Synthesis and characterization of copper(II), nickel(II) and cobalt(II/III) complexes with Schiff base ligands

Thesis submitted for the degree of

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By

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DEDICATED TO

My PhD Supervisor

Prof. Shouvik Chattopadhyay

My Beloved Parents

Mr. Tapan Kumar Dutta

&

Mrs. Swapna Dutta

"Any supervisor worth his salt would rather deal with people who attempt too much than with those who try too little"

-Lee lacocca

"I believe that parents who love their children do everything for them with love, even discipline"

-Ellen. J. Barr

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কলকাতা-৭০০ ০৩২, ভারত

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FACULTY OF SCIENCE : DEPARTMENT OF CHEMISTRY : INORGANIC CHEMISTRY SECTION

CERTIFICATE FROM THE SUPERVISOR

This is to certify that the thesis entitled **“Synthesis and characterization of copper(II), nickel(II) and cobalt(II/III) complexes with Schiff base ligands”** submitted by Sri Tamal Dutta, who got his name registered on 25.11.21 **(Index Number No. 115/21/chem./27)** for the award of Ph.D. (Science) degree of Jadavpur University, is absolutely based upon his own work under the supervision of Dr. Shouvik Chattopadhyay and that neither this 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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ELECTIVE UNITS :: CHEM/PHD/I-1 :: APPLICATION OF SPECTROSCOPIC STUDIES IN CHEMICAL RESEARCH CHEM/PHD/I-2 :: MATERIALS, CATELYSES & ELECTROCHEMICAL STUDIES CHEM/PHD/I-3 :: METALS IN LIFE & REACTION DYNAMICS CHEM/PHD/I-4 :: SINGLE CRYSTAL X-RAY STR. SUPRAMOLECULAR CHEM.& DFT COMPUTN.	8	80

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Checked by :

Bhattacharyya

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Preface

The entire work described in this thesis deals with Synthesis and characterization of copper(II), nickel(II) and cobalt(II/III) complexes with Schiff base ligands. The thesis consists of six chapters of which ***Chapter I*** deals with the literature survey on the coordination chemistry of copper(II), nickel(II) and cobalt(II/III) complexes with Schiff base ligands. The research works are presented in ***Chapters II-VI*** of the thesis. The interesting observations are highlighted in ***Chapter VII.***

The entire work was initiated in July, 2019. All information in this document have been obtained and presented in accordance with the academic rules and ethical conducts. I also declare that as required by these rules and conducts, I have cited and referenced all materials and results which are not original to this work. I take the responsibility of any unintentional oversight and errors, which might have crept in despite precautions.

Tamal Dutta.

Dated: Jadavpur
29.11.23

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At this moment of accomplishment, first of all I wish to record my sincere gratitude to my supervisor, **Prof. Shouvik Chattopadhyay** without whom, I would not have had the courage to embark on this journey, for his constant guidance, motivation, suggestions, and discussions throughout the work. Under his guidance, I successfully overcame many difficulties and each time learned a lot from his experience. Whenever, I had felt that I have reached the limits of my knowledge, it was his insightful advice that kept me going. Not only in the matter of academics, but also my interaction with him helped me to grow as a human being. His unflinching passion and conviction will always inspire me and I hope to extend the work to newer areas from this training that I received from him.

I take this opportunity to sincerely acknowledge **Prof. Subratanath Koner, Head of the Department of Chemistry, Jadavpur University, Prof. Saurabh Das Section-In-Charge, Inorganic Chemistry Section, for assisting me with infrastructure and supports.**

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I am very much grateful to my labmates for providing me moral support and friendly atmosphere always during my research work. Special thanks to my labmates **Dr. Tanmoy Basak**, **Dr. Snehasis Thakur**, **Dr. Kousik Ghosh, Dr. Abhisek Banerjee**, **Dr. Mainak Karmakar**, **Mr. Saikat Mirdya**, **Mrs. Ipsita Mondal**, **Mr**.**Sudip Bhunia** and **Mr. Rabi Shankar Sarkar, Mridul Karmakar**. My heartiest thank to my seniors **Dr. Sourav Roy**, **Dr. Nandita Sarkar**, **Dr. Samim Khan**, **Dr. Prasanta Bhowmik**, **Dr. Prasanta Kumar Bhaumik**, **Dr. Subrata Jana**, **Dr. Mithun Das, Dr. Sumit Roy**, **Dr. Anik Bhattacharyya** and **Dr. Pallab Bhowmik.**

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In conclusion, I would like to thank everybody who was important to the successful realization of this thesis, as well as expressing my apology that I could not mention personally all of them personally. I wish, I could continue the rest of my life as a successful educator

Tamal Dutta.

Tamal Dutta

Department of Chemistry

Jadavpur University

Date 29.11.23

Place Jadavpur

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Table of Content

Chapter I

General introduction, experimental section and summary of the thesis

“Somewhere, something incredible is waiting to be known”

-Carl Sagan

Section I.A

A brief overview on the coordination chemistry of copper (II), nickel (II) and cobalt (III) with N, O donor Schiff base ligands

The use of copper, nickel and cobalt has been known since the dawn of civilization. They are mentioned in the ancient literature and descriptions. In the Roman era, copper was principally mined on Cyprus, in the name of *cyprium* (metal of Cyprus), later shortened to *cuprum* and hence the English *copper*.[1] In medieval Germany, miners were tried to extract copper from a red mineral, but failed. They blamed a mischievous spirit, Nickel (a devil of German mythology), for besetting the copper and named this ore *Kupfernickel* (Old Nick's copper). In 1751, A. F. Cronstedt extracted a white metal from the very same ore and the new metal was named nickel.[2] On the other hand, miners had long used the name *kobold* ore (*goblin ore*) for some of the blue pigment producing minerals. In 1735, such ores were found to be reducible to a new metal and this was ultimately named for the *kobold* which later changed to cobalt.[3]

Copper is the first element of Group 11 in the periodic table and have one *s* electron outside a completely filled *d* subshell ($3d^{10}4s^{1}$) and shows oxidation states (0), (+1), (+II) and (+III).[4] The copper (0) complexes are extremely limited.[4a] It might be expected that (+I) oxidation state would be the most common and most stable because of the extra stability resulting from a fulfilled *d* subshell. Surprisingly, in aqueous solution.[4a,5] Copper(III) copper(1) is unstable and disproportionates rapidly is so strongly oxidizing that it reduces water and only occur when stabilized in complexes.[6] However, the most important and stable oxidation state of copper is (+II).[7] Most copper(II) complexes are typically blue or green coloured due to d-d transitions. Copper(II) forms numerous complexes with various geometries having coordination numbers four, five and six. The majority of hexacoordinated copper(II) complexes have elongated octahedral structures as a result of strong Jahn-Teller distortion.[8] In pentacoordinated system, copper(II) assumes either square pyramidal or trigonal bipyramidal geometry.[9] The tetrahedral geometry of copper(II) always 10 On the other hand, involves significant compression along the S_4 symmetry axis.[10] square planar complexes show very small tetrahedral distortion.[11]

Nickel $(3d^8 4s^2)$ is the first element of Group 10 and shows range of oxidation states from (–I) to (+IV), but its chemistry is predominantly that of the (+II) state.[12] Nickel(II) forms a large number of complexes with coordination numbers four, five and six, of which tetracoordinated and hexacoordinated nickel(II) complexes are common in literature.[13] Good π-donor ligands tend to stabilize tetrahedral geometries, whereas square planar geometries are favoured with π-acceptor ligands.[14] Steric bulk of the ligands may also influence the geometry of tetracoordinated nickel (II) complexes, since tetrahedral coordination is favored by bulky ligands.[15] Most of the hexacoordinated nickel(II) complexes are essentially octahedral.[16] A considerable number of pentacoordinated trigonal bipyramidal and square pyramidal nickel (II) complexes are also known.[17]

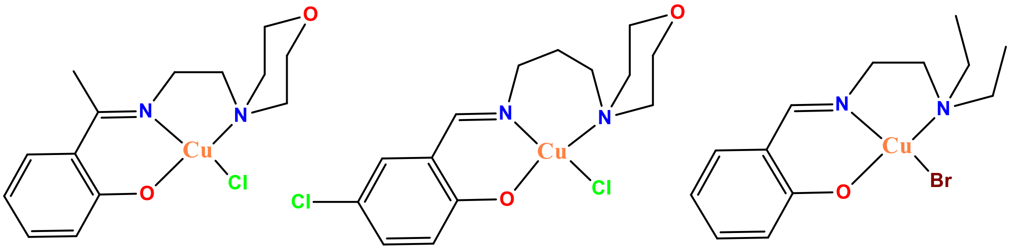
On the other hand, cobalt $(3d^7 4s^2)$ is the first element of Group 9. Although it shows various oxidation states ranging from (–I) to (+IV), the most common oxidation state of cobalt is (+III) with $3d^6$ electronic configuration.[18] The most favoured geometry of d^6 cobalt(III) is octahedral, where cobalt(III) is essentially low spin, the major stabilizing influence being probably the high CFSE associated with the t_{2g}^6 electronic configuration (-24 Dq_0, the maximum possible for any d^n configuration).[19] All such complexes are kinetically inert and, therefore, undergo only very slow substitution or ligand exchange reaction. No vacancy in t_{2g}, orbitals and no electrons in e_g orbitals do not allow the cobalt(III) complexes to undergo interchange reaction either via associative (S_N2) or dissociative (S_N1) pathway. It is this kinetic inertness of cobalt(III) which probably helped Werner (and many other synthetic inorganic chemists too) to prepare various isomers of cobalt(III) complexes.[20] Many researchers of current age are also exploiting this kinetic inertness of low spin cobalt(III) to prepare varieties of isomeric complexes.[21]

