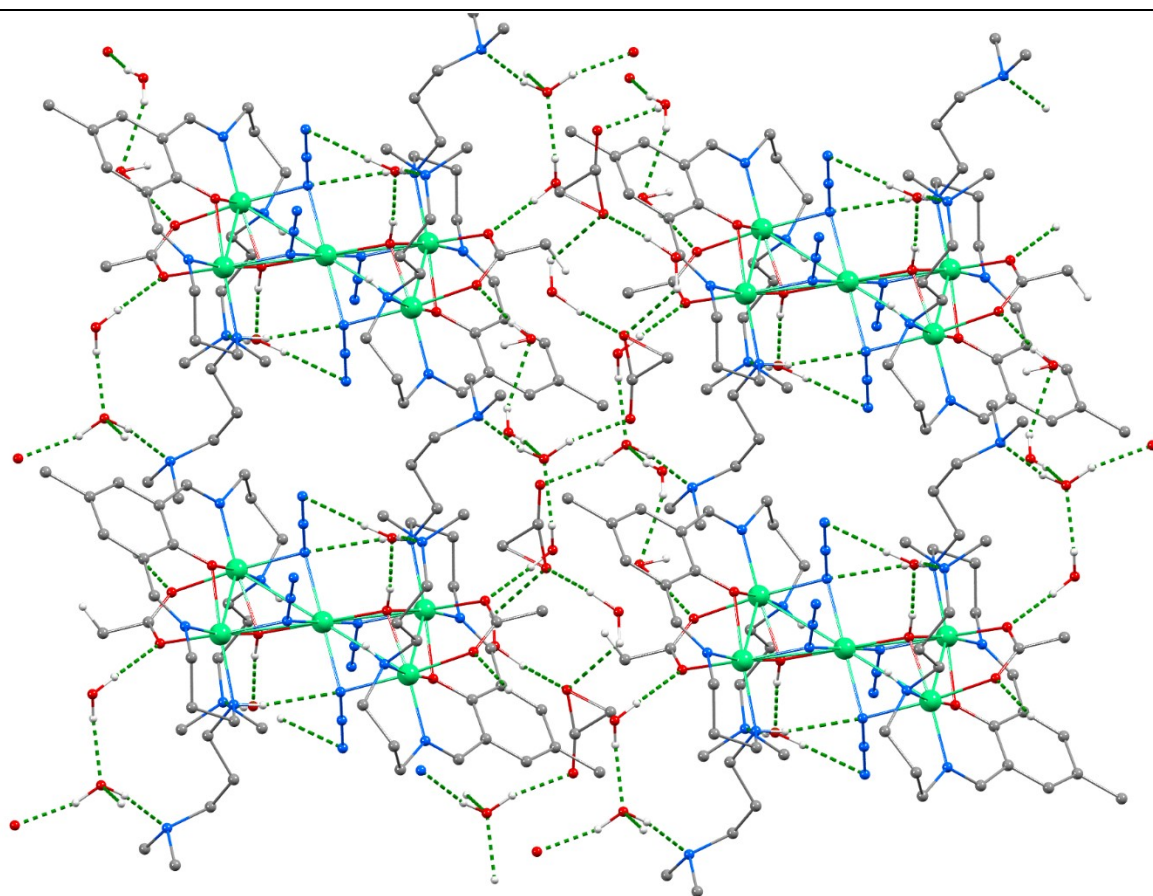


Figure 6.6: A part of the solid-state structure of **69** displaying hydrogen bonding interactions.

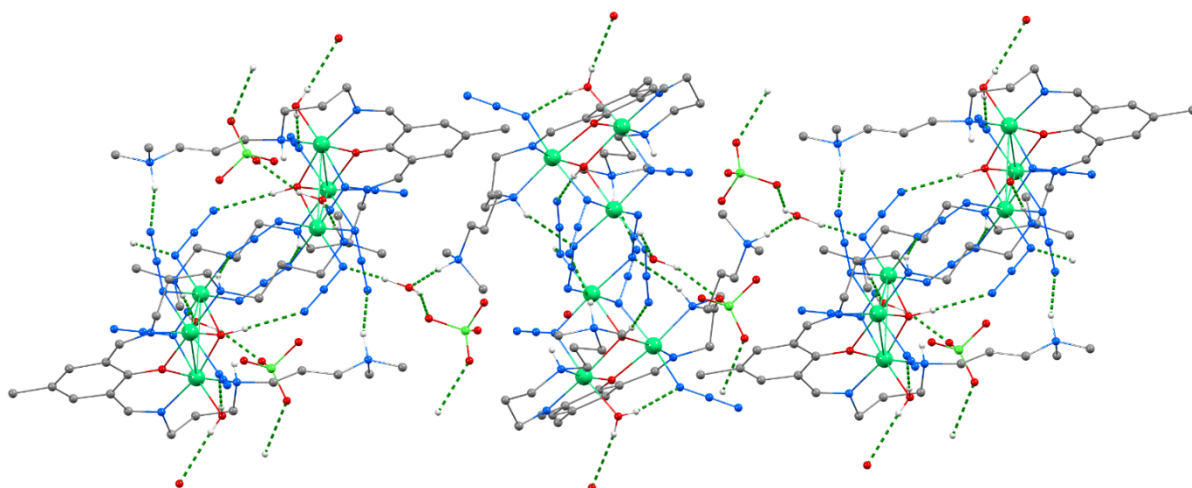


Figure 6.7: A part of the crystal packing of **70** displaying hydrogen bonding interactions.

6.3.4. Magnetic Studies

The effective magnetic moment for **68** at $T = 300$ K adopts a value of $\mu_{\text{eff}} = 7.25 \mu_{\text{B}}$ (Figure 6.8). This matches five $s = 1$ uncoupled spins for which the theoretical value is $\mu_{\text{eff}}/\mu_{\text{B}} = g[5s(s + 1)]^{1/2} = 7.27$ (typical $g = 2.3$). There is a slight increase of the effective magnetic moment on cooling that can be caused either by some uncompensated temperature-independent magnetism χ_{TIM} or an exchange coupling of the ferromagnetic nature ($J_{\text{f}} > 0$). Below 40 K a marked drop of the μ_{eff} value is registered due to either the exchange interaction of an antiferromagnetic nature ($J_{\text{a}} < 0$) prevailing in this temperature range, or the zero-field splitting (D) typical for the Ni(II) centers.

The magnetization per formula unit is temperature little dependent and it does not show features of the saturation: it adopts a value of $M_1 = 4.9$ at $B = 7.0$ T and $T_0 = 2.0$ K. Theoretical saturation limit for five uncoupled $S = 1$ spins is $M_1 = 5g = 11.5$. A considerable reduction is probably due to the intra-complex exchange coupling of an antiferromagnetic nature. Moreover, the first derivative of the magnetization is not a smooth curve (Figure 6.8 – inset) pointing to the interplay of the antiferromagnetic and ferromagnetic portions of the exchange interactions.

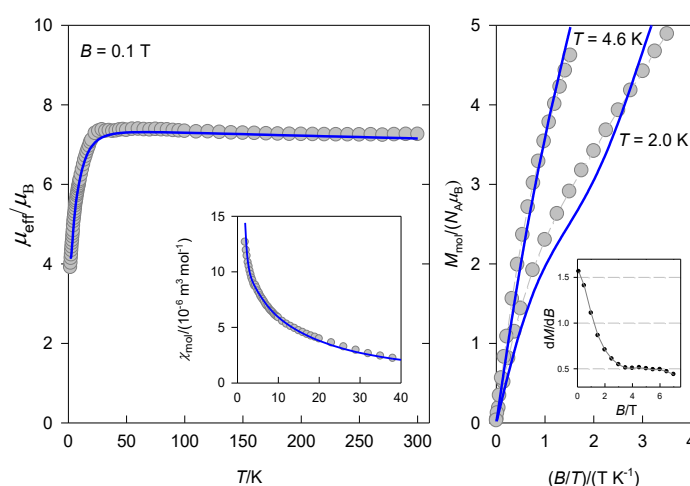


Figure 6.8: Magnetic functions for **68**. Left – temperature evolution of the effective magnetic moment (inset: temperature dependence of the molar magnetic susceptibility); right – reduced magnetization (inset: the first derivative at $T = 2.0$ K). Solid lines – fitted.

The magnetic data was analyzed by assuming the following form of the isotropic spin Hamiltonian

$$\hat{H}^{\text{iso}} = -J'[(\vec{S}_2 \cdot \vec{S}_3) + (\vec{S}_4 \cdot \vec{S}_5)]\hbar - J'' \sum_{A=2}^5 (\vec{S}_1 \cdot \vec{S}_A)\hbar - \frac{5}{\hbar} \hat{S}_1^2 \hbar \quad (\text{Eq. 6.1})$$

that involves the ferromagnetic interaction of the central Ni(II) atom (1) with its neighbors J' , the antiferromagnetic interaction between two distant pairs (2-3 and 4-5) J'' , along with the isotropic Zeeman term. The corresponding interaction matrix of the $N = 3^5 = 243$ size has been diagonalized and the field-dependent energy levels inserted into the formulae of the statistical thermodynamics in order to get the magnetic susceptibility and magnetization, respectively [38,39]. Both experimental datasets have been processed simultaneously by minimizing the common functional

$$F = w \frac{\sum_i^n |\chi_i^o - \chi_i^c|}{(1/n) \sum_i^n \chi_i^o} + (1-w)(1/m) \sum_j^m (M_j^o - M_j^c)^2 \rightarrow \min \quad (\text{Eq. 6.2})$$

with equal weights for the mean magnetic susceptibility and squared Euclidean norm of the magnetization ($w = 0.5$); n and m are the number of experimental points for the susceptibility and magnetization, respectively. The optimization routine converged to the following set of magnetic parameters: $J''/\hbar c = +4.4(8) \text{ cm}^{-1}$, $J'/\hbar c = -10.8(9) \text{ cm}^{-1}$, and $g = 2.31(9)$ with displayed standard deviations. Two additional corrections applied to the magnetic susceptibility read: temperature-independent magnetism $\chi_{\text{TIM}} = -15 \times 10^{-9} \text{ m}^3 \text{ mol}^{-1}$ (SI units) and molecular-field correction $(zj)/\hbar c = 0.12 \text{ cm}^{-1}$. The discrepancy factors of the fit are $R(\chi) = 0.04$ and $R(M) = 0.09$. Negative value of χ_{TIM} refers to the underlying diamagnetism.

The fit can eventually be improved by adding the anisotropic zero-field splitting term

$$\hat{H}^{\text{zfs}} = \hat{H}^{\text{iso}} + D \sum_{A=1}^5 (\hat{S}_{Az}^2 - \vec{S}_A \cdot \vec{S}_A / 3) \hbar \quad (\text{Eq. 6.3})$$

However, in the present case the fitting procedure converged to a negligible D -value, probably owing to a strong correlation with the antiferromagnetic exchange coupling constant. Notice, the applied model assumes uniform g -factors for peripheral and central Ni(II) centers which, probably, causes that the fitted magnetization data are not perfect. In the other words, the capabilities of the selected model are exhausted. A more serious problem arises from the fact that the model employed considers a single exchange coupling constant between magnetic centers despite the double (oxido-azido, and oxido-phenoxido) superexchange paths.

The ferromagnetic exchange coupling between centers 1-A ($A = 2, 3, 4, 5$) matches the end-on coordination mode of the azido ligand. On the contrary, the antiferromagnetic coupling of the peripheral pairs 2-3 and 4-5 is consistent with the μ -O bridge and obtuse angle Ni-O-Ni (99 and 100 deg).

Magnetic data for **69** reveal a considerable exchange interaction of the ferromagnetic nature. The effective magnetic moment increases from its room-temperature value of $\mu_{\text{eff}} = 9.61 \mu_{\text{B}}$ to $\mu_{\text{eff}} = 11.7 \mu_{\text{B}}$ at $T = 8.5 \text{ K}$ and then it drops down (Figure 6.9). The magnetic susceptibility on cooling is only increasing and an eventual maximum is not registered. The magnetization per formula unit saturates to $M_1 = 11.5$ at $T = 2.0 \text{ K}$ and $B = 7.0 \text{ T}$.

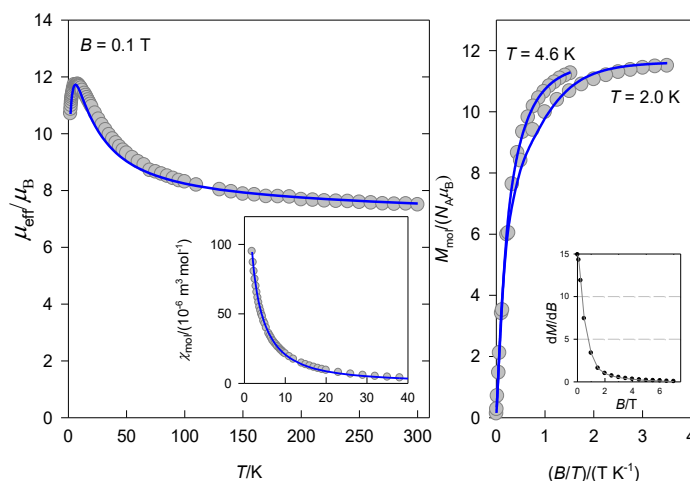


Figure 6.9: Magnetic functions for **69**. Left – temperature evolution of the effective magnetic moment (inset: temperature dependence of the molar magnetic susceptibility); right – reduced magnetization (inset: the first derivative at $T = 2.0$ K). Solid lines – fitted.

The data fitting with the help of the Hamiltonian (1) enlarged to (3) gave $J''/hc = +14.7 \text{ cm}^{-1}$, $J'/hc \sim -1.6$, $g = 2.33(9)$, $D/hc = 3.0(8) \text{ cm}^{-1}$, and $\chi_{\text{TIM}} = -17 \times 10^{-9} \text{ m}^3 \text{ mol}^{-1}$, $(zj)/hc = -0.007 \text{ cm}^{-1}$; $R(\chi) = 0.012$ and $R(M) = 0.016$. There is a substantial difference in the bond angles Ni-N₃-Ni between **68** and **69**; in **69** one of them is 93 deg that is very low and responsible for the dominating ferromagnetic exchange. Negative value of χ_{TIM} recovers the underlying diamagnetism.

The magnetic data for the hexanuclear complex **70** is displayed in Figure 6.10. The magnetic susceptibility on cooling is only increasing and no maximum is registered. The effective magnetic moment gradually decreases from its room-temperature value of $\mu_{\text{eff}} = 7.20 \mu_{\text{B}}$ to $\mu_{\text{eff}} = 2.74 \mu_{\text{B}}$ at $T = 1.9$ K. This indicates a more effective exchange coupling of the antiferromagnetic nature when compared to **68**. Also the magnetization saturates to a lower value of $M_1 = 1.20$ at $T = 2.0$ K and $B = 7.0$ T. There are neither features of the remnant magnetization nor of the slow magnetic relaxation. The fitting procedure is based upon the isotropic spin Hamiltonian

$$\begin{aligned} \hat{H} = & -J(\vec{S}_{\text{Ni}1} \cdot \vec{S}_{\text{Ni}1'})\hbar - J(\vec{S}_{\text{Ni}2} \cdot \vec{S}_{\text{Ni}2'})\hbar - J(\vec{S}_{\text{Ni}3} \cdot \vec{S}_{\text{Ni}3'})\hbar \\ & -J''[(\vec{S}_{\text{Ni}1} \cdot \vec{S}_{\text{Ni}2}) + (\vec{S}_{\text{Ni}1} \cdot \vec{S}_{\text{Ni}3}) + (\vec{S}_{\text{Ni}1'} \cdot \vec{S}_{\text{Ni}2'}) + (\vec{S}_{\text{Ni}1'} \cdot \vec{S}_{\text{Ni}3'})]\hbar \\ & + B_z \mu_B g \sum_{A=1}^6 (\hat{S}_{Az})\hbar \end{aligned} \quad (\text{Eq. 6.4})$$

where J' and J'' denote interactions within individual triangles and J between edges of two triangles mediated by two μ -1,3- N_3^- bridges. In such a case the interaction matrix of the total size $N = 3^6 = 729$ is factored according to the total spin ($S = 0$ through 6) to the blocks of the lower size: 15, 36, 40, 29, 15, 5, and 1. This is a tremendous simplification that allows a fast data-fitting when assuming uniform g-factors [40]. A continuous decrease of the effective magnetic moment indicates the overall antiferromagnetic coupling. In such a case, however, the magnetic susceptibility on cooling should pass through a maximum and then it turns to the zero. This effect is masked by a minor fraction of the paramagnetic impurity x_{PI} that often exists in even-center complexes.

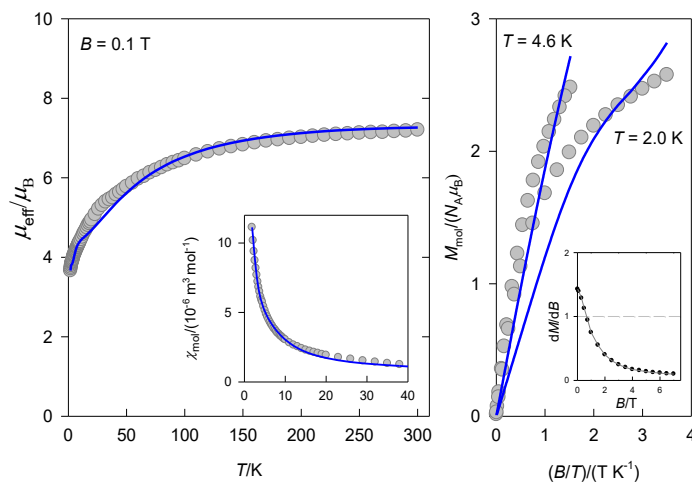


Figure 6.10: Magnetic functions for **70**. Left – temperature evolution of the effective magnetic moment (inset: temperature dependence of the molar magnetic susceptibility); right – reduced magnetization (inset: the first derivative at $T = 2.0$ K). Solid lines – fitted.

The fitting procedure yields the inter-triangle coupling constant $J/hc = -32 \text{ cm}^{-1}$, two times $J'/hc = -17 \text{ cm}^{-1}$, four times $J''/hc = -26 \text{ cm}^{-1}$, $g = 2.38$, $\chi_{\text{TIM}} \sim -30 \times 10^{-9} \text{ m}^3 \text{ mol}^{-1}$, $zj/hc = 0.53 \text{ cm}^{-1}$, and $x_{\text{PI}} = 0.03$; $R(\chi) = 0.026$ and $R(M) = 0.15$. It can be seen that the magnetic susceptibility is well recovered by the present model which is not the case of the low-temperature magnetization. Large negative value of χ_{TIM} refers to the underlying diamagnetism.

Among the several structural parameters that can influence the strength and sign of the magnetic exchange coupling constant between the paramagnetic centers, the bridging angle is largely considered the most crucial factor in determining the net magnetic interaction. Two different types of exchange pathways between the Ni(II) ions are operative through double μ -phenoxido/ μ_3 -hydroxido and double μ_3 -hydroxido/ $\mu_{1,1}$ -azido bridges in complex **68**. Experimental and theoretical magneto-structural correlations carried out by different groups have clearly shown that the magnetic coupling in hydroxido-, alkoxido- and phenoxido-bridged $\text{Ni}(\mu\text{-O})_2\text{Ni}$ complexes is expected to be ferromagnetic when the Ni–O–Ni angles are close to 90° , and a crossover from ferromagnetic to antiferromagnetic exchange coupling corresponds to a Ni–O–Ni angle of about $96\text{--}98^\circ$ [41]. The bridging angles of $98.90(11)$ and $100.31(11)$ are nicely agree with the antiferromagnetic interaction between the peripheral Ni(II) centers in complex **68**. As found in the most of mixed μ -phenoxido/ $\mu_{1,1}$ -azido bridges Ni(II) complexes, the magnetic interaction in **68** through this mixed bridges is observed to be ferromagnetic in nature [42].

Again two different types of exchange pathways between the Ni(II) ions are present in complex **69**: (i) triple μ -phenoxido/ μ_3 -hydroxido/*syn-syn* acetato bridges (described by J'), (ii) double μ_3 -hydroxido/ $\mu_{1,1}$ -azido bridges (described by J''). The ferromagnetic coupling through the mixed μ_3 -hydroxido/ $\mu_{1,1}$ -azido bridges is found again usual. The Ni–O–Ni

bridging angles of μ -phenoxido and μ_3 -hydroxido bridges are significantly shorter than that found in complex **68** and these angles are found to be $93.37(7)$ and $92.92(7)^\circ$, respectively, which is because of the presence of additional *syn-syn* $\mu_{1,3}$ -acetato bridge. It is well known that the *syn-syn* carboxylate bridge mediates the antiferromagnetic coupling between the paramagnetic metal centers [43]. Therefore, whether the overall magnetic coupling would be either ferromagnetic or antiferromagnetic that depends on the Ni–O–Ni bridging angles. The Ni–O–Ni bridging angles of $93.37(7)$ and $92.92(7)^\circ$ in **69** are more likely to transmit ferromagnetic interaction between the Ni(II) centers as they fall well below the crossover angles [41]. The observed almost zero coupling constant value propagated through the triple μ -phenoxido/ μ_3 -hydroxido/*syn-syn* acetato bridged Ni(II) centers is most likely due to orbital counter-complementary effects where the antiferromagnetic coupling interaction between the Ni(II) centers mediated by the *syn-syn* $\mu_{1,3}$ -acetato bridge is counterbalanced by the ferromagnetic interaction operating through μ -phenoxido and μ_3 -hydroxido bridges [44].

In complex **70**, the magnetic coupling proceeds through three different bridges, namely (i) double μ -phenoxido/ μ_3 -hydroxido bridges (described by J'), (ii) double μ_3 -hydroxido/ $\mu_{1,1}$ -azido bridges (described by J'') and (iii) double $\mu_{1,3}$ -azido bridges (described by J). It is well studied that the $\mu_{1,3}$ -azido bridge propagates antiferromagnetic interaction between the paramagnetic metal centers [19,40]. Therefore, the negative value of the exchange coupling constant value through this bridge is not unusual. Again, the magnetic coupling between the Ni(II) centers through μ -phenoxido/ μ_3 -hydroxido bridges with bridging angles $100.37(11)$ and $101.13(11)^\circ$ is nicely agree with the antiferromagnetic in nature, and somewhat larger Ni–O–Ni bridging angles in **70** compared to **68** is responsible for higher magnitude of the coupling constant value in **70**. Although the sign of the coupling constant through μ_3 -hydroxido/ $\mu_{1,1}$ -azido bridged Ni(II) centers is found unusual in the present case, but the dominating antiferromagnetic magnetic

exchange interaction through μ -phenoxido/ μ_3 -hydroxido bridges and double $\mu_{1,3}$ -azido bridges is consistent with the overall antiferromagnetic nature in **70**.

6.4. Conclusions

The present work extends the high nuclearity Ni(II)-clusters chemistry and emphasizes the ability of the Schiff base ligand (HL), derived from 2,6-diformyl-4-methylphenol and *N,N*-dimethyldipropylenetriamine, to form interesting structural types. The use of the Schiff base HL in Ni(II) chemistry has provided access to two pentanuclear complexes (**68** and **69**) and a hexanuclear cluster (**70**) under mild reaction conditions. It is also found that the counter anions and the stoichiometric ratio of the reactants played crucial role in the self-assembly processes, leading to the diverse nuclearity in these systems. The X-ray structural analyses reveal that the Ni_5 or Ni_6 clusters can be considered to be built from the assembly of two triangular $[\text{Ni}_3(\mu\text{-phenoxido})(\mu_3\text{-OH})(\mu\text{-N}_3)_4]$ subunits in different manners. Whereas, two bowtie-shaped Ni_5 clusters (in **68** and **69**) are formed by sharing a common vertex (Ni1) of the triangular subunits, the Ni_6 cluster on the other hand can be considered to be built from two triangular subunits by bis($\mu_{1,3}\text{-N}_3$) connectors. X-ray crystallography further shows that the tertiary amine nitrogen atoms remain either protonated or non-protonated to balance the charge of the system, which not only influence the self-assembly processes but participate in diverse hydrogen bonding pattern to stabilize the solid-state structures of the resulting complexes. Variable temperature magnetic properties of a penta- and the hexa-nuclear Ni(II) spin coupled clusters have been investigated and the magnetic studies reveal overall dominating antiferromagnetic interactions in **68** and **70** as opposed to **69** where the ferromagnetic coupling prevails. The dominating antiferromagnetic interaction between μ -hydroxido- and μ -phenoxido-bridged Ni_2 and Ni_3 centers over the ferromagnetic interaction between hetero μ -hydroxido- and $\mu_{1,1}\text{-N}_3^-$ -bridged Ni1 either with Ni_2 or Ni_3 is the

governing factor in **68**, while the additional antiferromagnetic coupling between Ni1 and Ni1' supported by bis($\mu_{1,3}$ -N₃⁻) bridges completely overshadowed the ferromagnetic coupling if any operating through the hetero-bridges.

References

- [1] E. K. Brechin, C. Boskovic, W. Wernsdorfer, J. Yoo, A. Yamaguchi, E. C. Sanudo, T. R. Concolino, A. L. Rheingold, H. Ishimoto, D. N. Hendrickson, G. Christou, *J. Am. Chem. Soc.* 2002, **124**, 9710.
- [2] D. Gatteschi, R. J. Sessoli, *Angew. Chem., Int. Ed.* 2003, **42**, 268.
- [3] R. Sessoli, D. Gatteschi, A. Caneschi, M. A. Novak, *Nature* 1993, **365**, 141.
- [4] R. Sessoli, H. L. Tsai, A. R. Schake, S. Y. Wang, J. B. Vincent, K. Folting, D. Gatteschi, G. Christou, D. N. Hendrickson, *J. Am. Chem. Soc.* 1993, **115**, 1804.
- [5] R. Bagai, W. Wernsdorfer, K. A. Abboud, G. Christou, *J. Am. Chem. Soc.* 2007, **129**, 12918.
- [6] D. Gatteschi, R. J. Sessoli, *J. Magn. Magn. Mater.* 2004, **272–276**, 1030.
- [7] C. J. Milios, A. Vinslava, W. Wernsdorfer, S. Moggach, S. Parsons, S. P. Perlepes, G. Christou, E. K. Brechin, *J. Am. Chem. Soc.* 2007, **129**, 2754.
- [8] M. Murugesu, M. Habrych, W. Wernsdorfer, K. A. Abboud, G. Christou, *J. Am. Chem. Soc.* 2004, **126**, 4766.
- [9] T. C. Stamatatos, K. A. Abboud, W. Wernsdorfer, G. Christou, *Angew. Chem., Int. Ed.* 2007, **46**, 884.
- [10] N. Aliaga-Alcalde, R. S. Edwards, S. O. Hill, W. Wernsdorfer, K. Folting, G. Christou, *J. Am. Chem. Soc.* 2004, **126**, 12503.

-
- [11] A. Caneschi, D. Gatteschi, N. Lalioti, C. Sangregorio, R. Sessoli, G. Ventiru, A. Vendigni, A. Retoori, M. G. Pini, M. A. Novak, *Angew. Chem., Int. Ed.* 2001, **40**, 1760.
- [12] R. Clérac, H. Miyasaka, M. Yamashita, C. Coulon, *J. Am. Chem. Soc.* 2002, **124**, 12837.
- [13] C. Coulon, H. Miyasaka, R. Clérac, *Struct. Bonding* (Berlin) 2006, **122**, 163.
- [14] C. J. Milios, R. Inglis, A. Vinslava, R. Bagai, W. Wernsdorfer, S. Parsons, S. P. Perlepes, G. Christou, E. K. Brechin, *J. Am. Chem. Soc.* 2007, **129**, 12505.
- [15] J. S. Miller, M. Drillon, *Magnetism: Molecules to Materials*; Wiley: Weinheim, 2001.
- [16] W. Wernsdorfer, R. Sessoli, *Science* 1999, **284**, 133.
- [17] a) A. Escuer, G. Aromi, *Eur. J. Inorg. Chem.* 2006, 4721-4736. b) M. Ferbinteanu, H. Miyasaka, W. Wernsdorfer, K. Nakata, K. Sugiura, M. Yamashita, C. Coulon, R. Clérac, *J. Am. Chem. Soc.* 2005, **127**, 3090. c) S. S. Massoud, F. A. Mautner, R. Vicente, A. A. Gallo, E. Ducasse, *Eur. J. Inorg. Chem.* 2007, 1091. d) A. J. Tasiopoulos, A. Vinslava, W. Wernsdorfer, K. A. Abboudand, G. Christou, *Angew. Chem., Int. Ed.* 2004, **43**, 2117. e) A. Panja, P. Guionneau, I. -R. Jeon, S. M. Holmes, R. Clérac, C. Mathonière, *Inorg. Chem.* 2012, **51**, 12350.
- [18] T. C. Stamatatos, D. Foguet-Albiol, S. C. Lee, C. C. Stoumpos, C. P. Raptopoulou, A. Terzis, W. Wernsdorfer, S. O. Hill, S. P. Perlepes and G. Christou, *J. Am. Chem. Soc.* 2007, **129**, 9484.
- [19] J. Ribas, A. Escuer, M. Monfort, R. Vicente, R. Cortes, L. Lezama and T. Rojo, *Coord. Chem. Rev.* 1999, **195**, 1027.
- [20] a) T. Liu, Y. -J. Zhang, Z. -M. Wang, S. Gao, *J. Am. Chem. Soc.* 2008, **130**, 130. b) C. -F. Lee, D. A. Leigh, R. G. Pritchard, D. Schultz, S. J. Teat, G. A. Timco, R. E. P. Winpenney, *Nature* 2009, **458**, 314. c) S. Schmitz, J. van Leusen, A. Ellern, P. Kögerler, K. Y. Monakhov, *Inorg. Chem. Front.* 2016, **3**, 523.
-

- [21] a) N. A. Rey, A. Neves, A. J. Bortoluzzi, C. T. Pich, H. Terenzi, *Inorg. Chem.* 2007, **46**, 348. b) S. Mandal, S. Mondal, C. Rajnák, J. Titiš, R. Boča, S. Mohanta, *Dalton Trans.* 2017, **46**, 13135.
- [22] a) K. Dhara, U. C. Saha, A. Dan, S. Sarkar, M. Manassero, P. Chattopadhyay, *Chem. Commun.* 2010, **46**, 1754. b) M. Sarkar, R. Clérac, C. Mathonière, N. G. R. Hearn, V. Bertolasi, D. Ray, *Inorg. Chem.* 2011, **50**, 3922.
- [23] M. Sarkar, R. Clérac, C. Mathonière, N. G. R. Hearn, V. Bertolasi, D. Ray, *Inorg. Chem.* 2010, **49**, 6575.
- [24] a) A. Das, F. J. Klinke, S. Demeshko, S. Meyer, S. Dechert, F. Meyer, *Inorg. Chem.* 2012, **51**, 8141. b) D. Mandal, C. S. Hong, H. C. Kim, H. -K. Fun, D. Ray, *Polyhedron* 2008, **27**, 2372. c) B. Bechlars, I. Issac, R. Feuerhake, R. Clérac, O. Fuhr, D. Fenske, *Eur. J. Inorg. Chem.* 2008, 1632.
- [25] S. Liu, S. Wang, F. Cao, H. Fu, D. Li, J. Dou, *RSC Adv.* 2012, **2**, 1310.
- [26] a) P. King, R. Clérac, W. Wernsdorfer, C. E. Anson, A. K. Powell, *Dalton Trans.* 2004, 2670. b) K. C. Mondal, O. Sengupta, P. S. Mukherjee, *Inorg. Chem. Commun.* 2009, **12**, 682.
- [27] a) F. -H. Zhao, Y. -X. Che, J. -M. Zheng, *Cryst. Growth Des.* 2012, **12**, 4712. b) A. Escuer, J. Esteban, S. P. Perlepes, T. C. Stamatatos, *Coord. Chem. Rev.* 2014, **275**, 87.
- [28] S. S. Tandon, S. D. Bunge, R. Rakosi, Z. Xu, L. K. Thompson, *Dalton Trans.* 2009, 6536.
- [29] a) A. Panja, N. Ch. Jana, P. Brandão, *Molecular Catalysis* 2018, **449**, 49. b) A. Panja, N. C. Jana, S. Adak, P. Brandão, L. Dlhán, J. Titiš, R. Boča, *New J. Chem.* 2017, **41**, 3143.
- [30] C. N. Verani, E. Rentschler, T. Weyhermüller, E. Bill, P. Chaudhuri, *J. Chem. Soc., Dalton Trans.* 2000, 251.

- [31] K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, (4th ed). Wiley: New York, 1986.
- [32] a) A. K. Ghosh, M. Shatruk, V. Bertolasi, K. Pramanik, D. Ray, *Inorg. Chem.* 2013, **52**, 13894. b) N. Dutta, G. C. Giri, S. Haldar, G. Vijaykumar, C. D. Stewart, L. Carrella, G. T. Musie, M. Bera, *ChemistrySelect*. 2019, **4**, 10260.
- [33] a) S. I. Sampani, E. Loukopoulos, M. Azam, K. Griffiths, A. Abdul-Sada, G. Tizzard, S. Coles, A. Escuer, A. Tsipis, G. E. Kostakis, *CrystEngComm*. 2018, **20**, 1411. b) P. S. Perlepe, L. Cunha-Silva, V. Bekiari, K. J. Gagnon, S. J. Teat, A. Escuere, T. C. Stamatatos, *Dalton Trans.* 2016, 45, 10256. c) J. Esteban, M. Font-Bardia, J. S. Costa, S. J. Teat, A. Escuer, *Inorg. Chem.* 2014, **53**, 3194.
- [34] a) A. Escuer, J. Esteban, J. Mayans, M. Font-Bardia, *Eur. J. Inorg. Chem.* 2014, 5443. b) J. Esteban, M. Font-Bardia, A. Escuer, *Inorg. Chem.* 2014, **53**, 1113. c) A. K. Boudalis, M. Pissas, C. P. Raptopoulou, V. Psycharis, B. Abarca, R. Ballesteros, *Inorg. Chem.* 2008, **47**, 10674. d) C. Papatriantafyllopoulou, T. C. Stamatatos, W. Wernsdorfer, S. J. Teat, A. J. Tasiopoulos, A. Escuer, S. P. Perlepes, *Inorg. Chem.* 2010, **49**, 10486. e) J. Esteban, E. Ruiz, M. Font-Bardia, T. Calvet, A. Escuer, *Chem. Eur. J.* 2012, **18**, 3637.
- [35] a) S. S. Tandon, S. D. Bunge, J. Sachiz, L. K. Thompson, *Inorg. Chem.* 2012, **51**, 3270. b) D. Mandal, V. Bertolasi, J. Ribas-Ariño, G. Aromi, D. Ray, *Inorg. Chem.* 2008, **47**, 3465. c) X. -T. Wang, B. -W. Wang, Z. -M. Wang, W. Zhang, S. Gao, *Inorg. Chim. Acta.* 2008, **361**, 3895. d) Y. -J. Liu, X. -J. Fu, X. -F. Li, T. -B. Qiu, H. -X. Yang, *Acta Crystallogr. E* 2011, **67**, m307.
- [36] a) A. N. Georgopoulou, C. P. Raptopoulou, V. Psycharis, R. Ballesteros, B. Abarca, A. K. Boudalis, *Inorg. Chem.* 2009, **48**, 3167. b) B. Sun, X. Chen, Z. Li, L. Zhang, Q. Zhao, *New J. Chem.* 2010, **34**, 190. c) M. Fondo, N. Ocampo, A. M. Garcia-Deibe, J.

-
- Cano, J. Sanmartin, *Dalton Trans.* 2010, **39**, 10888. d) M. Pait, A. Bauza, A. Frontera, E. Colacio, D. Ray, *Inorg. Chem.* 2015, **54**, 4709.
- [37] J. Esteban, E. Ruiz, M. Font-Bardia, T. Calvet, A. Escuer, *Chem. Eur. J.* 2012, **18**, 3637.
- [38] R. Boča, *A Handbook of Magnetochemical Formulae*, Elsevier, Amsterdam, 2012.
- [39] R. Boča, *Program MIF&FIT*, 2019. © University of SS Cyril and Methodius, Trnava, Slovakia.
- [40] O. Kahn, *Molecular Magnetism*, VCH, Weinheim, 1993.
- [41] a) M. P. Palacios, A. J. Mota, J. E. Perea-Buceta, F. J. White, E. K. Brechin, E. Colacio, *Inorg. Chem.* 2010, **49**, 10156. b) R. Biswas, S. Giri, S. K. Saha, A. Ghosh, *Eur. J. Inorg. Chem.* 2012, 2916. c) J. Ruiz, A. J. Mota, A. Rodríguez-Diéguez, I. Oyarzabal, J. M. Secob, E. Colacio, *Dalton Trans.* 2012, **41**, 14265.
- [42] a) S. Sasmal, S. Hazra, P. Kundu, S. Dutta, G. Rajaraman, E. C. Sanudo, S. Mohanta, *Inorg. Chem.* 2011, **50**, 7257. b) P. Ghorai, A. Chakraborty, A. Panja, T. K. Mondal, A. Saha, *RSC Adv.* 2016, **6**, 36020.
- [43] a) C. Ruiz-Pérez, J. Sanchiz, M. H. Molina, F. Lloret, M. Julve, *Inorg. Chem.* 2000, **39**, 1363. b) A. R. Fortea, P. Alemany, S. Alvarez, E. Ruiz, *Chem.–Eur. J.* 2001, **7**, 627.
- [44] a) S. N. Wang, J. F. Bai, Y. Z. Li, Y. Pan, M. Scheer, X. Z. You, *CrystEngComm.* 2007, **9**, 1084. b) M. Fondo, A. M. García-Deibe, N. Ocampo, J. Sanmartín, M. R. Bermejo, A. L. Llamas-Saiz, *Dalton Trans.* 2006, 4260. c) S. -Q. Guo, D. Tian, X. Zheng, H. Zhang, *CrystEngComm.* 2012, **14**, 3177.
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CHAPTER 7

CHAPTER-7

Highlights of the thesis

The outcome of this dissertation will serve as a basis for further studies and development of di and polynuclear paramagnetic transition metal complexes along with better understanding of the field of molecular magnetism as it provides design and synthesis of several dinuclear and polynuclear Ni(II) metal clusters with varieties of Schiff base ligands derived from *N,N*-dimethyldipropylenetriamine and salicylaldehyde / pyridine-2-aldehyde / diformylphenol (DFMP). Furthermore, this work provides the magneto-structural correlations of the synthesized complexes and details methods and mechanistic way of phenoxazinone synthase activity.

In the first part of the **chapter 1** of this dissertation, an update review has been elucidated about the synthesis and magnetic behavior of different di and polynuclear Ni(II) complexes derived from different Schiff base ligands. At the last part of it, the aim of this work has been explained.

In **chapter 2**, the preparation of a new tetradentate {N₃O}-donor ligand has been shown in free form by Schiff condensation. When it was reacted with Ni(II) salts both in presence and absence of pseudohalide ions, it yielded some mononuclear and dinuclear Ni(II) complexes, [Ni(HL^a)₂](ClO₄)₂ (**50**), [Ni(L^a)(sal)] (**51**), [Ni₂(L^a)₂(μ_{1,1}-N₃)₂] (**52**), [Ni₂(L^a)₂(μ_{1,1}-NCO)₂] (**53**) and [Ni₂(HL^a)₂(μ_{1,1}-NCS)₄].CH₃OH (**54**) whose structures were determined by single crystal X-ray structure analyses. The magnetic properties reveal the zero-field splitting for two mononuclear complexes and exchange coupling of ferromagnetic nature mediated by (μ_{1,1}-N₃), (μ_{1,1}-NCO) and (μ_{1,1}-NCS) bridging coligands. Most importantly, the (μ_{1,1}-NCO) and (μ_{1,1}-NCS) bridging complexes are not only rare dinickel(II) complexes, but also the (μ_{1,1}-NCS) bridging analogue is the first example of a ferromagnetically coupled dinickel(II) system.

In **chapter 3**, Synthesis and magnetic properties of four new complexes, [Ni₂(L^b)₂(NO₃)₂].CH₃OH (**55**), [Ni₂(L^b)₂(μ-Cl)₂] (**56**), [Ni₂(L^b)₂(μ_{1,1}-NCO)₂] (**57**) and

$[\text{Ni}_2(\text{L}^{\text{b}})_2(\mu_{1,1}\text{-N}_3)_2]$ (**58**) have been explored. All these complexes were prepared using a tetradentate Schiff base (HL^{b}), obtained from the condensation reaction of *N,N*-dimethyldipropylenetriamine and 5-bromosalicylaldehyde. X-ray crystallography reveals that they are isostructural and isomorphous dinickel(II) compounds with bridging chloride or pseudohalides. All these three dinickel(II) complexes exhibit ferromagnetic interaction through bridging chloride or pseudohalides and their coupling constants are in the order **58** > **56** > **57**, a replication of the average strength of exchange interactions found in such complexes characterised magnetically. Most importantly, compound **57** is a precious addition to the only four known examples of this family, and unprecedented high degree of structural and magnetic resemblances observed in **56–58** is the major achievement of the present work.

Synthesis of tetradentate ligands with $\{\text{N}_4\}$ -donor (L^{d} and L^{e}) and $\{\text{N}_3\text{O}\}$ -donor (HL^{e}) groups have been discussed in **chapter 4**. These ligands prepared from a traditional Schiff base condensation reaction of *N,N*-dimethyldipropylenetriamine with pyridine-2-aldehyde or 2-acetylpyridine or 3-ethoxysalicylaldehyde, respectively, were used to react with Ni(II) salts in the presence of different pseudohalide ions, resulting in six new Ni(II) dimers with different bridging modes: $[\text{Ni}_2(\text{L}^{\text{d}})_2(\mu_{1,3}\text{-N}_3)_2](\text{ClO}_4)_2$ (**59**), $[\text{Ni}_2(\text{L}^{\text{d}})_2(\mu_{1,3}\text{-NCO})_2](\text{ClO}_4)_2$ (**60**), $[\text{Ni}_2(\text{L}^{\text{d}})_2\{\mu_{1,5}\text{-N}(\text{CN})_2\}_2](\text{ClO}_4)_2$ (**61**), $[\text{Ni}_2(\text{L}^{\text{e}})_2(\mu_{1,3}\text{-N}_3)_2](\text{ClO}_4)_2$ (**62**), $[\text{Ni}_2(\text{L}^{\text{e}})_2(\mu_{1,1}\text{-N}_3)_2].0.5\text{MeCN}$ (**63**) and $[\text{Ni}_2(\text{L}^{\text{e}})_2(\mu_{1,1}\text{-NCO})_2].0.5\text{MeCN}$ (**64**). Their structures and magnetic properties have been studied and discussed. Double end-to-end (EE) and end-on (EO) bridging modes were observed for both the azide and cyanate ions in these complexes. While the EE or EO azido-bridged Ni(II) compounds are quite common, the doubly EE or EO cyanato-bridged dimeric Ni(II) complex **60** was quite rare. Furthermore, it is observed that in complex **62**, the double azido bridges cross each other to form a rarely observed twisted boat-type arrangement of the $\{\text{Ni}(\mu_{1,3}\text{-N}_3)_2\text{Ni}\}$ core, which leads to ferromagnetic interaction through the EE azide bridges. According to the present results, the

introduction of different bridges and bridging motifs affords overall diverse magnetic interactions in these Ni(II) dimers, which has been discussed and rationalized in terms of previous literature reports.

Chapter 5 describes the synthesis and structures of three dinickel(II) complexes, namely $[\text{Ni}_2(\mu\text{-L})(\mu\text{-OH})](\text{ClO}_4)_2$ (**65**), $[\text{Ni}_2(\mu\text{-H}_2\text{L})(\mu\text{-OH})(\text{NCS})_3](\text{NCS})$ (**66**), $[\text{Ni}_2(\mu\text{-HL})(\mu\text{-OBz})(\mu\text{-H}_2\text{O})(\text{OBz})](\text{ClO}_4)_2 \cdot 2.5\text{H}_2\text{O}$ (**67**) (where HOBz = benzoic acid), with an end-off compartmental ligand (HL) obtained via the Schiff base condensation of 2,6-diformyl-4-methylphenol and *N,N*-dimethyldipropylenetriamine in methanol. Structural characterization reveals that both **65** and **66** are phenoxo- and hydroxo-bridged compounds, while complex **67** is a unique triple aqua-, phenoxo- and carboxylato-bridged dinickel(II) complex. Although similar bridging patterns to that found in **67** are known, the combination of aqua-, carboxylato- and phenoxo-bridging in a dinickel(II) complex has not been reported in the literature. Variable temperature magnetic susceptibility analysis reveals that the two nickel centres are antiferromagnetically coupled, with *J* values ranging from -12 to -143 K, in these complexes. The phenoxazinone-synthase-like activities of these complexes have been investigated using *o*-aminophenol as a model substrate in methanol medium, as this area is yet to be explored for Ni(II) systems. Mass spectrometry and EPR spectroscopic studies were further carried out to gain insight into the course of the reaction, and the reactivity trend has been further explored. The present work highlights the novel triply bridged dinickel(II) complex and its magnetic properties, and also demonstrates a comparative biomimetic catalytic study relating to phenoxazinone synthase.

In **chapter 6**, the use of the Schiff base ligand (HL) derived from 2,6-diformyl-4-methylphenol and *N,N*-dimethyldipropylenetriamine in Ni(II) coordination chemistry has been investigated, and two pentanuclear $[\text{Ni}_5(\text{H}_2\text{L})_2(\mu_{1,1}\text{-N}_3)_4(\text{N}_3)_2(\mu_3\text{-OH})_2(\text{H}_2\text{O})_2](\text{NO}_3)_4 \cdot 6\text{H}_2\text{O}$ (**68**), $[\text{Ni}_5(\text{L})_2(\mu_{1,3}\text{-OAc})_2(\mu_{1,1}\text{-N}_3)_4(\mu_3\text{-OH})_2] \cdot 12\text{H}_2\text{O} \cdot 2\text{CH}_3\text{OH}$

(69) and one hexanuclear $[\text{Ni}_6(\text{H}_2\text{L})_2(\mu_{1,1}\text{-N}_3)_4(\mu_{1,3}\text{-N}_3)_2(\text{N}_3)_4(\mu_3\text{-OH})_2(\text{H}_2\text{O})_2](\text{ClO}_4)_2 \cdot 4\text{H}_2\text{O}$ (70) clusters were isolated under mild conditions. In these complexes, the nature of the anion and stoichiometry of the reactants seem to play important roles in directing the formation of the metal clusters. Their X-ray characterization shows that the Ni_6 cluster can be considered to be built from two triangular $[\text{Ni}_3(\mu\text{-phenoxido})-(\mu_3\text{-OH})(\mu\text{-N}_3)_4]$ subunits with bis($\mu_{1,3}\text{-N}_3$) connectors, while bowtie-shaped Ni_5 clusters are formed by sharing a common vertex. Variable temperature magnetic properties of the penta- and the hexanuclear Ni(II) spin coupled clusters have been investigated and interpreted. According to the present results, although the core structures of triangular Ni_3 units are identical in these systems, the introduction of different bridges bring overall diverse magnetic interaction (antiferromagnetic to ferromagnetic) in these Ni(II) clusters.

APPENDIX I

List of Publication and Seminar Attended

RSC Publication:	<i>New J. Chem.</i> 2017, 41 , 3143-3153. <i>CrystEngComm.</i> 2021, 23 , 3371–3382. <i>New J. Chem.</i> 2021, 45 , 7602–7613.
Wiley Publication:	<i>ChemistrySelect</i> 2020, 5 , 12924–12931. <i>Eur. J. Inorg. Chem.</i> 2020, 2362–2371. <i>ChemistrySelect</i> 2017, 2 , 2094–2105.
Elsevier Publication:	<i>Inorg. Chim. Acta.</i> 2017, 459 , 113–123. <i>Polyhedron</i> 2016, 107 , 48–56.
Seminar attended:	National-1

List of Publication (International journals):

1. “Structure and magnetism of mono- and di-nuclear Ni(II) complexes derived from {N₃O} donor Schiff base ligand.” Anangamohan Panja*, Narayan Ch. Jana, **Sarmistha Adak**, Paula Brandão, Lubor Dlháň, Ján Titiš, Roman Boča. *New J. Chem.* 2017, **41**, 3143-3153 (**Chapter 2**).
2. “Magneto-structural Studies in Double Chloro- and Pseudohalo-bridged Isomorphous Dinickel(II) Complexes” Moumita Patra, Paula Brandão, Adam P. Pikul, **Sarmistha Adak**, Anangamohan Panja*. *ChemistrySelect* 2020, **5**, 12924–12931 (**Chapter 3**).
3. “Tuneable structures and magnetic properties of pseudohalo-bridged dinuclear Ni(II) complexes derived from {N₄} and {N₃O} donor ligands” **Sarmistha Adak**, Yu-Chen Sun, Narayan Ch. Jana, Paula Brandão, Xin-Yi Wang, Anangamohan Panja*. *CrystEngComm*. 2021, **23**, 3371–3382 (**Chapter 4**).
4. “A novel triple aqua-, phenoxo- and carboxylatobridged dinickel(II) complex, its magnetic properties, and comparative biomimetic catalytic studies with analogous dinickel(II) complexes” Narayan Ch. Jana, Zvonko Jagličić, Paula Brandão, **Sarmistha Adak**, Amrita Saha, Anangamohan Panja*. *New J. Chem.* 2021, **45**, 7602–7613 (**Chapter 5**).
5. “Syntheses, Structures and Magnetic Properties of Ferromagnetically /Antiferromagnetically Coupled Penta- and Hexanuclear Azido-Bridged Nickel(II) Coordination Compounds” Anangamohan Panja*, **Sarmistha Adak**, Paula Brandão*, Lubor Dlháň, Roman Boča*. *Eur. J. Inorg. Chem.* 2020, 2362–2371 (**Chapter 6**).
6. “Insight into the origin of catechol oxidase activity in a rare mixed valence complex ion pairs of MnII/MnIII: an account of comparative biomimetic catalytic study.” Anangamohan Panja*, Narayan Ch. Jana, **Sarmistha Adak**, Kuheli Pramanik. *Inorg. Chim. Acta*. 2017, **459**, 113–123.