The rational design and synthesis of copper(II), nickel(II) and cobalt(III) complexes are of immense importance, for their potential use in catalysis,[22] in biological modeling applications,[23] in preparing liquid crystals[24] and also in magnetism.[25] Various polydentate ligands are widely used to prepare such complexes.[26] Schiff bases constitute a special class for their ease of synthesis, stability under a variety of oxidative and reductive conditions, and their structural versatility.[27] Among several Schiff bases, salicylaldimines are extensively explored for their ability to prepare phenoxo bridged polynuclear complexes with fascinating structures and properties.[28] Obviously, salen type ligands, prepared from the condensation of several diamines and salicylaldehyde or its derivatives in 1:2 ratio, are the most popular for this purpose,[29] although tridentate N_2O donor Schiff bases have also been used.[30] On the other hand, tetradentate N_4 donor Schiff bases, prepared by the condensation of several diamines with pyridine-2-carboxaldehyde or its derivative, have also been extensively used by several research groups since long.[31] Several copper(II) complexes of such ligands have been used to mimic SOD activity.[32] The imine bond(s) of these Schiff bases may be reduced with appropriate reducing agents in appropriate condition to prepare reduced Schiff bases, which are also used as important tools in synthetic coordination chemistry.[33] On the other hand, semicarbazone based Schiff bases, prepared by the condensation of several aldehyde and ketones with semicarbazide, constitute a special class as both their neutral and anionic forms may coordinate the metal ions to form a variety of complexes with diverse architecture.[34] Another important polydentate ligand is tetrazole which is also utilized for the preparation of various mono, di and polynuclear complexes.[35] Use of several halides and pseudohalides and to exploit their different bridging modes to prepare several polynuclear complexes are also well known since long.[36] All such ligands are used in the present work to prepare several mono, di and polynuclear copper(II), nickel(II) and cobal(III) complexes.

Salicylaldimine Schiff bases have been in the literature for many years and are linked with many advancement in chemistry.[55] Several salicylaldimine Schiff bases have been exploited by several researchers to form varieties of coordination polymers with structural diversities and tunable properties.[56] N_2O donor Salicylaldimine Schiff bases are prepared by condensation of several N-substituted diamines with salicylaldehyde/substituted salicylaldehydes.[56,57] Tridentate N_2O donor Salicylaldimine Schiff base ligands with an easily deprotonable phenoxo oxygen donor atom have a strong propensity to yield high nuclearity complexes.[57] Salicylaldimine Schiff base ligands with an easily deprotonatable phenoxo oxygen donor atom have a strong propensity to yield high nuclearity complexes.[39]

Synthesis and characterization of large number of mononuclear square planar copper(II) complexes with N_2O donor salicylaldimine Schiff bases in presence of halide coligands have been found in literature.[40] All such mononuclear tetracoordinated copper(II) halide complexes have been found to be square planar. Structures of some mononuclear copper (II) halide complexes have been shown in **Scheme I.A.1.** No such square planar nickel

(II) and cobalt (III) halide complexes with N_2O donor Schiff bases were characterized by single crystal X-ray diffraction studies.

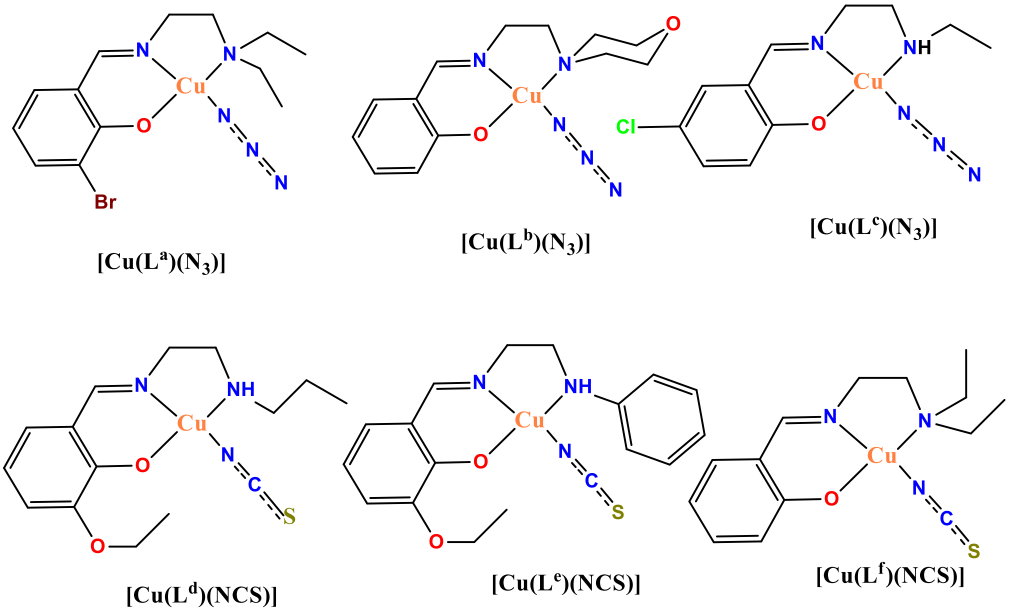


[Cu(L^a)(Cl)] **[Cu(L^b)(Cl)]** **[Cu(L^c)(Br)]**

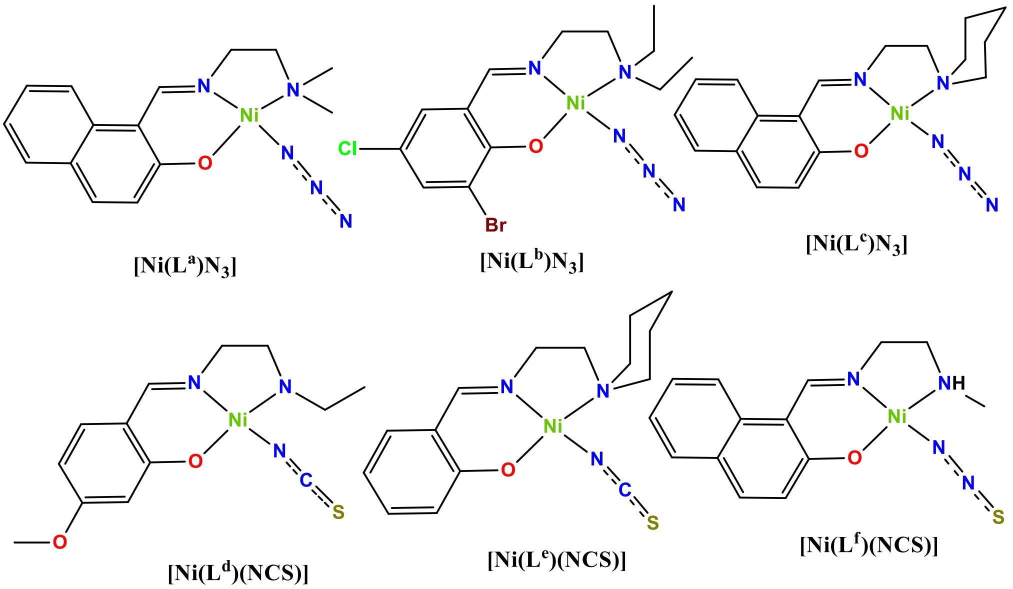
Scheme I.A.1. Schematic representation of mononuclear copper(II) halide complexes *[Cu(L^a) (CI)],*[40] *[Cu(L^b) (Cl)],*[40b,40c] and *[Cu(L^c) (Br)],*[40d] with N_2O donor salicylaldimine Schiff bases, HL^a = 2-(1-(2-morpholinoethylimino)ethyl) phenol, HL^b = 2-((3-morpholinopropylimino)methyl)-4-chlorophenol and HL^C = 2-((2-(diethylamino)ethylimino) methyl) phenol.

Pseudohalides (e.g. azide, thiocyanate etc.) have also been used to prepare similar mononuclear square planar copper(II) complexes. Some selected examples are shown in **Scheme I.A.2.** Several mononuclear square planar nickel(II) complexes could also be produced by using pseudohalides as coligands. [40d, 41-47] Structures of some mononuclear square planar nickel(II) complexes with azide and thiocyanate as coligands are gathered in **Scheme I.A.3.** Some of these complexes show urease inhibitory activity [43c] No such mononuclear square planar cobalt (III) pseudohalide complexes with N_20

donor salicylaldimine Schiff bases have been characterized by single crystal X-ray diffraction studies.

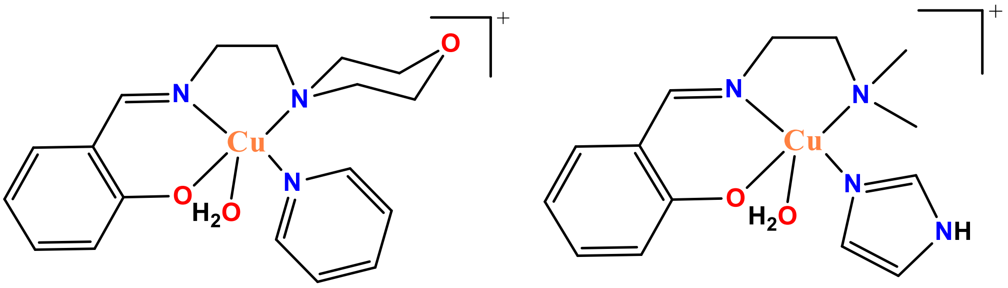


Scheme I.A.2. Schematic representation of some mononuclear copper(II) pseudohalide complexes, *$[Cu(L^a)(N_3)]$*[41a] *$[Cu(L^b)(N_3)]$*,[41b] *$[Cu(L^C)(N_3)]$*,[42c] *$[Cu(L^d)$ $(NCS)]$*,[43e] *$[Cu(L^e)$ $(NCS)]$*,[47h] and $[Cu(L^f)(NCS)]$,[43a] with N_2O donor salicylaldimine Schiff bases, *HL^a* = 2-((2-(diethylamino)ethylimino) methyl)-4, 6- dibromophenol, *HL^b* = 2-((2-morpholinoethylimino) methyl) phenol, *HL^c* = 2-((2- (ethylamino) ethylimino) methyl) -4-chlorophenol, HL^d = 2-((2 (propylamino) ethylimino) methyl) -6-ethoxyphenol, *HL^e* = 2-((2- (phenylamino)ethylimino)methyl)-6-ethoxyphenol and HL^f = 2-((2- (diethylamino) ethylimino) methyl) phenol.



Scheme I.A.3. Schematic representation of some mononuclear nickel(II) pseudohalide complexes, [Ni(L^a) (N_3)],[63a] [Ni(L^b) (N_3)],[63b] [Ni(L^C) (N_3)],[63h] [Ni(L^d) (NCS)],[64c] [Ni(L^e)(NCS)],[64f] and [Ni(L^f)(NCS)\],[64a] with N_2O donor salicylaldimine Schiff bases, HL^0 = 1-((2- (dimethylamino) ethylimino) methyl) naphthalen-2-ol, HL^b = 2-((2- (diethylamino) ethylimino) methyl) -6-bromo-4-chlorophenol, HL^c = 1-((2-(piperidin-1-yl) ethylimino) methyl) naphthalen-2-ol, HL^d = 2-((2-(ethylamino) ethylimino) methyl)- 5-methoxyphenol, HL^e = 2-((2-(piperidin-1-yl) ethylimino) methyl) phenol and HL^f = 1-((2-(methylamino) ethylimino) methyl) naphthalen-2-ol.

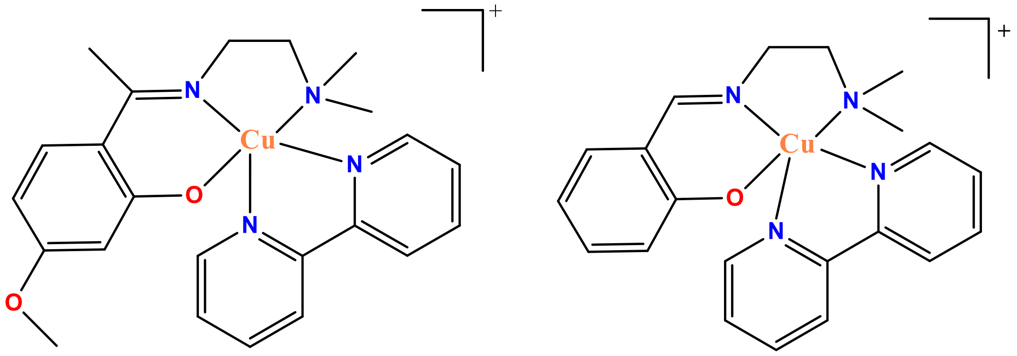
There are several examples of mononuclear pentacoordinated copper(II) complexes of tridentate N_2O donor salicylaldimine Schiff bases with monodentate (e.g. water, pyridine, imidazole etc.) or bidentate coligands (e.g. bipyridine, Schiff bases etc.).[48-50] Some pentacoordinated copper(II) complexes are gathered in **Scheme I.A.4.** Some of these complexes show catalytic activity in the oxidation of olefins to epoxides in the presence of 2-methylpropanal and molecular oxygen.[48d] Few other complexes also show type-2 copper (II) ascorbate oxidase activity.[48f]



$[Cu(L)'(L)''(H_2O)]^+$ **$[Cu(L)^b(L)''(H_2O)]^+$**

Scheme I.A.4. Schematic representation of mononuclear pentacoordinated copper(II) complexes, $[Cu(L)'(L)''(H_2O)]^+$,[48c] and $[Cu(L)^b(L)''(H_2O)]^+$,[48f] with tridentate $N_2$0 donor salicylaldimine Schiff bases. HLa = 2-((2-morpholinoethylimino) methyl) phenol and HL+$^{b\ =\ 2\text{-}((2\text{-}}$(dimethylamino) ethylimino) methyl) phenol and other monodentate ligands, L' = pyridine and L" = imidazole.

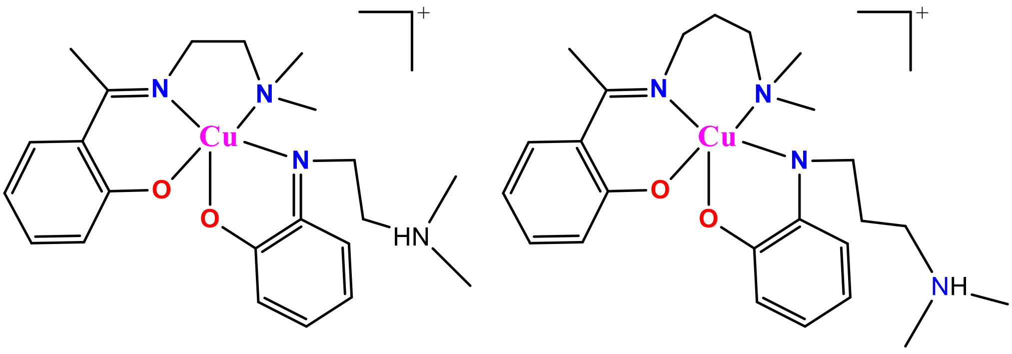
In presence of bidentate coligands (e.g. 2, 2-bipyridine), square pyramidal copper(II) complexes have been resulted in all cases (**Scheme I.A.5.**).[48b, 49c] Some of these complexes are found to show good DNA cleavage activity.[48h]



$[\mathrm{Cu(L^a)(L')}]^+$ $[\mathrm{Cu(L^b)(L')}]^+$

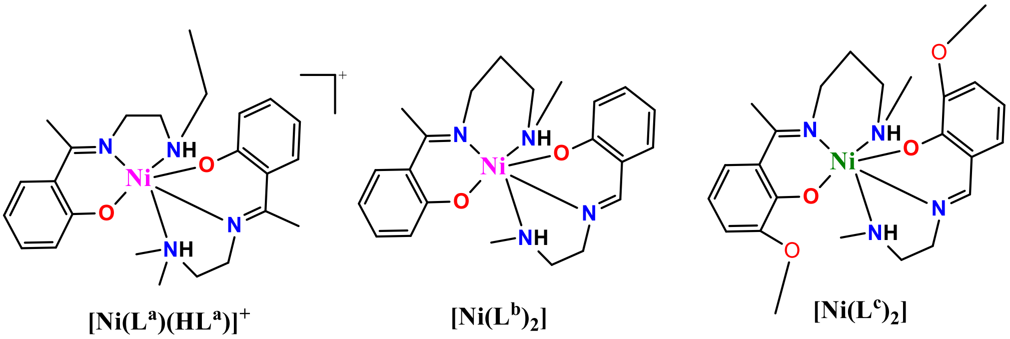
Scheme I.A.5. Schematic representation of mononuclear pentacoordinated copper(II) complexes $[\mathrm{Cu(L^a)\ (L')}]^+$,[48b] and $[\mathrm{Cu(L^b)(L')}]^+$,[49c] with 2,2'-bipyridine (L') and N_2O donor salicylaldimine Schiff bases, HL^a = 2-((2-(dimethylamino) ethylimino) ethyl)-5-methoxyphenol and HL^b = 2-((2-(dimethylamino) ethylimino) methyl)phenol.