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7. “Introducing supramolecular interactions into robust bis(tetrabromocatecholate) chelated manganese(III) systems and biomimetic catalytic activity.” Anangamohan Panja*, Narayan Ch. Jana, Antonio Bauzá, **Sarmistha Adak**, Tom M. Mwanja, David M. Eichhorn, Antonio Frontera*. *ChemistrySelect*. 2017, **2**, 2094–2105.
 8. “Synthesis, structure, electronic properties and DFT calculation of cobalt(II) complexes with a redox non-innocent naphthoquinone ligand.” Narayan Ch. Jana, **Sarmistha Adak**, Paula Brandão, Tarun Kanti Mandal, Anangamohan Panja*, *Polyhedron* 2016, **107**, 48–56.

Symposium Attended and Poster Presentation (International/National):

1. UGC Sponsored National Seminar on “Recent Development in Bio-Active Molecules (RDBAM-2016) on August 4th – 5th, 2016, Organized by Department of Chemistry, Haldia Govt. College. (Attended and Presented a Poster, **Awarded as the Best Poster**) “*Mechanistic investigation of dioxygen activation by Co(II) with N5 donor ligand: Inhibition of peroxo-bridging and Phenoxazinone synthase mimicking activity by thiocyanate ion.*”

APPENDIX II

Published Paper related to thesis chapters



Cite this: *New J. Chem.*, 2017, 41, 3143

The structure and magnetism of mono- and di-nuclear Ni(II) complexes derived from {N₃O}-donor Schiff base ligands†

Anangamohan Panja,^a Narayan Ch. Jana,^a Sarmistha Adak,^a Paula Brandão,^b Lubor Dlháň,^c Ján Titiš^d and Roman Boča^d

By Schiff condensation, a new tetradentate {N₃O}-donor ligand has been prepared in free form. It was combined with Ni(II) salts to yield mononuclear and dinuclear Ni(II) complexes whose structures were determined by single crystal X-ray structure analyses. The magnetic properties reveal some zero-field splitting for two mononuclear complexes and exchange coupling of ferromagnetic nature mediated by (μ_{1,1}-N₃), (μ_{1,1}-NCO) and (μ_{1,1}-NCS) bridging coligands. Most importantly, the (μ_{1,1}-NCO) and (μ_{1,1}-NCS) bridging complexes are not only rare dinickel(II) complexes, but also the (μ_{1,1}-NCS) bridging analogue is the first example of a ferromagnetically coupled dinickel(II) system.

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Introduction

The study of di- and polynuclear transition metal complexes bridged by pseudohalides is an attractive field of research because of their diverse magnetic properties.^{1–12} Among the pseudohalides, azido bridged complexes have been studied extensively because of their versatile coordination modes, end-on (μ_{1,1}) and end-to-end (μ_{1,3}) modes being the most common ones, and their effective transmittance of the magnetic interaction between the paramagnetic ions.^{13–21} In contrast, the heteroatomic pseudohalides, namely thiocyanate and cyanate, with polarizable π systems and two different donor atoms, which can coordinate the metal ions through either of the heteroatoms, or both, are less versatile than the azide ion. Therefore, in contrast to the vast chemistry of azido bridged complexes, both structurally and magnetically important compounds with these pseudohalides have been less investigated. The last two decades have witnessed rapid growth of azido-bridged nickel(II) systems,^{22–44} and accordingly, the sophisticated magneto-structural correlations are available on these

compounds to get insight into the fundamental aspects of the magnetic interactions.^{45,46} These comprehensive data reveal that the most characteristic feature of the azido bridges is the relationship between the coordination mode and magnetic behaviour. Generally, double μ_{1,3}-azido bridging leads to antiferromagnetic (AF) coupling, while μ_{1,1} coordination is associated with ferromagnetic (F) exchange between the Ni(II) centres with the only exception where low angles of μ_{1,1} bridging azido ligands lead to weak AF coupling.⁴¹ However, the double thiocyanato bridged Ni(II) complexes with the μ_{1,3} bridging mode exhibit F interaction although weakly,^{34,47–55} and mixed observations are made with μ_{1,3} bridged cyanato systems.^{49,56–59} Reported dinuclear Ni(II) compounds with cyanato and thiocyanato with μ_{1,1} bridging modes are too scarce in the literature to establish a proper magneto-structural correlation, and thus further attention is required for the development of these systems. It is worth noting that all three reported dinuclear systems with bis-μ_{1,1} bridged cyanato show weak F coupling,^{40,60} while the magnetically characterized lonely known μ_{1,1}-thiocyanato bridged dinuclear Ni(II) complex exhibits antiferromagnetic interaction.⁶¹

Literature reports reveal that the structural and magnetic diversities of pseudohalido bridged complexes are attributed to the diverse bonding modes of the bridging ligands and their orientation with respect to the paramagnetic centres. The major task in designing these compounds largely depends on the judicious choice of the blocking ligands and the stereochemical environment around the paramagnetic metal centres. Schiff-base ligands are extremely useful for the synthesis of such magnetically interesting compounds mainly because of their ease of synthesis and tremendous structural diversities. A large number of coordination compounds with Schiff base

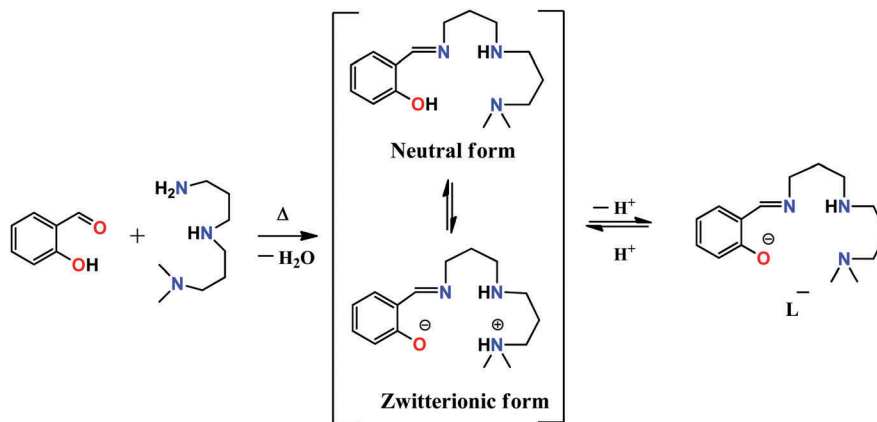
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† Electronic supplementary information (ESI) available. CCDC 1527392–1527396 contain the supplementary crystallographic data for 1 to 5, respectively, for this article. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c7nj00158d



Scheme 1 Schiff base HL employed in the present study.

ligands derived from *N*-substituted diamine at one end and salicylaldehyde or pyridine-2-aldehyde have been developed with interesting magnetic properties.^{28,29,62–65} A triamine protected at one end, namely *N,N*-dimethyldipropylenetriamine, may also provide {N₄}– or {N₃O}– donor Schiff base ligands, when reacted with pyridine-2-aldehyde or salicylaldehyde, respectively, for the development of coordination compounds. Moreover, the presence of bis(propylenic) linkers in this amine may allow the molecule to bend and rotate freely when binding to the metal centres so as to fulfil the coordinative requirements of the metal centres especially during the process of self-assembly. Surprisingly, only a single report of structurally characterized Cu(II) complexes with the Schiff base derived from *N,N*-dimethyldipropylenetriamine is available in the literature.⁶⁶ In this context, we intended to systematically develop the coordination chemistry of the transition metals derived from this triamine, with the goal of their applications in diverse fields including biomimetic catalysis and magnetic materials. Accordingly, in this present endeavour, a tetradentate Schiff base HL (Scheme 1) derived from *N,N*-dimethyldipropylenetriamine and salicylaldehyde has been reacted with Ni(II) salts both in the presence and absence of pseudohalides. Interestingly, we ended up with very diverse results of the isolation of some mono- and di-nuclear complexes of Ni(II) ions. Herewith, we report structures and magnetic properties of five new complexes, [Ni(HL)₂](ClO₄)₂ (1), [Ni(L)(sal)] (2), [Ni₂L₂(μ_{1,1}-N₃)₂] (3), [Ni₂L₂(μ_{1,1}-NCO)₂] (4) and [Ni₂(HL)₂(μ_{1,1}-NCS)₄]-CH₃OH (5). Among them, 4 and 5 are extremely rare bis-μ_{1,1}-bridged Ni(II) compounds with bridging cyanato and thiocyanato groups, respectively. Most importantly, compound 5 is the first example of a ferromagnetically coupled bis-μ_{1,1}-thiocyanato bridged dinickel(II) complex.

Experimental section

Materials and physical measurements

Chemicals such as nickel(II) perchlorate hexahydrate, nickel(II) acetate tetrahydrate, *N,N*-dimethyldipropylenetriamine and salicylaldehyde (Hsal) were purchased from commercial sources and used as received. Solvents and some other

chemicals were of reagent grade and used without further purification.

Caution! Perchlorate and azide salts of metal complexes coordinated with organic ligands are potentially explosive. Only a small amount of material should be prepared, and it should be handled with great care.

Elemental analyses (carbon, hydrogen and nitrogen) were performed in a PerkinElmer 240C elemental analyzer. The infrared spectra of the samples were recorded in the range of 400–4000 cm^{−1} on a PerkinElmer Spectrum Two FTIR spectrophotometer using KBr pellets. A SQUID magnetometer (MPMS-XL7, Quantum Design) has been used for magnetic data collection using the RSO mode of detection. The susceptibility taken at *B* = 0.1 T between *T* = 2–300 K was corrected for the underlying diamagnetism and converted to the effective magnetic moment. The magnetization was measured at two temperatures: *T* = 2.0 and *T* = 4.6 K.

Synthesis of Schiff base ligand HL

The tetradentate {N₃O}–donor ligand (HL) was prepared using the Schiff base condensation method. Briefly, 1.0 mmol of *N,N*-dimethyldipropylenetriamine (159 mg) and 1.0 mmol of salicylaldehyde (122 mg) were combined in 20 cm³ of methanol. The resulting solution was heated to reflux for *ca.* 1 h, and allowed to cool at room temperature. The dark orange methanol solution of HL was subsequently used for the synthesis of the following complexes.

Synthesis of complex [Ni(HL)₂](ClO₄)₂ (1)

Ni(ClO₄)₂·6H₂O (366 mg, 1.0 mmol) and HL (2.0 mmol) were mixed in 30 cm³ of methanol with stirring. To the resulting green solution was added Et₃N (101 mg, 1.0 mmol) and the solution was heated to reflux for 30 min. The reaction mixture was then filtered and kept at room temperature. Analytically pure dark-green crystals suitable for X-ray diffraction were obtained from slow evaporation of the solution after a couple of days, which was collected by filtration and washed with cold methanol/diethyl ether and air dried. Yield: 598 mg (77%). Anal. calcd for C₃₀H₅₀Cl₂N₆NiO₁₀: C 45.94%, H 6.43%, N 10.71%.

Found: C 46.31%, H 6.40%, N 10.60%. FTIR (KBr, cm^{-1}): 1635 m ($\nu_{\text{C}=\text{N}}$), 1076 s, 621s ($\nu_{\text{Cl}-\text{O}}$).

Synthesis of complex $[\text{Ni}(\text{L})(\text{sal})]$ (2)

Complex 2 was synthesized following a very similar procedure as described for 1, but $\text{Ni}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ was used instead of $\text{Ni}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$. Colour: dark-green. Yield: 753 mg (85%). Anal. calcd for $\text{C}_{22}\text{H}_{29}\text{N}_3\text{NiO}_3$: C 59.76%, H 6.61%, N 9.50%. Found: C 59.84%, H 6.70%, N 9.37%. FTIR (KBr, cm^{-1}): 1641 s ($\nu_{\text{C}=\text{N}}$ & $\nu_{\text{C}=\text{O}}$).

Synthesis of complex $[\text{Ni}_2\text{L}_2(\mu_{1,1}-\text{N}_3)_2]$ (3)

$\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (582 mg, 2.0 mmol) and HL (2.0 mmol) were combined in 30 cm^3 of methanol and stirred well for 15 min. Then, 10 cm^3 methanol–water solution (9 : 1, v/v) of NaN_3 (130 mg, 2 mmol) was added to it and the solution mixture was allowed to stir for an additional 10 min and filtered. Slow evaporation of the resulting green solution gave a dark-green crystalline compound containing X-ray diffraction quality plate like dark-green single crystals. Yield: 523 mg; 72%. Anal. calcd for $\text{C}_{30}\text{H}_{48}\text{N}_{12}\text{Ni}_2\text{O}_2$: C 49.62%, H 6.66%, N 23.15%. Found: C 49.84%, H 6.64%, 22.96%. FTIR (KBr, cm^{-1}): 2052 vs ($\nu_{\text{N}_3^-}$); 1626 s ($\nu_{\text{C}=\text{N}}$).

Synthesis of complex $[\text{Ni}_2\text{L}_2(\mu_{1,1}-\text{NCO})_2]$ (4)

Complex 4 was synthesized adopting an identical procedure as described for 3, except that NaNCO was used instead of NaN_3 . Colour: dark-green. Yield: 508 mg (70%). Anal. calcd for $\text{C}_{32}\text{H}_{48}\text{N}_8\text{Ni}_2\text{O}_4$: C 52.93%, H 6.66%, N 15.43%. Found: C 53.18%, H 6.50%, N 15.30%. FTIR (KBr, cm^{-1}): 2173 vs (ν_{NCO^-}); 1626 s ($\nu_{\text{C}=\text{N}}$).

Synthesis of complex $[\text{Ni}_2(\text{HL})_2(\mu_{1,1}-\text{NCS})_4] \cdot \text{CH}_3\text{OH}$ (5)

Complex 5 was synthesized following the same methodology applied for the synthesis of 3, but NH_4SCN was used in place of NaN_3 . (Yield: 724 mg; 80%). Anal. calcd for $\text{C}_{35}\text{H}_{54}\text{N}_{10}\text{Ni}_2\text{O}_3\text{S}_4$: C 46.27%, H 5.99%, N 15.42%. Colour: dark-green. Found: 46.50%, H 5.95%, N 15.35%. FTIR (KBr, cm^{-1}): 2085 vs, 2003 vs (ν_{NCS^-}); 1649 s ($\nu_{\text{C}=\text{N}}$).

X-ray crystallography

Single crystal X-ray data of 1–5 were collected using a Bruker Kappa Apex-II CCD diffractometer equipped with a fine focus sealed tube of monochromated Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$). The data were collected by scanning over the φ and ω directions and were averaged during refinement cycles. Data processing was performed using the Bruker APEX-II suite (v2.0-2) program. All available reflections to $2\theta_{\text{max}}$ were harvested and corrected for Lorentz and polarization factors with Bruker SAINT plus. The multiscan absorption correction method was applied for data correction using the SADABS program.⁶⁷ The structures were solved by a combination of direct methods and refined by means of the full matrix least-square technique based on F^2 using the SHELX-2013 suite.⁶⁸ All the non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms connected to carbon atoms were included in geometrically idealized positions with given thermal parameters related to where they are attached (1.5 times for methyl hydrogens and 1.2 times for

others). While hydrogen atoms connected to nitrogen atoms were located on the difference Fourier map and isotropically treated with given thermal parameters equivalent to 1.2 times the parent atoms. Only the structure of complex 1 was solved by adopting a disordered model in which both the metal centre and the pendent triamine part of the ligand are disordered over two positions. Drawings of the structures of 1–5 were generated with programs like MERCURY-3.8. Additional crystallographic data and refinement details for the complexes are given in Table 1.

Results and discussion

Syntheses and general characterization

The condensation reaction of *N,N*-dimethyldipropylenetriamine with salicylaldehyde in a 1 : 1 molar ratio in methanol resulted in Schiff base HL (Scheme 1). The reaction of this *in situ* generated Schiff base with $\text{Ni}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Ni}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ afforded dark-green crystalline compounds of $[\text{Ni}(\text{HL})_2](\text{ClO}_4)_2$ (1) and $[\text{Ni}(\text{L})(\text{sal})]$ (2), respectively. Synthesis of 1 and 2 is not sensitive to the stoichiometry of the reactants as both 1 : 1 and 1 : 2 molar ratios of metal salt and HL produced the same compounds. Among them, the later stoichiometry was adopted for better yields. Although we used triethylamine base for the synthesis of 1 and 2, the deprotonated Schiff base L binds the metal centre as a tetradentate ligand in 2, while the zwitterionic form of the Schiff base is coordinated to the metal centre in a tridentate fashion leaving the quaternary nitrogen free from coordination in 1. The reaction of Schiff base HL with $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and NaN_3 in aqueous methanol in a 1 : 1 : 1 molar ratio afforded dark-green compound 3 of molecular formula $[\text{Ni}_2\text{L}_2(\mu_{1,1}-\text{N}_3)_2]$. A similar reaction with NaNCO in aqueous methanol produced $[\text{Ni}_2\text{L}_2(\mu_{1,1}-\text{NCO})_2]$ (4), which is an isomorphous compound to complex 3 presenting cyanato as the bridging ligand. But under the identical reaction conditions if thiocyanate is used instead, dinuclear compound $[\text{Ni}_2(\text{HL})_2(\mu_{1,1}-\text{NCS})_4] \cdot \text{CH}_3\text{OH}$ (5) was isolated, featuring analogous bridging to that found in the azido (3) and cyanato (4) complexes. However, it is slightly different from the other two compounds as the zwitterionic form of the Schiff base is coordinated to the metal centre in a tridentate fashion instead of tetradentate anionic L bound to Ni(II) in 3 and 4. It is important to note that the addition of one equivalent of triethylamine eventually yielded the identical product. Although some dissimilarity associated with the mode of bonding of the Schiff base ligand to the metal centres is observed in these complexes, remarkable structural resemblances are found in the bridging regions of these compounds, which is very uncommon in pseudohalido bridged coordination chemistry in the presence of the same organic blocking ligands.

Among five compounds, only 1 is an ionic compound, having ClO_4^- as a counter anion. The characteristic stretching and bending vibrations of ClO_4^- ions are observed at 1076 and 621 cm^{-1} , respectively, in the IR spectrum of 1. The stretching vibrations of the azomethine ($\text{C}=\text{N}$) bond of the Schiff base are located in the range $1626\text{--}1649 \text{ cm}^{-1}$ in the IR spectra of 1 and 3–5. However, the stretching vibration of the azomethine bond together

Table 1 Crystallographic data and structural refinement parameters of **1–5**

	1	2	3	4	5
Empirical formula	C ₃₀ H ₄₂ Cl ₂ N ₆ NiO ₁₀	C ₂₂ H ₂₉ N ₃ NiO ₃	C ₃₀ H ₄₈ N ₁₂ Ni ₂ O ₂	C ₃₂ H ₄₈ N ₈ Ni ₂ O ₄	C ₃₅ H ₅₀ N ₁₀ Ni ₂ O ₃ S ₄
Formula weight (g mol ^{−1})	782.35	442.17	726.22	726.20	904.51
Temperature (K)	150(2)	150(2)	150(2)	150(2)	180(2)
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	<i>P</i> ₂ ₁ / <i>c</i>	<i>P</i> ₂ ₁ / <i>c</i>	<i>P</i> ₂ ₁ / <i>c</i>	<i>P</i> ₂ ₁ / <i>c</i>	<i>P</i> ₂ ₁ / <i>c</i>
<i>a</i> (Å)	8.9692(4)	8.0642(2)	10.8264(6)	10.8271(7)	10.8625(3)
<i>b</i> (Å)	9.8140(4)	15.4540(4)	15.9223(8)	15.8847(10)	12.3213(3)
<i>c</i> (Å)	20.2915(7)	17.5161(6)	19.0138(11)	19.0150(13)	15.8254(4)
α (deg)	90.00	90	90.00	90.00	90.00
β (deg)	101.814(2)	101.7440(10)	90.451(2)	90.578(2)	104.3490(10)
γ (deg)	90.00	90	90.00	90.00	90.00
Volume (Å ³)	1748.30(12)	2137.23(11)	3277.5(3)	3270.1(4)	2052.00(9)
<i>Z</i>	2	4	4	4	2
<i>D</i> _{calc} (g cm ^{−3})	1.486	1.377	1.472	1.475	1.464
μ (mm ^{−1})	0.771	0.935	1.198	1.202	1.169
<i>F</i> (000)	824	940	1536	1536	948
θ range (deg)	2.051–26.409	2.38–29.17	1.668–26.445	2.142–27.155	1.935–27.920
Reflections collected	35922	35679	30691	38986	24860
Independent reflections (<i>R</i> _{int})	3589(0.0416)	5749(0.0338)	6717(0.0571)	7233(0.0725)	4912(0.0474)
Observed reflections [<i>I</i> > 2 σ (<i>I</i>)]	2817	4789	4770	4734	3789
Restraints/parameters	147/295	1/268	2/427	0/427	1/257
Goodness-of-fit on <i>F</i> ²	1.044	1.026	1.180	1.035	1.064
Final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0448, <i>wR</i> ₂ = 0.1095	<i>R</i> ₁ = 0.0312, <i>wR</i> ₂ = 0.0699	<i>R</i> ₁ = 0.0775, <i>wR</i> ₂ = 0.1799	<i>R</i> ₁ = 0.0669, <i>wR</i> ₂ = 0.1603	<i>R</i> ₁ = 0.0360, <i>wR</i> ₂ = 0.0773
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0616, <i>wR</i> ₂ = 0.1216	<i>R</i> ₁ = 0.0436, <i>wR</i> ₂ = 0.750	<i>R</i> ₁ = 0.1132, <i>wR</i> ₂ = 0.1988	<i>R</i> ₁ = 0.1143, <i>wR</i> ₂ = 0.1603	<i>R</i> ₁ = 0.0518, <i>wR</i> ₂ = 0.0849
Largest diff. peak/hole (e Å ^{−3})	0.623/−0.431	0.483/−0.245	1.512/−0.709	3.200/−0.883	0.603/−0.584

with the carbonyl group of salicylaldehyde appeared at 1641 cm^{−1} in **2**. The IR spectrum of **3** exhibits a strong and sharp band at 2052 cm^{−1}, characteristic of the asymmetric stretching vibration of the bridging azido ligand, which is similar to those observed in analogous compounds.^{22–44} The asymmetric stretching vibration of the bridging NCO[−] ion for **4** is found at 2173 cm^{−1}.^{40,60} The IR spectrum of **5** consists of bifurcated bands at 2085 and 2003 cm^{−1} corresponding to the asymmetric stretching vibrations of NCS[−] ligands. The appearance of two strong peaks in the IR spectrum in **5** suggests the presence of both bridging and terminal thiocyanato ligands, consistent with the structural characterization of **5**. The higher frequency band is typical for a bridging thiocyanato group whereas the lower frequency is assigned to a N-coordinated terminal thiocyanato ligand.⁶⁹

Description of crystal structures

The crystal structures of complexes **1–5** along with partial atom-numbering schemes are depicted in Fig. 1–5, respectively, and selected metric parameters in the metal coordination spheres are listed in Table 2.

Mononuclear complexes **1** and **2**

Both **1** and **2** crystallize in the monoclinic space group *P*₂₁/*c*. Neutral complex **2** crystallizes on a general position, while the complex cation of **1** crystallizes on an inversion centre together with a perchlorate counter ion on a general position. Two perchlorate ions per Ni in **1** require protonation of the tertiary amine-N of the Schiff base ligands to balance the charge of the system *i.e.* the zwitterionic form of the Schiff base is bonded to the metal centre in **1**, while deprotonated Schiff base L binds

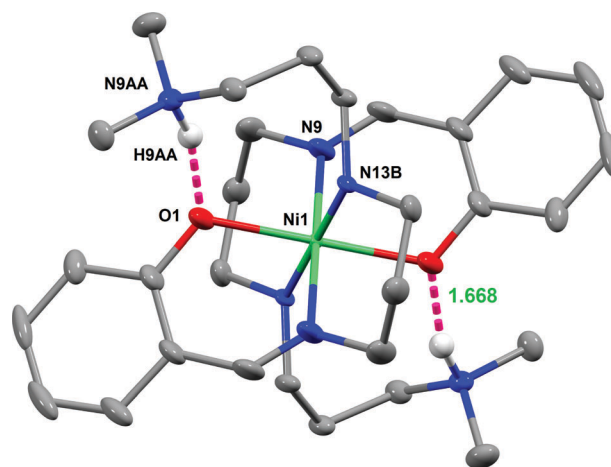


Fig. 1 Crystal structure of **1** showing the atom numbering scheme. Ellipsoids are drawn at the 30% probability level. Disordered portions and most of the H atoms are omitted for clarity. O–H...N bonding interactions are drawn as purple dashed lines.

the metal centre in **2**. The Ni(II) ion in both compounds is hexacoordinated, and the geometry around the metal centre can be best described as a distorted octahedron. The coordination sphere of Ni(II) in **1** is composed of the {N₄O₂} donor set, while it is {N₃O₃} in **2**. Two zwitterionic Schiff base ligands connect the metal centre through phenolato-O, imine-N and secondary amine-N leaving a protonated tertiary amine group free from coordination, and each of the zwitterionic ligands coordinates Ni(II) in the facial configuration in **1**. While only one deprotonated Schiff base binds the metal centre through

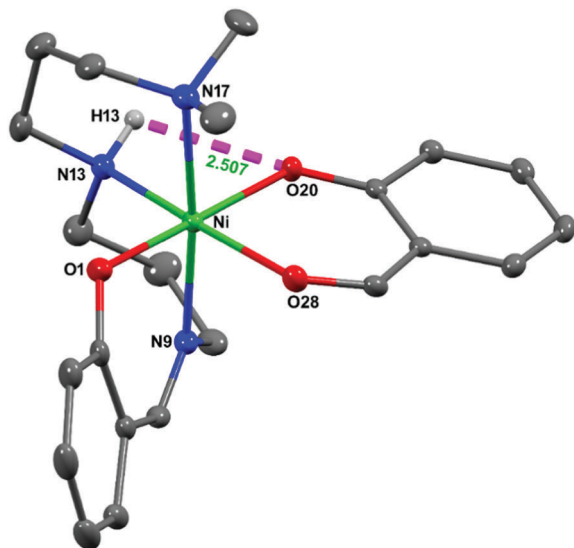


Fig. 2 Crystal structure of **2** showing the atom numbering scheme. Ellipsoids are drawn at the 30% probability level. O–H...N bonding interactions are drawn as purple dashed lines.

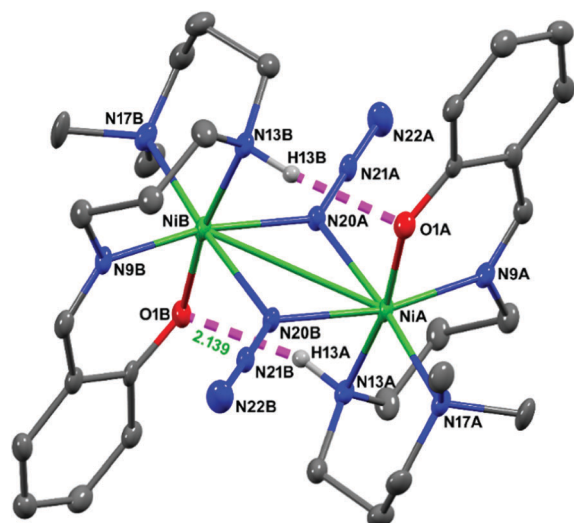


Fig. 3 Crystal structure of **3** showing the atom numbering scheme. Ellipsoids are drawn at the 50% probability level. O–H...N bonding interactions are drawn as purple dashed lines.

all four donor sites including tertiary amine-N in **2**. The coordination sphere in **2** is completed by the coordination of the deprotonated salicylaldehyde ligand using both phenolato-O and carbonyl-O. The imine, secondary amine and tertiary amine nitrogen atoms occupy one meridional position of hexacoordinate Ni(II) in **2**, while the other meridional position is occupied by the phenolato-O atom of the Schiff base together with two oxygen atoms from the deprotonated salicylaldehyde ligand. Ni–N distances of imine and secondary amine and Ni–O distances of the phenolato group of the Schiff base ligand in **1** are found to be 2.051(2), 2.162(3) and 2.075(2) Å, respectively, which are comparable to bond distances observed in analogues Ni(II) complexes with similar coordination environments.^{28,29,62–65}

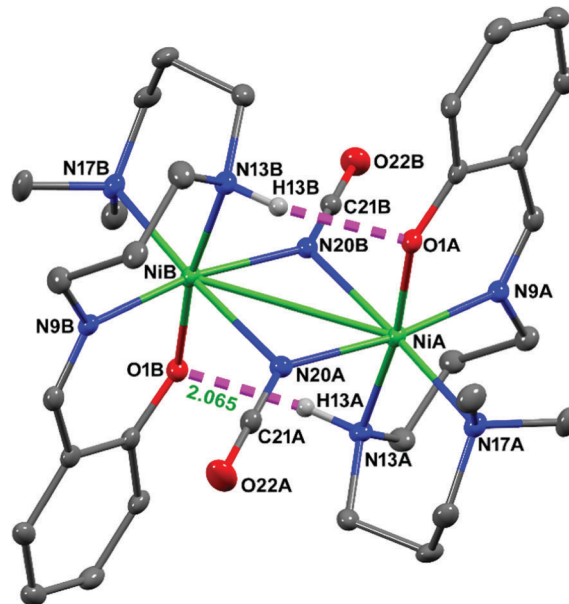


Fig. 4 Crystal structure of **4** showing the atom numbering scheme. Ellipsoids are drawn at the 30% probability level. O–H...N bonding interactions are drawn as purple dashed lines.

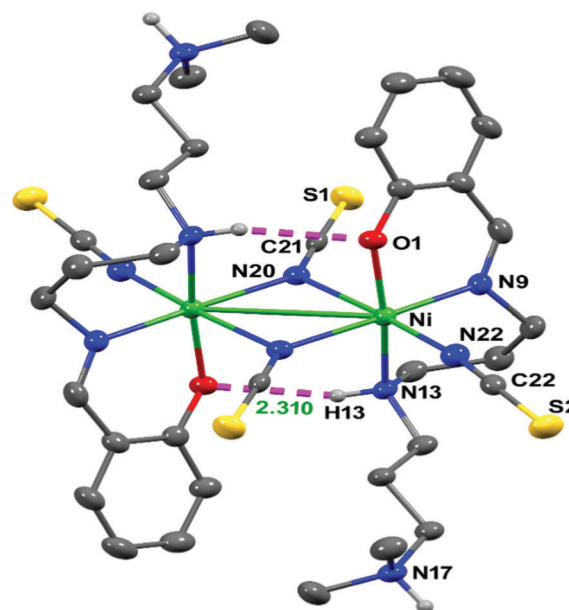


Fig. 5 Crystal structure of **5** showing the atom numbering scheme. Ellipsoids are drawn at the 30% probability level. O–H...N bonding interactions are drawn as purple dashed lines.

The imine bonds are somewhat shorter than the secondary amine nitrogen, which is along the line of their respective state of hybridization of coordinated nitrogen atoms. A similar observation is also made in **2** where the secondary amine nitrogen bond is found to be significantly longer than the imine nitrogen bond (Table 2). Furthermore, the significantly longer bond distance of the tertiary amine over a secondary amine group observed in the structure of **2** is probably due to the presence of two methyl substitutions at the tertiary amine, which in turn increased the

Table 2 Selected bond distances (Å) for 1–5

Bond	1	2	3	4	5
Ni(II)–N(imine)	2.051(2)	2.0507(13)	2.046(5)	2.059(4)	2.0298(17)
Ni(II)–N(secondary amine)	2.162(3)	2.1119(13)	2.053(5)	2.057(4)	2.1433(19)
Ni(II)–N(tertiary amine)	—	2.1979(13)	2.128(5)	2.154(4)	—
Ni(II)–O(phenolate)	2.075(2)	2.0078(10)	2.144(5)	2.132(4)	—
Ni(II)–N(pseudohalide)	—	2.0284(10)	2.186(5)	2.214(4)	—
			2.198(5)	2.205(4)	
			2.005(4)	2.020(3)	2.0570(15)
			2.014(4)	2.006(3)	
			2.121(5)	2.107(4)	2.1291(17)
			2.227(5)	2.244(4)	2.2871(19) ^a
			2.132(5)	2.115(4)	2.050(2)
			2.199(5)	2.280(4)	

^a Symmetry code: $-x, -y, -z$.

steric congestion around the donor site, thereby leading to the weaker binding ability of the tertiary amine to the metal centre. Whereas, complex **1** is stabilized in the solid state mainly by electrostatic force together with intramolecular hydrogen bonding interaction between the quaternary amine and phenolato-O (see Fig. 1), the solid state structure of complex **2** is stabilized by the combination of C–H... π and nonconventional C–H...O interactions as depicted in Fig. S1 (ESI†).

Dinuclear complexes 3–5

3 and **4** are isostructural and isomorphous compounds, and they crystallize in the monoclinic space group $P2_1/c$. The structures of **3** and **4** consist of neutral dimeric units of formulas $[\text{Ni}_2\text{L}_2(\mu_{1,1}\text{-N}_3)_2]$ and $[\text{Ni}_2\text{L}_2(\mu_{1,1}\text{-NCO})_2]$, respectively. In these complexes, each Ni(II) centre is hexacoordinated with a distorted octahedral geometry, being bonded with three N donor atoms and one phenolato-O atom of the deprotonated Schiff base ligand and two N atoms of the end-on bridging azido groups, which form a common edge within the dinuclear units, leading to an edge-sharing bioctahedral structure. Like in **2**, all the nitrogen atoms (imine, secondary amine and tertiary amine nitrogen atoms) of the triamine part of the deprotonated Schiff base coordinate Ni(II) in the meridional configuration, while the remaining meridional position is occupied by phenolato-O atom of the Schiff base together with two nitrogen atoms of bridging azido (in **3**) and cyanato (in **4**) ligands. Again, a similar trend of bond lengths as found in compound **2** *i.e.* Ni–N(tertiary amine) > Ni–N(secondary amine) > Ni–N(imine), is observed in these complexes (Table 2). Although the absence of an inversion centre brings two different bridging angles in these complexes ($100.7(2)$ and $102.0(2)^\circ$ for **3**; $97.84(15)$ and $98.74(15)^\circ$ for **4**), the central Ni_2Ni rings are found to be eventually planar. The azido and cyanato ligands are nearly linear with N–N–N and N–C–O angles varying in the range of $178.6(7)$ – $178.8(7)^\circ$ and $179.1(6)$ – $179.3(6)^\circ$, respectively. The slightly asymmetric double end-on azido bridge (with Ni–N bond distances of $2.121(5)/2.132(5)$ Å and $2.227(5)/2.199(5)$ Å) separates the two Ni(II) ions by $3.357(5)$ Å, which are comparable to those of the previously reported analogous Ni(II) complexes.^{22–44} Similar asymmetric double end-on cyanato bridging ($2.107(4)/2.115(4)$ Å *vs.* $2.244(4)/2.280(4)$ Å) with Ni...Ni separation of $3.357(5)$ Å is

observed in **4**. Unlike azido bridging, the doubly end-on bridging NCO^- is extremely uncommon in Ni(II) coordination chemistry, and it is important to note that only three dinickel(II) compounds with such a bridging motif are reported in the literature.^{40,60} However, in both compounds, the secondary amine hydrogen atom participates in an intramolecular hydrogen bond to the phenoxido oxygen atom within the dimeric unit with donor–acceptor distances of 3.009 Å and 3.013 Å in **3** and **4**, respectively. Moreover, non-conventional C–H...X (X = N for **3** and O for **4**) hydrogen bonding and C–H... π interactions stabilize the solid state structures of these isomorphic compounds (see Fig. S2, ESI†).

Compound **5** crystallizes in the monoclinic space group $P2_1/c$ and consists of a centrosymmetric dinuclear $[\text{Ni}_2(\text{HL})_2(\mu_{1,1}\text{-NCS})_4]$ unit and a disordered lattice methanol molecule. Ni(II) centres have a distorted octahedral structure with an $\{\text{NiN}_6\}$ coordination environment, being bonded with two N donor atoms (one each of imine and secondary amine) and the phenolato-O atom of the zwitterionic Schiff base, two N atoms of the $\mu_{1,1}$ -bridging thiocyanato groups, which form the common edge within the dinuclear unit, and a terminal thiocyanato ligand. Unlike **1**, the zwitterionic Schiff base connects the metal centre in the meridional configuration, while the remaining meridional position is occupied by thiocyanato ligands. Being centrosymmetric, the central $\{\text{NiN}_2\text{Ni}\}$ core is planar with a bridging angle of $98.50(7)^\circ$ and Ni...Ni separation of $3.347(7)$ Å. Both, bridging and terminal thiocyanato groups are quasilinear, with N–C–S angles of $178.2(2)$ and $179.4(2)^\circ$, respectively. Compound **5** is very similar to **3** and **4** in that NCS^- ions feature analogous end-on bridging to that found in the azido (**3**) and cyanato (**4**) complexes. However, the structural difference found in these systems is mainly associated with diverse binding propensity of the ligand – the tetradentate monoanionic Schiff base ligand binds Ni(II) in **3** and **4**, while the zwitterionic tridentate ligand binds the metal centre in **5** along with a terminal thiocyanato ligand to satisfy the coordination number six of the Ni(II) centre as well as to balance the charge of the system. Like in **3** and **4**, the secondary amine hydrogen atom is involved in an intradimer hydrogen bond to the phenoxido oxygen atom within the dimeric unit with a donor–acceptor distance of 3.122 Å. Remarkably, the quaternary amine hydrogens participate in intermolecular hydrogen bonding with phenolato-O atoms of the Schiff bases

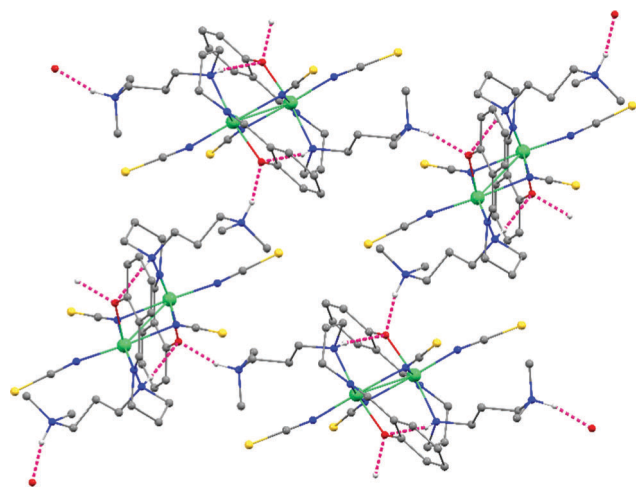


Fig. 6 Hydrogen bonded supramolecular 2D sheet of **5** in the *bc* plane showing both inter- and intra-molecular hydrogen bonding interactions.

from the adjacent dimeric units, resulting in the formation of a 2D supramolecular structure in the *bc* plane (Fig. 6). It is worth noting that end-to-end thiocyanato bridged dinickel(II) complexes are quite common in the literature.^{34,47–55} In contrast, the end-on bridging dinickel(II) complexes are extremely scarce in the literature. In fact, only three of such structurally characterized complexes are available in the literature.^{61,70,71}

Magnetic properties

Mononuclear complexes. The effective magnetic moment for **1** adopts its room temperature value of $\mu_{\text{eff}} = 3.09 \mu_{\text{B}}$ and it stays

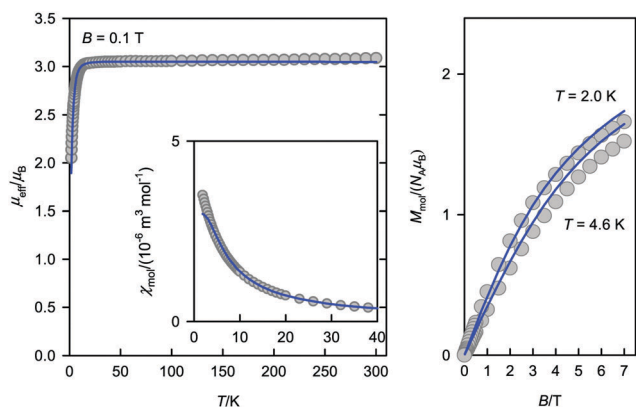


Fig. 7 Magnetic data for **1**. Lines – fitted.

constant down to 12 K where it drops down in an abrupt manner; at $T = 1.9$ K it is $\mu_{\text{eff}} = 2.05 \mu_{\text{B}}$ (Fig. 7). This feature is typical for the zero-field splitting (zfs) of the $S = 1$ spin system with the axial zfs parameter $D > 0$.⁷² The magnetization per formula unit at $T = 2.0$ K and $B = 7.0$ T adopts a subnormal value of $M_1 = M_{\text{mol}}/N_A \mu_{\text{B}} = 1.66$ which also confirms a considerable zfs.

The magnetic data (molar magnetic susceptibility and molar magnetization) were fitted simultaneously by minimizing a joint functional $F = w \cdot R(\chi) + (1 - w) \cdot R(M)$ with equal weights, $w = 0.5$. The spin Hamiltonian of the form

$$\hat{H}_k = D(\hat{S}_z^2 - \hat{S}^2/3)\hbar^{-2} + \mu_{\text{B}}B(g_z\hat{S}_z \cos \theta_k + g_{xy}\hat{S}_x \sin \theta_k)\hbar^{-1} \quad (1)$$

yields the eigenvalues which enter the partition function and consequently the susceptibility and magnetization are reconstructed by using the apparatus of statistical thermodynamics.⁷³ The fitting procedure gave the set of magnetic parameters as listed in Table 3; there is $D/hc = +7.2 \text{ cm}^{-1}$ and $g_z < g_x$ as predicted by spin Hamiltonian theory.⁷⁴

Complex **2** displays temperature-independent effective magnetic moment $\mu_{\text{eff}} = 3.10\text{--}3.06 \mu_{\text{B}}$ between room temperature and $T = 12$ K; below this temperature its decrease is registered towards a limit of $\mu_{\text{eff}} = 2.63 \mu_{\text{B}}$ at $T = 1.9$ K (Fig. 8). The magnetization data develop with the field differently when compared to **1**: there is a saturation of $M_1 = 2.0$ at $T = 2.0$ K and $B = 7.0$ T. Both these features are characteristics for $D < 0$. Indeed, the fitting procedure confirmed $D/hc = -5.2 \text{ cm}^{-1}$ and $g_z > g_x$.

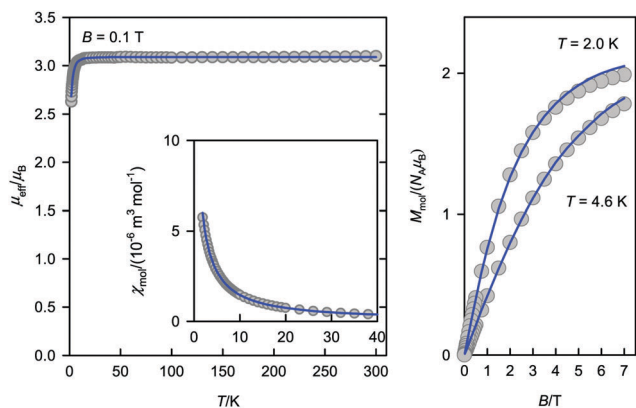
The difference in the sign of the D -parameter originates in the geometry of the chromophore $\{\text{NiN}_2\text{N}_2'\text{O}_2\}$ for **1** and $\{\text{NiN}_3\text{O}_3\}$ for **2**. The averaged bond lengths ($\text{\AA}$) in **1** are $d(\text{Ni-N9}) = 2.052$, $d(\text{Ni-N13}) = 2.190$, and $d(\text{Ni-O1}) = 2.075$; the displacements from the averaged distances $\bar{d}(\text{Ni-N}) = 2.145$ and/or $\bar{d}(\text{Ni-O}) = 2.055$ are $\delta_i = (d_i - \bar{d}_i)$, i.e. $\delta(\text{Ni-N}) = -0.093$, $\delta(\text{Ni-N}') = 0.045$, and $\delta(\text{Ni-O}) = 0.020 \text{ \AA}$. Two similar displacements define an equatorial plane of the bipyramid so that the chromophore behaves like a compressed bipyramid with the structural tetragonality parameter $D_{\text{str}} = \delta_z - (\delta_x - \delta_y)/2 = -12.55 \text{ pm}$. However, the situation is more complex since the occupation number of the Ni site is only 0.5 and there are two NiA centres with the occupation numbers 0.25 and the distances $d(\text{NiA-O1}) = 1.887$ and 2.297 , $d(\text{NiA-N9}) = 1.998$ and 2.158 , and $d(\text{NiA-N13}) = 1.917 \text{ \AA}$.

In complex **2** with the *mer*- $\{\text{NiN}_3\text{O}_3\}$ chromophore all metal-ligand distances are different: $d(\text{Ni-O1}) = 2.0078$, $d(\text{Ni-O20}) = 2.0284$, $d(\text{Ni-O28}) = 2.1062$, $d(\text{Ni-N9}) = 2.0507$, $d(\text{Ni-N13}) = 2.1119$, and $d(\text{Ni-N17}) = 2.1979 \text{ \AA}$; the displacements are

Table 3 Magnetic parameters for **1** through **5**

System	$J/hc/\text{cm}^{-1}$	$D/hc/\text{cm}^{-1}$	g_z	g_x	χ_{TIM}^a	$zj/hc/\text{cm}^{-1}$	$R(\chi)/\%$	$R(M)/\%$	Ni–N–Ni/deg
1	—	+7.21	2.093	2.180	0	0	6.3	5.8	
2	—	−5.16	2.320	2.121	0	0	1.8	1.9	
3	+20.0	+5.12	2.376	—	0	−0.060	1.3		100.7, 102.0
4	+13.7	+7.18	2.187	—	4.7		2.0	1.7	97.8, 98.7
5	+12.4	+6.87	2.118	—	10		4.3	2.1	98.5

^a χ_{TIM} in units of $10^{-6} \text{ m}^3 \text{ mol}^{-1}$. R – discrepancy factors of the fit.

Fig. 8 Magnetic data for **2**. Lines – fitted.

$\delta(\text{Ni-O1}) = -0.0472$, $\delta(\text{Ni-O20}) = -0.0266$, $\delta(\text{Ni-O28}) = 0.0512$, $\delta(\text{Ni-N9}) = -0.0943$, $\delta(\text{Ni-N13}) = -0.0331$, and $\delta(\text{Ni-N17}) = 0.0529$ Å. Thus it is difficult to simplify these data to a compressed or elongated tetragonal bipyramid in order to determine the structural tetragonality parameter D_{str} . However, this can be carried out by averaging *trans*-positioned distances: $\delta_1 = -0.0369$, $\delta_2 = 0.00905$, and $\delta_3 = -0.0207$. Now, the D_{str} parameter can be calculated in three ways using a constraint $E_{\text{str}} = (\delta_x - \delta_y)/2 < |D_{\text{str}}|/3$. Then $\delta_z = \delta_2$ and $\delta_{xy} = -0.0288$ gave $D_{\text{str}} = +3.785$, $E_{\text{str}} = 0.81$ pm, and $E/|D| = 0.21$.

It was found⁷⁵ that in a series of mononuclear Ni(II) complexes with the $\{\text{NiA}_4\text{B}_2\}$ chromophore the structural tetragonality parameter D_{str} correlates with the magnetic anisotropy parameter D along a straight line with a positive slope. The original dataset has been enriched by some recent investigations.^{76–79} Complexes **1** and **2**, however, do not match such a correlation probably owing to the problematic determination of the D_{str} parameter.

Dinuclear complexes. Dinuclear complex **5** shows that the effective magnetic moment on cooling increases from its room temperature value $\mu_{\text{eff}} = 4.51 \mu_{\text{B}}$ (Fig. 9). It passes through a maximum at $T = 8.7$ K and then drops down to $\mu_{\text{eff}} = 4.44 \mu_{\text{B}}$ at $T = 1.9$ K. The magnetization grows to $M_1 = 3.8$ at $T = 2.0$ K and $B = 7.0$ T. These data confirm a presence of the exchange interaction of a ferromagnetic nature ($J > 0$) and some zero-field splitting that operates at low temperature.

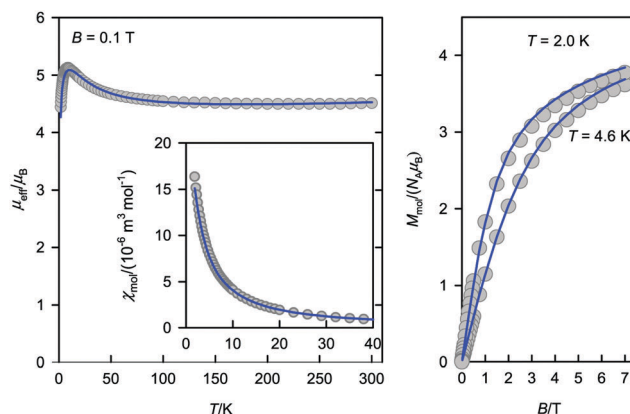
The magnetic data were fitted by using the spin Hamiltonian for a dinuclear system with isotropic exchange and zfs

$$\hat{H}_k = -J(\vec{S}_A \cdot \vec{S}_B)\hbar^{-2} + \sum_{A=1}^2 D(\hat{S}_{A,z}^2 - \vec{S}_A^2/3)\hbar^{-2} + \sum_{A=1}^2 \mu_B B(g_{A,z}\hat{S}_{A,z}\cos\theta_k + g_{A,xy}\hat{S}_{A,x}\sin\theta_k)\hbar^{-1} \quad (2)$$

Eventually the molecular field correction (*zj*) and temperature-independent magnetism χ_{TIM} can be applied

$$\chi = \chi^{\text{sh}}/[1 - (zj)\chi^{\text{sh}}] + \chi_{\text{TIM}} \quad (3)$$

In order to reduce the set of free parameters, the isotropic Zeeman term has been considered ($g_z = g_x$). The final set of magnetic parameters is listed in Table 3.

Fig. 9 Magnetic data for **5**. Lines – fitted.

The positive exchange coupling constant can be rationalized by the bonding angle Ni–N–Ni = 98.50 deg that is close to the critical value when the ferromagnetic exchange prevails.⁸⁰ The $\{\text{NiN}_5\text{O}\}$ chromophore is rather distorted with all metal–ligand distances being different.