Zwitterionic forms of several Schiff bases could also be trapped as pentacoordinated copper (II) complexes.[48g, 50c] Structures of these complexes reveal that the zwitterionic N_2O donor Schiff base behaves as pendant ligand (**Scheme I.A.6.**) Pendant ligands show variety of different chemical applications, in enzyme simulations, for the purpose of carrying a radionuclide into a target cell and in magnetic resonance imaging reagents.[50g-50i] No such pentacoordinated nickel(II) and cobalt(III) complexes are found in literature.



$[Cu(L^a)(HL^a)]^+$ **$[Cu(L^b)(HL^b)]^+$**

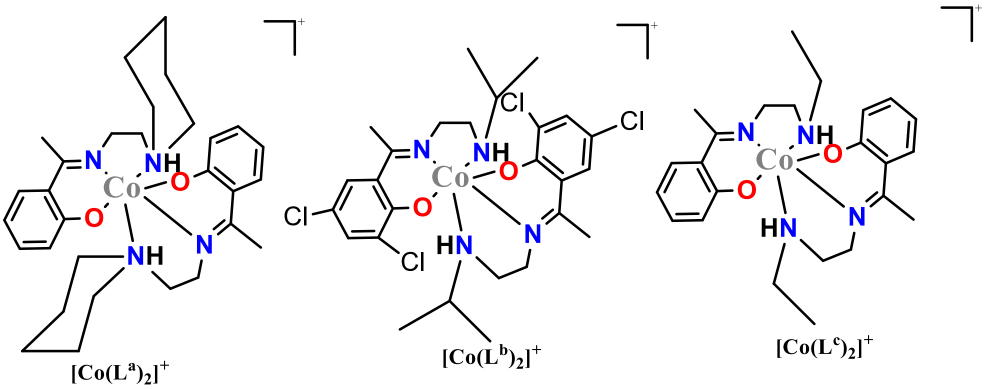
Scheme I.A.6. Schematic representation of mononuclear pentacoordinated copper (II) complexes $[Cu(L^a)(HL^a)]^+$,[48g] and $[Cu(L^b)(HL^b)]^+$,[50c] with zwitterionic Schiff bases having pendent arm, HL^a = 2-((2-(dimethylamino) ethylimino) methyl) phenol and HL^b = 2-((3-(dimethylamino) propylimino) methyl) phenol.



$[Ni(L^a)(HL^a)]^+$ **$[Ni(L^b)_2]$** **$[Ni(L^c)_2]$**

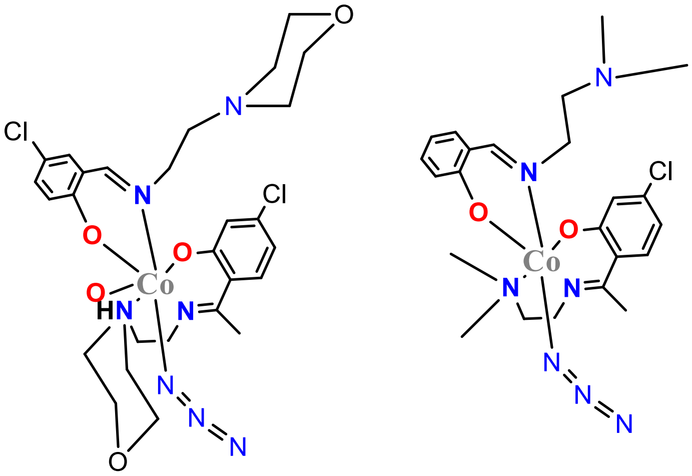
Scheme I.A.7. Schematic representation of some mononuclear octahedral bis-ligand nickel(II) complexes $[Ni(L^a)(HL^a)]$,[51a] $[Ni(L^b)_2]$,[51i] and $[Ni(L^c)_2]$,[52g] with N_2O donor salicylaldimine Schiff bases, HL^a = 2-((2-(ethylamino) ethylimino) methyl) phenol, HL^b = 2-((3-(methylamino) propylimino) methyl) phenol and HL^c = 2-((3- (methylamino) propylimino) methyl)-6-methoxyphenol.

Examples of mononuclear octahedral bis-ligand nickel (II) complexes with tridentate N_2O donor Schiff bases have also been reported in literature.[51,52, 45g] Both facial and meridonial orientations of ligand have been found in those complexes. Some selected bis-ligand nickel (II) complexes are gathered in **Scheme I.A.7.**



Scheme I.A.8. Schematic representation of some mononuclear bis-ligand cobalt(III) complexes, $[Co(L^a)_2]^+$ [54] $[Co(L^b)_2]^+$ [55g] with N_2O donor salicylaldimine Schiff bases, HL^a - 2-((3- (cyclohexylamino) propylimino) methyl) phenol, HL^b = 2-((2- (isopropylamino) ethylimino) methyl)-4,6-dichlorophenol and HL^c = 2-((2- (ethylamino) ethylimino) methyl) phenol.

Mononuclear octahedral cobalt(III) complexes with tridentate N_2O donor Schiff bases are also found in literature.[54-57] Mononuclear bis-ligand cobalt(III) complexes are most common in this category.[54-56] All such complexes show hexacoordinated distorted octahedral geometry of central cobalt(III).

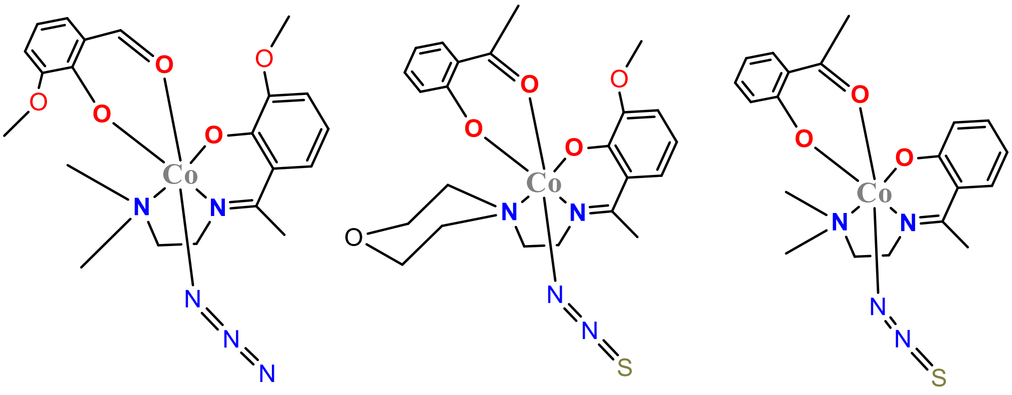


$[Co(L^a)_2(N_3)]^+$ $[Co(L^b)_2(N_3)]^+$

Scheme I.A.9. Schematic representation of two mononuclear quaternary cobalt (III) complexes $[Co(L^a)_2(N_3)]^+$,[75a] and $[Co(L^b)_2(N_3)]^+$,[75a] with azide and N_2O donor salicylaldimine Schiff bases, HL^a = 2-((2- morpholinoethylimino) methyl)-4- chlorophenol and HL^h-2-((2-(dimethylamino) ethylimino) methyl) phenol

.Structures of some monocationic bis-ligand cobalt (III) complexes are shown in **Scheme I.A.8.** some of these complexes are found to form intercalation with CT DNA.[55f]

Mononuclear octahedral cobalt(III) azide complexes with bidentate pendant ligand have also been found in literature.[57] Some structures of these complexes are shown in **Scheme I.A.9.**

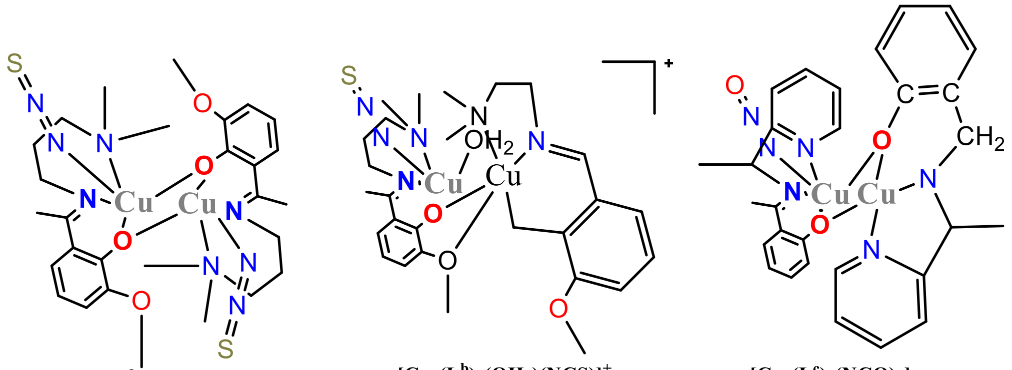


[Co(L^a)(L')(N$_3$)] **[Co(L^b)(L'')(NCS)]** **[Co(L^c)(L'')(NCS)]**

Scheme I.A.10. Schematic representation of some mononuclear quaternary cobalt(III) pseudohalide complexes [Co(L^a) (L') (N$_3$)],[57g] [Co(L^b)(L'')(NCS)],[57e] and [Co(L^c)(L'') (NCS)],[57f] with N$_2$O donor salicylaldimine Schiff bases, HL^a = 2-((2- (dimethylamino) ethylimino) methyl)-6-methoxyphenol, HL^b = 2-(1-(2- morpholinoethylimino) ethyl) phenol and HL^c = 2-(1-(2- (dimethylamino) ethylimino) ethyl)phenol. HL' = 3-methoxysalicylaldehyde and HL'' = Acetophenone