The remaining two dinuclear complexes, **3** and **4**, display analogous magnetic functions to **5** (Fig. 10 and 11) with the

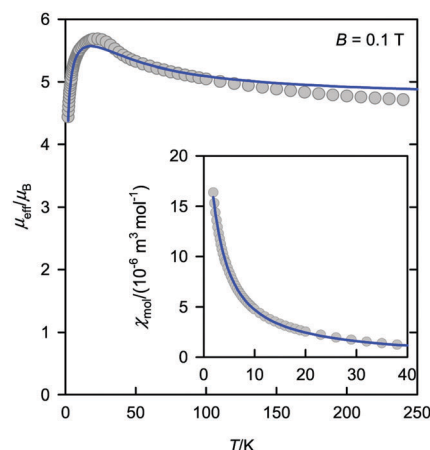
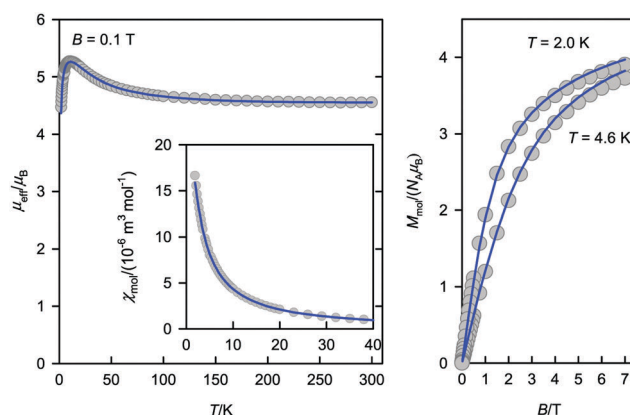
Fig. 10 Magnetic data for **3**. Lines – fitted.Fig. 11 Magnetic data for **4**. Lines – fitted.

Table 4 Selected structural and magnetic data of Ni(II) dimers with doubly end-on cyanato and thiocyanato bridges^a

Compounds	$D/hc/\text{cm}^{-1}$	g	M–N–M (°)	$J/hc/\text{cm}^{-1}$	Ref.
$[\text{Ni}_2(\text{L}^1)_2(\mu_{1,1}\text{-NCO})_2](\text{ClO}_4)_2$	+3.6	2.23	94.4(3), 95.8(4)	+3.4	40
$[\text{Ni}_2(\text{L}^2)_2(\mu_{1,1}\text{-NCO})_2](\text{ClO}_4)_2$	–12.32	2.21	95.33(13), 95.79(12)	+5.6	40
$[\text{Ni}_2(\text{terpy})_2(\mu_{1,1}\text{-NCO})_2(\text{H}_2\text{O})_2](\text{PF}_6)_2$	+3.6	2.23	97.7(4)	+9.2	60
$[\text{Ni}_2\text{L}_2(\mu_{1,1}\text{-NCO})_2]$ (4)	+7.18	2.187	97.84(15), 98.74(15)	+13.7	This work
$[\text{Ni}_2(\text{S-dept})_2(\mu_{1,1}\text{-NCS})_2(\text{NCS})_2]$	—	2.142	96.9(8)	–13.2	61
$[\text{Ni}_2(\text{HL})_2(\mu_{1,1}\text{-NCS})_4]\cdot\text{CH}_3\text{OH}$ (5)	+6.87	2.118	98.50(7)	+12.4	This work

^a Terpy = terpyridine; $\text{L}^1 = [N,N'\text{-bis}(2\text{-pyridinylmethylene})]\text{propane-1,3-diamine}$; $\text{L}^2 = [N,N'\text{-bis}(\text{pyridin-2-yl})\text{benzylidene}]\text{ethane-1,2-diamine}$; S-dept = N,N,N',N' -tetraethylpyridine-2,6-dithiocarboxamide.

ferromagnetic exchange coupling and sizable zero-field splitting of easy-plane character ($D > 0$).

Among the several structural parameters that can affect the strength and sign of the exchange coupling constant (J) between the paramagnetic centers, the bridging angle is considered the most crucial factor in determining the net magnetic interaction. Theoretical studies by Ruiz *et al.* on doubly $\mu_{1,1}$ -azido bridged dinickel(II) complexes have revealed that the interaction predicted to be ferromagnetic on all values of Ni–N(N_3)–Ni angles (θ) ranging from 80 to 115°, with J increasing upon increasing this angle, reaching a maximum at around 104° and then decreasing with increasing θ .^{45,46} In fact, all the reported $\mu_{1,1}$ -azido bridged nickel(II) dimers exhibit ferromagnetic coupling^{22–40,42–44} with only one exception where a very low bridging angle of 90.4° propagates the AF interaction between Ni(II) centers.⁴¹ The Ni–N–Ni angles of 100.7(2) and 102.0(2)° found in **3** are very typical for this kind of systems, and thus the sign and magnitude of calculated J in **3** is reasonable. For bis($\mu_{1,1}$ -NCO) bridged nickel(II) dimers, the existing data are extremely scarce, and only three data sets on such compounds are available in the literature where J values vary in the narrow range +3.4 to +9.2 cm^{-1} (Table 4).^{40,60} A similar ferromagnetic interaction is also observed in **4**, however, the magnetic coupling is found to be somewhat stronger in the present case. Although this dataset is too small to permit proper magneto structural correlation, a similar trend to that found in theoretical predictions with doubly $\mu_{1,1}$ -azido bridged dinickel(II) systems, *i.e.* J increasing with an increase in bridging angle, is observed in the cyanato bridged systems. However, the reason for weaker coupling for the cyanato bridged compounds compared to analogous azido systems can be understood by means of theoretical calculations.⁴⁰ Interestingly, in the only previous example with a doubly $\mu_{1,1}$ -thiocyanato bridged dinickel(II) complex, the magnetic coupling between the metal centers has been found to be an antiferromagnetic with the J value of –13.2 cm^{-1} (Table 4).⁶¹ In contrast, the observed magnetic coupling is ferromagnetic in nature in **5** with the coupling constant of +12.4 cm^{-1} . The Ni–N–Ni bridging angle found in that previously reported compound is 96.9°, while it is 98.50° in **5**. A careful inspection of the magneto-structural data of these doubly $\mu_{1,1}$ -pseudohalido bridged dinickel(II) systems reveals that, for azido bridged systems,⁴² the smallest experimentally found bridging angle 90.4° leads to very weak AF interaction (–1.77 cm^{-1}), while the next lowest angle of 95.5(3)/96.5(3) is responsible for significantly strong F interaction (+31.62 cm^{-1}).

Although ferromagnetic coupling is predicted in the range of bridging angles 80 to 115° by theoretical means, the overestimation of J values cannot be ruled out especially at lower bridging angles. However, these experimental facts suggest that the bis($\mu_{1,1}$ - N_3) bridging groups could not be the universal ferromagnetic coupler in Ni(II) systems and the crossover angle for bis($\mu_{1,1}$ -azido) bridged dinickel(II) is closely located near about 91°. Similarly, the experimental facts indicate that the crossover angle is situated in-between 96.9° and 98.50° for a thiocyanato system, and it might be just below 94° for cyanate bridging systems. It is interesting to note from these magneto-structural data that on moving from azido to cyanato to thiocyanato systems, the crossover angle is expected to move to higher values. More examples of doubly $\mu_{1,1}$ -NCO and $\mu_{1,1}$ -NCS bridged dinickel(II) systems and some data at lower $\mu_{1,1}$ - N_3 bridging angles along with sophisticated theoretical calculations are further required to reinforce the above conclusions.

Conclusions

We have synthesized some mono and dinuclear Ni(II) complexes with a new $\{\text{N}_3\text{O}\}$ donor Schiff base ligand. X-ray structural analyses reveal the diverse coordination ability of the Schiff base in these compounds as both the zwitterionic form and the deprotonated ligand can bind the metal centre through tridentate and tetradentate fashions, respectively. The magnetic properties disclose some zero-field splitting for mononuclear complexes as expected for the Ni(II) ion, and the exchange coupling of doubly end-on pseudohalido bridged complexes is found to be ferromagnetic in nature. Although a large number of bis($\mu_{1,1}$ - N_3) bridged Ni(II) dimers are known, the analogous ($\mu_{1,1}$ -NCO) and ($\mu_{1,1}$ -NCS) bridged dinickel(II) complexes are extremely scarce in the literature and thus these compounds are important additions in the family of such systems. Most remarkably, the thiocyanato compound is the first example of a ferromagnetically coupled system.

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References

- 1 S. Accorsi, A.-L. Barra, A. Caneschi, G. Chastanet, A. Cornia, A. C. Fabretti, D. Gatteschi, C. Mortalò, E. Olivieri, F. Parenti, P. Rosa, R. Sessoli, L. Sorace, W. Wernsdorfer and L. Zobbi, *J. Am. Chem. Soc.*, 2006, **128**, 4742–4755.
- 2 A. Ferguson, J. Lawrence, A. Parkin, J. Sanchez-Benitez, K. V. Kamenev, E. K. Brechin, W. Wernsdorfer, S. Hill and M. Murrie, *Dalton Trans.*, 2008, 6409–6414.
- 3 J. M. Clemente-Juan, E. Coronado, A. Forment-Aliaga, A. Gaita-Arino, C. Gimenez-Saiz, F. M. Romero, W. Wernsdorfer, R. Biagi and V. Corradini, *Inorg. Chem.*, 2010, **49**, 386–396.
- 4 H.-L. Sun, Z.-M. Wang and S. Gao, *Coord. Chem. Rev.*, 2010, **254**, 1081–1100.
- 5 M. Sarkar, R. Clerac, C. Mathoniere, N. G. R. Hearn, V. Bertolasi and D. Ray, *Inorg. Chem.*, 2011, **50**, 3922–3933.
- 6 M. Murugesu, M. Habrych, W. Wernsdorfer, K. A. Abboud and G. Christou, *J. Am. Chem. Soc.*, 2004, **126**, 4766–4767.
- 7 A. Bell, G. Aromí, S. J. Teat, W. Wernsdorfer and R. E. P. Winpenny, *Chem. Commun.*, 2005, 2808–2810.
- 8 S. Nayak, M. Evangelisti, A. K. Powell and J. Reedijk, *Chem. – Eur. J.*, 2010, **16**, 12865–12872.
- 9 F. Meyer, S. Demeshko, G. Leibel, B. Kersting, E. Kaifer and H. Pritzkow, *Chem. – Eur. J.*, 2005, **11**, 1518–1526.
- 10 G. Brunet, F. Habib, C. Cook, T. Pathmalingham, F. Loiseau, I. Korobkov, T. J. Burchell, A. M. Beauchemina and M. Murugesu, *Chem. Commun.*, 2012, **48**, 1287–1289.
- 11 J. Werner, M. Rams, Z. Tomkowicz, T. Runčevski, R. E. Dinnebier, S. Suckert and C. Näther, *Inorg. Chem.*, 2015, **54**, 2893–2901.
- 12 A. M. Ako, I. J. Hewitt, V. Mereacre, R. Clérac, W. Wernsdorfer, C. E. Anson and A. K. Powell, *Angew. Chem.*, 2006, **118**, 5048–5051.
- 13 J. Ribas, A. Escuer, M. Monfort, R. Vicente, R. Cortes, L. Lezama and T. Rojo, *Coord. Chem. Rev.*, 1999, **193–195**, 1027–1068.
- 14 A. Escuer and G. Aromí, *Eur. J. Inorg. Chem.*, 2006, 4721–4736.
- 15 Y.-F. Zeng, X. Hu, C.-F. Liu and X.-H. Bu, *Chem. Soc. Rev.*, 2009, **38**, 469–480.
- 16 C. Adhikary and S. Koner, *Coord. Chem. Rev.*, 2010, **254**, 2933–2958.
- 17 X.-Y. Wang, Z.-M. Wang and S. Gao, *Chem. Commun.*, 2008, 281–294.
- 18 S. Mukherjee and P. S. Mukherjee, *Acc. Chem. Res.*, 2013, **46**, 2556–2566.
- 19 T. C. Stamatatos and G. Christou, *Inorg. Chem.*, 2009, **48**, 3308–3322.
- 20 A. Escuer, J. Esteban, S. P. Perlepes and T. C. Stamatatos, *Coord. Chem. Rev.*, 2014, **275**, 87–129.
- 21 P. Ghorai, A. Chakraborty, A. Panja, T. K. Mondal and A. Saha, *RSC Adv.*, 2016, **6**, 36020–36030.
- 22 S. Liang, Z. Liu, N. Liu, C. Liu, X. Di and J. Zhang, *J. Coord. Chem.*, 2010, **63**, 3441–3452.
- 23 S. S. Massoud, F. R. Louka, Y. K. Obaid, R. Vicente, J. Ribas, R. C. Fischer and F. A. Mautner, *Dalton Trans.*, 2013, **42**, 3968–3978.
- 24 M. G. Barandika, R. Cortés, L. Lezama, M. K. Urriaga, M. I. Arriortua and T. Rojo, *J. Chem. Soc., Dalton Trans.*, 1999, 2971–2976.
- 25 H.-D. Bian, W. Gu, Q. Yu, S.-P. Yan, D.-Z. Liao, Z.-H. Jiang and P. Cheng, *Polyhedron*, 2005, **24**, 2002–2008.
- 26 S. Sarkar, A. Mondal, A. Banerjee, D. Chopra, J. Ribas and K. K. Rajak, *Polyhedron*, 2006, **25**, 2284–2288.
- 27 S. Deoghor, S. Sain, M. Soler, W. T. Wong, G. Christou, S. K. Bera and S. K. Chandra, *Polyhedron*, 2003, **22**, 257–262.
- 28 P. Mukherjee, M. G. B. Drew, C. J. Gómez-García and A. Ghosh, *Inorg. Chem.*, 2009, **48**, 5848–5860.
- 29 S. K. Dey, N. Mondal, M. S. E. Fallah, R. Vicente, A. Escuer, X. Solans, M. Font-Bardía, T. Matsushita, V. Gramlich and S. Mitra, *Inorg. Chem.*, 2004, **43**, 2427–2434.
- 30 S. Sarkar, A. Mondal, M. S. E. Fallah, J. Ribas, D. Chopra, H. Stoeckli-Evans and K. K. Rajak, *Polyhedron*, 2006, **25**, 25–30.
- 31 M. I. Arriortua, A. R. Cortes, L. Lezam, T. Rojo, X. Solans and M. Font-Bardía, *Inorg. Chim. Acta*, 1990, **174**, 263–269.
- 32 S. Nandi, D. Bannerjee, J.-S. Wu, T.-H. Lu, A. M. Z. Slawin, J. D. Woollins, J. Ribas and C. Sinha, *Eur. J. Inorg. Chem.*, 2009, 3972–3981.
- 33 A. Escuer, R. Vicente, M. S. E. Fallah, X. Solans and M. Font-Bardía, *Inorg. Chim. Acta*, 1996, **247**, 85–91.
- 34 R. Cortes, J. I. Ruiz de Larramendi, L. Lezama, T. Rojo, K. Urriaga and M. I. Arriortua, *J. Chem. Soc., Dalton Trans.*, 1992, 2723–2728.
- 35 S. Sain, S. Bid, A. Usman, H.-K. Fun, G. Aromí, X. Solans and S. K. Chandra, *Inorg. Chim. Acta*, 2005, **358**, 3362–3368.
- 36 R. Vicente, A. Escuer, J. Ribas, M. S. E. Fallah, X. Solans and M. Font-Bardía, *Inorg. Chem.*, 1993, **32**, 1920–1924.
- 37 J. Ribas, M. Monfort, C. Diaz, C. Bastos and X. Solans, *Inorg. Chem.*, 1994, **33**, 484–489.
- 38 X.-J. Lin, Z. Shen, Y. Song, H.-J. Xu, Y.-Z. Li and X.-Z. You, *Inorg. Chim. Acta*, 2005, **358**, 1963–1969.
- 39 A. Escuer, R. Vicente, J. Ribas and X. Solans, *Inorg. Chem.*, 1995, **34**, 1793–1798.
- 40 M. Habib, T. K. Karmakar, G. Aromí, J. Ribas-Ariño, H.-K. Fun, S. Chantrapromma and S. K. Chandra, *Inorg. Chem.*, 2008, **47**, 4109–4117.
- 41 P. Chaudhuri, R. Wagner, S. Khanra and T. Weyhermüller, *Dalton Trans.*, 2006, 4962–4968.
- 42 A. Bhattacharyya, P. K. Bhaumik, M. Das, A. Bauzá, P. P. Jana, K. Harms, A. Frontera and S. Chattopadhyay, *Polyhedron*, 2015, **101**, 257–269.
- 43 A. Solanki, M. Monfort and S. B. Kumar, *J. Mol. Struct.*, 2013, **1050**, 197–203.
- 44 S. Sarkar, A. Datta, A. Mondal, D. Chopra, J. Ribas, K. K. Rajak, S. M. Sairam and S. K. Pati, *J. Phys. Chem. B*, 2006, **110**, 12–15.
- 45 E. Ruiz, J. Cano, S. Alvarez and P. Alemany, *J. Am. Chem. Soc.*, 1998, **120**, 11122–11129.
- 46 G. Manca, J. Cano and E. Ruiz, *Inorg. Chem.*, 2009, **48**, 3139–3144.
- 47 F. A. Mautner, M. Scherzer, C. Berger, R. C. Fischer, R. Vicente and S. S. Massoud, *Polyhedron*, 2015, **85**, 20–26.

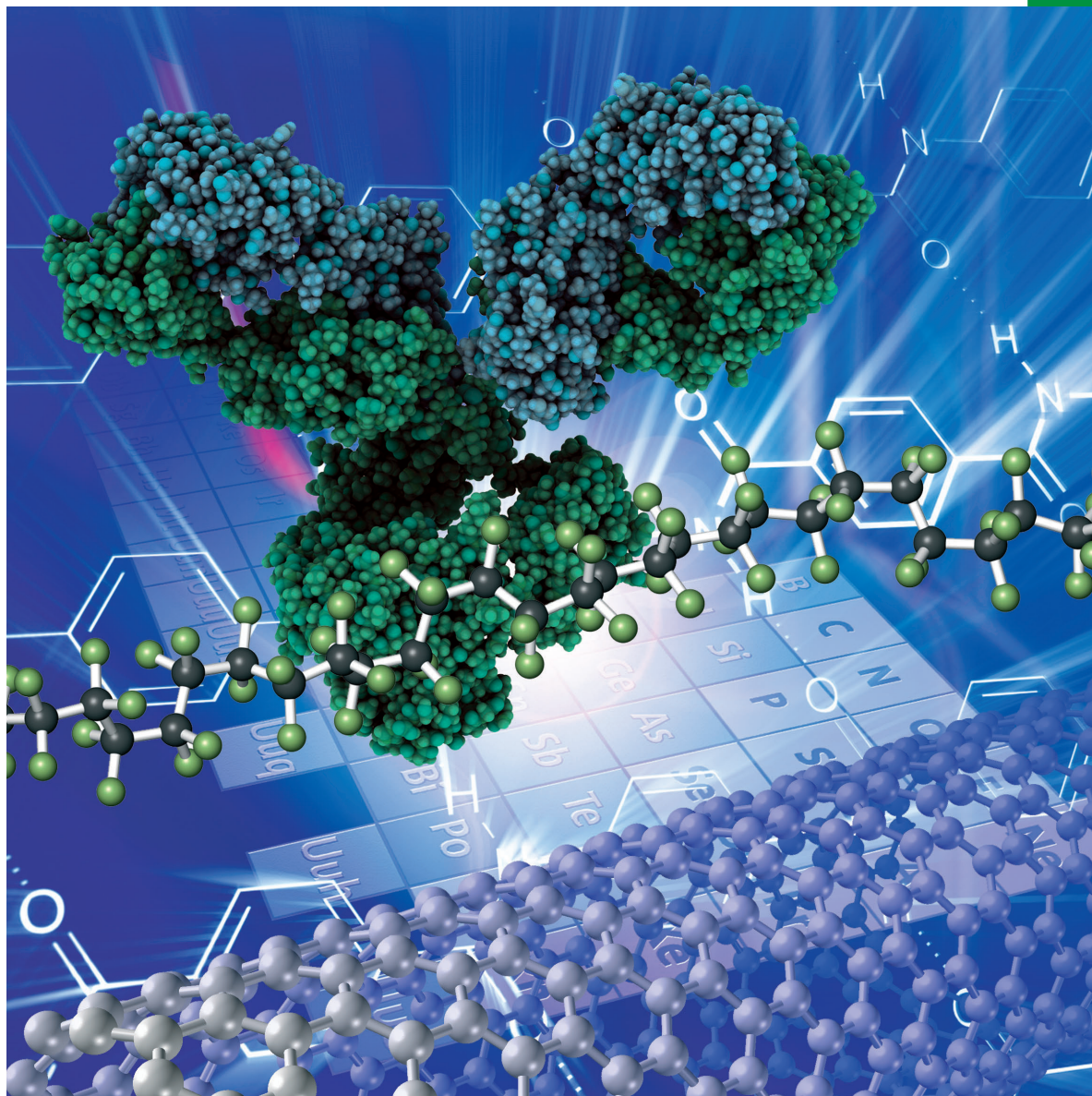
- 48 M. Monfort, J. Ribas and X. Solans, *Inorg. Chem.*, 1994, **33**, 4271–4276.
- 49 D. M. Duggan and D. N. Hendrickson, *Inorg. Chem.*, 1974, **13**, 2929–2940.
- 50 T. Rojo, R. Cortés, L. Lezama, M. I. Arriortua, K. Urtiaga and G. Villeneuve, *J. Chem. Soc., Dalton Trans.*, 1991, 1779–1783.
- 51 A. P. Ginsberg, R. C. Sherwood, R. W. Brookes and R. L. Martin, *J. Am. Chem. Soc.*, 1971, **93**, 5927–5928.
- 52 H. D. Bien, W. Gu, Q. Yu, S. P. Yan, D. Z. Liao, Z. H. Jiang and P. Cheng, *Polyhedron*, 2005, **24**, 2002–2008.
- 53 P. Bhowmik, S. Chattopadhyay, M. G. B. Drew, C. Diaz and A. Ghosh, *Polyhedron*, 2010, **29**, 2637–2642.
- 54 B. Larue, L.-T. Tran, D. Luneau and C. Reber, *Can. J. Chem.*, 2003, **81**, 1168–1179.
- 55 T. K. Maji, G. Mostafa, J. M. Clemente-Juan, J. Ribas, F. Lloret, K.-i. Okamoto and N. R. Chaudhuri, *Eur. J. Inorg. Chem.*, 2003, 1005–1011.
- 56 A. Escuer, R. Vicente, M. S. E. Fallah, X. Solans and M. Font-Bardia, *J. Chem. Soc., Dalton Trans.*, 1996, 1013–1019.
- 57 D. M. Duggan and D. N. Hendrickson, *Inorg. Chem.*, 1974, **13**, 2056–2062.
- 58 Z. Mahendrasinh, S. Ankita, S. B. Kumar, A. Escuer and E. Suresh, *Inorg. Chim. Acta*, 2011, **375**, 333–337.
- 59 S. Choubey, K. Bhar, S. Chattopadhyay, A. Hazra, T. K. Maji, J. Ribas and B. K. Ghosh, *Dalton Trans.*, 2012, **41**, 11551–11554.
- 60 M. I. Arriortua, R. Cortes, J. L. Mesa, L. Lezama, T. Rojo and G. Villeneuve, *Transition Met. Chem.*, 1988, **13**, 371–374.
- 61 R. Kapoor, A. Kataria, A. Pathak, P. Venugopalan, G. Hundal and P. Kapoor, *Polyhedron*, 2005, **24**, 1221–1231.
- 62 S. Jana, B. K. Shaw, P. Bhowmik, K. Harms, M. G. B. Drew, S. Chattopadhyay and S. K. Saha, *Inorg. Chem.*, 2014, **53**, 8723–8734.
- 63 S. Sasmal, S. Hazra, P. Kundu, S. Majumder, N. Aliaga-Alcalde, E. Ruiz and S. Mohanta, *Inorg. Chem.*, 2010, **49**, 9517–9526.
- 64 S. Sasmal, S. Hazra, P. Kundu, S. Dutta, G. Rajaraman, E. Carolina Sañudo and S. Mohanta, *Inorg. Chem.*, 2011, **50**, 7257–7267.
- 65 S. Mukherjee, B. Gole, Y. Song and P. S. Mukherjee, *Inorg. Chem.*, 2011, **50**, 3621–3631.
- 66 A. Company, L. Gomez, R. Mas-Balleste, I. V. Korendovych, X. Ribas, A. Poater, T. Parella, X. Fontrodona, J. Benet-Buchholz, M. Sola, L. Que Jr, E. V. Rybak-Akimova and M. Costas, *Inorg. Chem.*, 2007, **46**, 4997–5012.
- 67 G. M. Sheldrick, *SADABS*, University of Göttingen, Germany, 1996.
- 68 G. M. Sheldrick, *Acta Crystallogr., Sect. A: Found. Crystallogr.*, 2008, **64**, 112–122.
- 69 J. Palion-Gazda, B. Machura, F. Lloret and M. Julve, *Cryst. Growth Des.*, 2015, **15**, 2380–2388.
- 70 P. A. Harding, K. Henrick, L. F. Lindoy, M. McPartlin and P. A. Tasker, *J. Chem. Soc., Chem. Commun.*, 1983, 1300–1301.
- 71 H.-W. Lin, *Acta Crystallogr.*, 2008, **E64**, m295.
- 72 R. Boča and J. Titiš, *Coordination Chemistry Research Progress*, Nova Science Publishers, New York, 2008, pp. 247–304.
- 73 R. Boča, *Theoretical Foundations of Molecular Magnetism*, Elsevier, Amsterdam, 1999.
- 74 R. Boča, *Struct. Bonding*, 2006, **117**, 1–256.
- 75 J. Titiš and R. Boča, *Inorg. Chem.*, 2010, **49**, 3971–3973.
- 76 A. Packová, J. Miklovič, J. Titiš, M. Koman and R. Boča, *Inorg. Chem. Commun.*, 2013, **32**, 9–11.
- 77 J. Miklovič, A. Packová, P. Segla, J. Titiš, M. Koman, J. Moncol, R. Boča, V. Jorik, H. Krekuzska and D. Valigura, *Inorg. Chim. Acta*, 2015, **429**, 73–80.
- 78 J. Miklovič, P. Baran and R. Boča, *Nova Biotechnol. Chim.*, 2016, **15**, 182–189.
- 79 N. Farkašová, J. Černák, L. R. Falvello, M. Orendáč and R. Boča, *Acta Crystallogr., Sect. C: Struct. Chem.*, 2015, **71**, 252–257.
- 80 O. Kahn, *Molecular Magnetism*, VCH, Weinheim, 1993.

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Magneto-structural Studies in Double Chloro- and Pseudohalo-bridged Isomorphous Dinickel(II) Complexes

Moumita Patra,^[a] Paula Brandão,^[b] Adam P. Pikul,^[c] Sarmistha Adak,^[a, d] and Anangamohan Panja^{*[a, d]}

Four new complexes, $[\text{NiL}(\text{NO}_3)]\cdot\text{CH}_3\text{OH}$ (1), $[\text{Ni}_2\text{L}_2(\mu\text{-Cl})_2]$ (2), $[\text{Ni}_2\text{L}_2(\mu_{1,1}\text{-NCO})_2]$ (3) and $[\text{Ni}_2\text{L}_2(\mu_{1,1}\text{-N}_3)_2]$ (4) were synthesized from a tetradentate Schiff base (HL), prepared from the condensation reaction of *N,N*-dimethyldipropylenetriamine and 5-bromosalicylaldehyde. X-ray crystallography reveals that 2–4 are isostructural and isomorphous dinickel(II) compounds with bridging chloride or pseudohalides. All these three dinickel(II) complexes exhibit ferromagnetic interaction through bridging

chloride or pseudohalides and their coupling constants are in the order $4 > 2 > 3$, a replication of the average strength of exchange interactions found in such complexes characterised magnetically. Most importantly, compound 3 is a precious addition to the only four known examples of this family, and unprecedented high degree of structural and magnetic resemblances observed in 2–4 is the major achievement of the present work.

1. Introduction

Considerable attention has been directed towards the synthesis of di- and polynuclear transition metal complexes in recent years primarily because of their aesthetic structural diversity, relevance to the metalloenzymatic systems in biology^[1–2] and fascinating magnetic properties.^[3–8] In the field of molecular magnetism, Ni(II) ion is an automatic choice due to its large single-ion zero-field splitting, and as a consequence several di- and polynuclear Ni(II) complexes with interesting magnetic property have been developed.^[9–11] The investigation of magnetic properties of binuclear Ni(II) complexes and correlating them with the structures are quite significant to gain insight into the fundamental aspects of the magnetic interactions as well as to integrate the derived ideas into the large clusters or extended systems to develop molecule-based magnetic materials with predictable magnetic properties. A common strategy to prepare such complexes is the utilization of a multidentate ligand along with judicious choice of a bridging

ligand to transmit specific magnetic interactions between the paramagnetic metal centres.^[12] The pseudohalide ligand particularly azide ion is the most attractive bridging ligand because of its diverse bridging modes, end-on ($\mu_{1,1}$) and end-to-end ($\mu_{1,3}$) modes being the most common ones, leading to the rich magnetic property in such compounds.^[12] In contrast, the presence of two hetero-bridging atoms with polarizable π systems in other pseudohalides, namely cyanate, which can coordinate the metal ions through either of the heteroatoms, or both, are less versatile than the azide ion. Therefore, in contrast to the vast coordination chemistry of azido-bridged systems,^[13–20] both structurally and magnetically interesting compounds with other pseudohalides are limited.^[21] It is well known that halides and pseudohalides show great resemblances in several chemical and physical properties, but such similarity in coordination chemistry is quite limited, which is due to lack of coordinative versatility of one-atom halide ion compared to polyatomic pseudohalides. If pseudohalides bind the metal centre terminally or connect the metal centres through $\mu_{1,1}$ or $\mu_{1,1,1}$ bridging modes, then only it may have structural resemblance with halide analogues. Along with the rich coordination chemistry of azido-bridged complexes, sophisticated experimental and theoretical magneto-structural correlations are available for these complexes for better understanding the magnetic property of these systems, in which general tendency is that $\mu_{1,3}$ bridging mode exerts antiferromagnetic (AF) coupling, while $\mu_{1,1}$ coordination mode propagates ferromagnetic (F) exchange between the metal centres.^[13–21] Cyanate ion transmits magnetic interaction between the metal centres almost in similar way as that azide ion does but weakly and a scarcity of reports of such Ni(II) compounds is available in the literature to establish a sophisticated magneto-structural correlation for cyanato-bridged Ni(II) systems.^[19,21,24] When Ni(II) is five-coordinate, the magnetic coupling observed between the metal ions is usually dominantly AF in nature, while in octahedral or pseudo-

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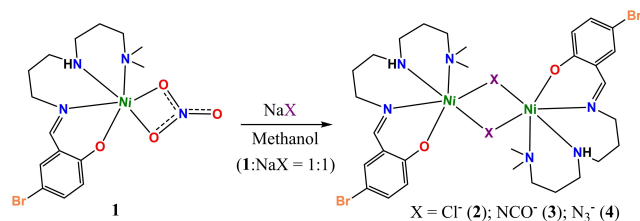
octahedral, the coupling is found generally ferromagnetic through chloro-bridge.^[25,26] Developing magneto-structural correlations by only experimental means is a very challenging task because that requires structurally similar or identical complexes with all but one governing parameter being identical. Several diazido- and dichloro-bridged dinickel(II) complexes have been both structurally and magnetically characterized, however for a particular ligand system no such structural and magnetic resemblance has yet been established. Therefore, working on a particular ligand system with varied bridging chloride and pseudohalides may provide us significant information of their communicating ability in these systems.

We observed previously that the Schiff base ligand with N₃O donor sites derived from condensation of salicylaldehyde with *N,N*-dimethyldipropylenetriamine is capable to stabilize ferromagnetically coupled dinickel(II) complexes with azide or cyanate ions in $\mu_{1,1}$ bridging fashion.^[21] Therefore, we anticipated that such organic ligands may be useful for the synthesis of ferromagnetically coupled dinickel(II) complexes with both bridging halides and pseudohalides with significant structural resemblance. Accordingly, in this present endeavour, a tetradentate Schiff base prepared from the condensation reaction of *N,N*-dimethyldipropylenetriamine and 5-bromosalicylaldehyde was reacted with nickel(II) nitrate in the presence of exogenous chloride, azide and cyanate ions and finally ended up with the isolation of isomorphous dinickel(II) complexes with bridging chloride and pseudohalides (Scheme 1). Herein, we report crystal structures and magnetic property of four new complexes, [NiL(NO₃)]·CH₃OH (1), [Ni₂L₂(μ-Cl)₂] (2), [Ni₂L₂(μ_{1,1}-NCO)₂] (3) and [Ni₂L₂(μ_{1,1}-N₃)₂] (4). All these dinickel(II) complexes show ferromagnetic coupling through bridging chloride and pseudohalides. Compound 3 is a precious addition to the only four known examples of this family, and unprecedented high degree of structural and magnetic resemblances found in 2–4 is the major achievement of the present work.

2. Results and Discussion

2.1. Syntheses and general characterizations

Schiff base ligand HL was synthesized following simple condensation reaction of *N,N*-dimethyldipropylenetriamine and 5-bromosalicylaldehyde in a 1:1 molar ratio in methanol. Subsequently, it was reacted with nickel(II) nitrate hexahydrate in methanol that resulted [NiL(NO₃)]·CH₃OH (1). High degree of solubility of complex 1 in common organic solvents like



Scheme 1. Schematic representation of the synthesized complexes.

alcohols and acetonitrile allowed us to use it as a precursor complex for the synthesis of other complexes. Accordingly, it was reacted with sodium salts of chloride, cyanate or azide, that afforded dark-green crystals of [Ni₂L₂(μ-Cl)₂] (2), [Ni₂L₂(μ_{1,1}-NCO)₂] (3) or [Ni₂L₂(μ_{1,1}-N₃)₂] (4), respectively, in high yields. All complexes were characterized by elemental analysis and by IR and UV-Vis spectroscopies methods and these data are given in the experimental section. All these complexes show a common feature of stretching vibration of the azomethine (C=N) bond of the Schiff base varying in the range 1623–1627 cm⁻¹. Additionally, the IR spectra of 3 and 4 exhibit strong and sharp bands at 2176 cm⁻¹ and 2049 cm⁻¹, respectively, characteristic of the asymmetric stretching vibration of the bridging cyanate and azide ions, respectively, typical for end-on cyanate and azide bridged transition metal complexes. The UV-Vis spectra of 1–4 in the solid state and in methanol are eventually similar and the spectra are displayed in Figure S1. The UV-Vis spectra reveal the presence of two well-resolved bands in the range 374–381 and 600–681 nm. The very intense former band can be assigned to phenolato-to-nickel(II) charge transfer transition, whereas the band observed at 639 nm could be assigned to a ³A_{2g}→³T_{1g}(F) as expected for octahedral nickel(II) complexes. Additional band for complex 1 is observed at around 930 nm, which is assigned to ³A_{2g}→³T_{2g} and for other complexes it is not clearly visible being shifted to NIR region. However, for all complexes the higher energy ³A_{2g}→³T_{1g}(P) band is obscured by the strong charge transfer transition.

3. Description of crystal structures

Neutral complex [NiL(NO₃)]·CH₃OH (1) crystallizes in the monoclinic space group *P*2₁/*n*. The crystal structure of 1 with atom numbering scheme is depicted in Figure 1 and the selected bond parameters are given in Table 1. The Ni(II) ion in 1 is hexacoordinated with distorted octahedral geometry, being bonded with N₃O donor sites from the deprotonated Schiff base ligand together with a bidentate nitrate ion. The Ni–O distances of the coordinated nitrate are 2.141(1) and 2.247(2) Å, with their difference Δ*d* being < 0.3 Å justify its coordination to

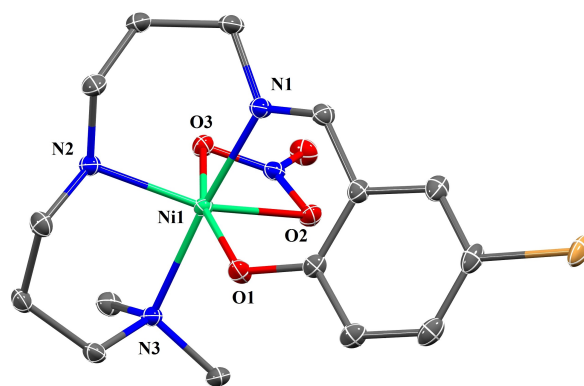


Figure 1. Crystal structure of 1 showing atom numbering scheme. The ellipsoids are drawn at 30% probability level and hydrogen atoms and solvent methanol have been omitted for clarity.

Table 1. Selected bond distances (Å) for 1–4.

Bond	1	2	3	4
Ni(II)–N(imine)	2.052(2)	2.060(2)	2.077(2)	2.069(2)
Ni(II)–N(secondary amine)	2.069(2)	2.125(2)	2.097(2)	2.094(2)
Ni(II)–N(tertiary amine)	2.138(2)	2.190(2)	2.120(2)	2.208(2)
Ni(II)–O(phenolate)	1.986(1)	2.011(2)	2.006(2)	2.006(2)
Ni(II)–X ^[a]	2.141(1) 2.247(2)	2.507(1) 2.467(1) ^[b]	2.225(2) 2.202(2) ^[b]	2.122(2) 2.173(2) ^[b]

[a] X = O(nitrate) for 1, Cl for 2, N(azide) for 3 and N(cyanate) for 4; [b] Symmetry code: $-x, -y, -z$.

the metal centre as a bidentate fashion rather than anisobidentate one.^[27,28] But significantly low bite angle of the nitrate ion of $58.90(5)^\circ$ is the main reason behind the significant distortion from the ideal octahedral geometry.^[29,30] All the nitrogen atoms from the Schiff base ligand occupy one meridional position of Ni(II) centre in 1, while three oxygen atoms, one from phenolate group of the Schiff base and two from bidentate nitrate ion, occupy other meridional position. The Ni–N distances of imine, secondary amine and tertiary amine and the Ni–O distance of phenolato-O of the Schiff base ligand in 1 are 2.052(2), 2.069(2), 2.1378(2) and 1.986(1) Å, respectively, which fall in line with reported Ni(II) complexes with similar coordination environments.^[13–20] The Br atom of the Schiff base ligand was solved considering the disorder model with about 0.66/0.34 occupancies over two sites with usual C–Br distances of 1.899(3) and 1.916(6) Å, respectively. The structure of 1 in the solid state is mainly stabilized by hydrogen bonding interactions as displayed in Figure S2. The phenolate oxygen is connected with solvent methanol molecule through hydrogen bond of donor-acceptor distance of 2.866 Å, while the secondary amine group forms an intermolecular hydrogen bond with non-coordinated oxygen atom of the nitrate group from the neighbouring molecule with donor-acceptor distance of 3.059 Å, leading to a hydrogen bonded zig-zag chain running along the crystallographic *b* axis.

Complexes $[\text{Ni}_2\text{L}_2(\mu\text{-Cl})_2]$ (2), $[\text{Ni}_2\text{L}_2(\mu_{1,1}\text{-NCO})_2]$ (3) and $[\text{Ni}_2\text{L}_2(\mu_{1,1}\text{-N}_3)_2]$ (4) are isostructural and isomorphous compounds, and they crystallize in the monoclinic unit cell with space group $P2_1/c$. These centro-symmetrical neutral complex molecules are formed by doubly bridged chloride or pseudohalide ions, and the structures of these compounds are depicted in Figures 2–4, respectively, and their important bond parameters are given in Table 1. The Ni(II) centres in these complexes are hexacoordinated with slightly distorted octahedral geometry in which, in addition to doubly bridging chloride or pseudohalide ions, the metal centres are bonded to three N donor atoms and one phenolato-O atom of the deprotonated Schiff base ligand. The bridging chloride or pseudohalide ions form the common edge within the dinuclear units, leading to edge-sharing bioctahedral structures (Figure 3). The Ni–($\mu\text{-Cl}$), Ni–N($\mu_{1,1}\text{-NCO}$) and Ni–N($\mu_{1,1}\text{-N}_3$) bond lengths of 2.467(1) and 2.507(1) Å, 2.202(2) and 2.225(2) Å, and 2.173(2) and 2.122(2) Å

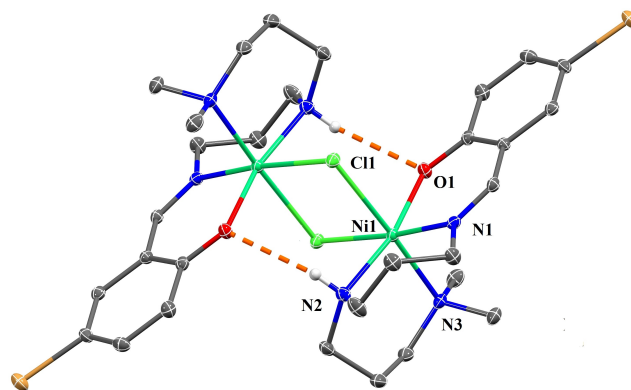


Figure 2. Crystal structure of 2 showing atom numbering scheme and intramolecular hydrogen bonds. The ellipsoids are drawn at 30% probability level.

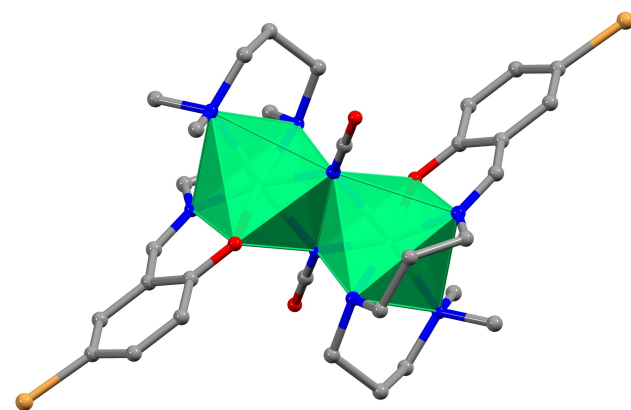


Figure 3. Crystal structure of 3 showing edge sharing bioctahedral structure and hydrogen atoms have been omitted for clarity.

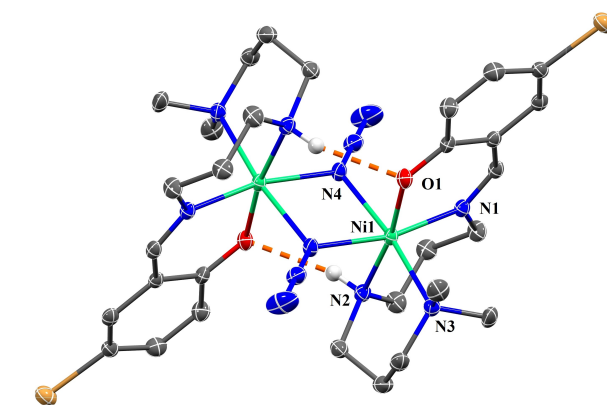


Figure 4. Crystal structure of 4 showing selected atom numbering scheme and intramolecular hydrogen bonding interaction. The ellipsoids are drawn at 30% probability level.

in complexes 2–4, respectively, justify that the bridging region is slightly asymmetric, accounting slight distortion around Ni(II) ions in these systems. Unlike 1, all the nitrogen atoms of the

triamine part of the deprotonated Schiff base coordinate Ni(II) ion in the facial configuration, while the remaining facial position is occupied by phenolato-O atom of the Schiff base together with two bridging chloride ions in **2** and two nitrogen atoms of two bridging cyanate or azide ions in **3** and **4**, respectively. The different coordination modes of the triamine part of the ligand, meridional (in **1**) and facial (in **2–4**) justify the flexibility and adoptability of *N,N*-dimethyldipropyltriamine in these systems, a key feature for being a good ligand in coordination chemistry. The Ni–N(imine), Ni–N (secondary amine) and Ni–N (tertiary amine) vary in the range 2.060(2)–2.077(2), 2.094(2)–2.125(2) and 2.120(2)–2.208(2) Å for **2–4**, respectively (Table 1), which are comparable to analogous

complexes reported in the literature.^[21] The centre of symmetry enforces the central Ni(μ-Cl)₂Ni (in **2**) and Ni(μ-N)₂Ni (in **3** and **4**) core structures to be perfectly planar. The bridging angles are 92.27(2), 98.47(2) and 101.99(1)° with metal-metal separations of 3.587(1), 3.274(1) and 3.338(1) Å for **2–4**, respectively, which are comparable to those reported earlier.^[13–26,31–33] Although handful examples of chloride and end-on azide bridged dinickel(II) complexes are known, complex **3** could be a precious addition in growing family of this type of complexes of totalling only five.^[19,21,24] Being isomorphous compounds, they display similar types of noncovalent interaction, one of such notable interaction is the intramolecular hydrogen bonding interaction involving secondary amine of a Schiff base ligand and phenolate oxygen atom of other Schiff base ligand in the dimeric unit with donor-acceptor distances in the range 2.992 to 3.180 Å.

It is interesting to note that all the structural parameters except at bridging region are almost identical in these complexes. The Ni–(μ-Cl) bond length in **2** is significantly longer than Ni–(μ-N) bond distances in bridging azide and cyanate ions in **3** and **4** as expected. Furthermore, the bridging angle in **3** is close to the orthogonal, while it is more obtuse in azide complex and an intermediate impression has been observed in the cyanate bridged one, resulting in a significant dissimilarity in bridging region. Remarkably, the system has overcome all these divergences and has crystallized them in the identical crystallographic parameters, which is rarely achieved in coordination chemistry and for dihalide and dipseudohalide bridged systems, it was not reported earlier.

Table 2. Selected structural and magnetic data of doubly end-on cyanato bridged Ni(II) dimers (following $\hat{H} = -2J\hat{S}_1\hat{S}_2$ convention).^[a]

Compounds	<i>J</i> (cm ^{−1})	<i>D</i> (cm ^{−1})	<i>g</i>	M–N (Å)	M–N–M (°)	Refs.
[Ni ₂ (L ⁴) ₂ (μ _{1,1} -NCO) ₂](ClO ₄) ₂	+1.7	+3.6	2.23	2.125, 2.090	94.4, 95.8	[19]
[Ni ₂ (L ⁵) ₂ (μ _{1,1} -NCO) ₂](ClO ₄) ₂	+2.8	+3.6	2.23	2.099, 2.115	95.33, 95.79	[19]
[Ni ₂ (terpy) ₂ (μ _{1,1} -NCO) ₂ (H ₂ O) ₂](PF ₆) ₂	+	−12.32	2.23	2.044, 2.195	97.7	[24]
[Ni ₂ L ⁶ ₂ (μ _{1,1} -NCO) ₂]	+6.85	+7.18	2.19	2.107, 2.244, 2.115, 2.280	97.84, 98.74	[21]
[Ni ₂ L ₂ (μ _{1,1} -NCO) ₂] (3)	+5.31	+5.00	2.19	2.225, 2.201	98.47	This work

[a] terpy = terpyridine; L⁴ = [*N,N'*-bis(2-pyridinylmethylene)]propane-1,3-diamine; L⁵ = *N,N'*-bis(pyridin-2-yl)benzylidene]ethane-1,2-diamine; L⁶ = a tetradentate N₄ donor ligand.

Table 3. Selected structural and magnetic data of doubly end-on cyanato bridged Ni(II) dimers (following $\hat{H} = -2J\hat{S}_1\hat{S}_2$ convention)^[b]

Compounds	<i>J</i> (cm ^{−1})	<i>D</i> (cm ^{−1})	<i>g</i>	M–N (Å)	M–N–M (°)	Refs.
Ni ₂ Cl ₂ (TTF ⁺) ₂ [(I ₃) ₄ (I ₂) ₃ ·(H ₂ O) ₂ ·(C ₄ H ₈ O) ₃]	5.0	−16	2.26	2.365, 2.391	90.5, 91.8	47
[[Ni(ATsc)(MeOH)] ₂ (μ-Cl) ₂]Cl ₂	5.7	−	2.29	2.348, 2.396	91.5	48
[[Ni(ATHAc)(H ₂ O)] ₂ (μ-Cl) ₂]Cl ₂	6.6	−	2.30	2.327, 2.471	92.7	48
[[Ni(TPA)Cl] ₂](ClO ₄) ₂ ·2HNEt ₃ ClO ₄	7.6	+0.51	2.07	2.365, 2.507	92.63	49
(C ₃ H ₆ N ₂ H ₆) ₂ [Ni ₂ Cl ₂ (H ₂ O) ₂]	8.13	−3.4	−	2.430, 2.459	95.05	50
[[Ni(eg) ₂ Cl] ₂]Cl ₂	9.0	−	−	2.383	93.03	51
[Ni ₂ (en) ₄ Cl ₂]Cl ₂	6.65	−3.6	2.21	2.461, 2.551	96.6	52
	4.83	−4.78	2.24			53
	10.5	+11.1	2.12			54
	3.48	+9.7	2.25			55
[[Ni(en) ₂ Cl] ₂](ClO ₄) ₂	8.9	−4.2	2.18	2.461, 2.512	95.4	52
[[Ni(en) ₂ Cl] ₂](Ph ₄ B) ₂	9.5	−7.7	2.16	2.403, 2.503	95.6	52,56
[[Ni(TPA)Cl] ₂](ClO ₄) ₂ ·H ₂ O	14.59	−	2.02	2.363, 2.503	92.7	57
[Ni ₂ (bipy) ₂ (μ-Cl) ₂ Cl ₂ (H ₂ O) ₂]	8.4	+3.5	2.09	2.396, 2.405	91.56	58
[[Ni(L ⁷) ₂ (μ-Cl) ₂](ClO ₄) ₂]	9.95	+12	2.06	2.381, 2.535	93.52	26,59
[Ni ₂ (H ₂ L ⁸) ₂ Cl ₂ ·4H ₂ O·2 C ₄ H ₈ O ₂]	7.6	−	2.12	2.393, 2.421	87.07	60
[Ni ₂ (H ₃ L ⁹) ₂ Cl ₂]Cl ₂	7.17	−7.5	2.35	2.433, 2.353	93.50	61
[Ni ₂ L ¹⁰ ₂ Cl ₂]	8.90	−7.52	−	2.416, 2.511	94.34	62
[Ni ₂ L ₂ (μ-Cl) ₂] (2)	+6.84	+5.51	2.21	2.507, 2.467	92.27	This work

[b] TTF = 4,5-bis(2-pyridylmethylsulfanyl)-4',5'-ethylenedithiotetrathiafulvene; ATsc = 2-acetyl-2-thiazoline semicarbazone; ATHAc = 2-acetyl-2-thiazoline acetylhydrazone; TPA = tris-(2-pyridylmethyl)amine; eg = ethylene glycol; en = ethylenediamine; bipy = 2,2'-bipyridine; L⁷ = 3,11-dithia-7,17-diazabicyclo[11.3.1]; heptadeca-1(17),13,15-triene; H₂L⁸ = bis[(pyridin-2-yl)-1,2,4-triazol-3-yl]methane; H₃L⁹ = triethanolamine; L¹⁰ = 1-(benzimidazolyl-2-methyl)-1,4,7-triazacyclononane.