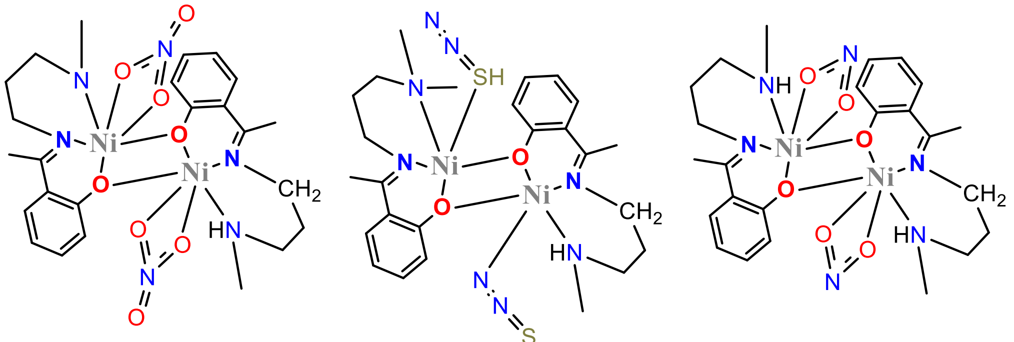
In some cases, Schiff bases hydrolyzed to give corresponding aldehyde which then bind metal center as coligand in presence of Schiff base ligand to produce mononuclear octahedral cobalt(III) complexes as shown in **Scheme I.A.10.**

N_2O donor salicylaldimine Schiff bases have widely been used to form dinuclear transition metal complexes exploiting the bridging ability of the phenoxo oxygen atom. Many such copper(II) and nickel(II) complexes have been reported in literature.[39a,39d,42h,49g,50f,53a,58-60] Some examples of such copper(II) and nickel(II) complexes are gathered in **Schemes I.A.11.** and **I.A.12.** respectively. Magnetic interactions between the phenoxo bridged metal centers are also investigated and most of the cases, antiferromagnetic interactions are found,[49g,50f,58c,58g] although ferromagnetic interactions may also be possible."[59]



$[Cu_2(L^a)_2(NCS)_2]$ $[Cu_2(L^b)_2(OH_2)(NCS)]^+$ $[Cu_2(L^c)_2(NCO)_2]$

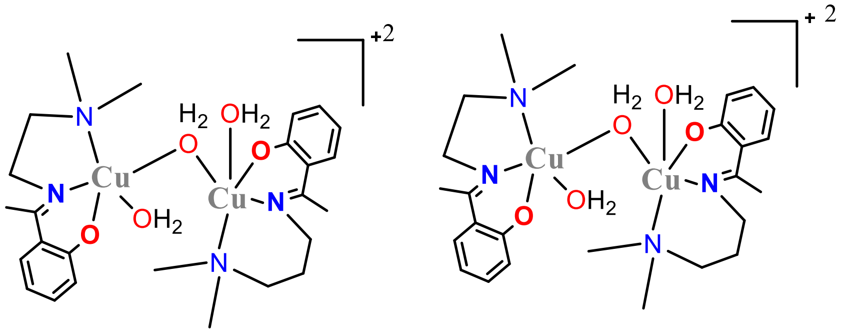
Scheme I.A.11. Schematic representation of three phenoxo bridged dinuclear copper(II) complexes, $[Cu_2(L^a)_2(NCS)_2]$,[58h] $[Cu_2(L^b)_2(OH_2)(NCS)]$, $[Cu_2(L^c)_2(NCO)_2]$,[58h] with N_2O donor salicylaldimine Schiff bases, HL^a = 2-((3- (dimethylamino) propylimino) methyl) -6-methoxyphenol, HL^b = 2-((2-(dimethylamino) ethylimino) methyl)-6-methoxyphenol and HL^c = 2-((3-(dimethylamino) propylimino) methyl)-6-methoxyphenol.



$[Ni_2(L^a)_2(NO_3)_2]$ $[Ni_2(L^b)_2(NCS)_2]$ $[Ni_2(L^c)_2(NO_2)_2]$

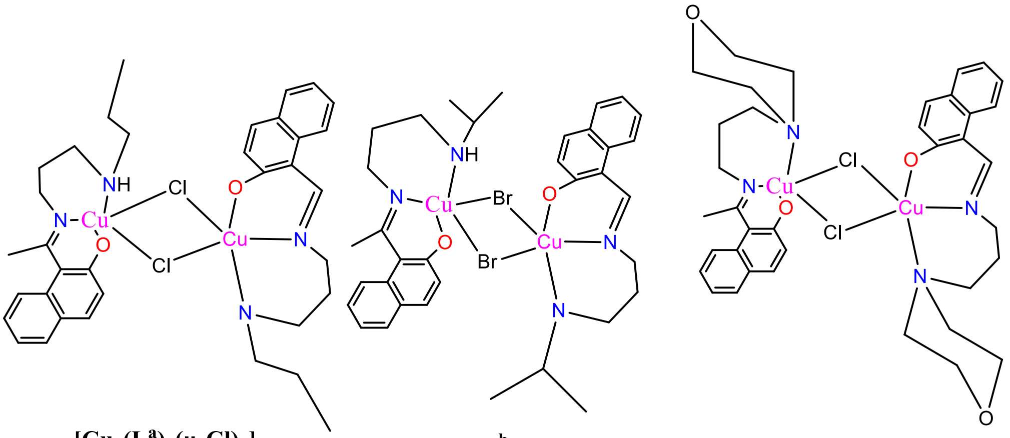
Scheme I.A.12. Schematic representation of three phenoxo bridged dinuclear nickel(II) complexes, $[Ni_2(L^a)_2(NO_3)_2]$,[78c] $[Ni_2(L^b)2(NCS)_2]$,[60c] and $[Ni_2(L^a)_2(NO_2)_2]$,[60b] with N_2O donor salicylaldimine Schiff bases, HL^a = 2-((3-(methylamino) propylimino) methyl) phenol, HL^b = 2-((2-(dimethylamino) ethylimino) methyl) phenol and HL^c = 2-(1-(3- (methylamino) propylimino) ethyl) phenol.

Reports of water bridged dinuclear copper (II) complexes are also found in literature.[61] Structures of two such copper(II) complexes are gathered in **Scheme I.A.13.** Variable temperature magnetic sucptibility measurement reveals antiferromagnetic interactions between copper (II) centers.[61c]



$[Cu_2(L^a)_2(\mu\text{-}OH_2)(OH_2)_2]^{+2}$ $[Cu_2(L^b)_2(\mu\text{-}OH_2)(OH_2)_2]^{+2}$

Scheme I.A.13. Schematic representation of water bridged dinuclear copper(II) complexes, $[Cu_2(L^a)_2(\mu\text{-}OH_2)(OH_2)2]^{2+}$,[61b] and $[Cu_2(L^b)_2(\mu\text{-}OH_2)(OH_2)_2]^{2+}$,[61c] with N_2O donor salicylaldimine Schiff bases, HL^a = 2-((2- (dimethylamino) ethylimino) methyl) phenol and HL^b = 2-((2-(dimethylamino) ethylimino) ethyl) phenol.

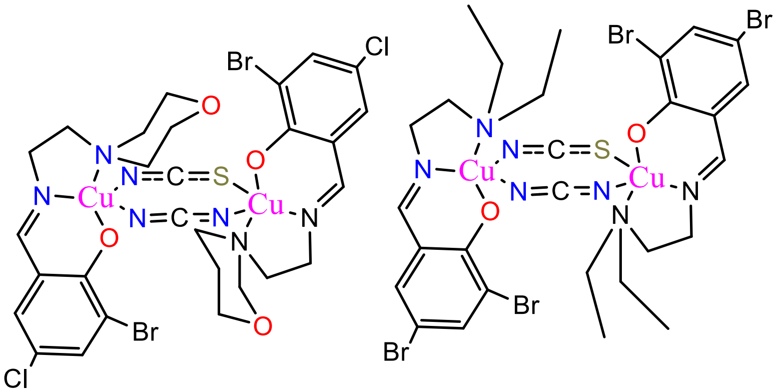


$[Cu_2(L^a)_2(\mu\text{-}Cl)_2]$ **$[Cu_2(L^b)_2(\mu\text{-}Br)_2]$** **$[Cu_2(L^c)_2(\mu\text{-}Cl)_2]$**

Scheme I.A.14. Schematic representation of dinuclear copper(II) complexes $[Cu_2(L^a)_2(\mu\text{-}Cl)_2]$,[62d] $[Cu_2(L^b)_2(\mu\text{-}Br)_2]$,[62c] and $[Cu_2(L^c)_2(\mu\text{-}Cl)_2]$,[62b] with N_2O donor salicylaldimine Schiff bases, HL^a = 1-((2-(propylamino) ethylimino)methyl) naphthalen-2-ol, HL^b = 2-((2-(isopropylamino) ethylimino) methyl) phenol and HL^c = 1-((2-morpholinoethylimino) methyl) naphthalen-2-ol.