3.1. Magnetic properties

The temperature dependence of the magnetic properties of dinuclear complexes **2–4** as χ_M and $\chi_M T$ product vs. T plots (χ_M being the molar magnetic susceptibility per dimer) under a constant magnetic field of 1.0 kOe in the temperature range 2–

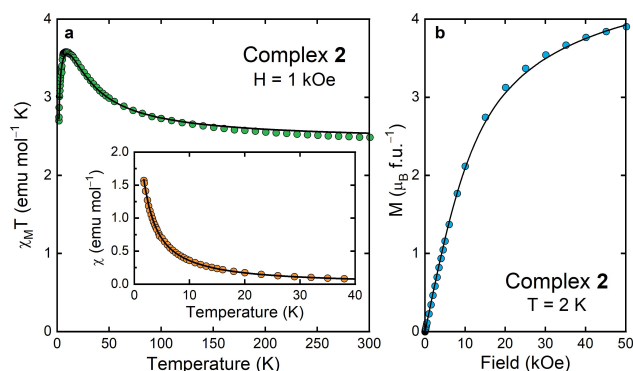


Figure 5. Magnetic data for **2**. (a) Thermal dependence of χ_M and $\chi_M T$ product measured at 1.0 kOe dc field. (b) Magnetisation data at 2 K. Symbols and solid lines represent experimental and best fitted data.

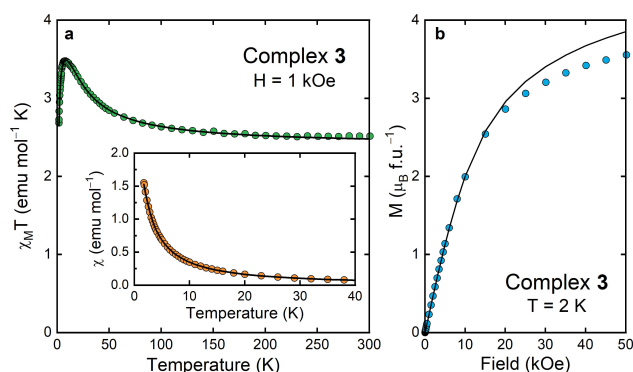


Figure 6. Magnetic data for **3**. (a) Thermal dependence of χ_M and $\chi_M T$ product measured at 1.0 kOe dc field. (b) Magnetisation data at 2 K. Symbols and solid lines represent experimental and best fitted data.

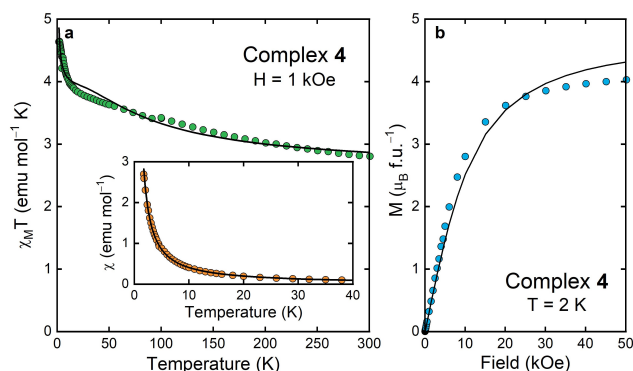


Figure 7. Magnetic data for **4**. (a) Thermal dependence of χ_M and $\chi_M T$ product measured at 1.0 kOe dc field. (b) Magnetisation data at 2 K. Symbols and solid lines represent experimental and best fitted data.

300 K and the molar magnetization as a function of applied dc magnetic field (M/μ_B f.u.^{−1} vs. H) are shown in Figures 5–7, respectively. The $\chi_M T$ product at room temperature for **2–4** is ca. 2.48, 2.51 and 2.80 emu mol^{−1} K, respectively, which are slightly larger than that expected for two magnetically non-interacting Ni(II) ions with $S=1$ (2.0 emu mol^{−1} K), which is mainly due to unquenched orbital angular momentum of Ni(II) ions. The $\chi_M T$ increases continuously with decreasing temperature reaching a maximum of 3.57 emu mol^{−1} K at 9.0 K for **2** and 3.47 emu mol^{−1} K at 8.0 K for **3** and then $\chi_M T$ decreases sharply to attain a value ca. 2.69 emu mol^{−1} K at 1.8 K. This feature is characteristic for an intramolecular ferromagnetic interaction between two Ni(II) ions with the influence of intermolecular interactions and/or zero-field splitting (ZFS) of ground state ($S=2$), manifested at low temperature. Almost similar feature has been observed for **4** but without noticeable decrease of $\chi_M T$ value even at very low temperature, indicating dominant ferromagnetic exchange interaction between these spin carriers. The high-temperature χ_M^{-1} data obeys the Curie-Weiss law and the linear fitting of the same above 100 K yielded Weiss constant (θ_p) values of 13.3(3), 6.3(6) and 29(2) K for **2–4**, respectively, with reasonable Curie constant values, which further indicate that the magnetic interaction between Ni(II) ions is ferromagnetic in nature (Figures S3–S5). A full-matrix diagonalization approach assuming isotropic exchange coupling Hamiltonian ($-2\hat{S}_1\hat{S}_2$), Zeeman effect (g_{Ni} , average), axial zero-field splitting (D), and intermolecular interaction (zJ') was employed to analyse further the magnetic data using *PHI* program.^[34] The simultaneous simulation of $\chi_M T$ and magnetisation data leads to good agreement between the calculated and observed data (Figures 5 and 7), and the best fittings afforded the following set of parameters: $J=6.84(10)$ cm^{−1}, $g_{Ni}=2.21(0.1)$, $D=5.51(2)$ cm^{−1} and $zJ'=0.003(4)$ cm^{−1} for complex **2**; $J=5.31(4)$ cm^{−1}, $g_{Ni}=2.19(0.1)$, $D=5.00(6)$ cm^{−1} and $zJ'=0.001(8)$ cm^{−1} for complex **3** and $J=18.8(7)$ cm^{−1}, $g_{Ni}=2.27(0.3)$, $D=3.31(14)$ cm^{−1} and $zJ'=0.038(1)$ cm^{−1} for complex **4**.

As we have stated earlier that for a particular ligand system none of the previous report deals with the structural and magnetic studies involving doubly bridged halide and pseudo-halide systems, so it is our privilege to analyse the magneto-structural data to gain insight into the magnetic properties in these systems. Although the ZFS parameter D and intermolecular coupling constant zJ' strongly interact with each other, thereby their overestimation cannot be ignored, yet the D values found in these complexes are comparable and fall in the region where it is clustered with several reported values even with same sign. However, these two parameters are poorly coupled with intramolecular exchange coupling constant J , leaving the exchange coupling constant J almost unaffected. The significantly stronger exchange interaction between two Ni(II) centres in **4** than other two complexes is well known, but the scenario is not so clear for chloro- and cyanato- bridged systems as their coexistence is one of the most scarcity in coordination chemistry. Our data provide us information that chloride ($J=6.84(10)$ cm^{−1}) is better magnetic coupler than cyanate ion ($J=5.31(4)$ cm^{−1}). If we look at the reported results,

it is seen that J values (considering $\hat{H} = -2J\hat{S}_1\hat{S}_2$) vary from 1.91 to 43.9 cm⁻¹ in doubly $\mu_{1,1}$ -azido-bridged dinickel(II) complexes,^[13–20,31–33,35–46] while the ranges are 1.7 to 6.85 cm⁻¹^[19,21,24] and 3.48 to 14.59 cm⁻¹^[47–62] for doubly $\mu_{1,1}$ -cyanato-bridged and doubly μ -chloro-bridged analogues, respectively, and the trend of their average values is exactly replicated in the present study, that help us to conclude that $\mu_{1,1}$ -azido is superior magnetic exchanger among them, followed by μ -chloro and $\mu_{1,1}$ -cyanato.

It is well known that the sign and magnitude of the exchange coupling constant (J) between the paramagnetic centres is governed by several structural parameters. Among them, the bridging angle plays the most crucial role in determining the overall magnetic interactions. Ruiz et al. theoretically established that doubly $\mu_{1,1}$ -azido-bridged dinuclear Ni(II) complexes exhibit ferromagnetic interactions throughout the Ni–N–Ni angles (θ) ranging from 80° to 115°, with J values increasing as the angle increases, reaching a maximum approximately at 104°, and then decreases further with increasing θ .^[22,23] In fact, all the reported $\mu_{1,1}$ -azido-bridged dinickel(II) systems exhibit ferromagnetic coupling with only one exception where a very low bridging angle of 90.4° transmits AF interaction between Ni(II) centres.^[20] The Ni–N–Ni angle found in **4** is 101.99(1)°, which falls within the range where strong ferromagnetic interaction prevail between two Ni(II) ions as suggested by the theoretical study, and therefore J value (18.8(7) cm⁻¹) found in **4** is quite reasonable. However, although a large number of $\mu_{1,1}$ -azido-bridged dinickel(II) systems are known, unlike theoretical prediction, the experimental data do not show clear relationship with Ni–N–Ni angles as a small variation of Ni–N–Ni angles in the narrow range ca. 98°–103.9°, show a large variation of the J values from 1.91 to 43.9 cm⁻¹.^[13–20,31–33,35–46] This is confirmed by the fact that the present bridging angle of 101.99(1)° is very close to the value of 101.0° in $[\text{Ni}_2(\text{L}^1)_2(\mu_{1,1}\text{-N}_3)_2(\text{N}_3)_2]$ (L^1 = a tridentate quinoline-based ligand)^[33] and 101.79° (average value) in $[\text{Ni}_2(\text{L}^2)_2(\text{N}_3)_2(\mu_{1,1}\text{-N}_3)_2]\cdot\text{CH}_3\text{OH}$ (L^2 = *N,N*-dimethyl-*N'*-(pyrid-2-ylmethyl)-ethylenediamine),^[63] but show quite different J values of 6.1 and 1.91 cm⁻¹, respectively. In contrast, the magnetic interaction of the present complex is nicely agreed with other reported results that displayed very similar bridging angles of 101.6° in $[\text{Ni}_2(\text{terpy})_2(\text{N}_3)_2(\mu_{1,1}\text{-N}_3)_2]\cdot\text{H}_2\text{O}$ ^[14] and 101.4° (average value) in $[\text{Ni}_2(\text{L}^3)_2(\text{N}_3)_2(\mu_{1,1}\text{-N}_3)_2]$ (L^3 = a multidentate ligand)^[40] with J values of 22.8 and 20.96 cm⁻¹, respectively. Notably, the present J value significantly differs from our previous result with similar ligand where salicylaldehyde was used instead of 5-bromosalicylaldehyde, in which average bridging angle and J value are 101.35° and 10 cm⁻¹, respectively.^[21] Slightly higher bridging angle together with shorter average M–N($\mu_{1,1}$ -N₃) bond distance of 2.148 Å in **4** compared to 2.169 Å in the previous reported complex, could justify the stronger coupling constant value in the present complex.

In contrast to $\mu_{1,1}$ -N₃ bridged Ni(II) complexes, only four doubly $\mu_{1,1}$ -NCO bridged dinickel(II) complexes are known. The magnetic and crystallographic data of these five complexes are presented in Table 2, which shows that J values span in a narrow range 1.7 to 6.85 cm⁻¹.^[19,21,24] The sign and magnitude

of J value of 5.31(4) cm⁻¹ in **4** is again reasonable for such complexes. Interestingly, a general trend can be found in which J value increases with increase in bridging angles, similar to theoretical prediction that has been done for azide analogues. As shown in Figure 8, the value found in our earlier report is slightly higher among this series,^[21] that prompted us for further inspection of the structural parameters and it is seen that in the present case though the bridging angle is slightly higher than the previous one, the average bond length in the bridging region found in reverse order, that may the reason for such difference.

Previous studies on doubly chloro-bridged Ni(II) dimers showed that the magnetic interaction are predominantly ferromagnetic if the geometry of the metal centre is octahedral (Table 3),^[26,47–62] and the strength of the coupling varies from 3.48 to 14.59 cm⁻¹, with only one exception where AF interaction is operative between the metal centres with high degree of distortion of Ni(II) centres from the octahedral geometry.^[64] Tamayo et al. have established that the strength of the ferromagnetic coupling become weaker with increase of the bridging angle from ideal value of 90°.^[26] The value of bridging angle in **2** is 92.27(2)°, so it is in good agreement with the ferromagnetic interaction observed in **2**. However, the experimental data do not show clear relationship between the strength of the coupling and the bridging angles, leaving an unsolved challenge which will require consideration of more than one structural parameter at once.

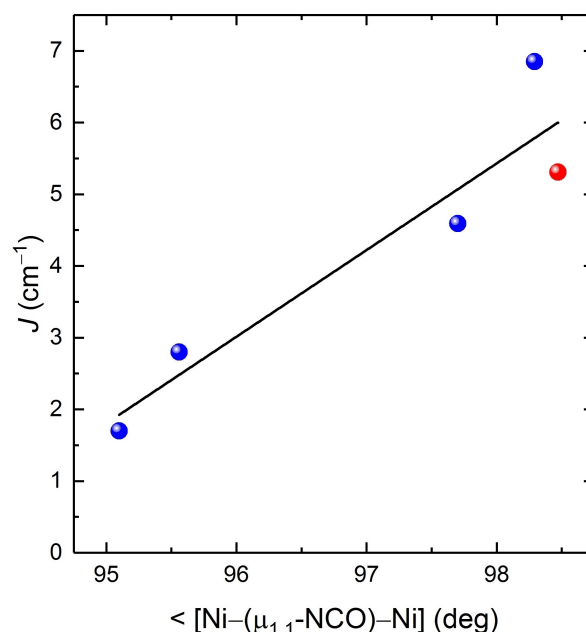


Figure 8. Magneto-structural correlation data showing dependence of J values with Ni– $\mu_{1,1}$ NCO–Ni bridging angles. The red symbol corresponds to the compound in this work.

4. Conclusions

Four new complexes, $[\text{NiL}(\text{NO}_3)]\cdot\text{CH}_3\text{OH}$ (**1**), $[\text{Ni}_2\text{L}_2(\mu\text{-Cl})_2]$ (**2**), $[\text{Ni}_2\text{L}_2(\mu_{1,1}\text{-NCO})_2]$ (**3**) and $[\text{Ni}_2\text{L}_2(\mu_{1,1}\text{-N}_3)_2]$ (**4**) were synthesized from a tetradentate N_3O -donor Schiff base (HL), derived from the condensation reaction of *N,N*-dimethyldipropylenetriamine and 5-bromosalicylaldehyde. X-ray crystallography reveals that complexes **2–4** are isostructural and isomorphous dinickel(II) compounds with doubly bridging chloride and pseudohalides, and the nickel(II) centres are in octahedral coordination environments. Such structural coincidence in halide and pseudihalide bridged complexes for a particular ligand system is rare in coordination chemistry and is not seen earlier in doubly halide and pseudohalide bridged nickel(II) systems. All these three dinickel(II) complexes exhibit ferromagnetic interaction through bridging chloride or pseudohalides with ferromagnetic coupling constant J are 6.84(10), 5.31(4) and 18.8(7) cm^{-1} for **2–4**, respectively, suggesting that azide ion is superior magnetic coupler among them followed by chloride and cyanate ions, a replication of the average strength of exchange interactions found in such complexes characterised magnetically. Most importantly, compound **3** is a precious addition to the only four known examples of this family, and unprecedented high degree of structural and magnetic resemblances of **2–4** is the major achievement of the present work.

Deposition Numbers 2022118 (for **1**), 2022119 (for **2**), 2022120 (for **3**), and 2022121 (for **4**) contain the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service www.ccdc.cam.ac.uk/structures.

Supporting Information Summary

Experimental, crystallographic data, crystal packing of **1**, UV-vis spectral plots and Curie-Weiss plots for **2–4**.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords: Dinickel(II) complexes · chloride and pseudohalide bridged complexes · isostructural and isomorphous compounds · magnetic study · Magneto-structural correlations

- [5] M. Andruh, *Chem. Commun.* **2018**, 54, 3559–3577.
- [6] S. Accorsi, A.-L. Barra, A. Caneschi, G. Chastanet, A. Cornia, A. C. Fabretti, D. Gatteschi, C. Mortalò, E. Olivieri, F. Parenti, P. Rosa, R. Sessoli, L. Sorace, W. Wernsdorfer, L. Zobbi, *J. Am. Chem. Soc.* **2006**, 128, 4742–4755.
- [7] H.-L. Sun, Z.-M. Wang, S. Gao, *Coord. Chem. Rev.* **2010**, 254, 1081–1100.
- [8] M. Sarkar, R. Clérac, C. Mathonière, N. G. R. Hearn, V. Bertolasi, D. Ray, *Inorg. Chem.* **2011**, 50, 3922–3933.
- [9] J. Ruiz, A. J. Mota, A. Rodríguez-Diéguez, I. Oyarzabal, J. M. Secob, E. Colacio, *Dalton Trans.* **2012**, 41, 14265–14273.
- [10] L. Botana, J. Ruiz, A. J. Mota, A. Rodríguez-Diéguez, J. M. Seco, I. Oyarzabal, E. Colacio, *Dalton Trans.* **2014**, 43, 13509–13524.
- [11] R. Boča, *Coord. Chem. Rev.* **2004**, 248, 757–815.
- [12] A. Escuer, J. Esteban, S. P. Perlepes, T. C. Stammatos, *Coord. Chem. Rev.* **2014**, 275, 87–129.
- [13] S. S. Massoud, F. R. Louka, Y. K. Obaid, R. Vicente, J. Ribas, R. C. Fischer, F. A. Mautner, *Dalton Trans.* **2013**, 42, 3968–3978.
- [14] M. G. Barandika, R. Cortés, L. Lezama, M. K. Urtiaga, M. I. Arriortua, T. Rojo, *J. Chem. Soc. Dalton Trans.* **1999**, 2971–2976.
- [15] P. Mukherjee, M. G. B. Drew, C. J. Gómez-García, A. Ghosh, *Inorg. Chem.* **2009**, 48, 5848–5860.
- [16] S. K. Dey, N. Mondal, M. S. E. Fallah, R. Vicente, A. Escuer, X. Solans, M. Font-Bardía, T. Matsushita, V. Gramlich, S. Mitra, *Inorg. Chem.* **2004**, 43, 2427–2434.
- [17] S. Sarkar, A. Mondal, M. S. E. Fallah, J. Ribas, D. Chopra, H. Stoeckli-Evans, K. K. Rajak, *Polyhedron*, **2006**, 25, 25–30.
- [18] S. Nandi, D. Bannerjee, J.-S. Wu, T.-H. Lu, A. M. Z. Slawin, J. D. Woollins, J. Ribas, C. Sinha, *Eur. J. Inorg. Chem.* **2009**, 3972–3981.
- [19] M. Habib, T. K. Karmakar, G. Aromí, J. Ribas-Ariño, H.-K. Fun, S. Chantrapromma, S. K. Chandra, *Inorg. Chem.* **2008**, 47, 4109–4117.
- [20] P. Chaudhuri, R. Wagner, S. Khanra, T. Weyhermüller, *Dalton Trans.* **2006**, 4962–4968.
- [21] A. Panja, N. C. Jana, S. Adak, P. Brandão, L. Dlhán, J. Titíš, R. Boča, *New J. Chem.* **2017**, 41, 3143–3153.
- [22] E. Ruiz, J. Cano, S. Alvarez, P. Alemany, *J. Am. Chem. Soc.* **1998**, 120, 11122–11129.
- [23] G. Manca, J. Cano, E. Ruiz, *Inorg. Chem.* **2009**, 48, 3139–3144.
- [24] M. I. Arriortua, R. Cortes, J. L. Mesa, L. Lezama, T. Rojo, G. Villeneuve, *Transition Met. Chem.* **1988**, 13, 371–374.
- [25] G. A. van Albada, J. J. A. Kolnaar, W. J. J. Smeets, Anthony L. Spek, J. Reedijk, *Eur. J. Inorg. Chem.* **1998**, 1337–1341.
- [26] A. Tamayo, L. Escriche, C. Lodeiro, J. Ribas-Ariño, J. Ribas, B. Covel, J. Casabó, *Inorg. Chem.* **2006**, 45, 7621–7627.
- [27] G. Parkin, *Chem. Rev.* **2004**, 104, 699–767.
- [28] A. Panja, T. Matsuo, S. Nagao, S. Hirota, *Inorg. Chem.* **2011**, 50, 11437–11445.
- [29] R. Biswas, S. Giri, S. K. Saha, A. Ghosh, *Eur. J. Inorg. Chem.* **2012**, 2916–2927.
- [30] P. Mukherjee, M. G. B. Drew, C. J. Gómez-García, A. Ghosh, *Inorg. Chem.* **2009**, 48, 5848–5860.
- [31] A. Bhattacharyya, P. K. Bhaumik, M. Das, A. Bauzá, P. P. Jana, K. Harms, A. Frontera, S. Chattopadhyay, *Polyhedron*, **2015**, 101, 257–269.
- [32] M. Č. Romanović, B. R. Čobeljić, A. Pevec, I. Turel, V. Spasojević, A. A. Tsaturyan, I. N. Shcherbakov, K. K. Anđelković, M. Milenković, D. Radanović, M. R. Milenković, *Polyhedron*, **2017**, 128, 30–37.
- [33] P. Ghorai, P. Brandão, S. Benmansour, C. J. Gómez García, A. Saha, *Polyhedron*, **2020**, 188, 114708.
- [34] N. F. Chilton, R. P. Anderson, L. D. Turner, A. Soncini, K. S. Murray, *J. Comput. Chem.* **2013**, 34, 1164–1175.
- [35] P. P. Chakrabarty, S. Giri, D. Schollmeyer, H. Sakiyama, M. Mikuriya, A. Sarkar, S. Saha, *Polyhedron*, **2015**, 89, 49–54.
- [36] H.-Z. Kou, S. Hishiy, O. Sato, *Inorg. Chim. Acta*, **2008**, 361, 2396–2406.
- [37] S. Sarkar, A. Mondal, A. Banerjee, D. Chopra, J. Ribas, K. K. Rajak, *Polyhedron*, **2006**, 25, 2284–2288.
- [38] S. Sarkar, A. Datta, A. Mondal, D. Chopra, J. Ribas, K. K. Rajak, S. M. Sairam, S. K. Pati, *J. Phys. Chem. B*, **2006**, 110, 12–15.
- [39] X.-J. Lin, Z. Shen, Y. Song, H.-J. Xu, Y.-Z. Li, X.-Z. You, *Inorg. Chim. Acta*, **2005**, 358, 1963–1969.
- [40] S. Sain, S. Bid, A. Usman, H.-K. Fun, G. Aromí, X. Solans, S. K. Chandra, *Inorg. Chim. Acta*, **2005**, 358, 3362–3368.

- [1] S. W. Ragsdale, *J. Biol. Chem.* **2009**, 284, 18571–18575.
- [2] M. A. Halcrow, G. Christou, *Chem. Rev.* **1994**, 94, 2421–2481.
- [3] G. A. Craig, M. Murrie, *Chem. Soc. Rev.* **2015**, 44, 2135–2147.
- [4] G. E. Kostakis, A. M. Ako, A. K. Powell, *Chem. Soc. Rev.* **2010**, 39, 2238–2271.

- [41] A. Escuer, R. Vicente, M. S. E. Fallah, X. Solans, M. Font-Bardia, *Inorg. Chim. Acta*. **1996**, 247, 85–91.
- [42] R. Cortes, J. I. Ruiz de Larramendi, L. Lezama, T. Rojo, K. Urtiaga, M. I. Arriortua, *J. Chem. Soc. Dalton Trans.* **1992**, 2723–2728.
- [43] R. Vicente, A. Escuer, J. Ribas, M. S. E. Fallah, X. Solans, M. Font-Bardia, *Inorg. Chem.* **1993**, 32, 1920–1924.
- [44] J. Ribas, M. Monfort, C. Diaz, C. Bastos, X. Solans, *Inorg. Chem.* **1994**, 33, 484–489.
- [45] A. Escuer, R. Vicente, J. Ribas, X. Solans, *Inorg. Chem.* **1995**, 34, 1793–1798.
- [46] A. Donmez, G. Oylumluoglu, M. B. Coban, C. Kocak, M. Aygun, H. Kara, *J. Mol. Struct.* **2017**, 1149, 569–575.
- [47] S. Liu, C. Ambrus, S. Dolder, A. Neels, S. Decurtins, *Inorg. Chem.* **2006**, 45, 9622–9624.
- [48] E. Viñuelas-Zahinos, F. Luna-Giles, P. Torres-García, A. Bernalte-García, *Polyhedron*, **2009**, 28, 1362–1368.
- [49] B. Tong, S.-C. Chang, E. E. Carpenter, C. J. O'Connor, J. O. Lay Jr, R. E. Norman, *Inorg. Chim. Acta*, **2000**, 300–302, 855–861.
- [50] C. P. Landee, R. D. Willett, *Inorg. Chem.* **1981**, 20, 2521–2525.
- [51] D. Knetsch, W. L. Groeneveld, *Inorg. Nucl. Chem. Lett.* **1976**, 12, 27–32.
- [52] Y. Journaux, O. Kahn, *J. Chem. Soc. Dalton Trans.* **1979**, 1575–1580.
- [53] R. Herchel, R. Boča, J. Krzystek, A. Ozarowski, M. Durán, J. van Slageren, *J. Am. Chem. Soc.* **2007**, 129, 10306–10307.
- [54] A. P. Ginsberg, R. L. Martin, R. W. Brookes, R. C. Sherwood, *Inorg. Chem.* **1972**, 11, 2884–2889.
- [55] K. O. Joung, C. J. O'Connor, E. Sinn, R. L. Carlin, *Inorg. Chem.* **1979**, 18, 804–808.
- [56] I. Bkouche-Waskman, Y. Journaux, O. Khan, *Transition Met. Chem.* **1981**, 6, 176–180.
- [57] Z. H. Zhang, X. H. Bu, Z. A. Zhu, Z. H. Jiang, Y. T. Chen, *Transition Met. Chem.* **1996**, 21, 235–237.
- [58] O. F. Ikotun, W. Ouellette, F. Lloret, M. Julve, R. P. Doyle, *Eur. J. Inorg. Chem.* **2007**, 2083–2088.
- [59] A. Tamayo, J. Casabó, L. Escriche, C. Lodeiro, B. Coveló, C. D. Brondino, R. Kivekäs, R. Sillampää, *Inorg. Chem.* **2006**, 45, 1140–1149.
- [60] A. N. Gusev, V. F. Shul'gin, I. O. Ryush, M. Hasegawa, M. A. Kiskin, N. N. Efimov, K. A. Lyssenko, I. L. Eremenko, W. Linert, *Eur. J. Inorg. Chem.* **2017**, 704–712.
- [61] A.-M.-C. Dumitriu, M. Cazacu, A. Bargan, S. Shova, C. Turta, *Polyhedron*, **2013**, 50, 255–263.
- [62] Q.-X. Li, Q.-H. Luo, Y.-Z. Li, C.-Y. Duan, Q.-Y. Tu, *Inorg. Chim. Acta*, **2005**, 358, 504–512.
- [63] H.-D. Bian, W. Gu, Q. Yu, S.-P. Yan, D.-Z. Liao, Z.-H. Jiang, P. Cheng, *Polyhedron*, **2005**, 24, 2002–2008.
- [64] A. I. Gallego, O. Castillo, F. Zamora, S. Delgado, *RSC Adv.* **2013**, 3, 18406–18413.

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Tuneable structures and magnetic properties of pseudohalo-bridged dinuclear Ni(II) complexes derived from {N₄} and {N₃O} donor ligands†

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Tetradentate ligands with {N₄}-donor (L¹ and L²) and {N₃O}-donor (HL³) groups prepared from a traditional Schiff base condensation reaction of *N,N*-dimethyldipropylenetriamine with pyridine-2-aldehyde or 2-acetylpyridine or 3-ethoxysalicylaldehyde, respectively, were used to react with Ni(II) salts in the presence of different pseudohalide ions, resulting in six new Ni(II) dimers with different bridging modes: [Ni₂(L¹)₂(μ_{1,3}-N₃)₂](ClO₄)₂ (**1**), [Ni₂(L¹)₂(μ_{1,3}-NCO)₂](ClO₄)₂ (**2**), [Ni₂(L¹)₂(μ_{1,5}-N(CN)₂)₂](ClO₄)₂ (**3**), [Ni₂(L²)₂(μ_{1,3}-N₃)₂](ClO₄)₂ (**4**), [Ni₂(L³)₂(μ_{1,1}-N₃)₂].0.5MeCN (**5**) and [Ni₂(L³)₂(μ_{1,1}-NCO)₂].0.5MeCN (**6**). Their structures and magnetic properties have been studied and discussed. Double end-to-end (EE) and end-on (EO) bridging modes were observed for both the azide and cyanate ions in these complexes. While the EE or EO azido-bridged Ni(II) compounds are quite common, the doubly EE or EO cyanato-bridged dimeric Ni(II) complex **2** was quite rare. Furthermore, we observed that in complex **4**, the double azido bridges cross each other to form a rarely observed twisted boat-type arrangement of the {Ni(μ_{1,3}-N₃)₂Ni} core, which leads to ferromagnetic interaction through the EE azide bridges. According to the present results, the introduction of different bridges and bridging motifs affords overall diverse magnetic interactions in these Ni(II) dimers, which has been discussed and rationalized in terms of previous literature reports.

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Introduction

Synthesis of di- and poly-nuclear transition metal complexes with bridging pseudohalides is still attracting considerable research interest worldwide because of their structural diversities and rich magnetic properties.^{1–6} In this context, the magnetochemistry of pseudohalo-bridged Ni(II) complexes has been extensively studied because of the presence of significant magnetic anisotropy in Ni(II) ions, arising from the second order spin–orbit coupling, in addition to the possible high spin ground states originating from the ferromagnetic coupling between the metal centres through the bridging

pseudohalides.^{7–9} Among all the pseudohalides, the azide anion is of special interest. It is well established that the azide ion with an end-on (EO, μ_{1,1}) bridging mode provides ferromagnetic (F) interaction, while end-to-end (EE, μ_{1,3}) azide usually transmits antiferromagnetic (AF) coupling between Ni(II) ions.¹⁰ Besides the azide anion, dicyanamide and cyanate ions are also frequently encountered in molecular magnetic materials. The μ_{1,5}-dicyanamide (dca) bridges mediate mostly a very weak AF interaction between Ni(II) centres, while the μ_{1,3}-mode of dca transfers moderate AF interactions, leading to some long-range magnetic materials.^{11–15} The cyanate ion, on the other hand, propagates magnetic interaction between Ni(II) centres in a similar fashion to that of the azide ion but weakly and there is a scarcity of reports of such Ni(II) compounds in the literature.^{16–22} In addition, unlike the azide ion, an experimental magneto-structural correlation is yet to be established for cyanato-bridged Ni(II) systems.^{23,24}

Magnetically speaking for all these pseudohalides, their controllable specific bridging modes are of great value to dictate the desired magnetic properties of the resulting molecular compounds. A better understanding of the stereo-electronic factors governing the magnetic exchange interaction between metal ions through the bridging pseudohalides would enable us to design Ni(II) clusters with

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† Electronic supplementary information (ESI) available. CCDC 2059601–2059606 contain the supplementary crystallographic data for **1–6**, respectively, for this article. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/d1ce00202c

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desired magnetic properties. However, the coordination behaviour of these ions is mostly serendipitous and the predicted bridging modes have been achieved only in a few cases. In this regard, organic ligands play crucial role in designing magnetically interesting Ni(II) cluster compounds as they may dictate the stereo-electronic structure at the metal centres and have a decisive influence on the bridging modes of the pseudohalides and thus the magnetic properties of the clusters.¹⁰ Among all the organic ligands, Schiff-base ligands are quite useful for developing large numbers of Ni(II) clusters with diverse structural and magnetic properties, mainly because of the synthetic simplicity and tuneable stereo-electronic structures of these ligands by varying carbonyl and amine counterparts.²⁵

We are now developing the coordination chemistry of 1st row transition metals with Schiff base ligands derived from a triamine protected at one end, namely *N,N*-dimethyldipropylenetriamine and salicylaldehyde or its derivatives for the interest in the fields of biomimetic catalysis and magnetic materials. We observed the diverse coordination adaptabilities of these ligands with varying denticity, which make these ligands suitable synthons for further exploration of coordination compounds with tuneable structures and properties.^{26,27} As we know the charge of the ligands strongly influences the self-assembled neutralization processes, and the ligands having the same number of donor centres but different charges could end up with diverse structures especially in the presence of exogenous bridging ligands. Given the aforementioned consideration, three tetradentate Schiff base ligands L^1 , L^2 and HL^3 (Scheme 1) were allowed to react with Ni(II) salts in the presence of different pseudohalide ions, resulting in a series of dinuclear Ni(II) complexes with diverse structures. Herein, the structures and magnetic properties of six new complexes $[Ni_2(L^1)_2(\mu_{1,3}-N_3)_2](ClO_4)_2$ (1), $[Ni_2(L^1)_2(\mu_{1,3}-NCO)_2](ClO_4)_2$ (2), $[Ni_2(L^1)_2(\mu_{1,5}-N(CN)_2)_2](ClO_4)_2$ (3), $[Ni_2(L^2)_2(\mu_{1,3}-N_3)_2](ClO_4)_2$ (4), $[Ni_2(L^3)_2(\mu_{1,1}-N_3)_2] \cdot 0.5MeCN$ (5) and $[Ni_2(L^3)_2(\mu_{1,1}-NCO)_2] \cdot 0.5MeCN$ (6) have been reported, with the magneto-structural relationship of these compounds being discussed.

Experimental section

Materials and physical measurements

All the chemicals such as nickel(II) perchlorate hexahydrate, 3-ethoxysalicylaldehyde, pyridine-2-aldehyde, 2-acetylpyridine

and *N,N*-dimethyldipropylenetriamine were purchased from commercial sources and used without further purification. Solvents were of reagent grade and used as received.

Caution! Perchlorate and azide salts of metal complexes coordinated with organic ligands are potentially explosive. Only a small amount of the material should be prepared, and it should be handled with great care.

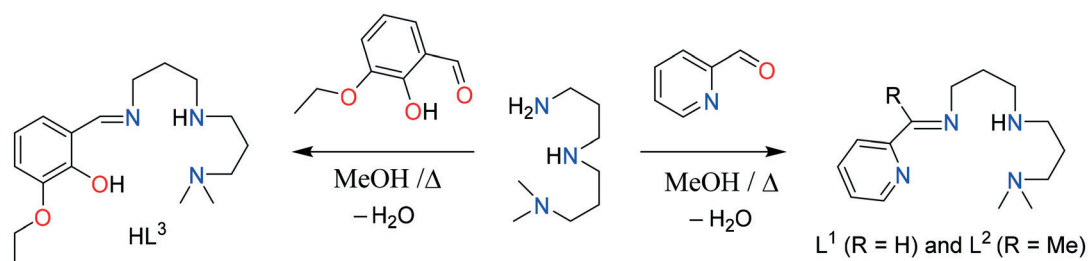
Elemental analyses (carbon, hydrogen and nitrogen) were conducted on a PerkinElmer 240C elemental analyser. Magnetic susceptibility measurements were performed using a Quantum Design SQUID VSM magnetometer for all the compounds. Direct current (DC) measurements were conducted in the temperature range of 300 to 2 K under an external magnetic field of 1000 Oe. The field dependent magnetizations were measured at 2–5 K with a dc magnetic field between 0 and 7 T. All magnetic data were corrected for the sample holder and for the diamagnetic contribution of the samples.

Synthesis of the Schiff base ligands L^1 , L^2 and HL^3

The ligands were prepared adopting the Schiff base condensation method.²⁷ When *N,N*-dimethyldipropylenetriamine was allowed to react with pyridine-2-aldehyde or 2-acetylpyridine or 3-ethoxysalicylaldehyde in methanol, tetradentate $\{N_4\}$ or $\{N_3O\}$ donor Schiff base ligands were produced. In a typical reaction, a mixture of 1.0 mmol of *N,N*-dimethyldipropylenetriamine (159 mg) and 1.0 mmol of pyridine-2-aldehyde (107 mg) in 20 mL methanol was placed in a round bottom flask and it was refluxed for *ca.* 1 h, and thereafter allowed to cool at room temperature. The deep orange methanol solution of L^1 was subsequently used for the synthesis of complexes 1–3. Using a similar protocol, where the condensation reaction was carried out using 2-acetylpyridine or 3-ethoxysalicylaldehyde instead of pyridine-2-aldehyde, it resulted in ligands L^2 and HL^3 which were subsequently used for the preparation of complexes 4–6.

Synthesis of $[Ni_2(L^1)_2(\mu_{1,3}-N_3)_2](ClO_4)_2$ (1)

$Ni(ClO_4)_2 \cdot 6H_2O$ (1.0 mmol, 366 mg) and Schiff base ligand L^1 (1.0 mmol) were combined in 30 mL of methanol with stirring. To the reaction mixture, NaN_3 (1.0 mmol, 65 mg) was added with continuous stirring and the resulting green solution was subjected to reflux for about 30 min. The



Scheme 1 Synthesis of the Schiff base ligands.

reaction mixture was then filtered and kept at room temperature for crystallization. Crops of dark-green crystals, suitable for X-ray diffraction, were obtained from slow evaporation of the solution after a few days. Then the crystals were collected by filtration and washed with cold methanol/diethyl ether and air dried to obtain analytically pure complex **1**. Yield: 332 mg (74%). Anal. calcd. for $C_{28}H_{48}Cl_2N_{14}Ni_2O_8$: C 37.49%, H 5.39%, N 21.86%. Found: C 37.74%, H 5.60%, N 21.67%. Selected FTIR bands (cm^{-1}): 1075 s and 621 s (ClO_4^-); 1599 m (pyridyl); 1651 w (azomethine); 2080 s (azide).

Synthesis of $[Ni_2(L^1)_2(\mu_{1,3}-NCO)_2](ClO_4)_2$ (**2**)

Complex **2** was prepared following a similar procedure to that described for **1**, but $NaNCO$ was used instead of NaN_3 . Colour: dark-green. Yield: 305 mg (68%). Anal. calcd. for $C_{30}H_{48}Cl_2N_{10}Ni_2O_{10}$: C 40.17%, H 5.39%, N 15.61%. Found: C 40.34%, H 5.58%, N 15.37%. Selected FTIR bands (cm^{-1}): 1076 s and 621 s (ClO_4^-); 1601 m (pyridyl); 1653 w (azomethine); 2222 s (cyanate).

Synthesis of $[Ni_2(L^1)_2(\mu_{1,5}-N(CN)_2)_2](ClO_4)_2$ (**3**)

Complex **3** was prepared following the same synthetic methodology applied for **1**, but $NaN(CN)_2$ was added instead of NaN_3 . Colour: dark-green. Yield: 364 mg (77%). Anal. calcd. for $C_{32}H_{48}Cl_2N_{14}Ni_2O_8$: C 40.67%, H 5.12%, N 20.75%. Found: C 40.54%, H 5.28%, N 20.57%. Selected FTIR bands (cm^{-1}): 1069 s and 621 s (ClO_4^-); 1600 m (pyridyl); 1646 w (azomethine); 2195 s, 2246 m, 2303 m (dicyanamide).

Synthesis of $[Ni_2(L^2)_2(\mu_{1,3}-N_3)_2](ClO_4)_2$ (**4**)

Complex **4** was synthesised following an identical procedure to that described for **1**, but ligand L^2 was used in place of L^1 . Colour: dark-green. Yield: 305 mg (66%). Anal. calcd. for $C_{30}H_{52}Cl_2N_{14}Ni_2O_8$: C 38.95%, H 5.67%, N 21.20%. Found: C 40.04%, H 5.58%, N 21.07%. Selected FTIR bands (cm^{-1}): 1080 s and 620 s (ClO_4^-); 1598 m (pyridyl); 1631 w (azomethine); 2073 s (azide).

Synthesis of $[Ni_2(L^3)_2(\mu_{1,1}-N_3)_2] \cdot 0.5MeCN$ (**5**)

A mixture of $Ni(ClO_4)_2 \cdot 6H_2O$ and Schiff base ligand HL^3 in methanol/acetonitrile (1 : 1, v/v) was used to prepare complex **5** adopting a very similar procedure to that described for **1** in the presence of Et_3N (1.0 mmol). Colour: dark-green. Yield: 338 mg (81%). Anal. calcd. for $C_{70}H_{114}N_{25}Ni_4O_8$: C 50.39%, H 6.89%, N 20.99%. Found: C 50.52%, H 6.99%, N 20.71%. Selected FTIR bands (cm^{-1}): 1619 s (azomethine); 2052 s (azide).

Synthesis of $[Ni_2(L^3)_2(\mu_{1,1}-NCO)_2] \cdot 0.5MeCN$ (**6**)

Complex **6** was prepared following the same methodology applied for the synthesis of **5**, but $NaNCO$ was used in place of NaN_3 . Colour: dark-green. Yield: 292 mg (70%). Anal. calcd. for $C_{74}H_{114}N_{17}Ni_4O_{12}$: C 53.27%, H 6.89%, N 14.27%.

Found: C 53.44%, H 6.99%, N 14.11%. Selected FTIR bands (cm^{-1}): 1619 s (azomethine); 2171 s (cyanate).

X-ray crystallography

Single crystal X-ray diffraction measurements of complexes **1–6** were carried out on a Bruker Kappa Apex-II CCD diffractometer equipped with a fine focus sealed tube of monochromated Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$) at 150(2) K. The program SAINT was used for integration of the diffraction profiles and multi-scan absorption corrections were applied using the SADABS program.²⁸ The structures were solved by direct methods (SHELXS) and refined by means of the full-matrix least squares method (SHELXL) on F^2 .²⁹ All the non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms bonded to carbon atoms were introduced in calculated positions and refined with a fixed geometry with respect to their carrier atoms, while hydrogen atoms connected to nitrogen atoms were found on the difference Fourier map and isotropically treated with given thermal parameters equivalent to 1.2 times the parent atoms. Crystallographic data and refinement details for the complexes are given in Table 1.

Results and discussion

Syntheses and general characterization

The tetradentate $\{N_4\}$ -donor ligand L^1 (or L^2) was prepared by adopting a traditional Schiff base condensation method in which N,N -dimethyldipropylenetriamine was allowed to react with pyridine-2-aldehyde (or 2-acetylpyridine) in a 1 : 1 molar ratio in methanol. Similarly, the tetradentate $\{N_3O\}$ -donor ligand (HL^3) was synthesised when the condensation reaction was carried out using 3-ethoxysalicylaldehyde (Scheme 1). Six new dark-green binuclear crystalline complexes $[Ni_2(L^1)_2(\mu_{1,3}-N_3)_2](ClO_4)_2$ (**1**), $[Ni_2(L^1)_2(\mu_{1,3}-NCO)_2](ClO_4)_2$ (**2**), $[Ni_2(L^1)_2(\mu_{1,5}-N(CN)_2)_2](ClO_4)_2$ (**3**), $[Ni_2(L^2)_2(\mu_{1,3}-N_3)_2](ClO_4)_2$ (**4**), $[Ni_2(L^3)_2(\mu_{1,1}-N_3)_2] \cdot 0.5MeCN$ (**5**) and $[Ni_2(L^3)_2(\mu_{1,1}-NCO)_2] \cdot 0.5MeCN$ (**6**) were readily obtained through a one-pot reaction of $Ni(ClO_4)_2 \cdot 6H_2O$, Schiff base ligand and pseudohalide salts in a 1 : 1 : 1 molar ratio in methanol (or a mixture of methanol and acetonitrile). Additionally, triethylamine was used to deprotonate ligand HL^3 for the synthesis of **5** and **6**. One important observation was that ligands L^1 and L^2 afforded double EE pseudohalo-bridged dinickel(II) complexes, while ligand HL^3 gave double EO azido (or cyanato) bridged dinickel(II) complexes. Therefore, the present study discloses that by replacing the pyridyl group with a phenolic moiety, different bridging modes of pseudohalides may be achieved.

The IR spectra of complexes **1**, **4** and **5** display a very strong absorption band in the region 2052–2080 cm^{-1} which is due to the asymmetric stretching frequency, $\nu(N_3^-)$, of the coordinated azido groups. The observed $\nu(N_3^-)$ frequencies for the complexes are consistent with those observed in other related end-to-end or end-on azido bridged dinickel(II) complexes.¹⁰ The asymmetric stretching vibrations of end-to-

Table 1 Crystallographic data and structural refinement parameters of 1–6

	1	2	3	4	5	6
Empirical formula	C ₂₈ H ₄₈ Cl ₂ N ₁₄ Ni ₂ O ₈	C ₃₀ H ₄₈ Cl ₂ N ₁₀ Ni ₂ O ₁₀	C ₃₂ H ₄₈ Cl ₂ N ₁₄ Ni ₂ O ₈	C ₃₀ H ₅₂ Cl ₂ N ₁₄ Ni ₂ O ₈	C ₇₀ H ₁₁₅ N ₂₅ Ni ₄ O ₈	C ₇₄ H ₁₁₅ N ₁₇ Ni ₄ O ₁₂
Formula weight (g mol ⁻¹)	897.12	897.10	945.16	925.17	1669.70	1669.66
Crystal system	Monoclinic	Monoclinic	Monoclinic	Orthorhombic	Triclinic	Triclinic
Space group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>n</i>	<i>Fdd</i> 2	<i>P</i> 1	<i>P</i> 1
<i>a</i> (Å)	8.2434(4)	8.3729(9)	8.1790(6)	26.3729(18)	15.0146(11)	15.0212(11)
<i>b</i> (Å)	13.7798(7)	13.6040(14)	27.2301(18)	43.882(4)	15.3326(10)	15.3518(12)
<i>c</i> (Å)	16.7261(8)	16.8216(19)	9.5177(7)	20.6839(16)	18.7906(14)	18.7416(14)
α (deg)	90	90	90	90	106.124(2)	106.273(3)
β (deg)	96.059(3)	94.390(4)	100.369(3)	90	106.924(2)	106.932(3)
γ (deg)	90	90	90	90	91.258(2)	91.228(3)
Volume (Å ³)	1889.34(16)	1910.4(4)	2085.1(3)	23 937(3)	3950.7(5)	3943.8(5)
<i>Z</i>	2	2	2	24	2	2
<i>D</i> _{calc} (g cm ⁻³)	1.577	1.560	1.505	1.540	1.404	1.406
μ (mm ⁻¹)	1.205	1.193	1.096	1.144	1.008	1.010
<i>F</i> (000)	936	936	984	11 616	1772	1772
θ range (deg)	1.919–27.174	1.927–27.138	1.496–29.193	1.334–25.832	2.079–29.195	2.236–27.984
Reflections collected	16 252	15 382	27 011	38 367	190 619	196 862
Independent reflections (<i>R</i> _{int})	4197 (0.0692)	4222 (0.0644)	5580 (0.0453)	11 119 (0.0791)	21 354 (0.0440)	18 959 (0.0535)
Observed reflections [<i>I</i> > 2 σ (<i>I</i>)]	2927	2773	4182	7773	17 043	15 699
Restraints/parameters	1/249	1/249	0/267	0/665	6/1004	12/1000
Goodness-of-fit on <i>F</i> ²	1.015	1.026	1.059	1.024	1.026	1.036
Final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0452 <i>wR</i> ₂ = 0.0912	<i>R</i> ₁ = 0.0501 <i>wR</i> ₂ = 0.1035	<i>R</i> ₁ = 0.0368 <i>wR</i> ₂ = 0.0746	<i>R</i> ₁ = 0.0974 <i>wR</i> ₂ = 0.2413	<i>R</i> ₁ = 0.0323 <i>wR</i> ₂ = 0.0733	<i>R</i> ₁ = 0.0323 <i>wR</i> ₂ = 0.0695
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0789 <i>wR</i> ₂ = 0.1054	<i>R</i> ₁ = 0.0930 <i>wR</i> ₂ = 0.1184	<i>R</i> ₁ = 0.0580 <i>wR</i> ₂ = 0.0824	<i>R</i> ₁ = 0.1392 <i>wR</i> ₂ = 0.2733	<i>R</i> ₁ = 0.0500 <i>wR</i> ₂ = 0.0811	<i>R</i> ₁ = 0.0464 <i>wR</i> ₂ = 0.0756
Largest diff. peak/hole (e Å ⁻³)	0.908/−0.414	1.313/−0.566	0.472/−0.442	1.987/−0.674	0.834/−0.570	1.092/−0.504
Flack value	—	—	—	0.45(5)	—	—

end or end-on NCO[−] for complexes 2 and 6 are found in the range 2171–2222 cm^{−1},^{16–22} while the asymmetric and symmetric stretching vibrations of dicyanamide ions in 3 are observed in the range 2195–2303 cm^{−1}.^{11–15} The IR spectra of 1–4 also display two strong bands; one broad band at around

1076 cm^{−1} and a sharp band at 621 cm^{−1}, which can be assigned to the stretching and bending vibrations of perchlorate counterions. The broadening of the stretching band may be attributed to the involvement of perchlorate ions in hydrogen bonding interaction in the solid state. In

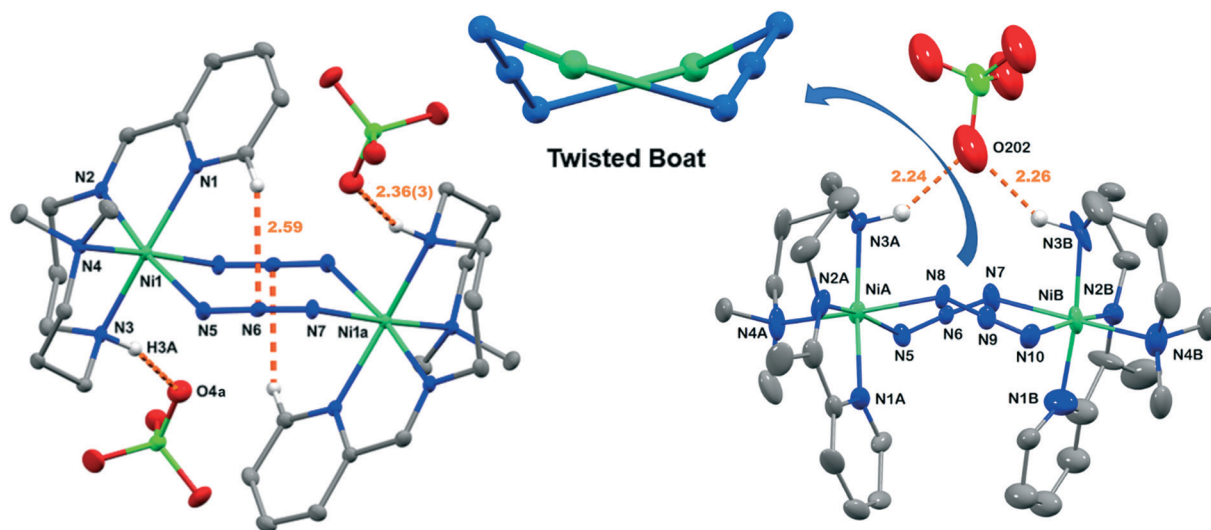


Fig. 1 Crystal structure of 1 (left) and a partial set of 4 (right) showing selected atom numbering scheme. Ellipsoids are drawn at the 30% probability level. The weak interactions are displayed as dashed lines. Symmetry code: *a* = 2 − *x*, −*y*, −*z*.

addition, the IR spectra of all the complexes consist of common bands in the region 1619–1653 cm^{-1} , which are attributable to the $\nu(\text{C}=\text{N})$ stretching frequency of the azomethine bond of the Schiff base ligands in **5** and **6**. The additional bands at around 1600 cm^{-1} for complexes **1–4** are attributed to the pyridyl groups.

Description of crystal structures

$[\text{Ni}_2(\text{L}^1)_2(\mu_{1,3}\text{-N}_3)_2](\text{ClO}_4)_2$ (**1**) and $[\text{Ni}_2(\text{L}^1)_2(\mu_{1,3}\text{-NCO})_2](\text{ClO}_4)_2$ (**2**) are isostructural and isomorphous compounds and both crystallized in the monoclinic space group $P2_1/n$ (Fig. 1 and 2). The centrosymmetric dimeric complex cations of **1** and **2** lie about an inversion centre and are constructed with doubly EE bridged pseudohalides (N_3^- and NCO^-), and the $\text{Ni}(\text{II})$ ions in these complexes are hexacoordinated with a distorted octahedral geometry. The coordination sites of $\text{Ni}(\text{II})$ ions in **1** are fulfilled by the $\{\text{N}_6\}$ donor set whereas it is $\{\text{N}_5\text{O}\}$ in **2**. Each $\text{Ni}(\text{II})$ centre in **1** or **2** is bonded with four nitrogen donor atoms of the Schiff base ligand and two nitrogen donor atoms from one each of the centro-symmetrically related EE bridging azide ions in **1** and one oxygen atom and one nitrogen atom from two centro-symmetrically related EE bridging cyanato groups in **2**. In both complexes, three N-atoms (imine, secondary amine and tertiary amine N-atoms) from the triamine part of the Schiff base ligand facially coordinate the $\text{Ni}(\text{II})$ centre. The Ni–N bond distances of pyridine, imine, secondary amine and tertiary amine of the Schiff base ligand vary in the range 2.072(3) to 2.135(3) Å in **1**, which are comparable to the literature reported values in closely related $\text{Ni}(\text{II})$ complexes.^{17,26} The bridging region is slightly asymmetric as can be seen from the Ni–N bond distances of 2.120(3) and 2.185(3) Å of the bridging azide ions. Similar bond lengths are observed in **2** (see Table 2), but the bridging region is more asymmetric as reflected from the different Ni–N (2.045(3) Å) and Ni–O (2.217(2) Å) bond distances of bridging cyanato ligands, which should be due

to the presence of hetero bridging atoms (oxygen and nitrogen atoms) in the cyanate ion in **2**. The EE pseudohalide bridges are almost linear with an angle N7–N6–N5 of 177.2(3)° for azide ions in **1** and an angle N5–C15–O1 of 176.3(5)° for cyanate ligands in **2**. The N6–N5–Ni angle of 133.5(2)° differs considerably from N6–N7–Ni1a of 116.7(2)° in **1** and the Ni1...Ni1a separation is 5.203 Å (symmetry code: $a = 2 - x, -y, -z$). Meanwhile in **2**, the C15–N5–Ni1b bond angle of 152.0(4)° differs significantly from C15–O1–Ni1 of 111.6(3)° with a Ni1...Ni1b separation of 5.326 Å (symmetry code: $b = 1 - x, 1 - y, z$). These values are consistent with the structural results obtained for other EE azido- and cyanato-bridged $\text{Ni}(\text{II})$ complexes.^{19–21,30–38} The two bridging pseudohalides in both **1** and **2** lie in the same plane and two $\text{Ni}(\text{II})$ centres deviate slightly out of that plane in either side, leading to a chair-like arrangement of the eight-membered $\{\text{Ni}(\mu_{1,3}\text{-N}_3/\text{NCO})_2\text{Ni}\}$ core. The dihedral angle (δ) between the plane defined by two pseudohalide ions and N–Ni–N (in **1**) or N–Ni–O (in **2**) are 34.51° and 17.74°, respectively. Further inspection of the crystal structures discloses that two edges of $\text{Ni}(\text{II})$ polyhedra are connected by EE bridging pseudohalides (see Fig. 2). Moreover, in both **1** and **2**, the secondary amine hydrogen atom of the Schiff base ligand participates in hydrogen bonding interaction with the oxygen atom of the perchlorate counter ion with $\text{N}\cdots\text{O}$ distances of 3.164(4) and 3.162(4) Å in **1** and **2**, respectively. The crystal packing is further stabilised by $\text{C-H}\cdots\pi$ interaction involving the C–H proton of the pyridyl group and π electrons of the pseudohalide ligands as shown in Fig. 1 and 2 for **1** and **2**, respectively. It is worth noting that, unlike azido bridged compounds,^{30–38} the doubly EE cyanato-bridged dimeric $\text{Ni}(\text{II})$ complexes are rare with only a limited number of examples reported in the literature.^{19–21}

$[\text{Ni}_2(\text{L}^1)_2\{\mu_{1,5}\text{-N}(\text{CN})_2\}_2](\text{ClO}_4)_2$ (**3**) crystallised in the monoclinic space group $P2_1/n$ where the asymmetric unit contains half of the dinuclear complex cation on an inversion centre and a perchlorate counter ion on a general position to balance the charge. The structure of complex **3** (Fig. 3) is very similar to the structures of **1** and **2**, but the central $\{\text{Ni}(\mu_{1,5}\text{-N}(\text{CN})_2)_2\text{Ni}\}$ core in **3** is somewhat different from $\{\text{Ni}(\mu_{1,3}\text{-N}_3)_2\text{Ni}\}$ in **1** or $\{\text{Ni}(\mu_{1,3}\text{-NCO})_2\text{Ni}\}$ in **2**. The Ni...Ni separation (7.346 Å) through the five-atom dicyanamide bridges is significantly larger in **3** than that found in three-atom bridged pseudohalides in **1** and **2** as expected. The coordinating fashion of the Schiff base ligand to the metal centre is exactly the same as that found in **1** and **2**. The $\text{Ni}(\text{II})$ ion in **3** is therefore again hexacoordinated in a distorted octahedral geometry with all four N donor atoms of the Schiff base ligand together with two N donor atoms from two symmetry related end-to-end bridging dicyanamide groups at *cis* positions (Table 2). The two N–C–N bond angles of the bridging dicyanamide group are 174.3(2)° (N5–C15–N6) and 175.0(2)° (N7–C16–N6), while the C16–N6–C15 angle is 118.91(17)°, which are typical for $\mu_{1,5}$ -dicyanamide bridges.^{11–15} Like in **1** and **2**, the secondary amine hydrogen atom of the Schiff base ligand in **3** is hydrogen bonded with

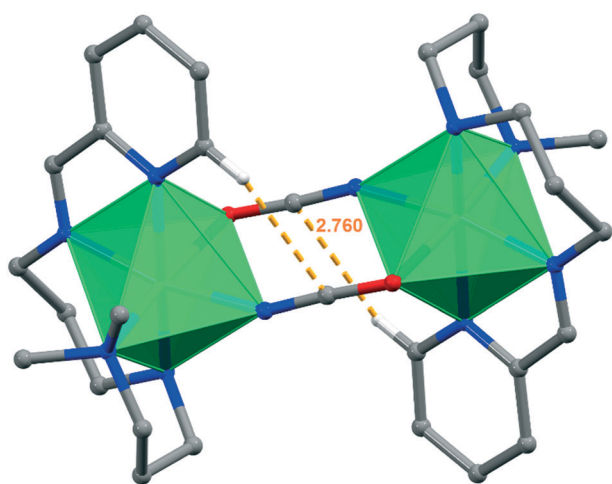


Fig. 2 Crystal structure of complex **2** along with local coordination geometry of $\text{Ni}(\text{II})$ ions.

Table 2 Selected bond distances (Å) for 1–6

Bond	1	2	3	4 [#]	5 [#]	6 [#]
Ni(II)–N(pyridine)	2.125(3)	2.124(3)	2.1331(17)	2.057(14)	—	—
Ni(II)–N(imine)	2.072(3)	2.067(3)	2.0704(17)	2.066(14)	2.0468(14)	2.0620(15)
Ni(II)–N(secondary amine)	2.102(3)	2.100(3)	2.0892(17)	2.074(12)	2.1192(14)	2.1095(15)
Ni(II)–N(tertiary amine)	2.135(3)	2.116(3)	2.1662(15)	2.164(13)	2.1949(14)	2.2164(16)
Ni(II)–O(phenolate)	—	—	—	—	2.0226(12)	2.0078(12)
Ni(II)–O(pseudohalide)	—	2.217(2)	—	—	—	—
Ni(II)–N(pseudohalide)	2.120(3)	2.045(3) ^b	2.1380(16)	2.164(13)	2.1192(14)	2.1143(14)
	2.185(3) ^a		2.0693(16) ^c	2.207(13) ^d	2.2048(14) ^e	2.2560(14) ^e

Symmetry codes: a = 2 – x, –y, –z; b = 1 – x, 1 – y, –z; c = 1 – x, –y, 1 – z; d = –x, –y, z; e = 1 – x, –y, –z and # denotes that the bond parameters of one of the crystallographically independent molecules are presented.

the oxygen atom of the perchlorate counter ion with N3...O bond distances of 3.223(2) and 3.320(3) Å. The solid-state packing is further stabilised by C–H... π interaction involving the C–H proton of the pyridyl group and π electrons of the bridging dicyanamide as shown in Fig. 3.

The crystallographic study reveals that similar to complex 1, $[\text{Ni}_2(\text{L}^2)_2(\mu_{1,3}\text{-N}_3)_2](\text{ClO}_4)_2$ (4) is also composed of doubly $\mu_{1,3}$ -azido-bridged dinickel(II) cations and two ClO_4^- ions (Fig. 1 and S1† and Table 2). But complex 4 crystallised in the orthorhombic *Fdd2* space group in which the asymmetric unit has one cation dimer in a general position as well as half of a cation dimer lying about a two-fold axis, and two perchlorate ions are in general positions and another two have their chlorine atoms on two-fold axes. Each Ni(II) ion is again six-coordinated, being bonded with four nitrogen atoms of ligand L^2 and two nitrogen atoms from two bridging azide ions in *cis* positions. However, the essential differences in these structures originate from the presence of different symmetry elements *i.e.* an inversion centre in 1 and a two-fold rotation axis in 2. This brings different hydrogen

bonding patterns in these structures as shown in Fig. 1. Secondary amine groups connected to Ni(II) centres in 1 are placed in opposite sides of the central $\{\text{Ni}(\mu_{1,3}\text{-N}_3)_2\text{Ni}\}$ core and thereby interact with different perchlorate ions through hydrogen bonds, while they reside at the same side, leading to a cooperative hydrogen bonding interaction with a perchlorate ion in 4 (Fig. 1). Remarkably, the $\{\text{Ni}(\mu_{1,3}\text{-N}_3)_2\text{Ni}\}$ core structure is quite different in two cases as it adopts a chair-like arrangement in 1 where both azide ions lie on the same plane, while the two azide bridges are non-coplanar and cross linked the Ni(II) ions with a twisted boat-type arrangement of the $\{\text{Ni}(\mu_{1,3}\text{-N}_3)_2\text{Ni}\}$ core in 4. The intramolecular Ni...Ni separations in two crystallographically independent dimeric units are 5.255(3) and 5.271(3) Å, whereas the closest intermolecular separation between the Ni(II) centres is 8.510(3) Å. It is noteworthy that the two bridging azides with cross-linked and non-coplanar $(\mu_{1,3}\text{-N}_3)_2$ structure are unusual, as the planarity is a common feature of dinickel(II) complexes with double $\mu_{1,3}\text{-N}_3$ bridges,^{30–38} and for the dinickel(II) system only four such compounds are both structurally and magnetically characterized.^{39–42} The Ni–($\mu_{1,3}\text{-N}_3$)–Ni (Ni–N...N–Ni) torsion angles (τ) are 66.24, 71.55 and 74.33°, which are close to those found in similar systems.^{39,40}

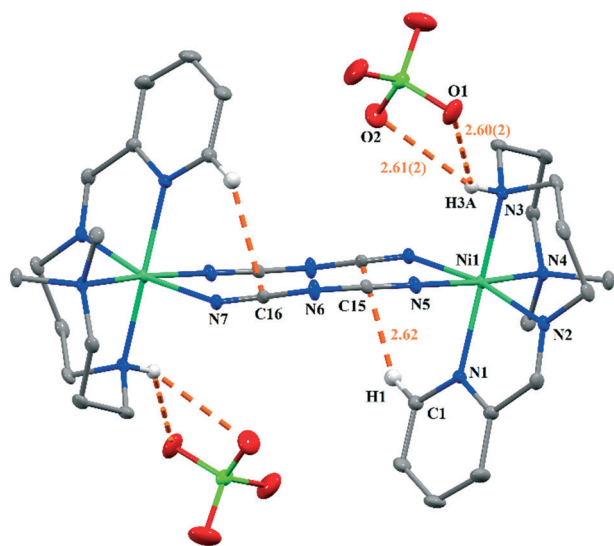


Fig. 3 Crystal structure of complex 3 with selected atom numbering scheme. Ellipsoids are drawn at the 30% probability level. The non-covalent interactions are shown as dashed lines.

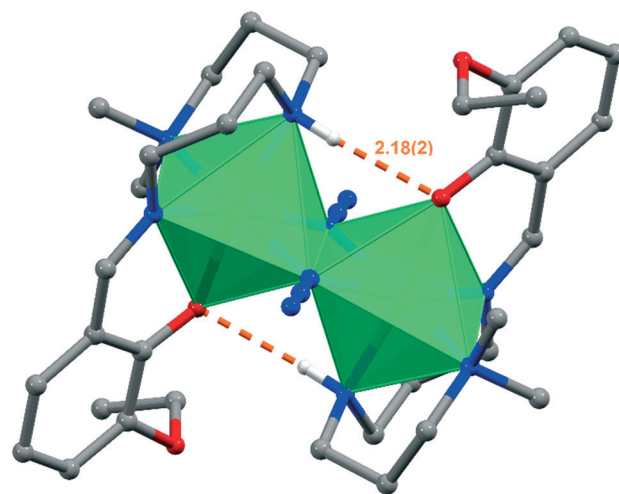


Fig. 4 Crystal structure of complex 5 along with local coordination geometry of Ni(II) ions.

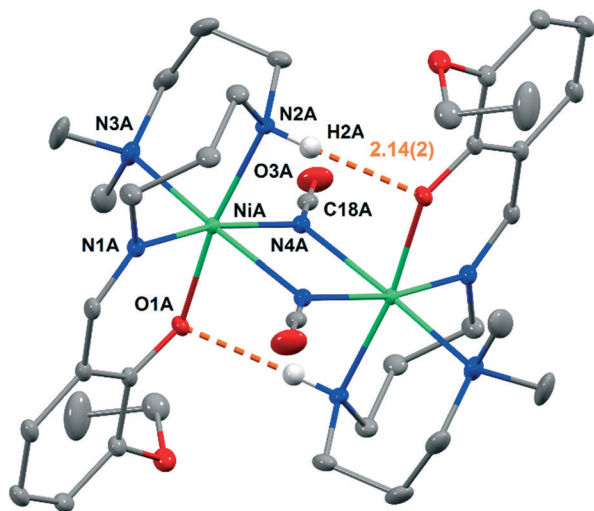


Fig. 5 Crystal structure of complex **6** with selected atom numbering scheme. Ellipsoids are drawn at the 30% probability level. The non-covalent interactions are shown as dashed lines.

Compounds $[\text{Ni}_2(\text{L}^3)_2(\mu_{1,1}\text{-N}_3)_2]\cdot 0.5\text{MeCN}$ (**5**) and $[\text{Ni}_2(\text{L}^3)_2(\mu_{1,1}\text{-NCO})_2]\cdot 0.5\text{MeCN}$ (**6**) are isostructural and isomorphous (Fig. 4 and 5), and they crystallised in the triclinic space group $P\bar{1}$ in which four crystallographically independent neutral complex molecules sit on inversion centres together with an acetonitrile molecule on a general position. In both complexes, the $\text{Ni}(\text{II})$ centres are hexacoordinated with a distorted octahedral structure. The coordination numbers of the $\text{Ni}(\text{II})$ ion are satisfied by three N donor atoms and one phenolate-O atom of the deprotonated Schiff base ligand and two N-atoms from either of the EO bridging azide ions (in **5**) or cyanate ions (in **6**). These *cis* disposed pseudohalide ions share common edges, leading to the edged-sharing bioctahedral structures (see Fig. 4). Like **1–4**, three N-atoms (imine, secondary amine and tertiary amine N-atoms) of the deprotonated Schiff base ligand facially coordinate the $\text{Ni}(\text{II})$ centres in **5** and **6**. The Ni–N bond distances in **5** and **6** are comparable to those observed in **1–4** (Table 2) and to related complexes reported in the literature.^{16–18,43–63} The central $\{\text{NiN}_2\text{Ni}\}$ cores are planar in both complexes as dictated by the centre of symmetry with the Ni–N–Ni bridging angles spanning the range $100.74(6)$ – $101.28(5)^\circ$ and $97.84(6)$ – $97.45(6)^\circ$ in **5** and **6**, respectively. The azide and cyanate ions are nearly linear with N–N–N and N–C–O bond angles of $178.55(18)^\circ$ and $179.3(2)^\circ$, respectively. The doubly EO pseudohalide bridges in both compounds are slightly asymmetric with Ni–N bond distances of 2.1192(2) and 2.2048(2) Å in **5** and 2.116(2) and 2.256(2) Å in **6**. The average separations of the metal centres in the dimeric units are 3.377 Å in **5** and 3.284 Å in **6**. The secondary amine hydrogen atom is involved in hydrogen bonding interaction with the phenoxido oxygen atom within the dimeric unit with average $\text{N}\cdots\text{O}$ distances of 3.033 and 3.002 Å in **5** and **6**, respectively, to provide the solid-state stability of these compounds. Additional stability in the

solid-state is gained by π – π interaction involving the π -electrons of the acetonitrile molecule and the aromatic ring of the Schiff base ligand (not shown). It is worth noting that, unlike azido bridging,^{43–63} the doubly EO cyanato-bridged dimeric $\text{Ni}(\text{II})$ complexes are scarce, and only a few dinuclear nickel(II) compounds with such a bridging motif are available in the literature.^{16–18,64}

From the structural studies, it is clear that just by fine tuning of the organic ligands, diverse bridging modes of pseudohalides can be achieved. For example, an additional methyl group in ligand L^2 affords the crossed linked and nonplanar double EE azido-bridged $\text{Ni}(\text{II})$ dimer in **4**, while EE bridging azides are planar in complex **1**. The central $\{\text{Ni}(\mu_{1,3}\text{-N}_3)_2\text{Ni}\}$ core structures in two cases are also significantly different as it is a chair like arrangement in **1** while a twisted boat like arrangement is observed in **4** (Fig. 1). Further inspection of the crystal structures reveals that although the connectivity of both ligands L^1 and deprotonated HL^3 to the metal centres is similar, leaving two *cis* positions of the metal centre for bridging azides, the bridging modes of azide ions are different in these systems *i.e.* EE ($\mu_{1,3}$) in **1** and EO ($\mu_{1,1}$) in **5**. It is reasonable to point out that the hydrogen bonding interaction between phenolate–O as an acceptor and secondary amine as a donor from either of the organic ligands in the dimeric unit could overcome the increased steric crowding in the system when azides bridge the metal centres in an EO fashion. In the absence of the hydrogen bond acceptor ability of the pyridyl group in **1**, the azide ions prefer to bridge the metal centres in an EE fashion to minimize steric repulsion in the system.

Magnetic studies

The temperature dependence of the magnetic properties of complexes **1** and **2** as χ_{M} and $\chi_{\text{M}}T$ product *vs.* T plots (χ_{M} being the molar magnetic susceptibility per dimer) under a constant magnetic field of 1.0 kOe is displayed in Fig. 6 and 7, respectively. At room temperature, the $\chi_{\text{M}}T$ values of 2.20 and 2.25 $\text{cm}^3 \text{mol}^{-1} \text{K}$ for **1** and **2**, respectively, are slightly

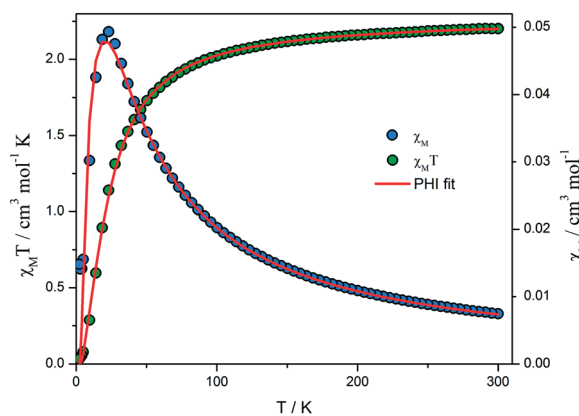


Fig. 6 Plots of χ_{M} and $\chi_{\text{M}}T$ *vs.* T for complex **1**. Symbols and solid lines represent experimental data and the best theoretical fits, respectively.

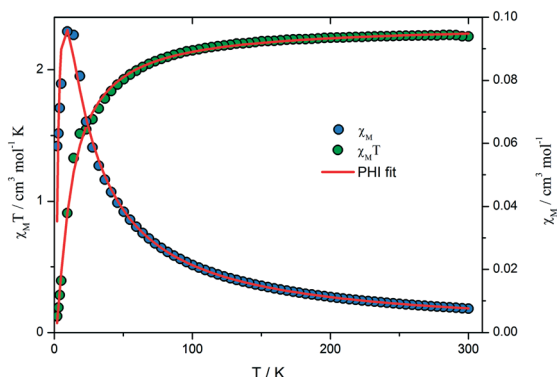


Fig. 7 Plots of χ_M and $\chi_M T$ vs. T for complex 2. Symbols and solid lines represent experimental data and the best theoretical fits, respectively.

higher than the calculated value of $2.0 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ for two isolated Ni(II) ions with $S = 1$ and $g = 2$, which is due to the spin-orbit coupling of the Ni(II) ion at room temperature. The $\chi_M T$ values decrease continuously from room temperature and approach zero at 2 K for both cases. This magnetic behaviour is typical for an intramolecular antiferromagnetic interaction between two Ni(II) ions. The Curie-Weiss analysis (Fig. S2 and S3†) of the magnetic susceptibility data above 100 K with negative Weiss values (-15.01 and -7.36 K , respectively) as well as the presence of distinct maxima in χ_M vs. T plots in 1 and 2 agrees well with the antiferromagnetic interaction between the metal centres. The isothermal magnetisation of 1 and 2 as depicted in Fig. S4 and S5†, respectively, justifies the diamagnetic ground state at low temperature, and therefore zero-field splitting (ZFS) does not have much influence on the magnetic properties of these systems. A full-matrix diagonalization approach assuming an isotropic spin exchange Hamiltonian ($-2J\hat{S}_1\hat{S}_2$), Zeeman interaction (g_{Ni} , average), and intermolecular interaction (zJ') was further employed to analyse the magnetic data using the PHI program.⁶⁵ The best fittings afforded the following set of parameters: $J = -6.95(1) \text{ cm}^{-1}$, $g_{\text{Ni}} = 2.13(1)$, and $zJ' = 0.39(10) \text{ cm}^{-1}$ for complex 1 and

$J = -2.71(2) \text{ cm}^{-1}$, $g_{\text{Ni}} = 2.17(1)$ and $zJ' = -0.48(6) \text{ cm}^{-1}$ for complex 2.

The $\chi_M T$ versus T plot per dimeric unit of 3 is shown in Fig. 8. At room temperature, the $\chi_M T$ value of $2.24 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ is again usual for two isolated Ni(II) ions. The $\chi_M T$ values remain almost constant down to 60 K and thereafter gradually decrease with lowering the temperature to attain a minimum value of $1.51 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ at 2 K. This magnetic behaviour is characteristic of very weak antiferromagnetically coupled Ni(II) ions through $\mu_{1,5}\text{-N}(\text{CN})_2$ -bridges.^{11–15} In addition, the isothermal field dependent magnetization data measured at 2 and 5 K are also depicted in Fig. 8, showing regular paramagnetic behaviour. The magnetic data were fitted simultaneously using the PHI program, assuming isotropic exchange Hamiltonian ($-2J\hat{S}_1\hat{S}_2$), Zeeman interaction (g_{Ni}) and axial zero-field splitting (D), and neglecting intermolecular interaction (zJ'). The best-fitting offers $J = -0.15(14) \text{ cm}^{-1}$, $g_{\text{Ni}} = 2.13(1)$ and $D = 2.64(5) \text{ cm}^{-1}$ for 3. The negligibly small exchange interaction is consistent with the intramolecular Ni...Ni separation of $7.346 \text{ \AA}$ through the bridging dicyanamide ligands. In fact, the analysis of the magnetic data, considering only the presence of single ion anisotropy and ignoring the exchange interaction, resulted in identical fitting with the best fit parameters $g_{\text{Ni}} = 2.12(1)$ and $D = 2.97(2) \text{ cm}^{-1}$.

The magnetic property per dimeric unit of 4 as χ_M and $\chi_M T$ product vs. T plots and the molar magnetization as a function of applied dc magnetic field ($M/N\beta$ vs. H) are displayed in Fig. 9. The $\chi_M T$ product at room temperature for 4, ca. $2.34 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$, is again typical for two magnetically isolated Ni(II) ions. Upon cooling, the $\chi_M T$ product increases continuously to a maximum of $3.18 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ at 19 K and thereafter decreases sharply to a value of $2.35 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ at 2 K. This behaviour is characteristic of an intramolecular ferromagnetic exchange between two Ni(II) ions together with the influence of an intermolecular interaction and/or zero-field splitting (ZFS) of the ground state ($S = 2$), manifested at low temperature. The Curie-Weiss plot (Fig. S6†) of the magnetic susceptibility data above 100 K with a positive

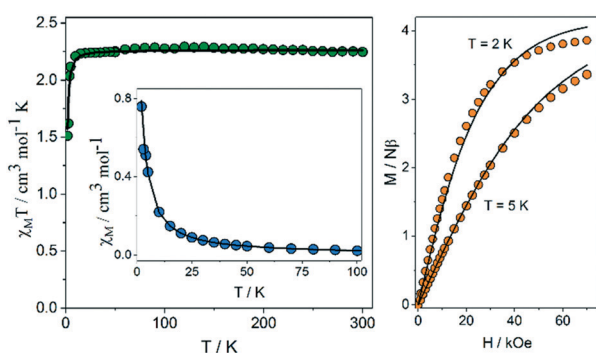


Fig. 8 Magnetic data for 3. Thermal dependence of χ_M and $\chi_M T$ product measured at 1.0 kOe dc field (left) and magnetisation data at different temperatures (right). Symbols and solid lines represent experimental data and the best fitted data, respectively.

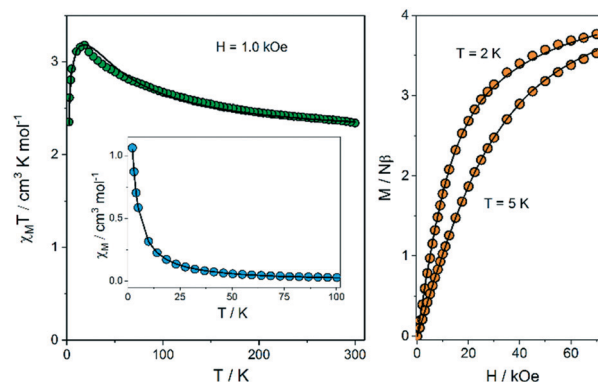


Fig. 9 Magnetic data for 4. Thermal dependence of χ_M and $\chi_M T$ product measured at 1.0 kOe dc field (left) and magnetisation data at different temperatures (right). Symbols and solid lines represent experimental data and the best fitted data, respectively.

Weiss value (12.92 K) further supports the ferromagnetic coupling between the metal centres. Analysis of the magnetic data applying isotropic exchange Hamiltonian ($-2J\hat{S}_1\cdot\hat{S}_2$), Zeeman effect (g_{Ni} , average), axial zero-field splitting (D), and intermolecular interaction (zJ') yielded the following set of best fit parameters: $J = 13.21(1) \text{ cm}^{-1}$, $g_{\text{Ni}} = 2.09(1)$, $D = 7.20(1) \text{ cm}^{-1}$ and $zJ' = -0.011(8) \text{ cm}^{-1}$ for complex 4.

The χ_{M} and $\chi_{\text{M}}T$ product vs. T plots per dimeric unit of 5 and 6 and the molar magnetization as a function of applied dc magnetic field ($M/N\beta$ vs. H) are shown in Fig. 10 and 11, respectively. The $\chi_{\text{M}}T$ product at room temperature for 5 and 6 is ca. 2.89 and $2.63 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$, respectively, which are slightly higher than those calculated for two magnetically non-interacting Ni(II) ions. The $\chi_{\text{M}}T$ product increases continuously with decreasing temperature, reaching a maximum of $3.57 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ at 50 K for 5 and $3.22 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ at 15 K for 6, and then $\chi_{\text{M}}T$ decreases sharply to attain a value ca. 1.38 and $1.69 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ at 2 K for 5 and 6, respectively. This feature is again typical for an intramolecular ferromagnetic exchange between two Ni(II) ions with the influence of intermolecular interactions and/or zero-field splitting (ZFS) of the ground state ($S = 2$), particularly at low temperature. The Curie-Weiss analysis (Fig. S7 and S8†) of the magnetic susceptibility data above 100 K is also consistent with ferromagnetic interaction. Analysis of the magnetic data considering isotropic spin exchange Hamiltonian ($-2J\hat{S}_1\cdot\hat{S}_2$), Zeeman effect (g_{Ni} , average), axial zero-field splitting (D), and intermolecular interaction (zJ') afforded the following set of best fit parameters: $J = 28.79(2) \text{ cm}^{-1}$, $g_{\text{Ni}} = 2.23(1)$, $D = 14.23(2) \text{ cm}^{-1}$ and $zJ' = -0.085(4) \text{ cm}^{-1}$ for complex 5 and $J = 3.70(2) \text{ cm}^{-1}$, $g_{\text{Ni}} = 2.28(1)$, $D = 8.05(4) \text{ cm}^{-1}$ and $zJ' = -0.067(2) \text{ cm}^{-1}$ for complex 6.

A handful of examples of double EE azido-bridged dinickel(II) complexes with $[\text{Ni}_2(\mu_{1,3}\text{-N}_3)_2]^{2+}$ core structures and planar bridging azides are known in which azide ions propagate AF interaction between the Ni(II) ions.^{30–38} The main factor that determines the magnitude of the J value in such systems is the dihedral angle (δ) between the planes

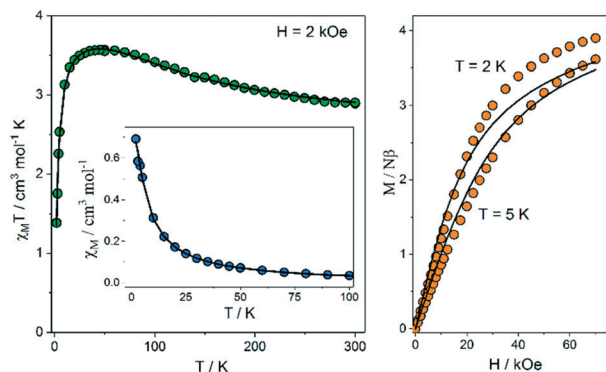


Fig. 10 Magnetic data for 5. Thermal dependence of χ_{M} and $\chi_{\text{M}}T$ product measured at 1.0 kOe dc field (left) and magnetisation data at different temperatures (right). Symbols and solid lines represent experimental data and the best fitted data, respectively.

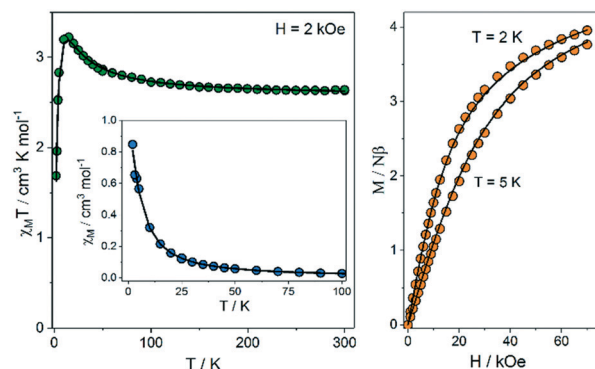


Fig. 11 Magnetic data for 6. Thermal dependence of χ_{M} and $\chi_{\text{M}}T$ product measured at 1.0 kOe dc field (left) and magnetisation data at different temperatures (right). Symbols and solid lines represent experimental data and the best fitted data, respectively.

defined by the six azide-N atoms and the N-Ni-N plane: the more planar the structure (δ is close to 0°), the more antiferromagnetic the interaction and hence the higher the $|J|$ value, whereas the Ni-N(azide) distance and other structural parameters are less important.²⁴ In complex 1, the dihedral angle δ of 34.51° should account for the relatively small J value of -6.95 cm^{-1} , which agrees well with the magneto-structural data available in these systems.^{30–38} Unlike azido-bridged analogues, the examples of double EE cyanato-bridged dinickel(II) complexes are limited (Table 3).^{19–21} It was also well predicted that cyanate ions transmit similar magnetic interaction between the metal centres but weakly, and the comparatively lower J values found for cyanato bridges as a consequence of the lower spin density on the N and O atoms.¹⁹ The relatively high δ value of 17.74° is responsible for the loss of overlap derived from the lower planarity of the bridging region and as a consequence the lowest J value of $-2.71(2) \text{ cm}^{-1}$ for 2 perfectly lies in the range of J values reported until now.

Although the general formula of $[\text{Ni}_2(\text{L}^2)_2(\mu_{1,3}\text{-N}_3)_2](\text{ClO}_4)_2$ (4) is identical with $[\text{Ni}_2(\text{L}^1)_2(\mu_{1,3}\text{-N}_3)_2](\text{ClO}_4)_2$ (1), the magnetic properties of these compounds are significantly different. Unlike in 1, the interaction between the Ni(II) centres in 4 is ferromagnetic in nature through double EE bridges. The difference in the magnetic properties arises essentially from the different connectivity in the bridging region. In 4, two bridging EE azides are not planar and crosslinked, and in such cases the nature of the magnetic interaction may be either F or AF, mainly depending on two structural parameters in the bridging region such as the Ni-N-N bond angles and the Ni- $\mu_{1,3}\text{-N}_3$ -Ni (Ni-N $\cdots$ N-Ni) torsion angle.⁶⁶ Maximum coupling was expected for a Ni-N-N angle of 108° and decreases when the Ni-N-N angle increases and the exchange interactions would be ferromagnetic if the angle exceeds 155° . Similarly, for a fixed Ni-N-N angle, AF coupling is expected to be maximum for a Ni-N $\cdots$ N-Ni torsion angle of 180° (or 0°) and decreases when the Ni-N $\cdots$ N-Ni torsion angle deviates from linearity and the interaction would be ferromagnetic if the torsion angle

Table 3 Selected structural and magnetic data of doubly EE cyanato bridged Ni(II) dimers (following $\hat{H} = -2J\hat{S}_1\hat{S}_2$ convention)^a

Compounds	J (cm ⁻¹)	g	Ni–O–C (°)	Ni–N–C (°)	Dihedral angle (δ , °) ^b	Ref.
[Ni(L ⁴)(NCO)] ₂ (BF ₄) ₂	-5.35	2.30	122.0	150.1	4.8	19
[Ni(tren)(NCO)] ₂ (BF ₄) ₂	-4.4	2.28	117.1	155.0	9.1	20
[Ni(L ⁵)(NCO)] ₂ (PF ₆) ₂	-3.1	2.16	110.9/111.4	147.9/152.0	18.6/20.8	21
2	-2.71	2.17	111.6(3)	152.0(4)	17.74	This work

^a L⁴ = DL-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane, tren = 2,2',2''-triiminotriethylamine; L⁵ = N,N-bis(3,5-dimethylpyrazol-1-ylmethyl)aminomethylpyridine. ^b The angle between the planes defined by the six azide-N atoms and the Ni–Ni–N plane.

Table 4 Selected structural and magnetic data of doubly crosslinked EE azido-bridged Ni(II) dimers (following $\hat{H} = -2J\hat{S}_1\hat{S}_2$ convention)^a

Compounds	J (cm ⁻¹)	D (cm ⁻¹)	g	Ni–N–N (°)	Torsion angle (τ , °) ^b	Ref.
{[Ni(L ⁶ N ₃) ₂ (ClO ₄) ₂ (CH ₃ OH) ₂]	+8.45	6.0	2.28	117.14–118.83	78.80	39
[Ni ₂ (L ⁷) ₂ (μ _{1,3} -N ₃) ₂](ClO ₄) ₂	+7.13	—	2.18	117.8–127.7	69.2	40
[Ni(L ⁸) ₂ (μ _{1,3} -N ₃) ₂](ClO ₄) ₂ ·8CH ₃ OH	-29	10	2.1	130.0	46.7	41
[L ⁹ Ni ₂ (N ₃) ₂ (μ _{1,3} -N ₃) ₂]	-36.4	0 (fixed)	2.04	124.5–128.2	34.28	42
4	+13.21	7.20	2.09	123.7–127.1	66.24–74.33	This work

^a L⁶ = N,N'-bis-(3,5-dipiperidin-1-yl-[2,4,6]triazin-1-yl)-pyridin-2-ylmethylethane-1,2-diamine; L⁷ = N,N',N''-tris(4-methoxybenzyl)tris(2-aminoethyl)amine; L⁸ = 2,6-dimethyl-2,3-bis(2-pyridyl)quinoxaline; L⁹ = 1,4,7-trimethyl-1,4,7-triazacyclononane. ^b The Ni–μ_{1,3}-N₃–Ni (Ni–N···N–Ni) torsion angle.

Table 5 Selected structural and magnetic data of doubly end-on cyanato bridged Ni(II) dimers (following $\hat{H} = -2J\hat{S}_1\hat{S}_2$ convention)^a

Compounds	J (cm ⁻¹)	D (cm ⁻¹)	g	M–N (Å)	M–N–M (°)	Ref.
[Ni ₂ (L ¹⁰) ₂ (μ _{1,1} -NCO) ₂](ClO ₄) ₂	+1.7	+3.6	2.23	2.125, 2.090	94.4, 95.8	16
[Ni ₂ (L ¹¹) ₂ (μ _{1,1} -NCO) ₂](ClO ₄) ₂	+2.8	+3.6	2.23	2.099, 2.115	95.33, 95.79	16
[Ni ₂ (terpy) ₂ (μ _{1,1} -NCO) ₂ (H ₂ O) ₂](PF ₆) ₂	+4.59	-12.32	2.23	2.044, 2.195	97.7	18
[Ni ₂ (L ¹²) ₂ (μ _{1,1} -NCO) ₂]	+6.85	+7.18	2.19	2.107, 2.244 2.115, 2.280	97.84, 98.74	17
[Ni ₂ (L ¹³) ₂ (μ _{1,1} -NCO) ₂]	+5.31	+5.00	2.19	2.225, 2.201	98.47	64
6	+3.70	+8.05	2.28	2.119, 2.205	97.45, 97.84	This work

^a L¹⁰ = [N,N'-bis(2-pyridinylmethylene)]propane-1,3-diamine; L¹¹ = [N,N'-bis(pyridin-2-yl)benzylidene]ethane-1,2-diamine; terpy = terpyridine; L¹² and L¹³ = tetradentate N₄ donor ligands.

approaches 90°. ⁶⁶ In general, the Ni–N–N angle does not exceed 155° and it is found that if the Ni–N–N angle exceeds 120° and the Ni–N···N–Ni torsion angle approaches 90°, a ferromagnetic coupling between the metal centres is observed. The average Ni–N–N angle of 124.54° and the average Ni–N···N–Ni torsion angle of 70.92° nicely agree with the overall ferromagnetic interaction in complex **4**. It is interesting to note that only four structurally and magnetically characterised crosslinked double EE azido-bridged systems are known in which only in two cases was the Ni–N···N–Ni torsion angle close to 90°, leading to a ferromagnetically coupled system (Table 4), ^{39,40} and thus compound **4** is a valuable addition to this series with perfect agreement of the magneto-structural data.

Unlike **1** and **4**, in complex **5**, two Ni(II) ions are bridged by double EO bridging azides, and working with such a system Ruiz *et al.* theoretically predicted the ferromagnetic interaction in all ranges of Ni–N(μ_{1,1}-N₃)–Ni angles, with J increasing upon increasing the bridging angle, reaching a maximum at 104° approximately. ²³ In fact, all the reported μ_{1,1}-azido bridged Ni(II) dimers exhibit ferromagnetic interaction with only one exception

where a very low bridging angle of 90.41° transmits AF interaction between Ni(II) centres. ⁴⁹ The average Ni–N–Ni angle found in **5** is 101.39°, which falls within the range where strong ferromagnetic interaction prevails between two Ni(II) ions, and therefore the J value of 28.79(2) cm⁻¹ found in **5** is quite reasonable. However, unlike theoretical prediction, the experimental data do not show a clear relationship with Ni–N–Ni angles as a small variation of Ni–N–Ni angles in a narrow range *ca.* 98–103.9° shows a large variation of the J values from 1.91 to 43.9 cm⁻¹, ^{43–63} leaving an unsolved challenge which will require consideration of more than one structural parameter at once. In contrast to μ_{1,1}-N₃ bridged Ni(II) complexes, only five doubly μ_{1,1}-NCO bridged dinickel(II) complexes are known. ^{16–18,64} The magnetic and crystallographic data of these complexes are presented in Table 5, which shows that J values span a narrow range of 1.7 to 6.85 cm⁻¹. The sign and magnitude of the J value of 3.70(2) cm⁻¹ in **6** is again reasonable for such complexes in which a general tendency is that the J value increases with increasing bridging angles, similar to the theoretical prediction carried out for azide analogues. ²³

Conclusion

We have synthesized and characterized six novel dinuclear Ni(II) complexes with different bridging modes of pseudohalides. The pyridyl containing neutral ligands favour EE bridged complexes **1**, **2** and **4**, while the phenolate containing anionic ligand stabilizes the EO bridged compounds **5** and **6**. Their magnetic properties were discussed based on their structures. For the isostructural and isomorphous compounds **1** and **2** with EE bridging pseudohalides, an intramolecular antiferromagnetic interaction is observed in which the doubly EE cyanato-bridged dimeric Ni(II) complexes are scarce in the literature. The magnetic behaviour of compound **3** is characteristic of weak antiferromagnetically coupled Ni(II) ions through $\mu_{1,5}$ -N(CN)₂-bridges. For complex **4**, an additional methyl group in ligand L² affords crossed and nonplanar double EE azido-bridges, which transfer ferromagnetic coupling between the metal centres. Unlike **1**, **2** and **4**, the Ni(II) centres of both complexes **5** and **6** are linked by doubly EO bridging modes. Apparently, complex **5** represents strong ferromagnetic interaction through the bridging azides as the average Ni–N–Ni angle (101.39°) falls within the range where strong ferromagnetic interaction prevails. Also, complex **6** expressing a positive *J* value is rational according to the similar theoretical prediction available on azide systems. Overall, there still exists an unsolved challenge to synthesize and study the rare linked motifs of the Ni(II) dimer to perfect the discipline.

Conflicts of interest

There are no conflicts to declare.

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Notes and references

- G. A. Craig and M. Murrie, *Chem. Soc. Rev.*, 2015, **44**, 2135–2147.
- G. E. Kostakis, A. M. Ako and A. K. Powell, *Chem. Soc. Rev.*, 2010, **39**, 2238–2271.
- M. Andruh, *Chem. Commun.*, 2018, **54**, 3559–3577.
- S. Accorsi, A.-L. Barra, A. Caneschi, G. Chastanet, A. Cornia, A. C. Fabretti, D. Gatteschi, C. Mortalò, E. Olivieri, F. Parenti, P. Rosa, R. Sessoli, L. Sorace, W. Wernsdorfer and L. Zobbi, *J. Am. Chem. Soc.*, 2006, **128**, 4742–4755.
- X.-Y. Wang, Z.-M. Wang and S. Gao, *Chem. Commun.*, 2008, 281–294.
- M. Sarkar, R. Clérac, C. Mathonière, N. G. R. Hearn, V. Bertolasi and D. Ray, *Inorg. Chem.*, 2011, **50**, 3922–3933.
- J. Ruiz, A. J. Mota, A. Rodríguez-Diéguez, I. Oyarzabal, J. M. Secob and E. Colacio, *Dalton Trans.*, 2012, **41**, 14265–14273.
- L. Botana, J. Ruiz, A. J. Mota, A. Rodríguez-Diéguez, J. M. Seco, I. Oyarzabal and E. Colacio, *Dalton Trans.*, 2014, **43**, 13509–13524.
- (a) R. Boča, *Coord. Chem. Rev.*, 2004, **248**, 757–815; (b) J. Miklovič, D. Valigura, R. Boča and J. Titiš, *Dalton Trans.*, 2015, **44**, 12484–12487.
- A. Escuer, J. Esteban, S. P. Perlepes and T. C. Stamatatos, *Coord. Chem. Rev.*, 2014, **275**, 87–129.
- R. Biswas, C. Diaz and A. Ghosh, *Polyhedron*, 2013, **56**, 172–179.
- D. Ghoshal, H. Bialas, A. Escuer, M. Font-Bardía, T. K. Maji, J. Ribas, X. Solans, R. Vicente, E. Zangrando and N. R. Chaudhuri, *Eur. J. Inorg. Chem.*, 2003, 3929–3933.
- F. A. Mautner, M. Mikuriya, H. Ishida, H. Sakiyama, F. R. Louka, J. W. Humphrey and S. S. Massoud, *Inorg. Chim. Acta*, 2009, **362**, 4073–4080.
- K. Ma, Q. Shi, M. Hu, X. Cai and S. Huang, *Inorg. Chim. Acta*, 2009, **362**, 4926–4930.
- R. Boca, M. Boca, M. Gembocký, L. Jäger, C. Wagner and H. Fuess, *Polyhedron*, 2004, **23**, 2337–2348.
- M. Habib, T. K. Karmakar, G. Aromí, J. Ribas-Ariño, H.-K. Fun, S. Chantrapromma and S. K. Chandra, *Inorg. Chem.*, 2008, **47**, 4109–4117.
- A. Panja, N. C. Jana, S. Adak, P. Brandão, L. Dlháň, J. Titiš and R. Boča, *New J. Chem.*, 2017, **41**, 3143–3153.
- M. I. Arriortua, R. Cortes, J. L. Mesa, L. Lezama, T. Rojo and G. Villeneuve, *Transition Met. Chem.*, 1988, **13**, 371–374.
- A. Escuer, R. Vicente, M. S. E. Fallah, X. Solans and M. Font-Bardía, *J. Chem. Soc., Dalton Trans.*, 1996, 1013.
- (a) D. M. Duggan and D. N. Hendrickson, *Inorg. Chem.*, 1974, **13**, 2056; (b) D. M. Duggan and D. N. Hendrickson, *Inorg. Chem.*, 1974, **13**, 2929.
- Z. Mahendrasinh, S. Ankita, S. B. Kumar, A. Escuer and E. Suresh, *Inorg. Chim. Acta*, 2011, **375**, 333–337.
- Z. Serna, N. De la Pinta, M. K. Urtiaga, L. Lezama, G. Madariaga, J. M. Clemente-Juan, E. Coronado and R. Cortés, *Inorg. Chem.*, 2010, **49**, 11541–11549.
- E. Ruiz, J. Cano, S. Alvarez and P. Alemany, *J. Am. Chem. Soc.*, 1998, **120**, 11122–11129.
- F. F. de Biani, E. Ruiz, J. Cano, J. J. Novoa and S. Alvarez, *Inorg. Chem.*, 2000, **39**, 3221–3229.
- P. S. Perlepe, L. Cunha-Silva, K. J. Gagnon, S. J. Teat, C. Lampropoulos, A. Escuer and T. C. Stamatatos, *Inorg. Chem.*, 2016, **55**(3), 1270–1277.
- A. Panja, S. Adak, P. Brandão, E. Dlháň and R. Boča, *Eur. J. Inorg. Chem.*, 2020, 2362–2371.
- A. Panja, N. C. Jana and P. Brandão, *Mol. Catal.*, 2018, **449**, 49–61.
- G. M. Sheldrick, SADABS, University of Göttingen, Germany, 1996.
- G. M. Sheldrick, *Acta Crystallogr., Sect. A: Found. Crystallogr.*, 2008, **64**, 112–122.
- Z. Mahendrasinh, S. B. Kumar, E. Suresh and J. Ribas, *Transition Met. Chem.*, 2010, **35**, 757–763.