Halides are also used as bridging ligands to prepare dinuclear complexes.[39d, 62] Structures of some selected dinuclear copper(II) complexes are shown in **Scheme I.A.14.** Some of these complexes show antibacterial activities against Bacillus subtilis, Staphylococcus aureus, Escherichia coli and

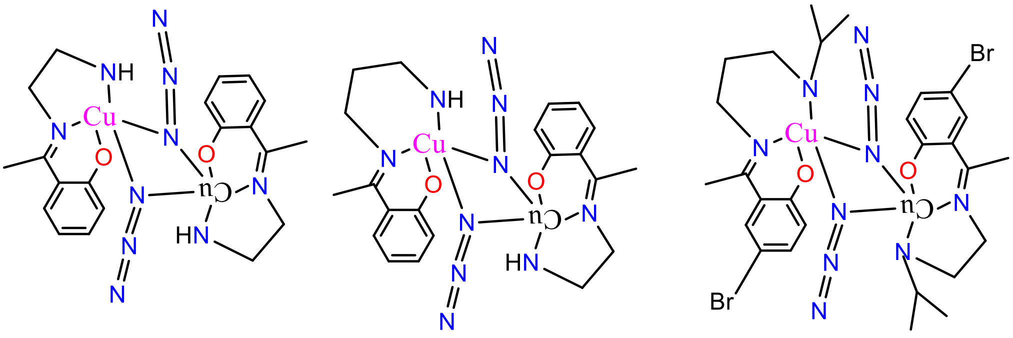
Pseudomonas fuorescens.[62b] No such nickel (II) and cobalt(III) complexes have been characterized by single crystal X- ray diffraction studies.



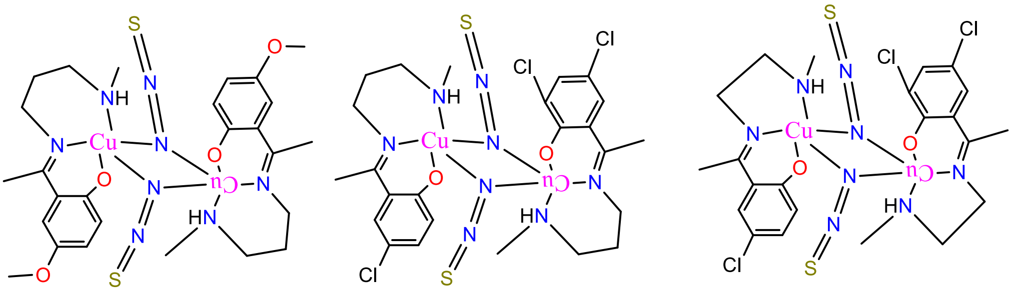
$[Cu_2(L^a)_2(\mu_{1,3}\text{-}NCS)_2]$ **$[Cu_2(L^b)_2(\mu_{1,3}\text{-}NCS)_2]$**

Scheme I.A.15. Schematic representation of two end to end thiocyanate bridged dinuclear copper(II) complexes $[Cu_2(L^a)_2(\mu_{1,3}\text{-}NCS)_2]$[66b] and $[Cu_2(L^b)_2(\mu_{1,3}\text{-}NCS)_2]$[66c] with N_2O donor salicylaldimine Schiff bases, HL^a = 2-((2- morpholinoethylimino) methyl) -6-bromo-4-chlorophenol.

On the other hand, pseudohalides (e.g. azide, thiocyanate etc.) are very popular because of their versatile coordination modes of which end to end $(\mu_{1.3})$ and end on $(\mu_{1,1})$ are the most common ones.[63-65] Two examples of end to end thiocyanate bridged dinuclear copper(II) complexes are shown in **Scheme I.A.15.**[59a,66] Varriable temperature magnetic susceptibility measurement of one such complex indicates the presence of weak antiferromagnetic interactions with $J=-1.71(1)\ cm^{-1}$. No such nickel (II) and cobalt (III) complexes have been reported in literature.



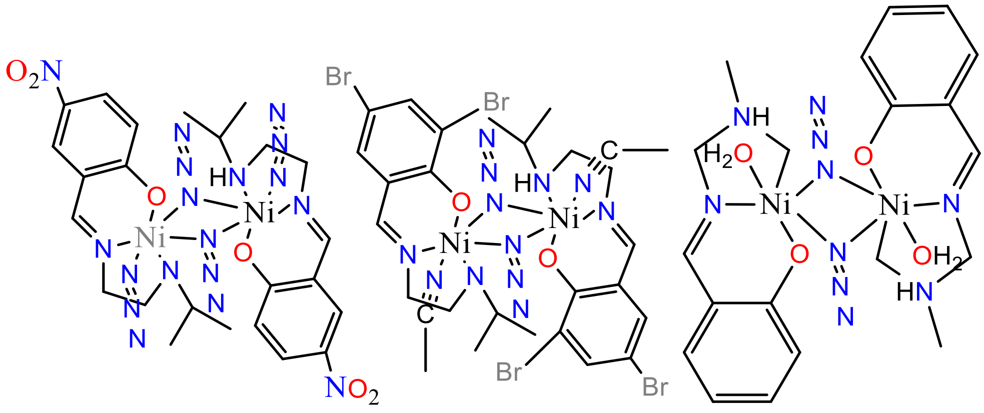
$[Cu_2(L^a)_2(\mu_{1,1}\text{-}N_3)_2]$ $[Cu_2(L^a)_2(\mu_{1,1}\text{-}N_3)_2]$ $[Cu_2(L^c)_2(\mu_{1,1}\text{-}N_3)_2]$



$[Cu_2(L^d)_2(\mu_{1,1}\text{-}NCS)_2]$ $[Cu_2(L^e)_2(\mu_{1,1}\text{-}NCS)_2]$ $[Cu_2(L^f)_2(\mu_{1,1}\text{-}NCS)_2]$

Scheme I.A.16. Schematic representation of some end on pseudohalide bridged dinuclear copper(II) complexes $[Cu_2(L^a)_2(\mu_{1,1}\text{-}N_3)_2]$,[69g] $[Cu_2(L^b)_2(\mu_{1,1}\text{-}N_3)_2]$,[70j] $[Cu_2(L^c)_2(\mu_{1,1}\text{-}N_3)_2]$,[69h] $[Cu_2(L^d)_2(\mu_{1,1}\text{-}NCS)_2]$,[71c] $[Cu_2(L^c)_2(\mu_{1,1}\text{-}NCS)_2]$,[71a] and $[Cu_2(L^f)_2(\mu_{1,1}\text{-}NCS)_2]$,[71c] with N_2O donor salicylaldimine Schiff bases, HL^D = 2-(1-(2- aminoethylimino) ethyl) phenol, HL^b = 2-((3- (methylamino) propylimino) methyl) phenol, HL^c = 2-((2-(isopropylamino) ethylimino) methyl)-4-bromophenol, HL^d = 2-((3-(methylamino) propylimino) methyl) -4-methoxyphenol, HL^c = 2-((3-(methylamino) propylimino) methyl) -4,6-dichlorophenol and HL^f = 2-((2-(methylamino) ethylimino) methyl) phenol.

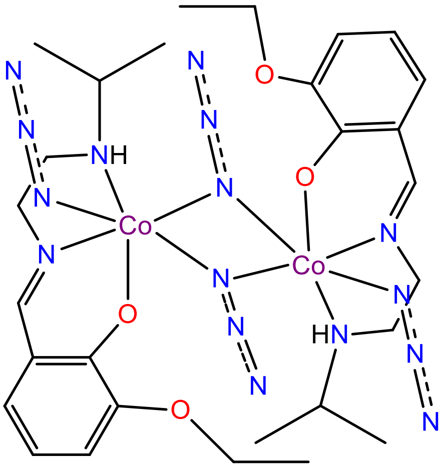
Literature shows that a large number of basal-apical and basal-basal end on pseudohalide bridged dinuclear copper(II) complexes have been studied thoroughly to establish the nature of magnetic interactions among the paramagnetic copper(II) centers.[67-71] Pseudohalides may bind two adjacent metal centers in basal-basal (symmetric)[67] and basal-apical (unsymmetric or antisymmetric) modes.[68] It is also to be noted here that end on pseudohalide bridged copper(II) complexes are essentially of basal-apical type in presence of tridentate N_2O donor Schiff bases. Several research groups have reported basal-apical end on pseudohalide bridged dinuclear copper (II) complexes with tridentate N_2O donor Schiff bases.[62d,69-71] Some examples of end on pseudohalide bridged dinuclear copper(II) complexes are gathered in **Scheme I.A.16.** Variable temperature magnetic susceptibility measurements of one such complexes indicates the presence of weak antiferromagnetic interaction with $J = 2.63(1)$ cm^{-1}



$[Ni_2(L^a)_2(N_3)_2(\mu\text{-}N_3)_2]$ **$[Ni_2(L^b)_2(NCCH_3)_2(\mu\text{-}N_3)_2]$** **$[Ni_2(L^c)_2(OH_2)_2(\mu\text{-}N_3)_2]$**

Scheme I.A.17. Schematic representation of three end on azide bridged dinuclear nickel(II) complexes, $[Ni_2(L^a)_2(N_3)_2(\mu_{1,1}\text{-}N_3)_2]$,[72a] $[Ni_2(L^b)_2(NCCH_3)_2(\mu_{1.1}\text{-}N_3)_2]$,[72b] $[Ni_2(L^b)_2(OH_2)_2(\mu_{1.1}\text{-}N_3)_2]$,[60c] with N_2O donor salicylaldimine Schiff bases, HL^a = 2-((2-(isopropylamino) ethylimino) methyl) -4-nitrophenol, HL^b = 2-((2- (ethylamino) ethylimino) methyl) -4, 6-dibromophenol and HL^c = 2-((2- (methylamino) ethylimino) methyl) phenol.

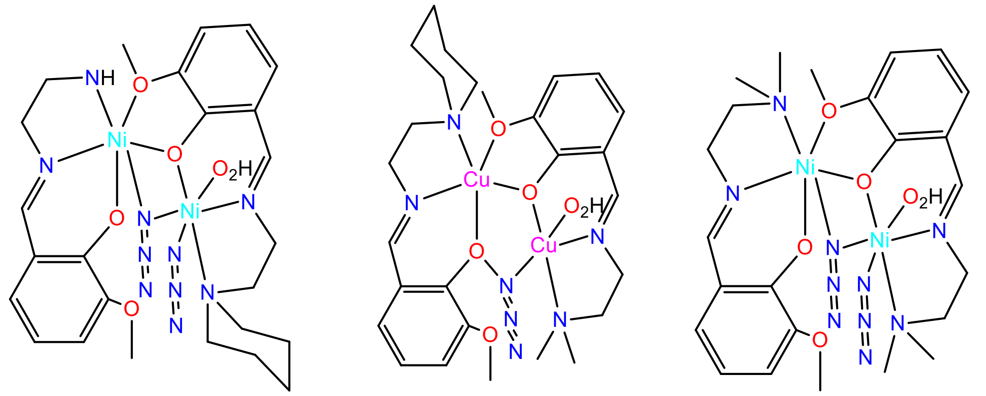
End of azide bridged dinuclear nickel (II) and cobalt (III) complexes with N_2O donor Schiff bases have also been reported by several groups.[60c,72-73] In most cases, coordination geometry around metal center is distorted octahedral. Structures of some selected nickel (II) complexes are gathered in **Scheme I.A.17.** Variable temperature magnetic susceptibility measurement of one such complex indicates the presence of moderately strong ferromagnetic interaction with J = 23.5(3) cm^{-1}.[60c] Structure of a double end on azide bridged dinuclear cobalt (III) complex is also shown in **Scheme I.A.30.** The complex has excellent antibacterial activity against B. subtilis, E. coli and S. aureus and moderate activity against P. fluorescens.[73]



$[Co_2(L^a)_2(\mu_{1,3}\text{-}N_3)_2(N_3)_2]$

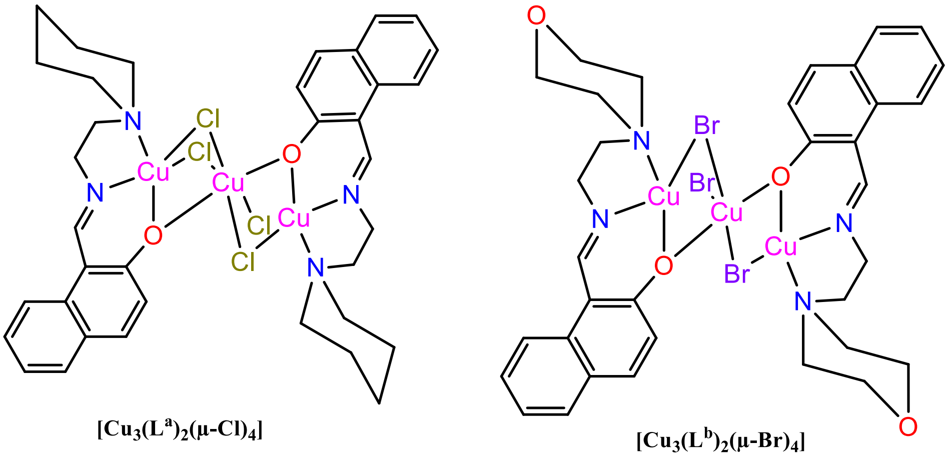
Scheme I.A.18. Schematic representation of end on azide bridged dinuclear cobalt (III) complex, $[Co_2(L^a)_2(\mu_{1.1}\text{-}N_3)_2(N_3)_2]$ with N_2O donor salicylaldimine Schiff base, HL^a = 2-((2- (isopropylamino) ethylimino) methyl) -6-ethoxyphenol.[73]

The study of magnetic exchange in N_2O donor Schiff base complexes mediated by azide in its different bridging modes is often complicated by the presence of additional bridging ligands as all these bridges may either add or counterbalance their effects.[74] Among the possibilities of innumerable combinations of different bridges, a combination of phenoxo and/or carboxylate group with the azide in one system is an interesting approach for modulating magnetic behaviors as both these ligand can transmit ferromagnetic or antiferromagnetic coupling between metal centers. Several research groups have reported the syntheses, crystal structures and magnetic properties of such metal complexes having combined phenoxo and azide bridged (μ-phenoxo- μ-azide).[43c,75,76] Structures of some combined phenoxo and azide bridged dinuclear metal complexes have been shown in **Scheme I.A.19.**[75,76] Magnetic property of combined phenoxo and azide bridged metal centers are also investigated and most of the cases, ferromagnetic interactions are found,[76b,76c] although weak antiferromagnetic interactions may also be possible.[76b]



[Cu$_2$(L^a)($\mu_{1,1}$-N$_3$)(N$_3$)(H$_2$O)] **[Ni$_2$(L^b)($\mu_{1,1}$-N$_3$)(N$_3$)(H$_2$O)]** **[Ni$_2$(L^a)($\mu_{1,1}$-N$_3$)(N$_3$)(H$_2$O)]**

Scheme I.A.19. Schematic representation of phenoxo and azide bridged dinuclear copper(II) and nickel(II) complexes, [Cu$_2$(L^a)$_2$($\mu_{1.1}$-N$_3$)(N$_3$)(H$_2$O)],[75a] [Ni$_2$(L^b)$_2$($\mu_{1.1}$-N3)(N$_3$)(H$_2$O)][43c,76c] and and [Ni$_2$(L^a)$_2$($\mu_{1.1}$-N$_3$)(N$_3$)(H$_2$O)],[75a] with N$_2$O donor salicylaldimine Schiff bases, HL^a = 2-((2-(dimethylamino) ethylimino) methyl) -6- methoxyphenol and HL^b = 2-((2-(piperidin-1-yl) ethylimino) methyl)-6-methoxyphenol.

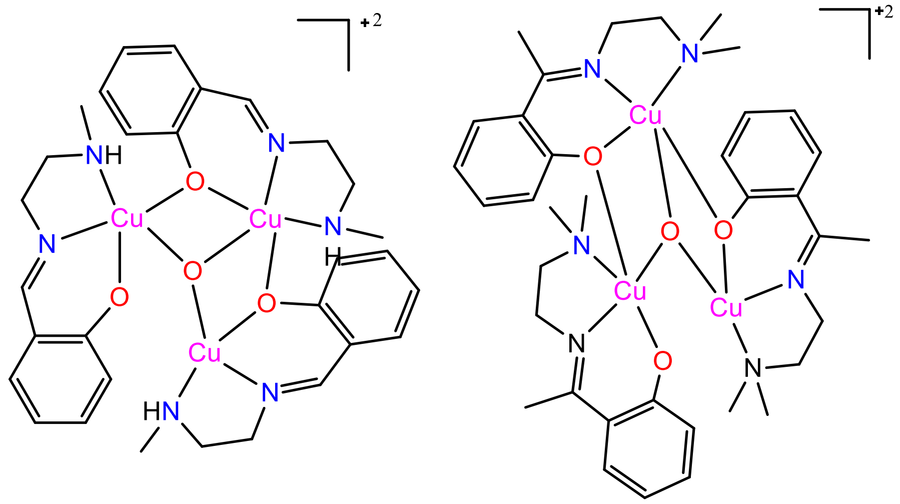


[$Cu_3(L^a)_2(\mu\text{-}Cl)_4$] **[$Cu_3(L^b)_2(\mu\text{-}Br)_4$]**

Scheme I.A.20. Schematic representation of trinuclear copper(II) complexes, [$Cu_3(L^a)_2(\mu\text{-}Cl)_4$],[76] and [$Cu_3(L^b)_2(\mu\text{-}Br)_4$],[62b] with N_2O donor salicylaldimine Schiff bases, HL^a = 1-((2-(piperidin-1-yl) ethylimino) methyl) naphthalen-2-ol and HL^b = 1-((2-morpholinoethylimino) methyl) naphthalen-2-ol.