- 31 S. S. Massoud, F. A. Mautner, R. Vicente, A. A. Gallo and E. Ducasse, *Eur. J. Inorg. Chem.*, 2007, 1091–1102.
- 32 M. Monfort, I. Resino, J. Ribas, X. Solans, M. Font-Bardia and H. Stoeckli-Evans, *New J. Chem.*, 2002, **26**, 1601–1606.
- 33 A. Escuer, R. Vicente, M. S. E. Fallah, X. Solans and M. Font-Bardia, *Inorg. Chim. Acta*, 1998, **278**, 43–50.
- 34 J. Ribas, M. Monfort, B. K. Ghosh, R. Cortés, X. Solans and M. Font-Bardia, *Inorg. Chem.*, 1996, **35**, 864–868.
- 35 J. Ribas, M. Monfort, C. Diaz, C. Bastos and X. Solans, *Inorg. Chem.*, 1993, **32**, 3557–3561.
- 36 C. G. Pierpont, D. N. Hendrickson, D. M. Duggna, F. Wagner and E. K. Barefield, *Inorg. Chem.*, 1975, **14**, 604.
- 37 P. Chaudhuri, M. Guttman, D. Ventur, K. Wieghardt, B. Nuber and J. Weiss, *J. Chem. Soc., Chem. Commun.*, 1985, 1618.
- 38 A. Escuer, I. Castro, F. Mautner, M. S. E. Fallah and R. Vicente, *Inorg. Chem.*, 1997, **36**, 4633.
- 39 I. I. Ebralidze, G. Leitus, L. J. W. Shimon and R. Neumann, *Inorg. Chim. Acta*, 2009, **362**, 4760–4766.
- 40 X.-T. Liu and Q.-L. Liu, *J. Mol. Struct.*, 2008, **889**, 160–164.
- 41 C.-Y. Liao, H.-H. Wei, S.-C. Cheng and S. Mohanta, *Tamkang Journal of Science and Engineering*, 2002, **5**, 201–208.
- 42 P. Chaudhuri, T. Weyhermiller, E. Bill and K. Wieghardt, *Inorg. Chim. Acta*, 1996, **252**, 195–202.
- 43 S. S. Massoud, F. R. Louka, Y. K. Obaid, R. Vicente, J. Ribas, R. C. Fischerc and F. A. Mautner, *Dalton Trans.*, 2013, **42**, 3968–3978.
- 44 M. G. Barandika, R. Cortés, L. Lezama, M. K. Urriaga, M. I. Arriortua and T. Rojo, *J. Chem. Soc., Dalton Trans.*, 1999, 2971–2976.
- 45 P. Mukherjee, M. G. B. Drew, C. J. Gómez-García and A. Ghosh, *Inorg. Chem.*, 2009, **48**, 5848–5860.
- 46 S. K. Dey, N. Mondal, M. S. E. Fallah, R. Vicente, A. Escuer, X. Solans, M. Font-Bardía, T. Matsushita, V. Gramlich and S. Mitra, *Inorg. Chem.*, 2004, **43**, 2427–2434.
- 47 S. Sarkar, A. Mondal, M. S. E. Fallah, J. Ribas, D. Chopra, H. Stoeckli-Evans and K. K. Rajak, *Polyhedron*, 2006, **25**, 25–30.
- 48 S. Nandi, D. Bannerjee, J.-S. Wu, T.-H. Lu, A. M. Z. Slawin, J. D. Woollins, J. Ribas and C. Sinha, *Eur. J. Inorg. Chem.*, 2009, 3972–3981.
- 49 P. Chaudhuri, R. Wagner, S. Khanra and T. Weyhermüller, *Dalton Trans.*, 2006, 4962–4968.
- 50 A. Bhattacharyya, P. K. Bhaumik, M. Das, A. Bauzá, P. P. Jana, K. Harms, A. Frontera and S. Chattopadhyay, *Polyhedron*, 2015, **101**, 257–269.
- 51 M. Č. Romanović, B. R. Čobeljić, A. Pevec, I. Turel, V. Spasojević, A. A. Tsaturyan, I. N. Shcherbakov, K. K. Andelković, M. Milenković, D. Radanović and M. R. Milenković, *Polyhedron*, 2017, **128**, 30–37.
- 52 P. Ghorai, P. Brandão, S. Benmansour, C. J. Gómez García and A. Saha, *Polyhedron*, 2020, **188**, 114708.
- 53 P. P. Chakrabarty, S. Giri, D. Schollmeyer, H. Sakiyama, M. Mikuriya, A. Sarkar and S. Saha, *Polyhedron*, 2015, **89**, 49–54.
- 54 H.-Z. Kou, S. Hishiya and O. Sato, *Inorg. Chim. Acta*, 2008, **361**, 2396–2406.
- 55 S. Sarkar, A. Mondal, A. Banerjee, D. Chopra, J. Ribas and K. K. Rajak, *Polyhedron*, 2006, **25**, 2284–2288.
- 56 S. Sarkar, A. Datta, A. Mondal, D. Chopra, J. Ribas, K. K. Rajak, S. M. Sairam and S. K. Pati, *J. Phys. Chem. B*, 2006, **110**, 12–15.
- 57 X.-J. Lin, Z. Shen, Y. Song, H.-J. Xu, Y.-Z. Li and X.-Z. You, *Inorg. Chim. Acta*, 2005, **358**, 1963–1969.
- 58 S. Sain, S. Bid, A. Usman, H.-K. Fun, G. Aromić, X. Solans and S. K. Chandra, *Inorg. Chim. Acta*, 2005, **358**, 3362–3368.
- 59 R. Cortes, J. I. Ruiz de Larramendi, L. Lezama, T. Rojo, K. Urriaga and M. I. Arriortua, *J. Chem. Soc., Dalton Trans.*, 1992, 2723–2728.
- 60 R. Vicente, A. Escuer, J. Ribas, M. S. E. Fallah, X. Solans and M. Font-Bardia, *Inorg. Chem.*, 1993, **32**, 1920–1924.
- 61 J. Ribas, M. Monfort, C. Diaz, C. Bastos and X. Solans, *Inorg. Chem.*, 1994, **33**, 484–489.
- 62 A. Escuer, R. Vicente, J. Ribas and X. Solans, *Inorg. Chem.*, 1995, **34**, 1793–1798.
- 63 A. Donmez, G. Oylumluoglu, M. B. Coban, C. Kocak, M. Aygun and H. Kara, *J. Mol. Struct.*, 2017, **1149**, 569–575.
- 64 M. Patra, P. Brandão, A. P. Pikul, S. Adak and A. Panja, *ChemistrySelect*, 2020, **5**, 12924–12931.
- 65 N. F. Chilton, R. P. Anderson, L. D. Turner, A. Soncini and K. S. Murray, *J. Comput. Chem.*, 2013, **34**, 1164–1175.
- 66 A. Escuer, R. Vicente, J. Ribas, M. S. E. Fallah, X. Solans and M. Font-Bardia, *Inorg. Chem.*, 1994, **33**, 1842.



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A novel triple aqua-, phenoxo- and carboxylato-bridged dinickel(II) complex, its magnetic properties, and comparative biomimetic catalytic studies with analogous dinickel(II) complexes†

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This paper describes the synthesis and structures of three dinickel(II) complexes, namely $[\text{Ni}_2(\mu\text{-L})(\mu\text{-OH})](\text{ClO}_4)_2$ (**1**), $[\text{Ni}_2(\mu\text{-H}_2\text{L})(\mu\text{-OH})(\text{NCS})_3](\text{NCS})$ (**2**), and $[\text{Ni}_2(\mu\text{-HL})(\mu\text{-OBz})(\mu\text{-H}_2\text{O})(\text{OBz})](\text{ClO}_4)_2 \cdot 2.5\text{H}_2\text{O}$ (**3**) (where HOBz = benzoic acid), with an end-off compartmental ligand (HL) obtained via the Schiff base condensation of 2,6-diformyl-4-methylphenol and *N,N*-dimethyldipropylenetriamine in methanol. Structural characterization reveals that both **1** and **2** are phenoxo- and hydroxo-bridged compounds, while complex **3** is a unique triple aqua-, phenoxo- and carboxylato-bridged dinickel(II) complex. Although similar bridging patterns to that found in **3** are known, the combination of aqua-, carboxylato- and phenoxo-bridging in a dinickel(II) complex has not been reported in the literature. Variable temperature magnetic susceptibility analysis reveals that the two nickel centres are antiferromagnetically coupled, with *J* values ranging from -12 to -143 K, in these complexes. The phenoxazinone-synthase-like activities of these complexes have been investigated using *o*-aminophenol as a model substrate in a methanol medium, as this area is yet to be explored for nickel(II) systems. Mass spectrometry and EPR spectroscopic studies were further carried out to gain insight into the course of the reaction, and the reactivity trend has been further explored. The present work highlights the novel triply bridged dinickel(II) complex and its magnetic properties and demonstrates a comparative biomimetic catalytic study relating to phenoxazinone synthase.

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Introduction

The synthesis and structural studies of transition metal complexes with a variety of bridging ligands still attract considerable research interest worldwide, mainly because of their relevance in biological systems, catalysis, and molecular magnetism.^{1–3} The literature has witnessed the vast development of studies on the coordination chemistry of compartmental ligands that consist of two symmetrical or asymmetrical pendent arms at the 2- and

6-positions of a phenolic group. These ligands are capable of producing both homo- and hetero-metallic phenoxo-bridged dinuclear transition metal complexes in which metal centres are simultaneously bridged by the phenolate group.^{4–7} In some cases, the presence of additional bridges, such as hydroxide, carboxylate, and pseudohalide ions, may lead to doubly or triply bridged dinuclear metal complexes in which two metal ions are placed in close proximity of 2.9–4.0 Å.^{8–15} In many of these compounds, the metal centres are coordinatively unsaturated and/or bonded with substitutionally labile ions or groups, making these types of compounds attractive candidates for biomimetic studies; consequently, they have been extensively employed in the structural and functional modelling of various metalloenzymes, like catechol oxidase,^{10,11} catalase,¹² urease,¹³ purple acid phosphatases,¹⁴ phosphoesterases, and DNA nucleases,¹⁵ to gain insight into the mechanistic aspects of metalloenzymes. In addition to modelling the structures and functions of the active sites of metalloenzymes, these compounds could provide a large number of ferro-/antiferromagnetically coupled discrete dinuclear metal complexes; this could help to provide insight into the fundamental aspects of

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pairwise exchange interactions, knowledge of which could at least allow qualitative assessments of the magnetic coupling in high nuclearity systems for the betterment of the field of molecular magnetism.¹⁶

We have been using N/O-donor Schiff bases derived from *N,N*-dimethyldipropylenetriamine for quite some time for the synthesis of transition-metal complexes with intriguing magnetic properties^{17,18} and biomimetic catalysts, modelling the function of phenoxazinone synthase.^{19–21} The diverse coordination abilities of this triamine have further prompted us to explore the coordination abilities of ligands derived from this triamine. We have also recently explored the coordination chemistry of a Schiff base ligand (HL, Scheme 1), resulting from the condensation of 2,6-diformyl-4-methylphenol and *N,N*-dimethyldipropylenetriamine, with Ni(II) salts in the presence of azide ions of different stoichiometries; these complexes exhibited diverse magnetic properties, ranging from antiferromagnetic to ferromagnetic.²² Phenoxazinone synthase is a multicopper oxidase that catalyses the oxidative coupling of two substituted *o*-aminophenols to the phenoxazinone chromophore through the catalytic activation of dioxygen in the final stage of the biosynthesis of a naturally occurring antitumor drug actinomycin D,²³ which is used clinically for the treatment of various cancers,^{24–26} and several other transition metal (mostly manganese and cobalt) complexes have been proved to be excellent functional models of this metalloenzyme.¹⁰ Ni(II) complexes, on the other hand, have been extensively studied as biomimetic catalysts for other oxidase metalloenzymes, like catechol oxidase, but the phenoxazinone synthase abilities of these metal complexes are yet to be explored.¹⁰ Therefore, in the present endeavour, three dinickel(II) complexes, [Ni₂(μ-L)(μ-OH)](ClO₄)₂ (1), [Ni₂(μ-H₂L)(μ-OH)(NCS)₃](NCS) (2), and [Ni₂(μ-HL)(μ-OBz)(μ-H₂O)(OBz)](ClO₄)₂·2.5H₂O (3) (where HOBz = benzoic acid), have been synthesised using a compartmental Schiff base ligand (HL). The crystal structures, magnetic properties, and biomimetic catalytic activities when modelling the function of phenoxazinone synthase of these complexes were further investigated and discussed. Interestingly, complex 3, consisting of triple

aqua-, phenoxo-, and carboxylato-bridges, is a unique example of dinickel(II) chemistry.

Experimental section

Materials

2,6-Diformyl-4-methylphenol (DFMP) was prepared following a literature-reported method,²⁷ and *N,N*-dimethyldipropylenetriamine was purchased from Aldrich. All other chemicals (metal salts and solvents) were analytical or reagent grade and used as received.

Warning! Perchlorate salts of metal complexes with organic ligands are potentially explosive. Only small quantities of the compounds should be prepared, and these should be handled with great care.

Synthesis of the Schiff base ligand HL

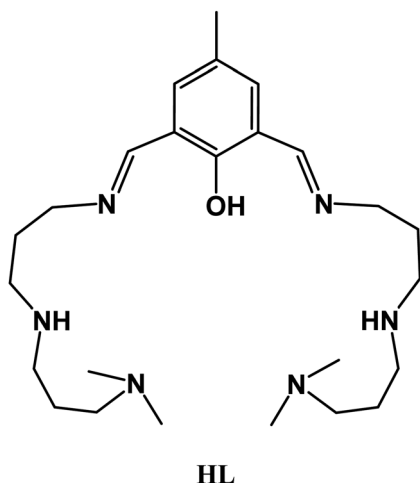
The Schiff base was prepared *via* the condensation of *N,N*-dimethyldipropylenetriamine and 2,6-diformyl-4-methylphenol in methanol, as reported earlier.²²

Synthesis of [Ni₂(μ-L)(μ-OH)](ClO₄)₂ (1)

Ni(ClO₄)₂·6H₂O (0.366 g, 1.0 mmol), HL (0.5 mmol), and triethylamine (0.5 mmol) were mixed together in 30 ml of methanol and were allowed to reflux for about 1 h. After cooling, the reaction mixture was filtered, and the clear deep-green solution was kept at room temperature for slow evaporation. Dark-green single crystals suitable for X-ray analysis were obtained from the filtrate after a few days. The crystals were collected *via* filtration, washed with methanol/ether, and air dried. Yield: 0.339 g; 87%. Anal. calcd for C₂₅H₄₆Cl₂N₆Ni₂O₁₀: C 38.55%, H 5.95%, N 10.79%; found: C 38.34%, H 6.04%, N 10.66%. Selected FTIR bands (cm⁻¹): 625 (s), 1088–1116 (vs) (νClO₄⁻), 1635 (s) (νC=N).

Synthesis of [Ni₂(μ-H₂L)(μ-OH)(NCS)₃](NCS) (2)

Ni(NO₃)₂·6H₂O (0.290 g, 1.0 mmol), the Schiff base ligand (0.5 mmol), and triethylamine (0.5 mmol) were combined in 30 ml of methanol. The resulting green solution was allowed to reflux for *ca.* 1 h. Thereafter, a solution of sodium thiocyanate (2.0 mmol, 0.162 g) dissolved in a minimum amount of methanol was added to the resulting green solution dropwise over a period of 5 min under constant stirring. The reaction mixture (bright dark-green) was stirred under reflux for *ca.* 30 min, and it was filtered to remove any minute quantities of precipitate. The clear dark-green filtrate was kept undisturbed at ambient temperature, affording dark-green crystals of 2 within a week, which were appropriate for single crystal X-ray diffraction measurements. The crystals were collected *via* filtration, washed with methanol/ether, and air dried. Yield: 0.327 g; 78%. Anal. calcd for C₂₉H₄₈N₁₀Ni₂O₂S₄: C 42.77%, H 5.94%, N 17.20%; found: C 42.64%, H 6.01%, N 17.01%. Selected FTIR bands (cm⁻¹): 1634 (s), 1644 (s) (νC=N), 2068 (vs), 2092 (vs) (νNCS⁻).



Scheme 1 The Schiff base HL employed in the present study.

Synthesis of $[\text{Ni}_2(\mu\text{-HL})(\mu\text{-OBz})(\mu\text{-H}_2\text{O})(\text{OBz})](\text{ClO}_4)_2 \cdot 2.5\text{H}_2\text{O}$ (**3**)

$\text{Ni}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (0.366 g, 1.0 mmol), the Schiff base ligand (0.5 mmol), and triethylamine (0.5 mmol) were combined in 30 ml of methanol. The resulting green solution was allowed to reflux for *ca.* 1 h. Thereafter, a methanolic solution of benzoic acid (0.122 g, 1.0 mM) and triethylamine (1.0 mmol) was added under stirring, and this was further allowed to stir for another 30 min. The resulting dark-green reaction mixture was filtered and left at room temperature for crystallisation. Green crystal-line single crystals were separated out from the solution within a couple of days with quality suitable for X-ray single crystal diffraction analysis. The crystals were then filtered and washed with methanol/ether and air dried. Yield: 0.395 g; 74%. Anal. calcd for $\text{C}_{39}\text{H}_{63}\text{Cl}_2\text{N}_6\text{Ni}_2\text{O}_{16.5}$: C 43.85%, H 5.94%, N 7.87%; found: C 43.99%, H 6.01%, N 7.71%. Selected FTIR bands (cm^{-1}): 623 (s), 1094 (vs) (νClO_4^-), 1601–1645 (s) ($\nu\text{C}=\text{N}$ and νCOO^-).

Kinetic studies of the oxidation of *o*-aminophenol

The phenoxazinone-synthase-like activities of **1–3** were examined *via* UV-vis spectrophotometry using *o*-aminophenol (OAPH) as a model substrate. Kinetic experiments for the formation of 2-aminophenoxazin-3-one were carried out *via* monitoring the increase of the spectral band at ~ 435 nm ($\epsilon = 9095 \text{ M}^{-1} \text{ cm}^{-1}$)²⁸ as a function of time in air-saturated methanol at ambient temperature (25 °C). Detailed kinetic studies were performed to gain insight into the reaction kinetics for the catalytic oxidation of OAPH and, for this purpose, varying amounts of the substrates (5×10^{-4} to 1×10^{-2} M) were allowed to react with a fixed complex concentration (5×10^{-5} M), maintaining pseudo-first-order reaction conditions. The rates of the reactions were calculated *via* adopting the initial rate method. The kinetic parameters K_M , V_{max} , and k_{cat} were determined *via* applying the Michaelis–Menten equation. The turnover number (k_{cat} value) was obtained *via* dividing the V_{max} values by the concentration of complex used.

Physical measurements

Elemental analyses for C, H, and N were carried out using a PerkinElmer 240C elemental analyser. IR spectra were recorded using a Thermo Scientific Nicolet iS5 FTIR spectrometer with a universal ATR sampling accessory from 4000 to 400 cm^{-1} . UV-vis spectra were recorded using an Agilent Carry-60 diode array UV-vis spectrophotometer at room temperature with a 1 cm path-length cuvette. The X-band EPR spectra were measured in methanol using a JEOL JES-FA 200 instrument at liquid nitrogen temperature (77 K). Electrospray ionization mass spectrometry (ESI-MS positive) was carried out using a Micromass Q-ToF-Micro Quadrupole mass spectrometer. DC susceptibility data were measured using a Quantum Design MPMS-XL-5 magnetometer in a constant magnetic field of 2 kOe between 2 and 300 K. All the presented data were corrected taking into account the contribution of the sample holder and the diamagnetic susceptibility of inner-shell electrons.

X-ray crystallography

Single crystal X-ray diffraction data from **1–3** were collected at 150 K using a Bruker Kappa Apex-II CCD diffractometer operating with graphite monochromated Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$) *via* applying φ - and ω -scan methods. The intensity data were processed in the Bruker APEX-II suite (v2.0-2) program and the data were corrected for Lorentz and polarization effects with Bruker SAINT plus. The multi-scan absorption correction method was applied for data correction using the SADABS program.²⁹ The structures were solved and refined by means of the full matrix least-squares technique based on F^2 using SHELXT 2014/5 and SHELXL2018/3,³⁰ respectively. All non-hydrogen atoms were refined with independent anisotropic displacement parameters. Hydrogen atoms were added geometrically and refined as riding atoms with fixed thermal parameters 1.2- or 1.5-times those of the corresponding parent atoms, with the exception of aqua ligands and molecules of water of crystallisation, whose H atoms were located in the difference Fourier map and further refined with O–H constrained distances if needed. The methyl groups associated directly with one of the tertiary amine nitrogen atoms and the oxygen atoms of one perchlorate ion in **1** and the sulphur atom of one of the coordinated thiocyanate ions in **2** were refined using a disordered model. One of the molecules of water of crystallisation in **3** was allowed to freely refine, and it was then rounded up with 0.33 occupancy to make it reasonable. The crystal structures of the complexes were generated through the program MERCURY-4.3.1. Data collection and structural refinement details for the complexes can be found in Table 1.

Results and discussion

Synthesis and general characterization

The reaction of a methanolic solution of the compartmental Schiff base ligand HL with $\text{Ni}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ at a 1 : 2 molar ratio in methanol afforded $[\text{Ni}_2(\mu\text{-L})(\mu\text{-OH})](\text{ClO}_4)_2$ (**1**). The corresponding reaction with $\text{Ni}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ in the presence of benzoic acid at a 1 : 2 : 1 molar ratio resulted in $[\text{Ni}_2(\mu\text{-HL})(\mu\text{-OBz})(\mu\text{-H}_2\text{O})(\text{OBz})](\text{ClO}_4)_2 \cdot 2.5\text{H}_2\text{O}$ (**3**). A similar reaction with $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ in the presence of NaSCN at a 1 : 2 : 2 molar ratio in refluxing methanol solution produced $[\text{Ni}_2(\mu\text{-H}_2\text{L})(\mu\text{-OH})(\text{NCS})_3](\text{NCS})$ (**2**). An equimolar amount of triethylamine was added for the deprotonation of the Schiff base ligand in all cases and also that of benzoic acid in **3**. These complexes were obtained in high yields, and the phenolic group of the ligand that is deprotonated bridges two metal ions, leading to dinickel(II) complexes. X-ray-quality single crystals of **1–3** were obtained *via* the slow evaporation of the reaction mixtures. The isolated complexes were characterized *via* elemental micro-analyses, IR and UV-vis spectroscopy (Fig. S1 and S2, ESI,[†] respectively), and single-crystal X-ray diffraction studies, and these complexes are fairly soluble in common organic solvents like methanol, acetonitrile, and DMF. A thermogravimetric study was performed to check the number of molecules of

Table 1 Crystal details and structure refinement parameters of complexes 1–3

	1	2	3
Empirical formula	C ₂₅ H ₄₆ Cl ₂ N ₆ Ni ₂ O ₁₀	C ₂₉ H ₄₈ N ₁₀ Ni ₂ O ₂ S ₄	C ₃₉ H ₆₃ Cl ₂ N ₆ Ni ₂ O _{16.5}
Formula weight (g mol ^{−1})	779.00	814.43	1068.27
Crystal system	Monoclinic	Triclinic	Triclinic
Space group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$
<i>a</i> (Å)	18.1138(11)	9.2680(4)	12.8331(12)
<i>b</i> (Å)	9.9392(6)	11.2105(4)	14.2244(13)
<i>c</i> (Å)	19.5105(10)	18.8811(7)	15.4895(15)
α (deg.)	90.00	87.895(2)	63.296(3)
β (deg.)	108.764(2)	78.990(2)	72.834(3)
γ (deg.)	90.00	77.785(2)	77.698(3)
Volume (Å ³)	3325.9(3)	1882.01(13)	2402.7(4)
<i>Z</i>	4	2	2
<i>D</i> _{calc} (g cm ^{−3})	1.556	1.437	1.477
μ (mm ^{−1})	1.354	1.264	0.969
<i>F</i> (000)	1632	856	1122
θ range (deg)	2.205–29.196	1.099–29.196	2.494–26.459
Reflections collected	113 948	96 578	38 722
Independent reflections (<i>R</i> _{int})	8997 (0.0469)	10 151 (0.0363)	9821 (0.0361)
Observed reflections [<i>I</i> > 2 σ (<i>I</i>)]	7329	8735	8027
Restraints/parameters	0/480	0/459	4/640
Goodness-of-fit on <i>F</i> ²	1.051	1.040	1.027
Final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0292, <i>wR</i> ₂ = 0.0648	<i>R</i> ₁ = 0.0248, <i>wR</i> ₂ = 0.0587	<i>R</i> ₁ = 0.0321, <i>wR</i> ₂ = 0.0726
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0441, <i>wR</i> ₂ = 0.0706	<i>R</i> ₁ = 0.0326, <i>wR</i> ₂ = 0.0623	<i>R</i> ₁ = 0.0456, <i>wR</i> ₂ = 0.0794
Largest diff. peak/hole (e Å ^{−3})	0.431/−0.487	0.391/−0.357	0.538/−0.590

water of crystallisation in 3 and it is found that the mass loss is comparable to the presence of about three molecules of water of crystallisation in bulk 3 (Fig. S3, ESI[†]); however, the single crystal X-ray crystallography study suggests that one of them is partially occupied.

The IR spectra of the complexes (Fig. S1, ESI[†]) display some common features, such as a band due to an N–H stretching vibration in the range of 3244–3278 cm^{−1}, an O–H stretching vibration at 3444–3465 cm^{−1} due to bridging hydroxide and/or water of crystallisation (in 3), and an azomethine (C=N) band from the Schiff base in the range of 1601–1645 cm^{−1}. However, the azomethine and carboxylate bands are hardly distinguishable in 3. Additionally, the IR spectra of 1 and 3 display the stretching vibration of ClO₄[−] ions as a split band over the range of 1088–1116 cm^{−1}. The splitting of the ν (Cl–O) band is attributed to the involvement of counter ClO₄[−] ions in H-bonding interactions in the solid state. Moreover, the bending vibration of ClO₄[−] ions is observed at 623–625 cm^{−1} in the IR spectra of these complexes.^{18,21} The IR spectrum of 2 also displays a bifurcated band at 2068 and 2092 cm^{−1}, which is characteristic of the asymmetric stretching vibrations of NCS[−] ions. The appearance of two strong peaks in the IR spectrum in 2 is consistent with the presence of both coordinated and non-coordinated NCS[−] ions, as evidenced by the structural characterization.^{21,31}

Description of the crystal structures

Crystal structures of all the complexes were determined *via* single-crystal X-ray diffraction studies. The data collection and structural refinement details for the complexes are assembled in Table 1, and selected bond distances and angles can be found in Table 2 and Table S1 (ESI[†]), respectively. Complex 1 crystallized in the monoclinic *P*2₁/*n* space group, and the crystal structure consists of a dinuclear [Ni₂(μ -L)(μ -OH)]²⁺ cation and

Table 2 Selected bond distances (Å) for complexes 1–3

Bond	1	2	3
Ni1–O1	2.0315(11)	2.0829(9)	2.0406(14)
Ni1–O2	1.9675(12)	2.0484(9)	2.1691(15)
Ni1–O3	—	—	2.0000(14)
Ni1–O5	—	—	2.0785(14)
Ni1–N1	2.0307(13)	2.0370(11)	2.0460(17)
Ni1–N2	2.0782(14)	2.1301(11)	2.1107(17)
Ni1–N3	2.0806(14)	—	—
Ni1–N7	—	2.0628(12)	—
Ni1–N8	—	2.1327(12)	—
Ni2–O1	2.0328(11)	2.0188(9)	2.0221(14)
Ni2–O2	1.9727(12)	2.0257(9)	2.2545(15)
Ni2–O4	—	—	2.0683(14)
Ni2–N4	2.0305(14)	2.0124(11)	2.0640(17)
Ni2–N5	2.0605(14)	2.0570(11)	2.0991(18)
Ni2–N6	2.0812(14)	—	2.1620(17)
Ni2–N9	—	2.0129(12)	—

two ClO₄[−] anions (Fig. 1). Within the dimeric unit, Ni(II) ions are bridged by the phenoxo group of the Schiff base ligand together with an exogenous hydroxo ligand, with a Ni–Ni distance of 3.154 Å and phenoxo and hydroxo bridging angles of 101.78(5) and 106.33(6)°, respectively. Both Ni(II) centres exhibit a NiN₃O₂ coordination sphere, which is made up of the bridging phenoxo and hydroxo oxygen atoms and three nitrogen atoms from the triamine part of the ligand. The coordination polyhedrons around the metal centres are best described as distorted square pyramidal structures, as indicated by the structural parameter τ (square pyramid: $\tau = 0$, trigonal bipyramid: $\tau = 1$; $\tau = (\alpha - \beta)/60^\circ$, where α and β are the two largest angles around the central atom) values of 0.05 and 0.15.³² The Ni(II) centres are displaced out of the least squares planes constructed from the exogenous hydroxo group and phenoxo oxygen atom and the imine and secondary amine

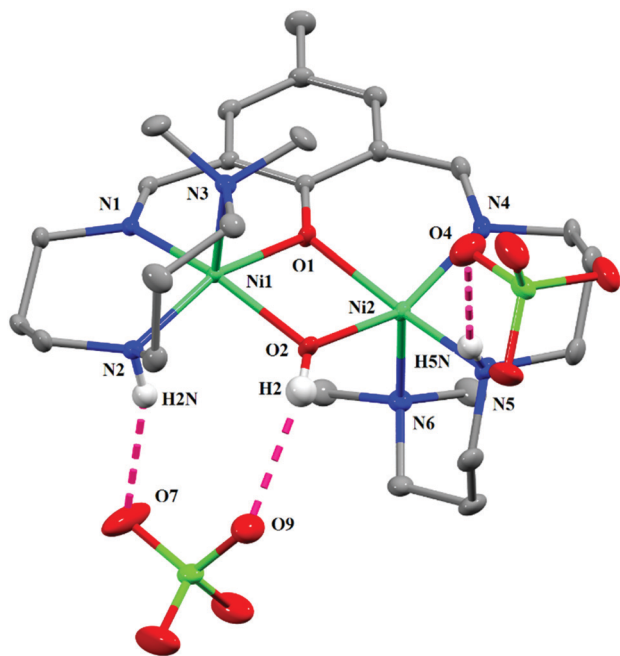


Fig. 1 The crystal structure of **1** displaying the labelling scheme of selected atoms and hydrogen bonding interactions. Ellipsoids are drawn at the 30% probability level, and most of the hydrogen atoms are omitted for clarity. Only one of the positions of disordered atoms is shown.

nitrogen atoms from the Schiff base ligand towards the apically coordinated tertiary amine nitrogen atom, with a deviation of 0.357 Å. The bond distances around the metal coordination spheres are usual for Ni(II) complexes (see Table 2).^{13,33–48} Both perchlorate counter-anions form moderate to strong hydrogen bonding interactions, one of them with the secondary amine group (N5...O4; 3.147(3) Å) only, and the other with both the secondary amine group (N2...O7; 3.009(3) Å) and the bridging hydroxo group (O2...O9; 3.104(2) Å), as shown in Fig. 1 and Fig. S4 (ESI[†]). The closest separation between Ni(II) centres in neighbouring dimeric units is 8.550 Å.

Complex **2** crystallized in the triclinic $P\bar{1}$ space group, and the crystal structure (Fig. 2) consists of a dinuclear [Ni₂(μ-H₂L)-(μ-OH)(NCS)₃]⁺ cation and a thiocyanate anion. Like **1**, within the dinuclear unit, Ni(II) ions are bridged by the phenoxo group together with an exogenous hydroxo ligand, with a Ni–Ni distance of 3.149 Å and phenoxo and hydroxo bridging angles of 100.30(4) and 101.25(4)°, respectively, but the two metal centres are in different coordination environments, i.e., there is a NiN₄O₂ coordination sphere for the Ni1 ion and a NiN₃O₂ coordination sphere for the Ni2 centre. In addition to the bridging hydroxo and phenoxo groups, the coordination sphere around Ni1 is made up of two N-bound trans-disposed thiocyanate ions and imine and secondary amine nitrogen atoms from one arm of the Schiff base, while the coordination sphere of Ni2 is made up of one terminal N-bound thiocyanate ion and imine and secondary amine nitrogen atoms from the other arm of the Schiff base ligand with the usual bond distances (Table 2).^{13,33–48} The coordination polyhedron around the Ni1 centre is best described as a distorted octahedron, as reflected by the significant deviation of the cisoid (78.19(4)–96.62(4)°) and transoid (166.87(4)–174.46(5)°) angles from the ideal values, while the geometry around Ni2 centre is close to square pyramidal, with a structural parameter τ value of 0.27.³² Unlike **1**, the tertiary amine groups in **2** are protonated and, thus, are involved in H-bonding interactions, as depicted in Fig. 2, in which one protonated tertiary amine is connected with the oxygen atom of the bridging hydroxide through an intramolecular hydrogen bond with an N3...O2 distance of 2.585(2) Å, while the other protonated tertiary amine group establishes an intermolecular hydrogen bond with the nitrogen atom of a non-coordinated thiocyanate ion with an N6...N10 distance of 2.824(2) Å. The sulphur atom of the non-coordinated thiocyanate ion is further involved in bifurcated hydrogen bonding with the bridging O–H (O2...S4 = 3.414(1) Å) and secondary amine N–H (N5...S4 = 3.5773(12) Å) from a neighbouring complex cation, leading to the formation of a supramolecular hydrogen-bonded dimer of dimers, as depicted in Fig. 2 and Fig. S5 (ESI[†]).

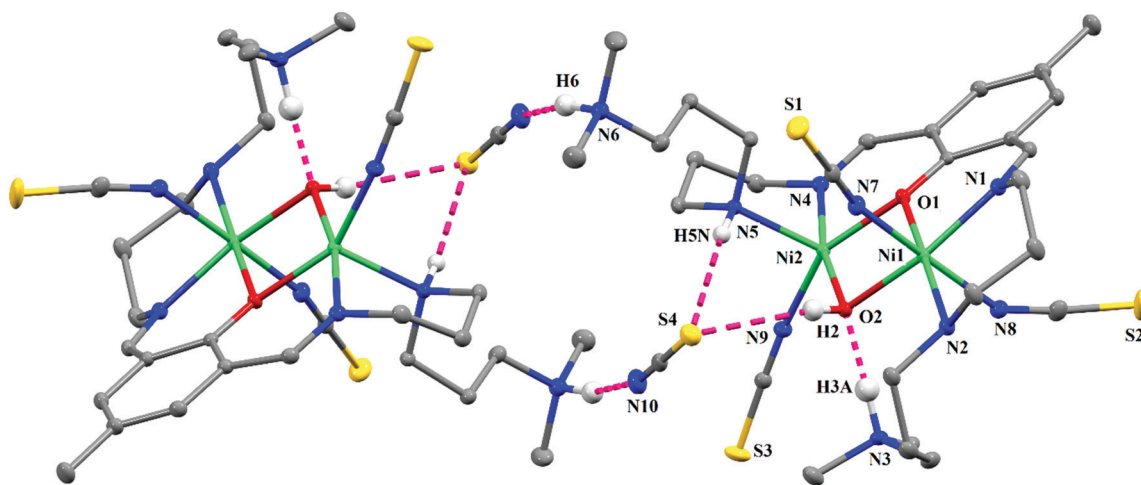


Fig. 2 The crystal structure of **2** showing the atom numbering scheme and hydrogen bonding interactions. Ellipsoids are drawn at the 30% probability level and most of the hydrogen atoms are omitted for clarity. Only one of the positions of disordered atoms is shown.

The closest separation between Ni(II) centres of neighbouring dimeric units is 9.268 Å, which is slightly higher than that found in **1**.

Complex **3** crystallized in the triclinic $P\bar{1}$ space group, and the crystal structure (Fig. 3) consists of a dinuclear $[\text{Ni}_2(\mu\text{-HL})(\mu\text{-OBz})(\mu\text{-H}_2\text{O})(\text{OBz})]^{2+}$ cation, two ClO_4^- anions, and a few water of crystallization molecules. In this dimeric entity, both Ni(II) centres are in an octahedral environment, being triply bridged by a phenoxo group from the Schiff base ligand, a benzoate ion in *syn-syn* configuration, and an aqua ligand, with Ni–Ni separation in the dimeric unit of 3.217 Å and phenoxo and aqua bridging angles of 104.73(6) and 93.30(6)°, respectively. The remaining coordination sites are filled by three nitrogen atoms from one triamine arm of the Ni2 centre, while imine and secondary amine nitrogen atoms from the other arm of the Schiff base and one oxygen atom of the monodentate benzoate ion fill the coordination sites around the Ni1 centre. The non-coordinated oxygen atom of the monodentate benzoate ion in turn is involved in strong hydrogen bonding interactions with the bridging aqua ligand ($\text{O2}\cdots\text{O6}$; 2.544(2) Å), as depicted in Fig. 3, thereby stabilising the triply bridged structure. Therefore, in the present case, the zwitterionic form of the Schiff base ligand is coordinated to the metal centres; the phenolic group is deprotonated and is bridged by the two metal centres, leaving one of the tertiary amine groups protonated. This protonated tertiary amine group participates in strong

hydrogen bonding interactions with one of the water of crystallisation molecules ($\text{N3}\cdots\text{O15}$; 2.675(3) Å). Furthermore, the solid-state structure of complex **3** is stabilised by a complex network of moderate to strong hydrogen bonding interactions with the involvement of perchlorate counter anions, lattice water molecules, and secondary amine groups of the Schiff base ligands, with donor–acceptor distances varying in the range of 2.545(2)–3.245(3) Å (Fig. S6, ESI†). Although it is a triply bridged system, the Ni–Ni separation in the dimeric unit of 3.217 Å is slightly longer than that found in **1** and **2**, while the closest separation between neighbouring dimeric units is found to be 7.740 Å.

The structural studies reveal the diverse coordination abilities of the Schiff base ligand HL in the present systems; the monoanionic L^- form of the ligand is bonded to the metal centres in **1**, while monocationic H_2L^+ and the zwitterionic form of the ligand coordinate the metal centres in **2** and **3**, respectively. Another notable observation is the geometrical differences around the metal centres in these complexes, as both Ni(II) centres in **1** have a five-coordinated and square-pyramidal structure, one Ni(II) ion adopts square-pyramidal geometry and the other one adopts octahedral geometry in **2**, and both metal centres adopt octahedral geometry in **3**. However, the most remarkable structural feature is the unique bridging pattern found in complex **3**. Literature reports reveal that aqua-bridged dinickel(II) complexes are not very abundant, and they have generally involved examples of triple-bridged systems, which are mostly associated with either double phenoxo bridges^{33–39} or double carboxylato bridges.^{40–46} A further observation is that when di(phenoxo) bridges are involved, the bridging aqua angle is less than 90°, and when two *syn-syn* carboxylate bridges are involved, the bridging aqua angles are quite large and always greater than 100°. In the present system (complex **3**), an intermediate aqua bridging angle of 93.30(6)° was observed, as it is associated with one phenoxo and one *syn-syn* carboxylate bridge. The structure of **3** is very close to dinickel(II) complexes where the bridging phenoxo is replaced by an alkoxo group.⁴⁷ Despite all sorts of notable dissimilarities, all these complexes are constructed with edge-sharing bi-polyhedral structures; two bridging phenoxo and hydroxo groups form the common edge in **1** and **2**, while it is formed from the bridging phenoxo and aqua ligands in **3** (see Fig. S7, ESI†). Also, both bridging atoms occupy the equatorial positions of the metal centres, irrespective of the geometry. The *syn-syn* carboxylate bridge occupies the apical positions of the two adjacent bi-octahedral structures in **3**.

Magnetic properties

DC magnetic susceptibility data were measured using polycrystalline samples of **1–3** in the temperature range of 300–2 K under a constant applied magnetic field of 2 kOe. The temperature dependent susceptibility per mole χ and χT values are displayed in Fig. 4. As can be seen from the figure, the susceptibility values increase with decreasing temperature from room temperature, reach maximum values at approximately 130 K for **1**, 45 K for **2**, and 11 K for **3**, and decrease

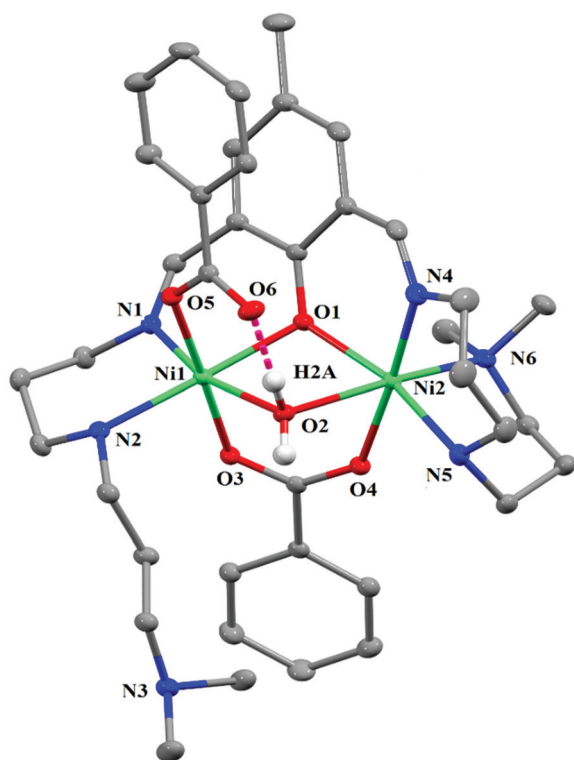


Fig. 3 The crystal structure of the complex cation of **3**, displaying the labelling scheme of selected atoms and the hydrogen bonding interactions. Ellipsoids are drawn at the 30% probability level and most of the hydrogen atoms are omitted for clarity.

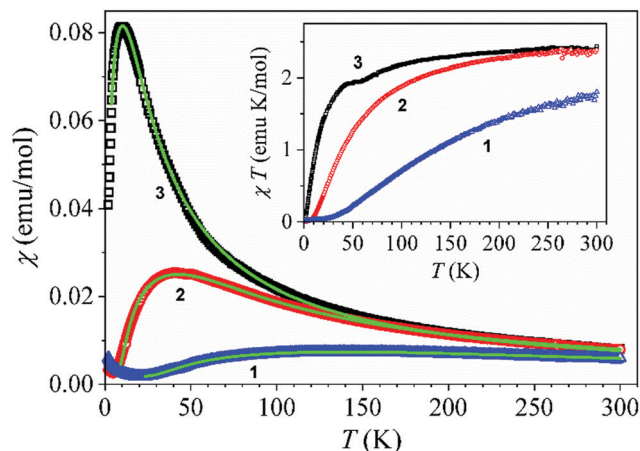


Fig. 4 The temperature-dependent molar magnetic susceptibility data for **1–3**. The solid green lines are fitted using eqn (1) and the parameters shown in Table 3. The inset shows χT vs. T plots.

thereafter, which is a clear indication of antiferromagnetic interactions between the Ni(II) ions in the dimeric units. At room temperature, the χT values of $2.4 \text{ emu K mol}^{-1}$ for **2** and **3** are slightly higher than the calculated value of $2.0 \text{ emu K mol}^{-1}$ for two noninteracting Ni(II) ions with $S = 1$ and $g = 2$, which is due to orbital contributions from Ni(II) ions at room temperature. However, the χT value of $1.8 \text{ emu K mol}^{-1}$ for **1** is slightly lower than the theoretical value, indicating that antiferromagnetic coupling between the two Ni(II) centres is operative even at room temperature. The isotropic Heisenberg model, $H = -J\mathbf{S}_1 \cdot \mathbf{S}_2$, where $\mathbf{S}_1$ and $\mathbf{S}_2$ are equal to 1 and J is an interaction parameter, can be applied to describe the temperature-dependent magnetic susceptibility values of these systems using the following equation:⁴⁹

$$\chi = \frac{g^2 N_A \mu_B^2}{k_B T} \frac{2(e^x + 5e^{3x})}{1 + 3e^x + 5e^{3x}} (1 - \rho) + \frac{4g^2 N_A \mu_B^2}{3k_B T} \rho \quad (1)$$

where $x = J/k_B T$ and the other symbols have their usual meanings. The second term accounts for a small amount of non-coupled magnetic moment, and ρ is the molar fraction of these noncoupled species. The best fits to the experimental data were obtained (solid green lines in Fig. 4) with $J/k_B = -143 \text{ K}$, $g = 2.3$, and $\rho = 1\%$ for **1**; $J/k_B = -42 \text{ K}$, $g = 2.3$, and $\rho = 0\%$ for **2**; and $J/k_B = -12 \text{ K}$, $g = 2.2$, and $\rho = 5\%$ for **3**.

As already described in the structural section, complexes **1** and **2** are dinickel(II) systems with phenoxo and hydroxo bridges. Experimental and theoretical magneto-structural correlations reveal that the major factor controlling the exchange coupling in double phenoxo-/alkoxo-/hydroxo-bridged Ni(μ-O)₂Ni complexes is the bridging Ni–O–Ni angle, and ferromagnetic coupling is expected when the Ni–O–Ni angle is close to 90° .⁵⁰ As the Ni–O–Ni angle deviates from 90° , the ferromagnetic coupling decreases, and above the critical Ni–O–Ni angle of $\sim 98^\circ$, the coupling becomes antiferromagnetic and the strength of the coupling constant increases upon increasing the angle. The phenoxo and hydroxo bridging angles in **2** of $100.30(4)$ and $101.25(4)^\circ$, respectively, are significantly larger than the critical

angle and, thus, the antiferromagnetic coupling between the Ni(II) centres is quite reasonable. The same angles ($101.78(5)$ and $106.33(6)^\circ$, respectively) in **1** are even larger than those found in **2**, which is consistent with the J/k_B value of -143 K for **1**. Furthermore, the geometries of both metal centres in **1** are square pyramidal, while they are octahedral and square pyramidal for the metal ions in **2**. Thus, the average bridging Ni–O distances for equatorially coordinated bridging atoms in **1** (range: $1.9674(14)$ – $2.0333(13) \text{ \AA}$) are somewhat shorter than those of **2** (range: $2.0188(9)$ – $2.0829(9) \text{ \AA}$), which is expected to increase the effective overlap in the super-exchange pathway executed through the bridged atoms in **1**, leading to stronger antiferromagnetic coupling in **1** than in **2**. The connectivity of the two Ni(II) centres in **3** is significantly different from the cases of **1** and **2**, as it is a triply bridged system, comprising *syn-syn* carboxylato, phenoxo, and aqua bridges. The *syn-syn* carboxylato bridge generally propagates antiferromagnetic interactions between the two metal centres.⁵¹ When it is coupled with an aqua bridge and the aqua bridging angle is larger than 100° , the Ni(II) ions experience stronger antiferromagnetic interactions due to the complementary effects of these bridging ligands. Similarly, almost all aqua and phenoxo triply bridged systems transmit weak to moderate ferromagnetic interactions, as all the bridging angles fall well below the critical angle in these systems. In the present case, antiferromagnetic coupling is expected as usual through the *syn-syn* carboxylato bridge and also through the phenoxo bridge, as the phenoxo bridging angle is $104.72(6)^\circ$. However, the bridging aqua angle of $93.30(6)^\circ$, being significantly lower than the critical angle, likely transmits ferromagnetic interactions between the metal ions. Therefore, the counter-complimentary effect of the aqua bridge is responsible for the weaker overall antiferromagnetic coupling in **3**.⁴⁷

The catalytic oxidation of *o*-aminophenol

The phenoxazinone-synthase-like activities of all the complexes were examined using *o*-aminophenol (OAPH) as a model substrate. The progress of the catalytic reaction of a mixture of OAPH (0.01 mM) and a complex ($5.0 \times 10^{-5} \text{ M}$ or $1.0 \times 10^{-4} \text{ M}$) in dioxygen-saturated methanol is monitored *via* UV-vis spectrophotometry at ambient temperature (25°C). The time-dependent spectral profiles, as depicted in Fig. 5, disclose the gradual development of a spectral band at *ca.* 435 nm , indicating the catalytic formation of the phenoxazinone chromophore. Detailed kinetic studies were further carried out to gain insight into the catalytic efficiencies of these complexes; for that, all the complexes ($5.0 \times 10^{-5} \text{ M}$) were allowed to react with excess OAPH, maintaining pseudo-first-order conditions, and the initial rates of the reactions were extracted. Plots of the initial rates against the concentrations of substrate (Fig. 6) follow rate-saturation kinetics, which can be modelled using Michaelis-Menten kinetics and the double-reciprocal Lineweaver-Burk plot (Fig. S8, ESI†) to extract the parameters V_{max} , K_M , and K_{cat} ; these values can be found in Table 4.

Reaction mechanism and comparative catalytic activities

Structural studies of metalloenzymes and several efficient functional models have disclosed that available vacant sites

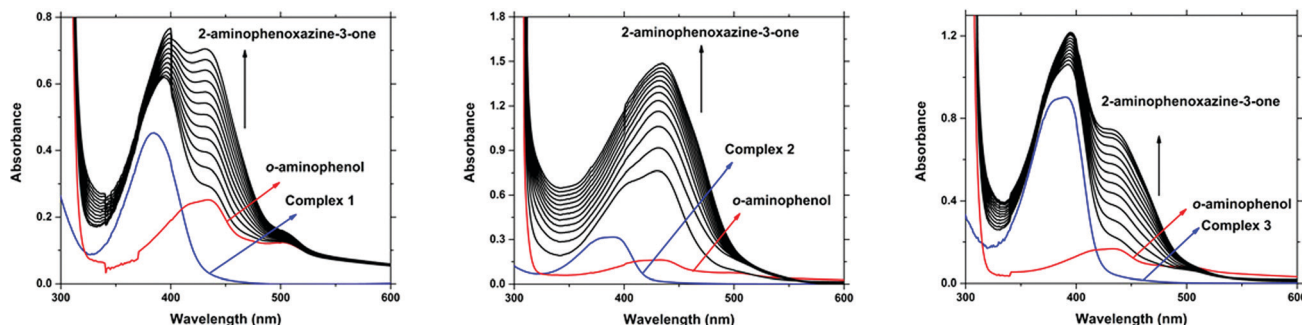


Fig. 5 Absorption vs. wavelength plots for the biomimetic oxidation of *o*-aminophenol in methanol showing the increase in the 2-aminophenoxazine-3-one product at 435 nm with the use of **1–3**. Reactions were conducted under aerobic conditions with 1×10^{-2} M OAPH, 5×10^{-5} M **1** or **2**, and 1×10^{-4} M **3** in methanol at room temperature.

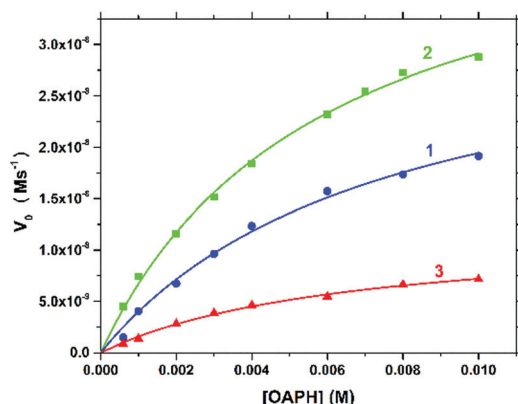


Fig. 6 Michaelis–Menten plots for the oxidation of OAPH in dioxygen-saturated methanol catalysed by complexes **1–3** at room temperature. The points and solid lines represent the experimental and simulated profiles, respectively.

or labile positions for substrate binding are a prerequisite for efficient catalytic activity.^{10,11,52} In complexes **1** and **2**, the metal centres are either coordinatively unsaturated and/or bonded with substitutionally labile thiocyanate ions, favouring the coordination of OAPH to the metal centres and leading to the efficient catalytic conversion of the substrate to the product 2-aminophenoxazine-3-one. The observed rate saturation kinetics further support the idea of complex-substrate adduct formation in these systems. However, in complex **3**, only one Ni(II) centre (Ni1) is bonded with a monodentate benzoate ion, which is strongly connected with the bridging aqua ligand through intramolecular hydrogen bonding; therefore, the formation of a complex-substrate adduct *via* the replacement of the monodentate benzoate ion in **3** is not much more favourable, leading to the weaker conversion of the substrate to the product.

Further information regarding the formation of the complex-substrate intermediate and the course of the reaction can be obtained from mass spectral studies, and for this, the mass spectra of one of the most reactive complexes (complex **2**) alone and in the presence of an excess amount of OAPH (20 equivalents) were recorded and are displayed in Fig. S9 and S10 (ESI[†]), respectively. The peaks at m/z values of 651.22, 664.20, 677.17, 701.49, and 736.17 are from dinickel species

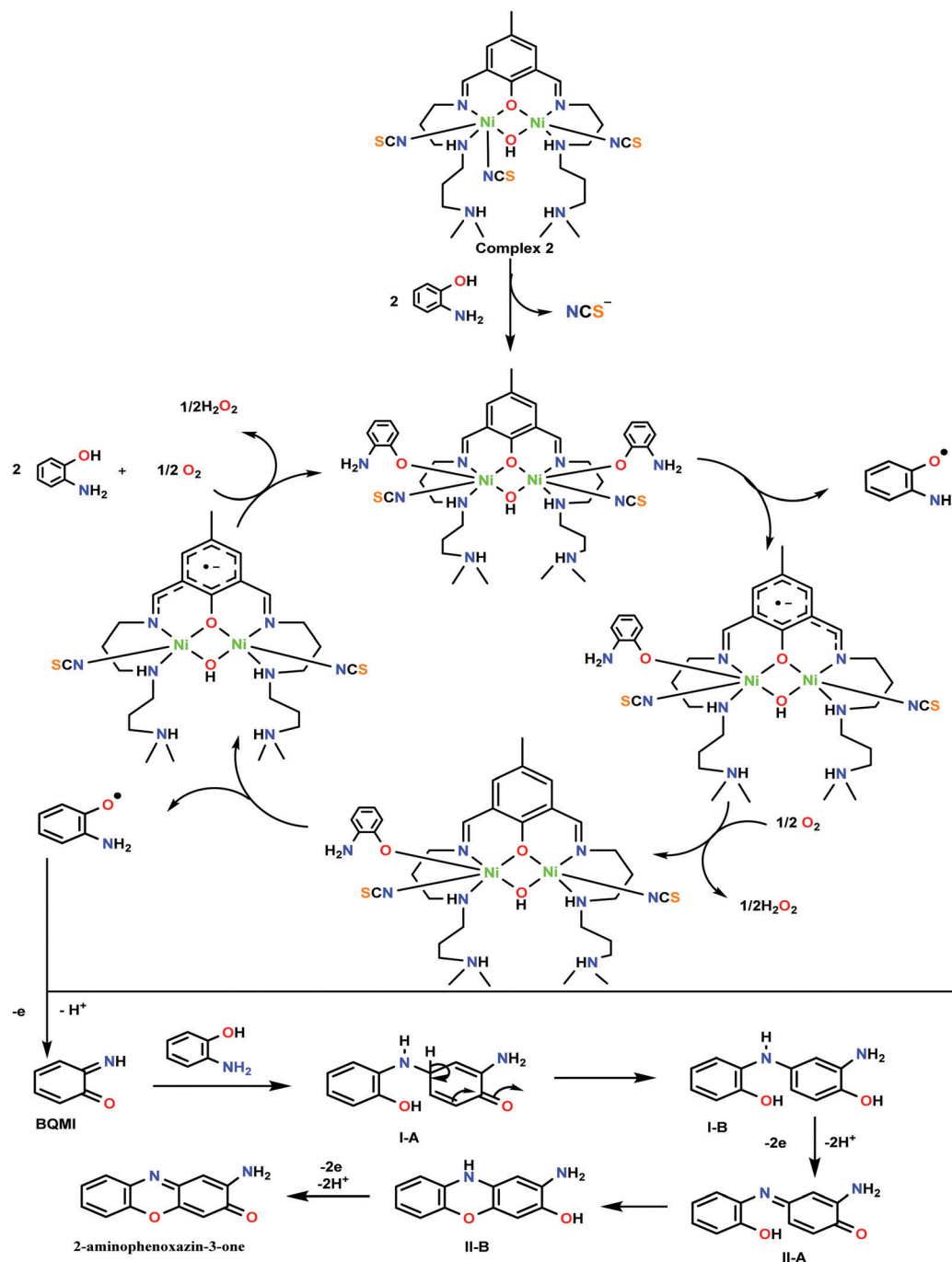
Table 3 Magnetic parameters for **1–3**

	χT (emu K mol ⁻¹)	$\mu_{\text{eff}} = \sqrt{8\chi T/2}$ (μ_B per Ni ion)	J (K)	g	ρ (%)
1	1.8	2.7	−143	2.3	1
2	2.4	3.1	−42	2.3	0
3	2.4	3.1	−12	2.2	5

Table 4 The kinetic parameters of the phenoxazinone-synthase-like activities of **1–3**

Catalyst	V_{max} (M s ⁻¹)	K_M (M)	k_{cat} (h ⁻¹)
1	$(3.41 \pm 0.24) \times 10^{-8}$	$(7.57 \pm 0.99) \times 10^{-3}$	12.30
2	$(4.64 \pm 0.15) \times 10^{-8}$	$(5.92 \pm 0.38) \times 10^{-3}$	16.70
3	$(1.19 \pm 0.06) \times 10^{-8}$	$(6.68 \pm 0.61) \times 10^{-3}$	4.32

with the compositions $[\text{Ni}_2(\text{L})(\text{NCS})(\text{MeOH})]^+$, $[\text{NaNi}_2(\text{L})(\text{OH})(\text{MeO})(\text{MeOH})]^+$, $[\text{Ni}_2(\text{L})(\text{NCS})_2]^+$ or $[\text{NaNi}_2(\text{L})(\text{NCS})(\text{OH})(\text{OH}_2)]^+$, $[\text{NaNi}_2(\text{HL})(\text{NCS})_2]^+$, and $[\text{NaNi}_2(\text{HL})(\text{NCS})(\text{OH})(\text{OH}_2)]^+$, respectively, and these assignments are well supported by the isotopic distribution patterns. A mononuclear Ni species is also found at $m/z = 562.27$, which is matched with a monocationic species with the composition $[\text{Ni}(\text{HL})(\text{NCS})_2]^+$. Interestingly, when mass spectra were recorded in the presence of excess OAPH, most of the peaks relating to the complex itself disappeared. The new major peaks are again well assignable, and these are either substrate-, product-, or intermediate-related species. The peak at $m/z = 213.06$ is consistent with a protonated species of the product 2-aminophenoxazine-3-one (calculated $m/z = 213.07$). The peak at $m/z = 215.08$ is quite interesting as it matched with a protonated species of an important reactive intermediate, II-B (calculated $m/z = 215.09$), generated during the course of the oxidative coupling of *o*-aminophenol in the penultimate step of the formation of 2-aminophenoxazine-3-one, as depicted in Scheme 2. The peaks at m/z values of 950.96, 964.95, 982.99, and 1028.00 are the most important peaks, as their peak-to-peak separation values and isotopic distribution patterns match with those of complex-substrate intermediate species with the compositions $[\text{NaNi}_2(\text{L})(\text{OH})(\text{OAP})_2(\text{NCS})_2(\text{H}_2\text{O})]^+$, $[\text{NaNi}_2(\text{L})(\text{OH})(\text{OAP})_2(\text{NCS})_2(\text{MeOH})]^+$, $[\text{NaNi}_2(\text{L})(\text{OH})(\text{OAP})_2(\text{NCS})_2(\text{H}_2\text{O})(\text{MeOH})]^+$, and $[\text{NaNi}_2(\text{L})(\text{OH})(\text{OAP})_2(\text{NCS})_2(\text{H}_2\text{O})_4]^+$, respectively. The peak at $m/z = 514.50$ is a dicationic



Scheme 2 The most probable mechanistic pathway for the catalytic oxidation of the substrate under aerobic conditions.

species, as suggested by the peak-to-peak separation of 0.5 and, therefore, this dicationic species is a conjugate acid of the mono-cationic species found at $m/z = 1028.00$.

Therefore, mass spectrometry together with rate saturation kinetics studies disclose that the coordination of the substrates to the metal centres is the key step in the catalytic cycle, as depicted in Scheme 2. The catalytic cycle starts with the formation of a complex-substrate adduct in which two thiocyanate ions and two OAPH molecules are bonded to the metal centres, as suggested by the mass spectrometry results where

all the complex-substrate intermediate species consist of two thiocyanate ions and two OAPH molecules. Thereafter, intra-molecular electron transfer occurs from the substrate to the complex. In order to better understand the electron transfer process, we have recorded the X-band EPR spectra at 77 K of complex 2 both in the presence and absence of the substrate. As usual, the compound itself is found to be EPR silent. But when excess OAPH (20 equivalents) was added to the complex, an isotropic signal at $g = 2.008$ appeared, indicating the generation of an organic free radical during the course of this

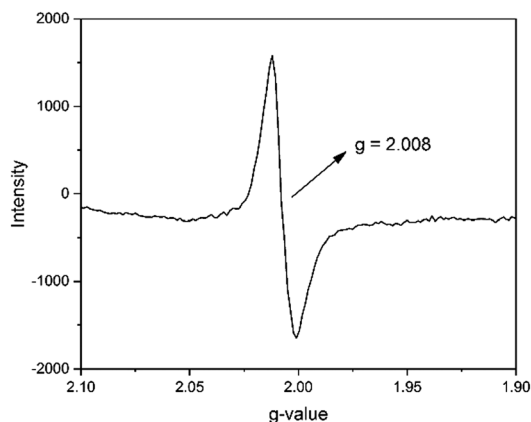


Fig. 7 The X-band EPR spectrum of complex **2** in the presence of excess OAPH.

reaction (Fig. 7). Therefore, the EPR study excludes the possible redox-based participation of the metal centre in an electron-transfer process, leaving ligand-centred base-reduction to be involved in the formation of the imine radical anion intermediate with the concomitant oxidation of OAPH to an OAP radical. The present results are consistent with most previously reported Ni(II) complexes with Schiff base ligands, showing catechol-oxidase-like activity where the Schiff base undergoes a one-electron reduction during the catalytic cycle.⁵³ The slightly higher reactivity of **2** over **1** could be due to the overall positive charge of the ligand (H_2L^+) in **2** compared to the negative charge of the ligand (L^-) in **1**, favouring the reduction of the imine bond towards the formation of the imine radical anion intermediate in the case of **2**. The OAP radical is thereafter converted to *o*-benzoquinone monoamine (BQMI) in many ways, including the disproportionation of the OAP radical itself, finally producing 2-aminophenoxazin-3-one through multiple steps, as shown in Scheme 2. However, H_2O_2 generated in the catalytic cycle was not detected, as it is probably utilised in the non-catalytic pathway for the production of 2-aminophenoxazin-3-one from *o*-benzoquinone monoamine, which requires a couple of oxidative dehydrogenation steps, as depicted in Scheme 2.

Conclusions

In conclusion, three dinickel(II) complexes, namely $[\text{Ni}_2(\mu\text{-L})(\mu\text{-OH})(\text{ClO}_4)_2]$ (**1**), $[\text{Ni}_2(\mu\text{-H}_2\text{L})(\mu\text{-OH})(\text{NCS})_3](\text{NCS})$ (**2**), and $[\text{Ni}_2(\mu\text{-HL})(\mu\text{-OBz})(\mu\text{-H}_2\text{O})(\text{OBz})(\text{ClO}_4)_2 \cdot 2.5\text{H}_2\text{O}]$ (**3**) (where HOBz = benzoic acid), have been synthesized with an end-off compartmental ligand (HL) derived from the Schiff base condensation of 2,6-diformyl-4-methylphenol and *N,N*-dimethyldipropylamine in methanol. X-Ray crystallography studies reveal that both **1** and **2** are phenoxo- and hydroxo-bridged compounds, while complex **3** is a unique triple aqua-, phenoxo-, and carboxylato-bridged dinickel(II) complex. Although similar bridging patterns to that found in **3** are known in the literature, the combination of aqua, carboxylate and phenoxo bridges could be a new addition to the field of dinickel(II) coordination chemistry.

The synthesized complexes display weak to moderate antiferromagnetic coupling between the Ni(II) centres within the dimeric units, with J values spanning the range of -12 to -143 K, and magneto-structural correlation has been investigated to gain insight into the exchange pathway. All these complexes exhibit moderate catalytic activity in comparison to phenoxazinone synthase and the extent of the catalytic reactivity has been further explored, with substitutionally labile sites and/or vacant sites at the metal centres being responsible for the higher reactivities of **1** and **2**. Mass spectrometry analysis further supports the idea of complex-substrate adduct formation and EPR spectroscopy indicates the possible involvement of ligand-centre-based reduction in the catalytic cycle; altogether, these studies provide mechanistic insight into the catalytic activity. Although a number of examples of Ni(II)-based efficient models for other metallo-oxidases, such as catechol oxidase, are available, the present modelling of Ni(II) complexes in relation to phenoxazinone synthase activity could be an important addition to the field of biorelevant catalytic activity.

Conflicts of interest

There are no conflicts to declare.

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References

- (a) S. Ciurli, in *Metal Ions in Life Sciences*, ed. A. Sigel, H. Sigel and R. K. O. Sigel, John Wiley & Sons, Chichester, 2007, vol. 2, p. 241; (b) A. L. Noffke, A. Habtemariam, A. M. Pizarro and P. J. Sadler, *Chem. Commun.*, 2012, **48**, 5219; (c) J. X. Liang, H. J. Zhong, G. Yang, K. Vellaisamy, D. L. Ma and C. H. Leung, *J. Inorg. Biochem.*, 2017, **177**, 276; (d) M. Odachowski, C. Marschner and B. Blom, *Eur. J. Med.*, 2020, **204**, 112613.
- (a) G. Ambrosi, M. Formica, V. Fusi, L. Giorgi and Ma. Micheloni, *Coord. Chem. Rev.*, 2008, **252**, 1121; (b) H. Suo, G. A. Solan, Y. Ma and W.-H. Sun, *Coord. Chem. Rev.*, 2018, **372**, 101; (c) P. Sun, D. Yang, Y. Li, B. Wang and J. Qu, *Dalton Trans.*, 2020, **49**, 2151; (d) A. R. Jeong, J. W. Shin, J. H. Jeong, K. H. Bok, C. Kim, D. Jeong, J. Cho, S. Hayami and K. S. Min, *Chem. – Eur. J.*, 2017, **23**, 3023.
- (a) J. A. DeGayner, I.-R. Jeon and T. D. Harris, *Chem. Sci.*, 2015, **6**, 6639; (b) S. Sasmal, S. Roy, L. Carrella, A. Jana, E. Rentschler and S. Mohanta, *Eur. J. Inorg. Chem.*, 2015, 680; (c) X. Ma, E. A. Suturina, M. Rouzières, M. Platunov,

- F. Wilhelm, A. Rogalev, R. Clérac and P. Dechambenoit, *J. Am. Chem. Soc.*, 2019, **141**, 7721; (d) M. D. Santana, G. García, M. Julve, F. Lloret, J. Pérez, M. Liu, F. Sanz, J. Cano and G. López, *Inorg. Chem.*, 2004, **43**, 2132.
- 4 S. S. Massoud, M. Spell, C. Ledet, T. Junk, R. Herchel, R. C. Fischer, Z. Travnicek and F. A. Mautner, *Dalton Trans.*, 2015, **44**, 2110.
 - 5 G. Ambrosi, M. Formica, V. Fusi, L. Giorgi and M. Micheloni, *Coord. Chem. Rev.*, 2008, **252**, 1121.
 - 6 (a) S. Svane, F. Kryuchkov, C. J. Lennarston, C. K. McKenzie and F. Kjeldsen, *Angew. Chem., Int. Ed.*, 2012, **51**, 3216; (b) R. K. Edgal, A. D. Bond and C. J. Mckenzie, *Dalton Trans.*, 2009, 3833; (c) R. K. Edgal, F. B. Larsen, A. D. Bond and C. J. Mckenzie, *Inorg. Chim. Acta*, 2005, **358**, 376.
 - 7 (a) A. Boisen, A. Hazell and C. J. Mckenzie, *Chem. Commun.*, 2001, 2136; (b) P. Dalgaard, A. Hazell, C. J. McKenzie, B. Moubaraki and K. S. Murray, *Polyhedron*, 2000, **19**, 1909; (c) H. Adams, D. Bradshaw and D. E. Fenton, *Inorg. Chim. Acta*, 2002, **332**, 195.
 - 8 F. R. Xavier, A. Neves, A. Casellato, R. A. Peralta, A. J. Bortoluzzi, B. Szpoganicz, P. C. Severino, H. Terenzi, Z. Tomkowicz, S. Ostrovsky, W. Haase, A. Ozarowski, J. Krzystek, J. Telser, G. Schenk and L. R. Gahan, *Inorg. Chem.*, 2009, **48**, 7905.
 - 9 F. Michel, P. Torelli, St. F. Thomas, C. Duboc, C. Philouze, S. Belle, E. Hamman, S. Saint-Aman and J. L. Pierre, *Angew. Chem., Int. Ed.*, 2005, **44**, 438.
 - 10 S. K. Dey and A. Mukherjee, *Coord. Chem. Rev.*, 2016, **310**, 80.
 - 11 (a) S. J. Smith, C. J. Noble, R. C. Palmer, G. R. Hanson, G. Schenk, L. R. Gahan and M. J. Riley, *J. Biol. Inorg. Chem.*, 2008, **13**, 499; (b) T. P. Camargo, F. F. Maia, C. Chaves, B. de Souza, A. J. Bortoluzzi, N. Castilho, N. T. Bortolotto, H. Terenzi, E. E. Castellano, W. Haase, Z. Tomkowicz, R. A. Peralta and A. Neves, *J. Inorg. Biochem.*, 2015, **146**, 77; (c) K. S. Banu, T. Chattopadhyay, A. Banerjee, S. Bhattacharya, E. Suresh, M. Nethaji, E. Zangrando and D. Das, *Inorg. Chem.*, 2008, **47**, 7083.
 - 12 (a) R. L. Lomoth, P. Huang, J. Zheng, L. Sun, L. Hammarström, B. Akermark and S. Styring, *Eur. J. Inorg. Chem.*, 2002, 5965; (b) Y. Gultneh, Y. T. Tesema, T. B. Yisgedu, R. J. Butcher, G. Wang and G. T. Yee, *Inorg. Chem.*, 2006, **45**, 3023.
 - 13 (a) H. Carlsson, M. Haukka, A. Bousseksou, J.-M. Latour and E. Nordlander, *Inorg. Chem.*, 2004, **43**(26), 8252; (b) F. Meyer, *Prog. Inorg. Chem.*, 2009, **56**, 487; (c) T. Koga, H. Furutachi, T. Nakamura, N. Fukita, M. Ohba, K. Takahashi and H. Okawa, *Inorg. Chem.*, 1998, **37**, 989.
 - 14 (a) C. Pathak, S. K. Gupta, M. K. Gangwar, A. P. Prakasham and P. Ghosh, *ACS Omega*, 2017, **2**(8), 4737; (b) X. Zhou, X.-P. Zhang, W. Li, D. L. Phillips, Z. Ke and C. Zhao, *Inorg. Chem.*, 2020, **59**(17), 12065; (c) P. V. Bernhardt, S. Bosch, P. Comba, L. R. Gahan, G. R. Hanson, V. Mereacre, C. J. Noble, A. K. Powell, G. Schenk and H. Wadepohl, *Inorg. Chem.*, 2015, **54**(15), 7249.
 - 15 (a) T. P. Camargo, A. Neves, R. A. Peralta, C. Chaves, E. C. P. Maia, E. H. Lizarazo-Jaimes, D. A. Gomes, T. Bortolotto, D. R. Norberto, H. Terenzi, D. L. Tierney and G. Schenk, *Inorg. Chem.*, 2018, **57**(1), 187; (b) S. K. Barman, T. Mondal, D. Koley, F. Lloret and R. Mukherjee, *Dalton Trans.*, 2017, **46**, 4038.
 - 16 (a) M. Jarenmark, M. Haukka, S. Demeshko, F. Tuczek, L. Zuppiroli, F. Meyer and E. Nordlander, *Inorg. Chem.*, 2011, **50**(9), 3866; (b) S. S. Massoud, C. C. Ledet, T. Junk, S. Bosch, P. Comba, R. Herchel, J. Hošek, Z. Trávníček, R. C. Fischer and F. A. Mautner, *Dalton Trans.*, 2016, **45**, 12933; (c) S. Mandal, S. Mondal, C. Rajnák, J. Titiš, R. Boča and S. Mohanta, *Dalton Trans.*, 2017, **46**, 13135.
 - 17 M. Patra, P. Brandão, A. P. Pikul, S. Adak and A. Panja, *ChemistrySelect*, 2020, **5**, 12924.
 - 18 A. Panja, N. C. Jana, S. Adak, P. Brandão, Ľ. Dlháň, J. Titiš and R. Boča, *New J. Chem.*, 2017, **41**, 3143.
 - 19 N. C. Jana, P. Brandão, A. Frontera and A. Panja, *Dalton Trans.*, 2020, **49**, 14216.
 - 20 A. Panja, N. C. Jana and P. Brandão, *Mol. Catal.*, 2018, **449**, 49.
 - 21 A. Panja, N. C. Jana and P. Brandão, *New J. Chem.*, 2017, **41**, 9784.
 - 22 A. Panja, S. Adak, P. Brandão, Ľ. Dlháň and R. Boča, *Eur. J. Inorg. Chem.*, 2020, 2362.
 - 23 C. E. Barry, P. G. Nayar and T. P. Begley, *J. Am. Chem. Soc.*, 1988, **110**, 3333.
 - 24 Z. Farhane, F. Bonnier and H. J. Byrne, *J. Biophotonics*, 2018, **11**, 1.
 - 25 X. Mu, L. Song, Q. Li, R. Yin, X. Zhao and D. Wang, *Internet J. Gynecol. Obstet.*, 2018, **143**, 225.
 - 26 J. Koshibu-Koizumi, M. Akazawa, T. Iwamoto, M. Takasaki, F. Mizuno, R. Kobayashi, A. Abe, A. Tomoda, M. Hamatake and R. Ishida, *J. Cancer Res. Clin. Oncol.*, 2002, **128**, 363.
 - 27 C. N. Verani, E. Rentschler, T. Weyhermüller, E. Bill and P. Chaudhuri, *J. Chem. Soc., Dalton Trans.*, 2000, 251.
 - 28 A. C. Sousa, M. C. Oliveira, L. O. Martins and M. P. Robalo, *Green Chem.*, 2014, **16**, 4127.
 - 29 G. M. Sheldrick, *SADABS*, University of Göttingen, Germany, 1996.
 - 30 G. M. Sheldrick, *Acta Crystallogr., Sect. A: Found. Crystallogr.*, 2008, **64**, 112.
 - 31 M. Shyamal, T. K. Mandal, A. Panja and A. Saha, *RSC Adv.*, 2014, **4**, 53520.
 - 32 A. W. Addison, T. N. Rao, J. Reedijk, J. V. Rijn and G. C. Verschoor, *J. Chem. Soc., Dalton Trans.*, 1984, 1349.
 - 33 R. Modak, Y. Sikdar, S. Mandal, S. Chatterjee, A. Bieńko, J. Mroziński and S. Goswami, *Inorg. Chim. Acta*, 2014, **416**, 122.
 - 34 L. Rodríguez, E. Labisbal, A. Sousa-Pedrares, J. A. García-Vázquez, J. Romero, M. L. Durán, J. A. Real and A. Sousa, *Inorg. Chem.*, 2006, **45**, 7903.
 - 35 R. Biswas, P. Kar, Y. Song and A. Ghosh, *Dalton Trans.*, 2011, **40**, 5324.
 - 36 R. Biswas, S. Giri, S. K. Saha and A. Ghosh, *Eur. J. Inorg. Chem.*, 2012, 2916.
 - 37 R. Biswas, C. Diaz, A. Bauzá, M. Barceló-Oliver, A. Frontera and A. Ghosh, *Dalton Trans.*, 2014, **43**, 6455.

- 38 R. Biswas, C. Diaz and A. Ghosh, *Polyhedron*, 2013, **56**, 172.
- 39 S. Banerjee, M. G. B. Drew, C.-Z. Lu, J. Tercero, C. Diaz and A. Ghosh, *Eur. J. Inorg. Chem.*, 2005, 2376.
- 40 A. A. Nikiforov, E. N. Dubrov, D. O. Blinou, V. V. Gurzhiy, A. A. Selyutin, I. N. Klykin, A. P. Zhdanov, A. E. Minkovich, N. S. Panina and A. V. Eremin, *Polyhedron*, 2021, **195**, 114971.
- 41 B.-H. Ye, I. D. Williams and X.-Y. Li, *J. Inorg. Biochem.*, 2002, **92**, 128.
- 42 A. Karmakar, K. Deka, R. J. Sarma and J. B. Baruah, *Inorg. Chem. Commun.*, 2006, **9**, 836.
- 43 A. Karmakar, R. J. Sarma and J. B. Baruah, *Eur. J. Inorg. Chem.*, 2006, 4673.
- 44 K. Müller, M. Korb, C. Koo, R. Klingeler, D. Miesel, A. Hildebrandt, T. Rüffer and H. Lang, *Polyhedron*, 2017, **138**, 185.
- 45 J. P. S. Walsh, S. Sproules, N. F. Chilton, A.-L. Barra, G. A. Timco, D. Collison, E. J. L. McInnes and R. E. P. Winpenny, *Inorg. Chem.*, 2014, **53**, 8464.
- 46 J. Overgaard, J. P. S. Walsh, V. R. Hathwar, M. R. V. Jørgensen, C. Hoffman, J. A. Platts, R. Piltz and R. E. P. Winpenny, *Inorg. Chem.*, 2014, **53**, 11531.
- 47 D. Volkmer, B. Hommerich, K. Griesar, W. Haase and B. Krebs, *Inorg. Chem.*, 1996, **35**, 3792.
- 48 (a) A. Greatti, M. Scarpellini, R. A. Peralta, A. Casellato, A. J. Bortoluzzi, F. R. Xavier, R. Jovito, M. A. de Brito, B. Szpoganicz, Z. Tomkowicz, M. Rams, W. Haase and A. Neves, *Inorg. Chem.*, 2008, **47**, 1107; (b) M. Fondo, A. M. García-Deibe, N. Ocampo, J. Sanmartín, M. R. Bermejo and A. L. Llamas-Saiz, *Dalton Trans.*, 2006, 4260; (c) R. Vinayak, A. Harinath, C. J. Gómez-García, T. K. Panda, S. Benmansour and H. P. Nayek, *ChemistrySelect*, 2016, **1**, 6532; (d) J.-P. Costes, R. Maurice and L. Vendier, *Chem. – Eur. J.*, 2012, **18**, 4031; (e) A. Paul, A. Figuerola, H. Puschmann and S. C. Manna, *Polyhedron*, 2019, **157**, 39; (f) P. Mukherjee, M. G. B. Drew, C. J. Gómez-García and A. Ghosh, *Inorg. Chem.*, 2009, **48**, 4817; (g) A. Biswas, L. K. Das, M. G. B. Drew, G. Aromí, P. Gamez and A. Ghosh, *Inorg. Chem.*, 2012, **51**, 7993; (h) S. Mandal, V. Balamurugan, F. Lloret and R. Mukherjee, *Inorg. Chem.*, 2009, **48**, 7544.
- 49 O. Kahn, *Molecular Magnetism*, VCH Publishers, New York, 1993, p. 211.
- 50 (a) M. P. Palacios, A. J. Mota, J. E. Perea-Buceta, F. J. White, E. K. Brechin and E. Colacio, *Inorg. Chem.*, 2010, **49**, 10156; (b) J. Ruiz, A. J. Mota, A. Rodríguez-Diéguez, I. Oyarzabal, J. M. Secob and E. Colacio, *Dalton Trans.*, 2012, **41**, 14265.
- 51 (a) C. Ruiz-Pérez, J. Sanchiz, M. H. Molina, F. Lloret and M. Julve, *Inorg. Chem.*, 2000, **39**, 1363; (b) A. R. Fortea, P. Alemany, S. Alvarez and E. Ruiz, *Chem. – Eur. J.*, 2001, **7**, 627.
- 52 A. Panja, M. Shyamal, A. Saha and T. K. Mandal, *Dalton Trans.*, 2014, **43**, 5443.
- 53 (a) M. Mondal, P. M. Guha, S. Giri and A. Ghosh, *J. Mol. Catal. A: Chem.*, 2016, **424**, 54; (b) T. Chakraborty, S. Mukherjee, S. Dasgupta, B. Biswas and D. Das, *Dalton Trans.*, 2019, **48**, 2772; (c) S. Dasgupta, J. Adhikary, S. Giri, A. Bauza, A. Frontera and D. Das, *Dalton Trans.*, 2017, **46**, 5888; (d) T. Ghosh, J. Adhikary, P. Chakraborty, P. K. Sukul, M. S. Jana, T. K. Mondal, E. Zangrando and D. Das, *Dalton Trans.*, 2014, **43**, 841.

Nickel(II) Clusters

Syntheses, Structures and Magnetic Properties of Ferromagnetically/Antiferromagnetically Coupled Penta- and Hexanuclear Azido-Bridged Nickel(II) Coordination Compounds

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Abstract: The use of the Schiff base ligand (HL) derived from 2,6-diformyl-4-methylphenol and *N,N*-dimethyldipropylene-triamine in nickel(II) coordination chemistry has been investigated and two pentanuclear $[\text{Ni}_5(\text{H}_2\text{L})_2(\mu_{1,1}\text{-N}_3)_4(\text{N}_3)_2(\mu_3\text{-OH})_2(\text{H}_2\text{O})_2](\text{NO}_3)_4 \cdot 6\text{H}_2\text{O}$ (**1**), $[\text{Ni}_5(\text{L})_2(\mu_{1,3}\text{-OAc})_2(\mu_{1,1}\text{-N}_3)_4(\mu_3\text{-OH})_2] \cdot 12\text{H}_2\text{O} \cdot 2\text{CH}_3\text{OH}$ (**2**) and one hexanuclear $[\text{Ni}_6(\text{H}_2\text{L})_2(\mu_{1,1}\text{-N}_3)_4(\mu_{1,3}\text{-N}_3)_2(\text{N}_3)_4(\mu_3\text{-OH})_2(\text{H}_2\text{O})_2](\text{ClO}_4)_4 \cdot 4\text{H}_2\text{O}$ (**3**) clusters were isolated under mild conditions. In these complexes, the nature of the anion and stoichiometry of the reactants seem to play important roles in directing the formation of the metal clusters. Their X-ray characterization shows that the Ni_6 cluster can be

considered to be built from two triangular $[\text{Ni}_3(\mu\text{-phenoxido})(\mu_3\text{-OH})(\mu\text{-N}_3)_4]$ subunits with bis($\mu_{1,3}\text{-N}_3$) connectors, while bowtie-shaped Ni_5 clusters are formed by sharing a common vertex. Variable temperature magnetic properties of the penta- and the hexanuclear nickel(II) spin coupled clusters have been investigated and interpreted. According to the present results, although the core structures of triangular Ni_3 units are identical in these systems, the introduction of different bridges bring overall diverse magnetic interaction (antiferromagnetic to ferromagnetic) in these nickel(II) clusters.

Introduction

The last few decades witnessed rapid development of polynuclear coordination clusters with spin-coupled paramagnetic transition metal ions not only because of understanding of their fundamental magnetic phenomena but also for their potential applications as single-molecule magnets (SMMs)^[1–9] and single-chain magnets (SCMs),^[10–14] and in magnetic refrigeration and

quantum computing and nanotechnological devices.^[15,16] A rational approach to synthesize discrete exchange-coupled transition metal clusters depends on the synthetic strategy that involves the use of transition metal ions, multidentate blocking ligands in conjunction with the flexidentate bridging ligands to propagate specific magnetic interactions between the metal centers. In majority, the doubly or triply bridging anions like N_3^- , NCS^- , $\text{N}(\text{CN})_2^-$, CN^- , $\text{C}_2\text{H}_3\text{O}_2^-$, $\text{C}_6\text{H}_5\text{O}^-$ and OH^- are used for the construction of magnetically interesting coordination clusters.^[17] The sign and magnitude of the magnetic exchange interactions between the metal centers in coordination clusters depend on a number of factors; the most important of these are the type of bridging ligands and bridge angles. Among all, azido and hydroxo (phenoxido and alkoxido) bridges are the most versatile mediators of magnetic exchange interactions between paramagnetic ions due to their diverse coordination ability.^[18] In most of the reported complexes, azido bridges propagate antiferromagnetic (end-to-end, $\mu_{1,3}$ bridges) or ferromagnetic interactions (end-on, $\mu_{1,1}$ bridges) depending upon the nature of the bridges.^[19]

New ligands could provide us the opportunity to attain new structural types and spin topologies. Schiff-base ligands have been extensively used as blocking ligands in developing magnetically interesting compounds mainly because of their synthetic simplicity and tremendous structural diversities. The choice of ligands is always a major issue in the development of new synthetic routes to produce such type of coordination clusters.^[20] Phenol-based dinucleating Schiff base ligands are needed to be special mentioned as they are capable to bind simultaneously two metal ions,^[21] leading to the formation of

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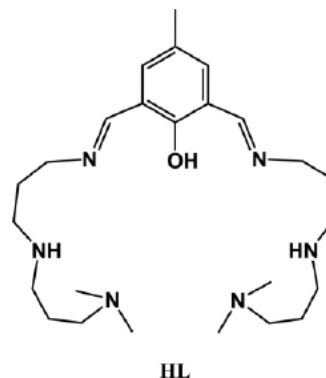
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M₂L type complexes in absence of any bridging ligand. Introduction of secondary bridging units, such as HO[−] and N₃[−], may result in assembly of the transition metal coordination clusters from two or more M₂L units.^[22] Such clusters display a variety of topologies, such as, tetrahedron,^[23] cubane,^[24] open dicubane,^[25] fused defective open dicubane,^[26] pentanuclear vertex-shared double cubane,^[27] and stepped cubane.^[28] We recently initiated a project towards development of coordination chemistry with Schiff bases derived from a triamine, *N,N*-dimethyldipropylenetriamine, in which the diverse coordination adaptabilities of the triamine part of the ligands were observed.^[29] We speculated that the dinucleating Schiff base ligands derived from this triamine would provide enough flexibility to self-assembly of the transition metal ions when react with additional bridging ligands to afford high nuclearity transition metal clusters. With this aim, a new dinucleating Schiff base ligand (HL, Scheme 1) was synthesized in situ by the condensation reaction of 2,6-diformyl-4-methylphenol (DFMP) and *N,N*-dimethyldipropylenetriamine, which thereafter yielded two pentanuclear and one hexanuclear Ni^{II} coordination compounds when reacted with Ni^{II} salts in presence of azide ions. Herein, we report the syntheses of three new complexes, [Ni₅(H₂L)₂(μ_{1,1}-N₃)₄(N₃)₂(μ₃-OH)₂(H₂O)₂](NO₃)₄·6H₂O (**1**), [Ni₅(L)₂(μ_{1,3}-OAc)₂(μ_{1,1}-N₃)₄(μ₃-OH)₂·12H₂O·2CH₃OH (**2**) and [Ni₆(H₂L)₂(μ_{1,1}-N₃)₄(μ_{1,3}-N₃)₂(N₃)₄(μ₃-OH)₂(H₂O)₂](ClO₄)₂·4H₂O (**3**), derived from multinutate dinucleating Schiff base ligand (HL). The crystal structures and magnetic properties of the complexes were further investigated and discussed.



Scheme 1. Schiff base HL employed in the present study.

Results and Discussion

Syntheses and IR Spectra

In the search for ligands that can induce new structural features and capable of synthesizing high nuclearity clusters, a Schiff base ligand (HL) with a high degree of conformational flexibility was prepared in situ by the reaction of 2,6-diformyl-4-methylphenol (DFMP) and *N,N*-dimethyldipropylenetriamine in 1:2 molar ratio in methanol under refluxing conditions (Scheme 1). This in situ generated Schiff base ligand was thereafter allowed to react with different nickel(II) salts and sodium azide in varied stoichiometry and in presence of triethylamine base to obtain diverse high nuclearity nickel(II) clusters. One-pot four-compo-



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Paula Brandão graduated in Biological Engineering from the University of Minho in 1993 and completed a Ph. D. degree in Inorganic Chemistry at the University of Aveiro in 1999. Currently Paula is responsible for the single-crystal X-ray diffraction laboratory, its maintenance, as well as the training of new users, contributing to the knowledge of the students not only to handle the single-crystal X-ray machine but also in solving structures using different methodologies. Simultaneously to the research on crystallography, she is working in the design, synthesis and characterization of polynuclear Cu and Fe complexes with different bio-ligands (DNA bases, Vitamin B₃ and Vitamin B₆), and polypyridyl ligands as alternative anti-tumoral drugs, including their cytotoxicity and DNA studies; bio-metal-organic frameworks as potential delivery vehicles for therapeutic nitric oxide; multinuclear transition metal compounds with important magnetic properties.



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ment reaction of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ with HL and NaN_3 in MeOH in the presence of triethylamine base in 2:1:4 stoichiometry afforded a green solution which gave crystalline compound $[\text{Ni}_5(\text{H}_2\text{L})_2(\mu_{1,1}\text{-N}_3)_4(\text{N}_3)_2(\mu_3\text{-OH})_2(\text{H}_2\text{O})_2](\text{NO}_3)_4 \cdot 6\text{H}_2\text{O}$ (**1**). Similar reaction when carried out using $\text{Ni}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ instead of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $[\text{Ni}_5(\text{L})_2(\mu_{1,3}\text{-OAc})_2(\mu_{1,1}\text{-N}_3)_4(\mu_3\text{-OH})_2] \cdot 12\text{H}_2\text{O} \cdot 2\text{CH}_3\text{OH}$ (**2**) was isolated in crystalline form. Although the structures of both **1** and **2** are very similar, the distinct role of counterions is noticed. The weaker coordinating nitrate ions involve in balancing the charge of the complex cation in **1**, while better coordinating acetato ligand bridges nickel(II) centers in **2**, leading to the formation of an electroneutral complex. The stoichiometric ratio of the reactants also played crucial role in the complex formation, such as when the similar reaction is carried out using $\text{Ni}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$, HL and NaN_3 in MeOH in the presence of triethylamine base in 3:1:6 molar ratio, it resulted only isolable product $[\text{Ni}_6(\text{H}_2\text{L})_2(\mu_{1,1}\text{-N}_3)_4(\mu_{1,3}\text{-N}_3)_2(\text{N}_3)_4(\mu_3\text{-OH})_2(\text{H}_2\text{O})_2](\text{ClO}_4)_2 \cdot 4\text{H}_2\text{O}$ (**3**) in reasonable yield. The presence of counterion in the crystal structure of **3** suggests that, in addition to the stoichiometry of the reactants, use of perchlorate salt seems to have significant role in the formation this complex.

Compound **2** is an electroneutral complex, while both **1** and **3** are ionic compounds having NO_3^- and ClO_4^- as counter anions, respectively, to balance the charge of complex cations. The characteristic stretching band of nitrate ion at 1384 cm^{-1} in the IR spectrum of **1** is consistent with the above fact. Similarly, the stretching and bending vibrations of ClO_4^- ion at 1076 and 621 cm^{-1} , respectively, in the IR spectrum of **3**, ensure the presence of ClO_4^- ions in the crystal lattices.^[30] The stretching vibrations of the azomethine ($\text{C}=\text{N}$) bonds of the Schiff base are located in the range $1627\text{--}1643\text{ cm}^{-1}$ in the IR spectra of **1** and **3**. However, the stretching vibration of the azomethine bond together with the acetate ion is appeared at 1644 cm^{-1} in **2**. The IR spectrum of **1** exhibits a bifurcated strong and sharp band at 2051 and 2070 cm^{-1} , characteristic of the asymmetric stretching vibration of the azido ligands. The bifurcation of the band is indicative of the presence of at least two different kinds of azido ligands, consistent with the structural characterization of **1**. Similar bifurcation of the asymmetric stretching vibration of the azido ligands at 2053 and 2072 cm^{-1} was also observed in the IR spectrum of complex **3**. Unlike **1** and **3**, the IR spectrum of complex **2** is composed of a single strong and sharp asymmetric stretching vibration of the azido ligands at 2061 cm^{-1} , indicating the presence of only one type of azido ligand in this complex.

Description of Crystal Structures

The solid-state molecular structures of compounds **1–3** were established by single-crystal X-ray diffraction analyses and the perspective views the crystal structures of complexes **1–3** along with partial atom numbering scheme are displayed in Figure 1, Figure 2, and Figure 3, respectively. Selected bond lengths and bond angles around the metal coordination spheres in **1–3** are given in Table 1, Table S1 and Table 2, respectively. X-ray diffraction study reveals that compound **1** crystallizes in the monoclinic space group $P2_1/c$, while complex **2** crystallizes in the

triclinic space group $P\bar{1}$. As the structures of both **1** and **2** are very similar, only the structure of the representative compound **1** has been described in detail. The asymmetric unit of **1** is comprised with a trinuclear Ni^{II} cationic part, two nitrate ions and three lattice water molecules in which all atoms are in full occupancy except Ni1 that resides on an inversion center with half occupancy. The symmetry operation through a crystallographic inversion center produces a full set of the centrosymmetric compound $[\text{Ni}_5(\text{H}_2\text{L})_2(\mu_{1,1}\text{-N}_3)_4(\text{N}_3)_2(\mu_3\text{-OH})_2(\text{H}_2\text{O})_2](\text{NO}_3)_4 \cdot 6\text{H}_2\text{O}$ (**1**). Structural analysis discloses that the

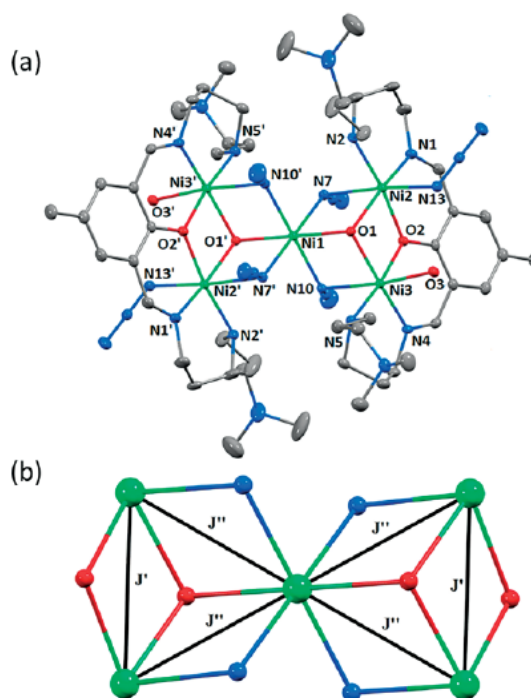


Figure 1. (a) Crystal structure of **1** with partial atom numbering scheme. Primed and unprimed atoms are related by the crystallographic inversion center. Ellipsoids are drawn at the 30 % probability level. H atoms, NO_3^- ions and solvent molecules are omitted for clarity. (b) Skeletal representation of the Ni_5 core structure displaying magnetic coupling scheme.

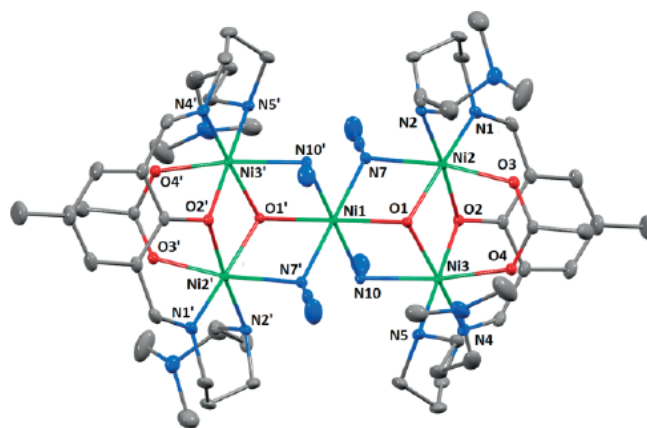


Figure 2. Crystal structure of **2** with partial atom numbering scheme. Primed and unprimed atoms are related by the crystallographic inversion center. Ellipsoids are drawn at the 30 % probability level. H atoms and solvent molecules are omitted for clarity.

complex cation is composed of five Ni^{II} ions held together by two doubly bridging phenoxido groups (μ -O2 and its symmetry equivalent) from Schiff base ligands, two triply bridging hydroxido groups (μ_3 -O1 and its symmetry equivalent), four end-on (EO) doubly bridging N_3^- ions (N7, N10 and their symmetry equivalents). Peripheral ligation is provided by eight nitrogen atoms from two Schiff base ligand H_2L (N1, N2, N4 and N5 and their symmetry equivalents), two azido ligands (N13 and its symmetry equivalent) and aqua ligands (O3 and its symmetry equivalent). Four non-coordinating NO_3^- ions are present in the molecular structures along with six lattice water molecules. Therefore, the protonation of the tertiary amine-N atoms of the Schiff base ligands is required to balance the charge of the system.

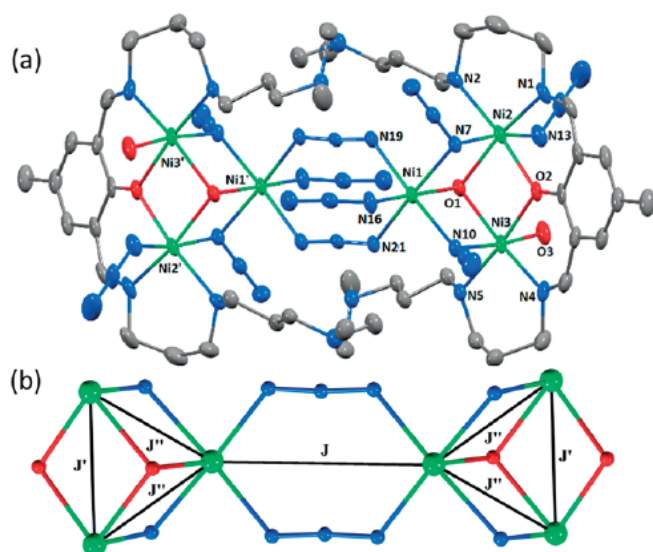


Figure 3. (a) Crystal structure of **3** with partial atom numbering scheme. Primed and unprimed atoms are related to the crystallographic inversion center. Ellipsoids are drawn at the 30 % probability level. H atoms, ClO_4^- ions and solvent molecules are omitted for clarity. (b) Skeletal representation of core structure displaying magnetic coupling scheme.

Table 1. Selected bond lengths [Å] and angles [deg] for complex **1**.

Distances			
Ni1–O1	2.062(2)	Ni1–N10	2.126(3)
Ni1–N7	2.160(3)	Ni2–N1	2.037(4)
Ni2–O2	2.063(3)	Ni2–O1	2.086(3)
Ni2–N2	2.117(3)	Ni2–N13	2.120(3)
Ni3–N4	2.025(3)	Ni3–O2	2.051(3)
Ni3–O1	2.071(2)	Ni3–O3	2.095(3)
Ni3–N5	2.106(3)	Ni3–N10	2.160(3)
Angles			
O1–Ni1–N10	82.88(10)	O1–Ni1–N7	81.59(11)
N10–Ni1–N7	87.54(12)	O2–Ni2–O1	79.46(10)
N1–Ni2–N2	96.59(14)	O1–Ni2–N7	79.97(10)
O2–Ni3–O1	80.11(10)	O1–Ni3–N10	81.84(10)
N4–Ni3–N5	97.25(13)	O2–Ni3–N10	91.70(11)
Ni1–O1–Ni2	102.44(11)	Ni1–N7–Ni2	95.60(12)
Ni1–O1–Ni3	99.95(10)	Ni1–N10–Ni3	95.19(12)
Ni3–O1–Ni2	98.90(11)	Ni3–O2–Ni2	100.31(11)

The core topology of five Ni^{II} atoms can be best described as a symmetric bowtie in which two reverse triangles (Ni1–Ni2–

Table 2. Selected bond lengths [Å] and angles [deg] for complex **3**.

Distances			
Ni2–N1	2.009(3)	Ni2–O1	2.061(3)
Ni2–O2	2.074(3)	Ni2–N13	2.108(4)
Ni2–N2	2.150(4)	Ni2–N7	2.219(3)
Ni3–N4	2.036(4)	Ni3–O2	2.057(3)
Ni3–O1	2.092(3)	Ni3–O3	2.113(3)
Ni3–N10	2.117(3)	Ni3–N5	2.127(3)
Ni1–N16	2.066(4)	Ni1–O1	2.068(3)
Ni1–N10	2.068(3)	Ni1–N19	2.096(4)
Ni1–N21	2.097(3)#	Ni1–N7	2.145(3)
Angles			
O1–Ni1–N10	82.49(12)	N10–Ni1–N7	91.89(13)
O1–Ni1–N7	82.07(11)	O1–Ni2–N7	80.45(11)
N1–Ni2–N2	95.71(15)	O2–Ni2–N7	86.38(12)
O1–Ni2–O2	78.88(11)	O2–Ni3–O1	78.57(11)
O2–Ni3–N10	90.39(11)	N4–Ni3–N5	97.11(14)
O1–Ni3–N10	80.77(12)	Ni2–O1–Ni1	102.20(12)
Ni2–O1–Ni3	100.37(11)	Ni1–O1–Ni3	98.64(12)
Ni3–O2–Ni2	101.13(11)	Ni1–N7–Ni2	94.81(12)
Ni1–N10–Ni3	97.81(13)		

Symmetry code: $-x, 1 - y, -z$

Ni3 and Ni1–Ni2'–Ni3') share a common vertex Ni1.^[31–33] All Ni^{II} centers reside on a same plane which is because of the presence of a crystallographic inversion center located at middle Ni1 atom. Each triangle is best described as nearly isosceles with Ni···Ni separations of 3.159 and 3.165 Å and 3.233 Å. Each of the four end-on doubly bridging N_3^- bridges the central Ni^{II} ion and one peripheral Ni^{II} ion in asymmetric fashion, while triply bridging μ_3 -HO⁻ groups almost symmetrically links the central Ni^{II} atom with the two peripheral metal ions on either side of the complex cation (see Table 1 and Figure 1). The peripheral metal ions are further connected by the doubly bridging phenoxido groups from the Schiff base ligands. Therefore, the formation of Ni_5 -cluster can be viewed as an aggregation of two dinuclear $[Ni_2(\mu-H_2L)(N_3)(H_2O)]$ fragments with an additional Ni^{II} ion from $Ni(NO_3)_2 \cdot 6H_2O$ salt supported by the exogenous azido and hydroxido bridges. Further inspection of the crystal structure reveals that the three-dimensional arrangement of the $[Ni_5(\mu-N_3)_4(\mu-OH)_2(\mu-phenoxido)_2]$ core has the shape of a defective vertex-shared (Ni1) dicubane where one vertex is missing from each cubane. The bond angles in the defective dicubane vary in the range 79.46 to 102.44°. In addition to the bridging atoms in $[Ni_5(\mu-N_3)_4(\mu-OH)_2(\mu-phenoxido)_2]$ core structure, Ni2 and Ni3 centers are further bonded with two N-donor atoms from either arm of the Schiff base along with a terminal azido and an aqua ligands, respectively. Same thing is also applicable for their symmetry equivalents. Overall, the coordination environments of Ni1 and Ni2 are comprised with N_4O_2 donor sets, while it is N_3O_3 for Ni3 center. Thus, all of the Ni^{II} atoms are six-coordinated with slightly distorted octahedral geometry in which the Ni–O and Ni–N bond lengths span in the range 2.025(3) to 2.160(3) Å (see Table 1).

The structure of $[Ni_5(L)_2(\mu_{1,3}-OAc)_2(\mu_{1,1}-N_3)_4(\mu_3-OH)_2] \cdot 12H_2O \cdot 2CH_3OH$ (**2**) is very similar to that of **1**, with the essential differences being the replacement of the terminal azido and aqua ligands bonded to Ni2 and Ni3, respectively, by the bridg-

ing acetato group (Figure 2). The Ni2...Ni3 distance in **2** is found somewhat shorter (2.975 Å) than that in **1** (3.159 Å) because of the presence of this additional bridging acetato ligand. As a further consequence, the phenoxido- and hydroxido-bridging angles are also reduced significantly (92.92° and 93.98°, respectively) in comparison to 100.31° and 98.91°, respectively, that found in **1**. Moreover, the neutral complex molecule crystallizes with twelve water and two disordered methanol molecules in the crystal lattices in **2**. The electroneutrality of the complex molecule ensures that the non-coordinated tertiary amine-N atoms are not protonated in **2** but they remain protonated in **1** that resulted different hydrogen bonding patterns in the solid-state structures of these compounds. Whereas the tertiary amine nitrogen atoms in the Schiff base ligand are protonated in **1**, thereby participating in strong hydrogen bonding interaction with the oxygen atoms of the nitrate counterions with N...O distances of 2.802 and 2.885 Å. The tertiary amine nitrogen in **2** is on the other hand not protonated, which is involved in strong hydrogen bonding interactions as an acceptor with the lattice water molecules with N...O distances of 2.748 and 2.851 Å. Additionally, a large numbers of solvent molecules present in the crystal lattices stabilize the solid-state structures of **1** and **2** by the participation of moderate to strong hydrogen bonding interactions as shown in Figures S1 and S2, respectively.

Complex $[\text{Ni}_6(\text{H}_2\text{L})_2(\mu_{1,1}\text{-N}_3)_4(\mu_{1,3}\text{-N}_3)_2(\text{N}_3)_4(\mu_3\text{-OH})_2(\text{H}_2\text{O})_2](\text{ClO}_4)_2 \cdot 4\text{H}_2\text{O}$ (**3**) crystallizes in the monoclinic space group $P2_1/n$ in which the crystallographic asymmetric unit is built up by a trinuclear Ni^{II} fragment with triangular arrangements of the metal centers with Ni...Ni separations of 3.155, 3.190 and 3.213 Å, one perchlorate ion and two lattice water molecules (Figure 3). The symmetry operation through an inversion center generates the full set of **3** in which Ni1 atom and its symmetry equivalent Ni1' center are connected by doubly bridging end-to-end azido ($\mu_{1,3}\text{-N}_3$) ligands and the inversion center is located at the midpoint of the central $[\text{Ni}_2(\mu_{1,3}\text{-N}_3)_2]$ core, made up with Ni1, Ni1' and doubly bridging end-to-end azido ligands. Interestingly, the core structure of the Ni^{II} triangle in **3** is identical as that found in **1** where triply bridging hydroxido group ($\mu_3\text{-OH}$) connects the metal centers in association with a doubly bridging phenoxido group ($\mu_2\text{-O}$) to connect the peripheral metal centers and four end-on (EO) doubly bridging N_3^- ions to connect Ni1 either with Ni2 or Ni3. Metric parameters inside the triangular unit in **3** are very similar to those found in **1** without significant differences (see Table 2). Now if we consider all the bridging phenoxido-O, hydroxido-O and azido-N atoms together with three Ni centers, it results a defective cubane with a missing vertex, identical to that found in **1**. Whereas in **1**, a defective dicubane is formed by sharing a vertex (Ni1) of symmetry related two defective cubanes, the two defective cubes on the other hand in **3** are connected to each other by Ni1 and its symmetry equivalent Ni1' through doubly $\mu_{1,3}\text{-N}_3^-$ bridges with Ni1...Ni1' distance of 5.174 Å. In addition to bridging donor atoms constituting the core structure, Ni1 center is bonded with a terminal azido ligand, while Ni2 and Ni3 are bonded with two nitrogen donor atoms from either arm of the Schiff base ligands and a terminal azido ligand to Ni2 and an

aqua ligand to Ni3 atom. Overall, the coordination environments around the metal centers are N_5O , N_4O_2 and N_3O_3 for Ni1, Ni2 and Ni3 atoms, respectively. Thus, all of the Ni^{II} atoms are six-coordinated with slightly distorted octahedral geometry in which the Ni–O and Ni–N bond lengths are comparable to that found in **1** and **2** and to the reported compounds having closely related structures.^[31–33]

A large number of pentanuclear Ni^{II} coordination clusters with different topological structures, such as linear, cross-like, trigonal bipyramidal-like, ring-like, bowtie-like and pentagonal-like motifs, are reported in the literature.^[32] Among them bowtie/twisted bowtie is the most popular motif in Ni₅ coordination chemistry. Notably, only seven azido-bridged Ni₅ clusters have been structurally characterized with bowtie/twisted bowtie topology.^[33] Interestingly, the present core structure is unique in that, although several azido-bound Ni-clusters have been reported in the literature, the core found in **1** has not been observed either in discrete Ni₅-clusters or as a recognizable subfragment of high-nuclearity Ni^{II}-clusters.^[27,33] Therefore, complexes **1** and **2** are important addition to the growing family of Ni₅-cluster with bowtie-like topology. The hexanuclear azido-based nickel(II) clusters reported in the literature mostly belong to a motif featuring four fused defective cubanes.^[28,34] Some cyclic or hexagonal topological displacements were also observed in Ni₆ clusters.^[35] However, the topology found in **3** is closely related to a Ni₆-cluster reported recently where two Ni₃ triangles are connected by a singly $\mu\text{-1,5}$ -bridged dicyanamide ion.^[36] The solid-state structure of **3** is stabilized by means of strong hydrogen bonding interactions. As the tertiary amine-N atoms of the Schiff base ligand are protonated to balance the charge of the system, they participate in strong hydrogen bonding interactions as hydrogen-bond acceptors. Interestingly, one tertiary amine-N atom forms the intramolecular hydrogen bond with a coordinated azido ligand with N...N distance of 2.951 Å, while other tertiary amine-N atom from other arm of the Schiff base constitutes the intermolecular hydrogen bond with a lattice water molecule (N...O, 2.740 Å), which simultaneously participates in the hydrogen bonding interactions with a perchlorate counterion (O...O, 2.904 Å) and a coordinated azido ligand (O...N, 2.666 Å) from the neighboring complex cation. Several other hydrogen bonding interactions as shown in Figure S3 are responsible for overall stability of **3** in the solid state.

Magnetic Data

The effective magnetic moment for **1** at $T = 300$ K adopts a value of $\mu_{\text{eff}} = 7.25 \mu_{\text{B}}$ (Figure 4). This matches five $s = 1$ uncoupled spins, for which the theoretical value is $\mu_{\text{eff}}/\mu_{\text{B}} = g[5s(s+1)]^{1/2} = 7.27$ (typical $g = 2.3$). There is a slight increase of the effective magnetic moment on cooling that can be caused either by some uncompensated temperature-independent magnetism χ_{TIM} or an exchange coupling of the ferromagnetic nature ($J_{\text{f}} > 0$). Below 40 K a marked drop of the μ_{eff} value is registered due to either the exchange interaction of an antiferromagnetic nature ($J_{\text{a}} < 0$) prevailing in this temperature range, or the zero-field splitting (D) typical for the Ni^{II} centers.

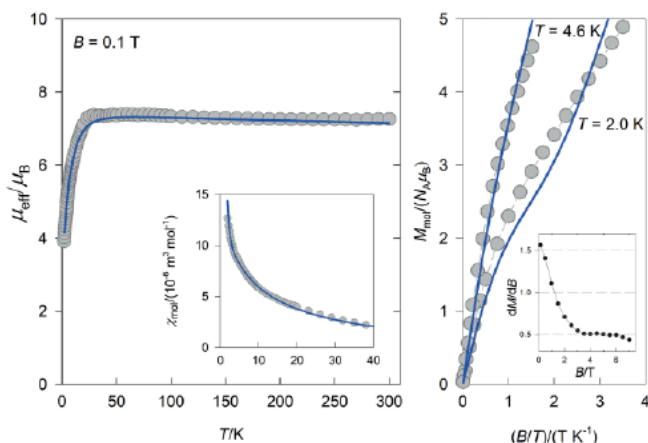


Figure 4. Magnetic functions for **1**. Left: temperature evolution of the effective magnetic moment (inset: temperature dependence of the molar magnetic susceptibility). Right: reduced magnetization (inset: the first derivative at $T = 2.0$ K). Solid lines: fitted.

The magnetization per formula unit is temperature little dependent and it does not show features of the saturation: it adopts a value of $M_1 = 4.9$ at $B = 7.0$ T and $T_0 = 2.0$ K. Theoretical saturation limit for five uncoupled $S = 1$ spins is $M_1 = 5g = 11.5$. A considerable reduction is probably due to the intra complex exchange coupling of an antiferromagnetic nature. Moreover, the first derivative of the magnetization is not a smooth curve (Figure 4 – inset) pointing to the interplay of the antiferromagnetic and ferromagnetic portions of the exchange interactions.

The magnetic data was analyzed by assuming the following form of the isotropic spin Hamiltonian

$$\hat{H}^{\text{iso}} = -J'[(\vec{S}_2 \cdot \vec{S}_3) + (\vec{S}_4 \cdot \vec{S}_5)]\hbar^{-2} - J'' \sum_{A=2}^5 (\vec{S}_1 \cdot \vec{S}_A)\hbar^{-2} + B_2 \mu_B g \sum_{A=1}^5 (\hat{S}_{Az})\hbar^{-1} \quad (1)$$

that involves the ferromagnetic interaction of the central Ni^{II} atom (1) with its neighbors J'' , the antiferromagnetic interaction between two distant pairs (2–3 and 4–5) J' , along with the isotropic Zeeman term. The corresponding interaction matrix of the $N = 3^5 = 243$ size has been diagonalized and the field-dependent energy levels inserted into the formulae of the statistical thermodynamics in order to get the magnetic susceptibility and magnetization, respectively.^[37,38] Both experimental datasets have been processed simultaneously by minimizing the common functional

$$F = w \frac{\sum_i |\chi_i^o - \chi_i^c|}{(1/n) \sum_i \chi_i^o} + (1-w)(1/m) \sum_j (M_j^o - M_j^c)^2 \rightarrow \min \quad (2)$$

with equal weights for the mean magnetic susceptibility and squared Euclidean norm of the magnetization ($w = 0.5$); n and m are the number of experimental points for the susceptibility and magnetization, respectively. The optimization routine converged to the following set of magnetic parameters: $J''/hc = +4.4(8)$ cm⁻¹, $J'/hc = -10.8(9)$ cm⁻¹, and $g = 2.31(9)$ with displayed standard deviations. Two additional corrections applied to the magnetic susceptibility read: temperature-independent

magnetism $\chi_{\text{TIM}} = -15 \times 10^{-9}$ m³ mol⁻¹ (SI units) and molecular-field correction $(zj)/hc = 0.12$ cm⁻¹. The discrepancy factors of the fit are $R(\chi) = 0.04$ and $R(M) = 0.09$. Negative value of χ_{TIM} refers to the underlying diamagnetism.

The fit can eventually be improved by adding the anisotropic zero-field splitting term

$$\hat{H}^{\text{zfs}} = \hat{H}^{\text{iso}} + D \sum_{A=1}^5 (\hat{S}_{Az}^2 - \hat{S}_A^2/3)\hbar^{-2} \quad (3)$$

However, in the present case the fitting procedure converged to a negligible D -value, probably owing to a strong correlation with the antiferromagnetic exchange coupling constant. Notice, the applied model assumes uniform g -factors for peripheral and central Ni^{II} centers which, probably, causes that the fitted magnetization data are not perfect. In the other words, the capabilities of the selected model are exhausted. A more serious problem arises from the fact that the model employed considers a single exchange coupling constant between magnetic centers despite the double (oxido-azido, and oxido-phenoxido) super-exchange paths.

The ferromagnetic exchange coupling between centers 1-A ($A = 2, 3, 4, 5$) matches the end-on coordination mode of the azido ligand. On the contrary, the antiferromagnetic coupling of the peripheral pairs 2–3 and 4–5 is consistent with the μ -O bridge and obtuse angle Ni–O–Ni (99 and 100 deg).

Magnetic data for **2** reveal a considerable exchange interaction of the ferromagnetic nature. The effective magnetic moment increases from its room-temperature value of $\mu_{\text{eff}} = 9.61$ μ_B to $\mu_{\text{eff}} = 11.7$ μ_B at $T = 8.5$ K and then it drops down (Figure 5). The magnetic susceptibility on cooling is only increasing and an eventual maximum is not registered. The magnetization per formula unit saturates to $M_1 = 11.5$ at $T = 2.0$ K and $B = 7.0$ T.

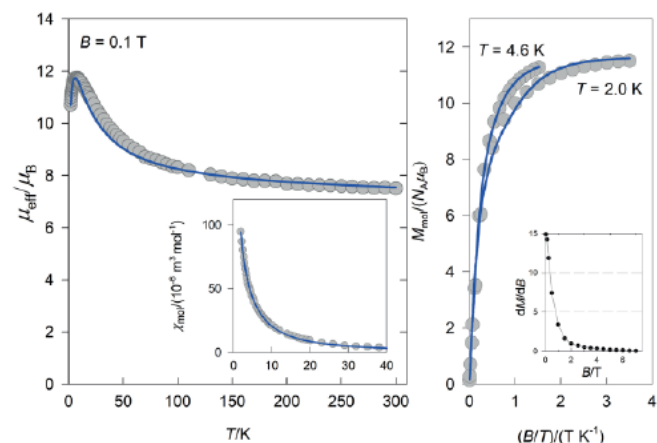


Figure 5. Magnetic functions for **2**. Left: temperature evolution of the effective magnetic moment (inset: temperature dependence of the molar magnetic susceptibility). Right: reduced magnetization (inset: the first derivative at $T = 2.0$ K). Solid lines: fitted.

The data fitting with the help of the Hamiltonian (1) enlarged to (3) gave $J''/hc = +14.7$ cm⁻¹, $J'/hc \approx -1.6$, $g = 2.33(9)$, $D/hc = 3.0(8)$ cm⁻¹, and $\chi_{\text{TIM}} = -17 \times 10^{-9}$ m³ mol⁻¹, $(zj)/hc = -0.007$ cm⁻¹; $R(\chi) = 0.012$ and $R(M) = 0.016$. There is a substantial difference in the bond angles Ni–N₃–Ni between **1** and **2**;

in **2** one of them is 93 deg that is very low and responsible for the dominating ferromagnetic exchange. Negative value of χ_{TIM} recovers the underlying diamagnetism.

The magnetic data for the hexanuclear complex **3** is displayed in Figure 6. The magnetic susceptibility on cooling is only increasing and no maximum is registered. The effective magnetic moment gradually decreases from its room-temperature value of $\mu_{\text{eff}} = 7.20 \mu_{\text{B}}$ to $\mu_{\text{eff}} = 2.74 \mu_{\text{B}}$ at $T = 1.9$ K. This indicates a more effective exchange coupling of the antiferromagnetic nature when compared to **1**. Also the magnetization saturates to a lower value of $M_1 = 1.20$ at $T = 2.0$ K and $B = 7.0$ T. There are neither features of the remnant magnetization nor of the slow magnetic relaxation. The fitting procedure is based upon the isotropic spin Hamiltonian

$$\hat{H} = -J(\vec{S}_{\text{Ni1}} \cdot \vec{S}_{\text{Ni1'}})\hbar^{-2} - J'[(\vec{S}_{\text{Ni2}} \cdot \vec{S}_{\text{Ni3}}) + (\vec{S}_{\text{Ni2'}} \cdot \vec{S}_{\text{Ni3'}})]\hbar^{-2} - J''[(\vec{S}_{\text{Ni1}} \cdot \vec{S}_{\text{Ni2}}) + (\vec{S}_{\text{Ni1'}} \cdot \vec{S}_{\text{Ni2'}}) + (\vec{S}_{\text{Ni2}} \cdot \vec{S}_{\text{Ni3'}}) + (\vec{S}_{\text{Ni2'}} \cdot \vec{S}_{\text{Ni3}})]\hbar^{-2} + B_z \mu_{\text{B}} g \sum_{i=1}^6 (\hat{S}_{z_i})\hbar^{-1} \quad (4)$$

where J' and J'' denote interactions within individual triangles and J between edges of two triangles mediated by two μ -1,3- N_3^- bridges. In such a case the interaction matrix of the total size $N = 3^6 = 729$ is factored according to the total spin ($S = 0$ through 6) to the blocks of the lower size: 15, 36, 40, 29, 15, 5, and 1. This is a tremendous simplification that allows a fast data-fitting when assuming uniform g -factors.^[39] A continuous decrease of the effective magnetic moment indicates the overall antiferromagnetic coupling. In such a case, however, the magnetic susceptibility on cooling should pass through a maximum and then it turns to the zero. This effect is masked by a minor fraction of the paramagnetic impurity x_{PI} that often exists in even-center complexes.

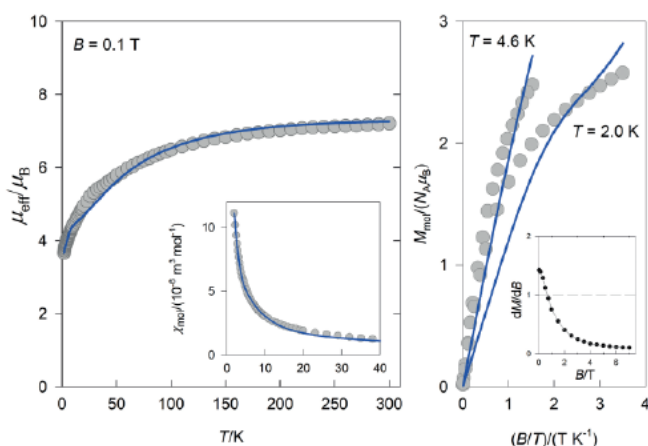


Figure 6. Magnetic functions for **3**. Left: temperature evolution of the effective magnetic moment (inset: temperature dependence of the molar magnetic susceptibility). Right: reduced magnetization (inset: the first derivative at $T = 2.0$ K). Solid lines: fitted.

The fitting procedure yields the inter-triangle coupling constant $J/hc = -32 \text{ cm}^{-1}$, two times $J'/hc = -17 \text{ cm}^{-1}$, four times $J''/hc = -26 \text{ cm}^{-1}$, $g = 2.38$, $\chi_{\text{TIM}} \approx -30 \times 10^{-9} \text{ m}^3 \text{ mol}^{-1}$, $zj/hc = 0.53 \text{ cm}^{-1}$, and $x_{\text{PI}} = 0.03$; $R(\chi) = 0.026$ and $R(M) = 0.15$. It can be seen that the magnetic susceptibility is well recovered by the present model which is not the case of the low-temperature

magnetization. Large negative value of χ_{TIM} refers to the underlying diamagnetism.

Among the several structural parameters that can influence the strength and sign of the magnetic exchange coupling constant between the paramagnetic centers, the bridging angle is largely considered the most crucial factor in determining the net magnetic interaction. Two different types of exchange pathways between the Ni^{II} ions are operative through double μ -phenoxido/ μ_3 -hydroxido and double μ_3 -hydroxido/ $\mu_{1,1}$ -azido bridges in complex **1**. Experimental and theoretical magnetostructural correlations carried out by different groups have clearly shown that the magnetic coupling in hydroxido-, alkoxido- and phenoxido-bridged $\text{Ni}(\mu\text{-O})_2\text{Ni}$ complexes is expected to be ferromagnetic when the Ni-O-Ni angles are close to 90° , and a crossover from ferromagnetic to antiferromagnetic exchange coupling corresponds to a Ni-O-Ni angle of about $96\text{--}98^\circ$.^[40] The bridging angles of $98.90(11)$ and $100.31(11)$ are nicely agree with the antiferromagnetic interaction between the peripheral Ni^{II} centers in complex **1**. As found in the most of mixed μ -phenoxido/ $\mu_{1,1}$ -azido bridges Ni^{II} complexes, the magnetic interaction in **1** through this mixed bridges is observed to be ferromagnetic in nature.^[41]

Again two different types of exchange pathways between the Ni^{II} ions are present in complex **2**: (i) triple μ -phenoxido/ μ_3 -hydroxido/*syn-syn* acetato bridges (described by J'), (ii) double μ_3 -hydroxido/ $\mu_{1,1}$ -azido bridges (described by J''). The ferromagnetic coupling through the mixed μ_3 -hydroxido/ $\mu_{1,1}$ -azido bridges is found again usual. The Ni-O-Ni bridging angles of μ -phenoxido and μ_3 -hydroxido bridges are significantly shorter than that found in complex **1** and these angles are found to be $93.37(7)$ and $92.92(7)^\circ$, respectively, which is because of the presence of additional *syn-syn* $\mu_{1,3}$ -acetato bridge. It is well known that the *syn-syn* carboxylate bridge mediates the antiferromagnetic coupling between the paramagnetic metal centers.^[42] Therefore, whether the overall magnetic coupling would be either ferromagnetic or antiferromagnetic that depends on the Ni-O-Ni bridging angles. The Ni-O-Ni bridging angles of $93.37(7)$ and $92.92(7)^\circ$ in **2** are more likely to transmit ferromagnetic interaction between the Ni^{II} centers as they fall well below the crossover angles.^[40] The observed almost zero coupling constant value propagated through the triple μ -phenoxido/ μ_3 -hydroxido/*syn-syn* acetato bridged Ni^{II} centers is most likely due to orbital counter-complementary effects where the antiferromagnetic coupling interaction between the Ni^{II} centers mediated by the *syn-syn* $\mu_{1,3}$ -acetato bridge is counterbalanced by the ferromagnetic interaction operating through μ -phenoxido and μ_3 -hydroxido bridges.^[43]

In complex **3**, the magnetic coupling proceeds through three different bridges, namely (i) double μ -phenoxido/ μ_3 -hydroxido bridges (described by J'), (ii) double μ_3 -hydroxido/ $\mu_{1,1}$ -azido bridges (described by J'') and (iii) double $\mu_{1,3}$ -azido bridges (described by J). It is well studied that the $\mu_{1,3}$ -azido bridge propagates antiferromagnetic interaction between the paramagnetic interaction between the paramagnetic metal centers.^[19,39] Therefore, the negative value of the exchange coupling constant value through this bridge is not unusual. Again, the magnetic coupling between the Ni^{II} centers through μ -phenoxido/

μ_3 -hydroxido bridges with bridging angles 100.37(11) and 101.13(11)° is nicely agree with the antiferromagnetic in nature, and somewhat larger Ni–O–Ni bridging angles in **3** compared to **1** is responsible for higher magnitude of the coupling constant value in **3**. Although the sign of the coupling constant through μ_3 -hydroxido/ $\mu_{1,1}$ -azido bridged Ni^{II} centers is found unusual in the present case, but the dominating antiferromagnetic magnetic exchange interaction through μ -phenoxido/ μ_3 -hydroxido bridges and double $\mu_{1,3}$ -azido bridges is consistent with the overall antiferromagnetic nature in **3**.

Conclusions

The present work extends the high nuclearity Ni^{II}-cluster chemistry and emphasizes the ability of the Schiff base ligand (HL), derived from 2,6-diformyl-4-methylphenol and *N,N*-dimethyldipropylenetriamine, to form interesting structural types. The use of the Schiff base HL in Ni^{II} chemistry has provided access to two pentanuclear complexes (**1** and **2**) and a hexanuclear cluster (**3**) under mild reaction conditions. It is also found that the counter anions and the stoichiometric ratio of the reactants played crucial role in the self-assembly processes, leading to the diverse nuclearity in these systems. The X-ray structural analyses reveal that the Ni₅ or Ni₆ clusters can be considered to be built from the assembly of two triangular [Ni₃(μ -phenoxido)(μ_3 -OH)(μ -N₃)₄] subunits in different manners. Whereas, two bowtie-shaped Ni₅ clusters (in **1** and **2**) are formed by sharing a common vertex (Ni1) of the triangular subunits, the Ni₆ cluster on the other hand can be considered to be built from two triangular subunits by bis($\mu_{1,3}$ -N₃[−]) connectors. X-ray crystallography further shows that the tertiary amine nitrogen atoms remain either protonated or non-protonated to balance the charge of the system, which not only influence the self-assembly processes but participate in diverse hydrogen bonding pattern to stabilize the solid-state structures of the resulting complexes. Variable temperature magnetic properties of a penta- and the hexanuclear nickel(II) spin coupled clusters have been investigated and the magnetic studies reveal overall dominating antiferromagnetic interactions in **1** and **3** as opposed to **2** where the ferromagnetic coupling prevails. The dominating antiferromagnetic interaction between μ -hydroxido- and μ -phenoxido-bridged Ni₂ and Ni₃ centers over the ferromagnetic interaction between hetero μ -hydroxido- and $\mu_{1,1}$ -N₃[−]-bridged Ni1 either with Ni₂ or Ni₃ is the governing factor in **1**, while the additional antiferromagnetic coupling between Ni1 and Ni1' supported by bis($\mu_{1,3}$ -N₃[−]) bridges completely overshadowed the ferromagnetic coupling if any operating through the hetero-bridges.

Experimental Section

Materials and Physical Measurements

2,6-diformyl-4-methylphenol (DFMP) was prepared according to literature reported method,^[44] and *N,N*-dimethyldipropylenetriamine was purchased from Aldrich. All other chemicals (metal salts and solvents) were analytical or reagent grade and used without further purification.

Caution! Azido complexes of metal ions consisting of organic ligands are potentially explosive. Only small quantities of the complexes should be prepared, and these should be handled with great care.

Microanalyses were carried out with a PerkinElmer 240C elemental analyzer. The infrared spectra of the samples as KBr pellets were recorded in the range of 400–4000 cm^{−1} on a PerkinElmer Spectrum Two FTIR spectrophotometer.

Samples of the nominal mass about 20 mg have been encapsulated into gelatine-made containers and inserted into the SQUID magnetometer (MPMS-XL7, Quantum Design). At the external field $B_0 = 0.1$ T the magnetic data was taken between $T = 1.9$ –300 K and raw magnetic moment of the specimen has been converted into the molar magnetic susceptibility, and displayed as the effective magnetic moment μ_{eff}/μ_B vs. T . The measured magnetic susceptibility was not corrected for the underlying diamagnetic susceptibility because of high uncertainties and/or non-existence of the constitutive Pascal constants in the present cases. The field scan between $B = 0$ and 7 T at low temperature ($T_0 = 2.0$ or 4.6 K) enables evaluating the molar magnetization that is expressed per formula unit and bohr magneton, $M_1 = M_{\text{mol}}/N_{\text{A}}\mu_B$ vs. B .

Synthesis of Schiff Base Ligand HL

The ligand (HL) used in the present work was prepared by single step Schiff base condensation method. Briefly, 1.0 mmol of *N,N*-dimethyldipropylenetriamine (159 mg) and 0.5 mmol of 2,6-diformyl-4-methylphenol (DFMP) (82 mg) were mixed in 20 mL of methanol. The resulting solution was heated to reflux for ca. 1 h, and cooled at room temperature. The dark orange methanol solution of HL was subsequently used for the synthesis of the following complexes.

Synthesis of Ni^{II} Compounds

[Ni₅(H₂L)₂($\mu_{1,1}$ -N₃)₄(μ_3 -OH)₂(H₂O)₂](NO₃)₄·6H₂O (1**):** Ni(NO₃)₂·6H₂O (0.145 g, 0.50 mmol), dissolved in 20 mL of methanol was added to a 20 mL of methanol solution of the Schiff-base ligand (0.25 mmol) dropwise with stirring, resulting in a green solution. A solution of sodium azide (NaN₃) (1.0 mmol, 0.065 g) dissolved in minimum amount of methanol was added to the resulting green solution dropwise over a period of 5 min with constant stirring. The reaction mixture (bright dark-green) was stirred under reflux for ca. 30 min, and it was filtered to remove if any minute quantity of precipitate. The filtrate was kept undisturbed at ambient temperature that afforded dark green crystals of **1** suitable for X-ray diffraction within couple of days. The crystals of **1** were collected by filtration and washed with methanol/ether and air dried. Yield: 0.31 g, 43.8 %. Anal. calcd. for C₅₀H₁₁₂N₃₄Ni₅O₂₄: C 32.21 %, H 6.06 %, N 25.56 %. Found: C 32.34 %, H 6.04 %, 24.46 %. Selected FTIR bands (KBr, cm^{−1}): 1384 s (νNO₃[−]); 1627 s, 1643 s (νC=N); 2051 s, 2070 s (νN₃[−]).

[Ni₅(L)₂($\mu_{1,3}$ -OAc)₂($\mu_{1,1}$ -N₃)₄(μ_3 -OH)₂·12H₂O·2CH₃OH (2**):** Compound **2** was synthesised following an identical procedure as that described for **1** except the use of Ni(CH₃CO₂)₂·4H₂O in place of Ni(NO₃)₂·6H₂O. Yield: 0.67 g, 43.8 %. Anal. calcd. for C₅₆H₁₃₀N₂₄Ni₅O₂₂: C 37.44 %, H 7.09 %, N 19.07 %. Found: C 37.52 %, H 7.14 %, 18.96 %. Selected FTIR bands (KBr, cm^{−1}): 1634 s, 1644 s (νC=N & νOAc[−]); 2061 s (νN₃[−]).

[Ni₆(H₂L)₂($\mu_{1,1}$ -N₃)₄($\mu_{1,3}$ -N₃)₂(N₃)₄(μ_3 -OH)₂(H₂O)₂](ClO₄)₂·4H₂O (3**):** Ni(ClO₄)₂·6H₂O (0.549 g, 1.5 mmol), and HL (0.5 mmol) were mixed together in a 30 mL of methanol and were allowed to reflux for about 30 min. To the resulting green solution 5 mL of methanol/water (4:1. v/v) solution of NaN₃ (0.185 mg, 3 mmol) was added

Table 3. Crystallographic data and structural refinement parameters of **1–3**.

	1	2	3
Empirical formula	C ₅₀ H ₁₁₂ N ₃₄ Ni ₅ O ₂₄	C ₅₅ H ₁₂₄ N ₂₄ Ni ₅ O ₂₂	C ₅₀ H ₁₀₄ Cl ₂ N ₄₂ Ni ₆ O ₁₈
Formula weight [g mol ⁻¹]	1867.28	1767.32	2004.91
Crystal system	Monoclinic	Triclinic	Monoclinic
Space group	P2 ₁ /c	P $\bar{1}$	P2 ₁ /n
a [Å]	12.6955(7)	11.9859(9)	14.0521(2)
b [Å]	22.6202(14)	12.9619(9)	15.2166(3)
c [Å]	14.2401(9)	15.3454(12)	20.1598(4)
α [deg]	90.00	93.929(3)	90.00
β [deg]	97.044(2)	97.194(3)	106.750(1)
γ [deg]	90.00	116.601(3)	90.00
Volume [Å ³]	4058.5(4)	2094.0(3)	4127.78(13)
Z	2	1	2
D _{calc} [g cm ⁻³]	1.528	1.402	1.613
μ [mm ⁻¹]	1.229	1.182	1.493
F(000)	1964	938	2088
θ Range [deg]	2.220–29.203	2.074–27.171	1.576–26.442
Reflections collected	94041	35912	25465
Independent reflections (R_{int})	10969 (0.0723)	9252 (0.0286)	8432 (0.0343)
Observed reflections [$I > 2\sigma(I)$]	7414	7815	6155
Restraints/parameters	7/612	44/542	3/599
Goodness-of-fit on F^2	1.069	1.051	1.034
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0524$, $wR_2 = 0.1474$	$R_1 = 0.0390$, $wR_2 = 0.1116$	$R_1 = 0.0478$, $wR_2 = 0.1237$
R indices (all data)	$R_1 = 0.0975$, $wR_2 = 0.1808$	$R_1 = 0.0488$, $wR_2 = 0.1181$	$R_1 = 0.0722$, $wR_2 = 0.1397$
Largest diff. peak/hole (e Å ⁻³)	0.884/–1.060	1.524/–0.950	1.119/–0.691

with stirring for a period of 5 min and the solution mixture was heated to reflux for about 30 min and filtered. The filtrate was kept undisturbed at ambient temperature that afforded **3** containing X-ray diffraction quality dark-green single crystals. They were collected by filtration and washed with methanol/ether and air dried. Yield: 0.67 g, 43.8 %. Anal. calcd. for C₅₀H₁₀₄Cl₂N₄₂Ni₆O₁₈: C 35.40 %, H 6.29 %, N 28.60 %. Found: C 35.52 %, H 6.14 %, N 28.55 %. Selected FTIR bands (KBr, cm⁻¹): 623 m, 1120 s (νClO₄⁻); 1636 s (νC=N); 2053 s, 2072 (νN₃⁻).

X-ray Crystallography

X-ray diffraction data of the suitable single crystals of all complexes were collected using a Bruker Kappa Apex-II CCD diffractometer equipped with fine focus sealed tube of monochromated Mo- K_{α} radiation ($\lambda = 0.71073$ Å) at 150 K. The data were collected by scanning over φ and ω directions and were averaged during refinement cycles. Bruker SMART software was used for data collection and procession. Space group determination, data integration and reduction were performed with Bruker SAINT plus software. Reflection intensities were corrected for absorption by the multi-scan method using the SADABS program.^[45] The structures were solved by a combination of direct methods and refined by means of full-matrix least-square technique based on F^2 using the SHELX-2018 suite.^[46] All the non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms attached to carbon atoms were included in geometrically idealized positions with given thermal parameters related to those they are attached (1.5 times for methyl hydrogens and 1.2 times for others). While hydrogen atoms connected to some nitrogen and oxygen atoms were located on the difference Fourier map and isotropically treated with given thermal parameters equivalent to 1.2 or 1.5 times of the parent atoms. Drawings of the structures of **1–3** were generated with the program MERCURY-4.1. Important crystallographic data and refinement details for the complexes are given in Table 3.

CCDC 1916987 (for **1**), 1916988 (for **2**), and 1916989 (for **3**) contain the supplementary crystallographic data for this paper.

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Keywords: Polynuclear complexes · Nickel clusters · Schiff-base · Crystal structure · Magnetic properties

- [1] E. K. Brechin, C. Boskovic, W. Wernsdorfer, J. Yoo, A. Yamaguchi, E. C. Sanudo, T. R. Concolino, A. L. Rheingold, H. Ishimoto, D. N. Hendrickson, G. Christou, *J. Am. Chem. Soc.* **2002**, 124, 9710–9711.
- [2] D. Gatteschi, R. J. Sessoli, *Angew. Chem. Int. Ed.* **2003**, 42, 268–297; *Angew. Chem.* **2003**, 115, 278.
- [3] R. Sessoli, D. Gatteschi, A. Caneschi, M. A. Novak, *Nature* **1993**, 365, 141–143.
- [4] R. Sessoli, H. L. Tsai, A. R. Schake, S. Y. Wang, J. B. Vincent, K. Folting, D. Gatteschi, G. Christou, D. N. Hendrickson, *J. Am. Chem. Soc.* **1993**, 115, 1804–1816.
- [5] R. Bagai, W. Wernsdorfer, K. A. Abboud, G. Christou, *J. Am. Chem. Soc.* **2007**, 129, 12918–12919.
- [6] D. Gatteschi, R. J. Sessoli, *J. Magn. Magn. Mater.* **2004**, 272–276, 1030–1036.
- [7] C. J. Milios, A. Vinslava, W. Wernsdorfer, S. Moggach, S. Parsons, S. P. Perlepes, G. Christou, E. K. Brechin, *J. Am. Chem. Soc.* **2007**, 129, 2754–2755.
- [8] M. Murugesu, M. Habrych, W. Wernsdorfer, K. A. Abboud, G. Christou, *J. Am. Chem. Soc.* **2004**, 126, 4766–4767.
- [9] T. C. Stamatatos, K. A. Abboud, W. Wernsdorfer, G. Christou, *Angew. Chem. Int. Ed.* **2007**, 46, 884–888; *Angew. Chem.* **2007**, 119, 902.

- [10] N. Aliaga-Alcalde, R. S. Edwards, S. O. Hill, W. Wernsdorfer, K. Folting, G. Christou, *J. Am. Chem. Soc.* **2004**, *126*, 12503–12516.
- [11] A. Caneschi, D. Gatteschi, N. Lalioti, C. Sangregorio, R. Sessoli, G. Venturi, A. Vindigni, A. Retoort, M. G. Pini, M. A. Novak, *Angew. Chem. Int. Ed.* **2001**, *40*, 1760–1763; *Angew. Chem.* **2001**, *113*, 1810.
- [12] R. Clérac, H. Miyasaka, M. Yamashita, C. Coulon, *J. Am. Chem. Soc.* **2002**, *124*, 12837–12844.
- [13] C. Coulon, H. Miyasaka, R. Clérac, *Struct. Bonding* **2006**, *122*, 163–206.
- [14] C. J. Milios, R. Inglis, A. Vinslava, R. Bagai, W. Wernsdorfer, S. Parsons, S. P. Perlepes, G. Christou, E. K. Brechin, *J. Am. Chem. Soc.* **2007**, *129*, 12505–12511.
- [15] J. S. Miller, M. Drillon, *Magnetism: Molecules to Materials*; Wiley: Weinheim, **2001**.
- [16] W. Wernsdorfer, R. Sessoli, *Science* **1999**, *284*, 133–135.
- [17] a) A. Escuer, G. Aromi, *Eur. J. Inorg. Chem.* **2006**, 4721–4736; b) M. Ferbinteanu, H. Miyasaka, W. Wernsdorfer, K. Nakata, K. Sugiura, M. Yamashita, C. Coulon, R. Clérac, *J. Am. Chem. Soc.* **2005**, *127*, 3090–3099; c) S. S. Massoud, F. A. Mautner, R. Vicente, A. A. Gallo, E. Ducasse, *Eur. J. Inorg. Chem.* **2007**, 1091–1102; d) A. J. Tasiopoulos, A. Vinslava, W. Wernsdorfer, K. A. Abboudand, G. Christou, *Angew. Chem. Int. Ed.* **2004**, *43*, 2117–2121; *Angew. Chem.* **2004**, *116*, 2169; e) A. Panja, P. Guionneau, I.-R. Jeon, S. M. Holmes, R. Clérac, C. Mathonière, *Inorg. Chem.* **2012**, *51*, 12350–12359.
- [18] a) T. C. Stamatatos, D. Foguet-Albiol, S. C. Lee, C. C. Stoumpos, C. P. Raptopoulou, A. Terzis, W. Wernsdorfer, S. O. Hill, S. P. Perlepes, G. Christou, *J. Am. Chem. Soc.* **2007**, *129*, 9484–9489.
- [19] J. Ribas, A. Escuer, M. Monfort, R. Vicente, R. Cortes, L. Lezama, T. Rojo, *Coord. Chem. Rev.* **1999**, *195*, 1027–1068.
- [20] a) T. Liu, Y.-J. Zhang, Z.-M. Wang, S. Gao, *J. Am. Chem. Soc.* **2008**, *130*, 130; b) C.-F. Lee, D. A. Leigh, R. G. Pritchard, D. Schultz, S. J. Teat, G. A. Timco, R. E. P. Winpenny, *Nature* **2009**, *458*, 314–318; c) S. Schmitz, J. van Leusen, A. Ellern, P. Kögerler, K. Y. Monakhov, *Inorg. Chem. Front.* **2016**, *3*, 523–531.
- [21] a) N. A. Rey, A. Neves, A. J. Bortoluzzi, C. T. Pich, H. Terenzi, *Inorg. Chem.* **2007**, *46*, 348–350; b) S. Mandal, S. Mondal, C. Rajnák, J. Titiš, R. Boča, S. Mohanta, *Dalton Trans.* **2017**, *46*, 13135–13144.
- [22] a) K. Dhara, U. C. Saha, A. Dan, S. Sarkar, M. Manassero, P. Chattopadhyay, *Chem. Commun.* **2010**, *46*, 1754–1756; b) M. Sarkar, R. Clérac, C. Mathonière, N. G. R. Hearn, V. Bertolasi, D. Ray, *Inorg. Chem.* **2011**, *50*, 3922–3933.
- [23] M. Sarkar, R. Clérac, C. Mathonière, N. G. R. Hearn, V. Bertolasi, D. Ray, *Inorg. Chem.* **2010**, *49*, 6575–6585.
- [24] a) A. Das, F. J. Klinke, S. Demeshko, S. Meyer, S. Dechert, F. Meyer, *Inorg. Chem.* **2012**, *51*, 8141–8149; b) D. Mandal, C. S. Hong, H. C. Kim, H.-K. Fun, D. Ray, *Polyhedron* **2008**, *27*, 2372–2378; c) B. Bechlars, I. Issac, R. Feuerhake, R. Clérac, O. Fuhr, D. Fenske, *Eur. J. Inorg. Chem.* **2008**, 1632–1644.
- [25] S. Liu, S. Wang, F. Cao, H. Fu, D. Li, J. Dou, *RSC Adv.* **2012**, *2*, 1310–1313.
- [26] a) P. King, R. Clérac, W. Wernsdorfer, C. E. Anson, A. K. Powell, *Dalton Trans.* **2004**, 2670–2676; b) K. C. Mondal, O. Sengupta, P. S. Mukherjee, *Inorg. Chem. Commun.* **2009**, *12*, 682–685.
- [27] a) F.-H. Zhao, Y.-X. Che, J.-M. Zheng, *Cryst. Growth Des.* **2012**, *12*, 4712–4721; b) A. Escuer, J. Esteban, S. P. Perlepes, T. C. Stamatatos, *Coord. Chem. Rev.* **2014**, *275*, 87–129.
- [28] S. S. Tandon, S. D. Bunge, R. Rakos, Z. Xu, L. K. Thompson, *Dalton Trans.* **2009**, 6536–6551.
- [29] a) A. Panja, N. ChJana, P. Brandão, *Mol. Catal.* **2018**, *449*, 49; b) A. Panja, N. C. Jana, S. Adak, P. Brandão, L. Dlhán, J. Titiš, R. Boča, *New J. Chem.* **2017**, *41*, 3143–3153.
- [30] K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, (4th ed). Wiley: New York, **1986**.
- [31] a) A. K. Ghosh, M. Shatruk, V. Bertolasi, K. Pramanik, D. Ray, *Inorg. Chem.* **2013**, *52*, 13894–13903; b) N. Dutta, G. C. Giri, S. Halder, G. Vijaykumar, C. D. Stewart, L. Carrella, G. T. Musie, M. Bera, *ChemistrySelect* **2019**, *4*, 10260–10269.
- [32] a) S. I. Sampani, E. Loukopoulou, M. Azam, K. Griffiths, A. Abdul-Sada, G. Tizzard, S. Coles, A. Escuer, A. Tsipis, G. E. Kostakis, *CrystEngComm* **2018**, *20*, 1411–1421; b) P. S. Perlepe, L. Cunha-Silva, V. Bekiari, K. J. Gagnon, S. J. Teat, A. Escuer, T. C. Stamatatos, *Dalton Trans.* **2016**, *45*, 10256–10270; c) J. Esteban, M. Font-Bardia, J. S. Costa, S. J. Teat, A. Escuer, *Inorg. Chem.* **2014**, *53*, 3194–3203; d) P. Wix, G. E. Kostakis, V. A. Blatov, D. M. Proserpio, S. P. Perlepes, A. K. Powell, *Eur. J. Inorg. Chem.* **2013**, 520–526.
- [33] a) A. Escuer, J. Esteban, J. Mayans, M. Font-Bardia, *Eur. J. Inorg. Chem.* **2014**, 5443–5450; b) J. Esteban, M. Font-Bardia, A. Escuer, *Inorg. Chem.* **2014**, *53*, 1113–1121; c) A. K. Boudalis, M. Pissas, C. P. Raptopoulou, V. Psycharis, B. Abarca, R. Ballesteros, *Inorg. Chem.* **2008**, *47*, 10674–10681; d) C. Papatriantafyllopoulou, T. C. Stamatatos, W. Wernsdorfer, S. J. Teat, A. J. Tasiopoulos, A. Escuer, S. P. Perlepes, *Inorg. Chem.* **2010**, *49*, 10486–10496; e) A. Escuer, G. Vlahopoulou, F. A. Mautner, *Dalton Trans.* **2011**, *40*, 10109–10116.
- [34] a) S. S. Tandon, S. D. Bunge, J. Sachiz, L. K. Thompson, *Inorg. Chem.* **2012**, *51*, 3270–3282; b) D. Mandal, V. Bertolasi, J. Ribas-Ariño, G. Aromi, D. Ray, *Inorg. Chem.* **2008**, *47*, 3465–3467; c) X.-T. Wang, B.-W. Wang, Z.-M. Wang, W. Zhang, S. Gao, *Inorg. Chim. Acta* **2008**, *361*, 3895–3902; d) Y.-J. Liu, X.-J. Fu, X.-F. Li, T.-B. Qiu, H.-X. Yang, *Acta Crystallogr., Sect. E* **2011**, *67*, m307.
- [35] a) A. N. Georgopoulou, C. P. Raptopoulou, V. Psycharis, R. Ballesteros, B. Abarca, A. K. Boudalis, *Inorg. Chem.* **2009**, *48*, 3167; b) B. Sun, X. Chen, Z. Li, L. Zhang, Q. Zhao, *New J. Chem.* **2010**, *34*, 190; c) M. Fondo, N. Ocampo, A. M. García-Deibe, J. Cano, J. Sanmartín, *Dalton Trans.* **2010**, 39, 10888; d) M. Pait, A. Bauza, A. Frontera, E. Colacio, D. Ray, *Inorg. Chem.* **2015**, *54*, 4709–4723.
- [36] J. Esteban, E. Ruiz, M. Font-Bardia, T. Calvet, A. Escuer, *Chem. Eur. J.* **2012**, *18*, 3637–3648.
- [37] R. Boča, *A Handbook of Magnetochemical Formulae*, Elsevier, Amsterdam, **2012**.
- [38] R. Boča, *Program MIF&FIT*, **2019**. © University of SS Cyril and Methodius, Trnava, Slovakia.
- [39] O. Kahn, *Molecular Magnetism*, VCH, Weinheim, **1993**.
- [40] a) M. P. Palacios, A. J. Mota, J. E. Perea-Buceta, F. J. White, E. K. Brechin, E. Colacio, *Inorg. Chem.* **2010**, *49*, 10156–10165; b) R. Biswas, S. Giri, S. K. Saha, A. Ghosh, *Eur. J. Inorg. Chem.* **2012**, 2916–2927; c) J. Ruiz, A. J. Mota, A. Rodríguez-Diéguez, I. Oyarzabal, J. M. Secob, E. Colacio, *Dalton Trans.* **2012**, *41*, 14265–14273.
- [41] a) S. Sasmal, S. Hazra, P. Kundu, S. Dutta, G. Rajaraman, E. C. Sanudo, S. Mohanta, *Inorg. Chem.* **2011**, *50*, 7257–7267; b) P. Ghorai, A. Chakraborty, A. Panja, T. K. Mondal, A. Saha, *RSC Adv.* **2016**, *6*, 36020–36030.
- [42] a) C. Ruiz-Pérez, J. Sanchiz, M. H. Molina, F. Lloret, M. Julve, *Inorg. Chem.* **2000**, *39*, 1363–1370; b) A. R. Fortea, P. Alemany, S. Alvarez, E. Ruiz, *Chem. Eur. J.* **2001**, *7*, 627–637.
- [43] a) S. N. Wang, J. F. Bai, Y. Z. Li, Y. Pan, M. Scheer, X. Z. You, *CrystEngComm* **2007**, *9*, 1084–1095; b) M. Fondo, A. M. García-Deibe, N. Ocampo, J. Sanmartín, M. Rodríguez-Bermejo, A. L. Llamas-Saiz, *Dalton Trans.* **2006**, 4260–4270; c) S.-Q. Guo, D. Tian, X. Zheng, H. Zhang, *CrystEngComm* **2012**, *14*, 3177–3188.
- [44] C. N. Verani, E. Rentschler, T. Weyhermüller, E. Bill, P. Chaudhuri, *J. Chem. Soc., Dalton Trans.* **2000**, 251–258.
- [45] G. M. Sheldrick, *SADABS*, University of Göttingen, Germany, **1996**.
- [46] G. M. Sheldrick, *Acta Crystallogr., Sect. C* **2015**, *71*, 3.

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