Examples of combined phenoxo and halide bridged trimuclear copper (II) complexes have also been found in literature. [62b, 77] Structures of two selected antibacterial activities against Bacillus subtilis, Staphylococcus aureus. Escherichio coli and Pseudomonas fuorescens.[77]

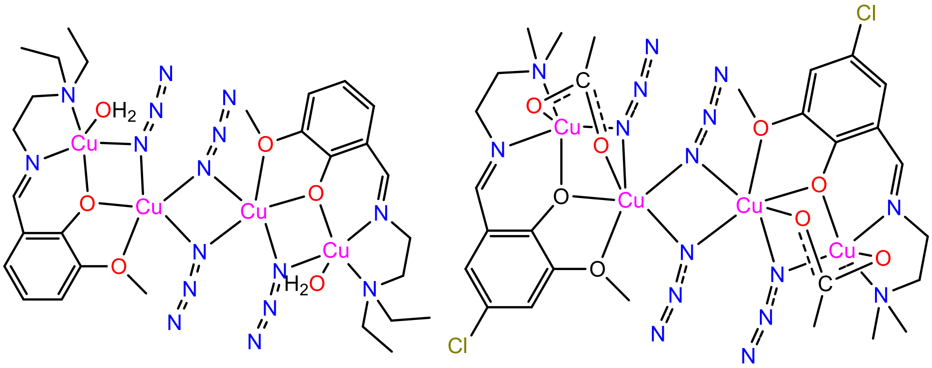
Hydroxide bridged (μ_3-OH) trinuclear copper(II) complexes have also been found in literature.[49g,78,79] Structural study of such complexes reveal trinuclear partial cubane [Cu_3O_4] cores in all cases (**Scheme I.A.21.**). Magnetic interaction between hydroxide bridged copper(II) centers are also investigated and most of the cases, antiferromagnetic interactions are found,[78,79a,79c] although ferromagnetic interactions could also be possible.[79a,79b]



$[Cu_3(L^a)_3(\mu\text{-}OH)]^{+2}$ **$[Cu_3(L^b)_3(\mu\text{-}OH)]^{+2}$**

Scheme I.A.21. Schematic representation of trinuclear copper(II) complexes, $[Cu_3(L^a)_3(\mu_3\text{-}OH)]^{2+}$[79] and $[Cu_3(L^b)_3(\mu_3\text{-}OH)]^{2+}$[79a] with N_2O donor salicylaldimine Schiff bases, HL^a-2-((2-(methylamino) ethylimino) methyl) phenol and HL^b = 2-(1-(2- (dimethylamino) ethylimino) ethyl) phenol.

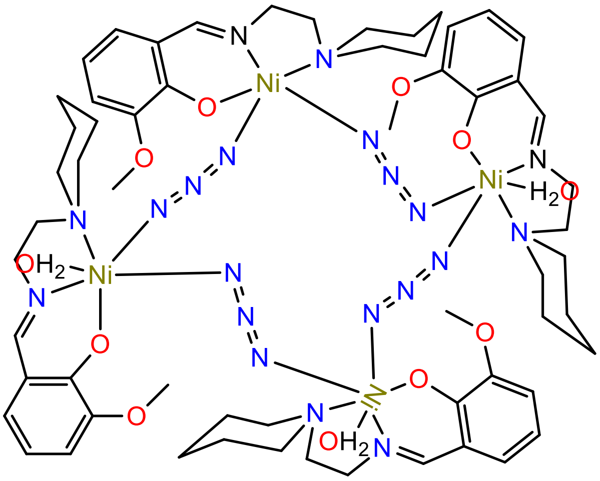
Examples of combined phenoxo and azide bridged tetranuclear copper (II) complexes are found in literature.[70a,75b,80] Structures of two such complexes are gathered in **Scheme I.A.22.** Variable temperature magnetic susceptibility measurements reveal antiferromagnetic interactions between combined phenoxo and aide bridged copper (II) centers inn most of the cases.[80a] although ferromagnetic interactions may also be possible.[75b]



$[Cu(L^a)_2(\mu\text{-}N_3)_4(N_3)_2(H_2O)_2]$

$[Cu(L^b)_2(\mu\text{-}N_3)_4(\mu\text{-}O_2CCH_3)_2]$

Scheme I.A.22. Schematic representation of tetranuclear copper(II) complexes, $[Cu_4(L^a)_2(\mu_{1,1}\text{-}N_3)_4(N_3)_2(H_2O)_2]$, and $[Cu_4(L^b)_2(\mu_{1,1}\text{-}N_3)_4(\mu\text{-}O_2CCH_3)_2]$,[80b] with N_2O donor salicylaldimine Schiff bases, HL^a = 2-((2-(diethylamino) ethylimino) methyl)-6- methoxyphenol and HL^b 2-((2-(dimethylamino) ethylimino) methyl) -4-chloro-6- methoxyphenol.

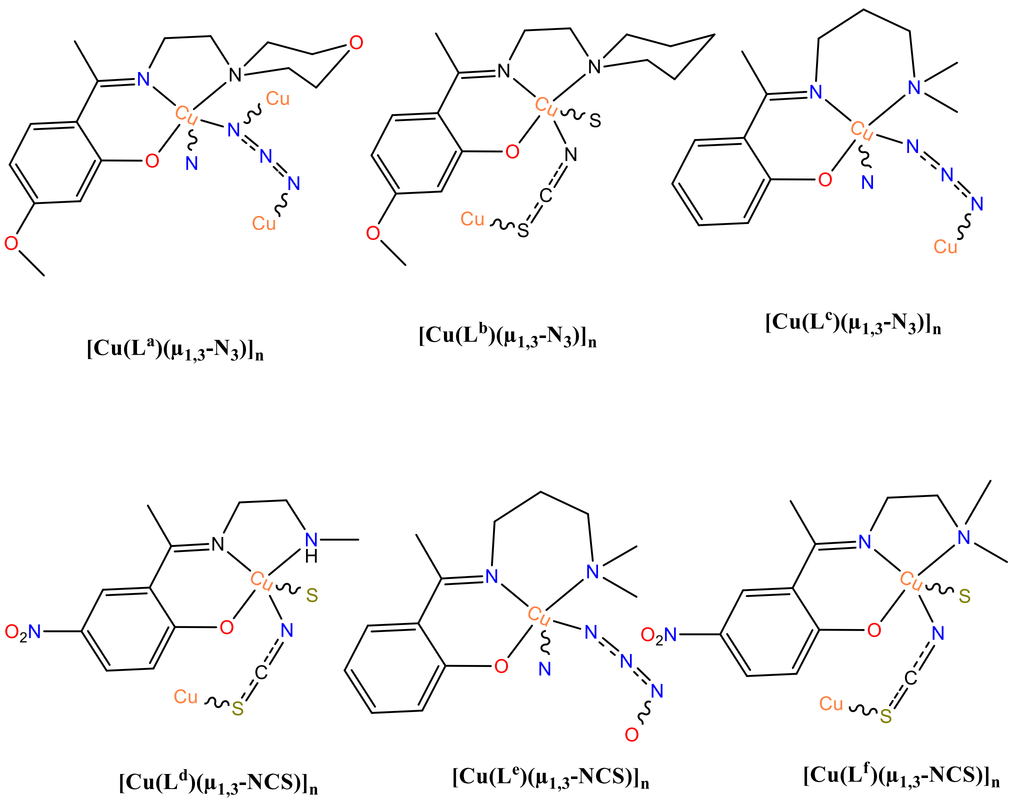


$[Ni_4(L^b)_4(\mu\text{-}N_3)_4]$

Scheme I.A.23. Schematic representation of cyclic tetranuclear nickel(II) complex, $[Ni_4(L^b)_4(\mu_{1,3}\text{-}N_3)_4]_n$ with N_2O donor salicylaldimine Schiff bases, HL^b = 2-((2- (piperidin-1-yl) ethylimino) methyl)-6-methoxyphenol.[81]

There are few reports of the synthesis and charecterisation of end to end azide bridged tetranuclear cyclic nickel (II) complexes.[81] Structure of a cyclic tetranuclear nickel(II) complex with tridentate N_2O donor salicylaldimine Schiff bases is shown in **Scheme I.A.23.** Magnetic interactions between end to end azide bridged copper (II) Centers are also investigated. Fitting of the measured data have been carried out by means of the marked differences among the torsion angles; for that, three exchange coupling constants have been considered in the following Heisenberg-spin Hamiltonian, $H = -J_a(S_1S_2 + S_3S_4) - J_bS_2S_3 - J_aS_4S_1$. Least squares fitting of the experimental data led to the overall antiferromagnetic interactions with J_a = 35.5, J_b= -70.5 and J_c=-15.5 cm^{-1} [81]

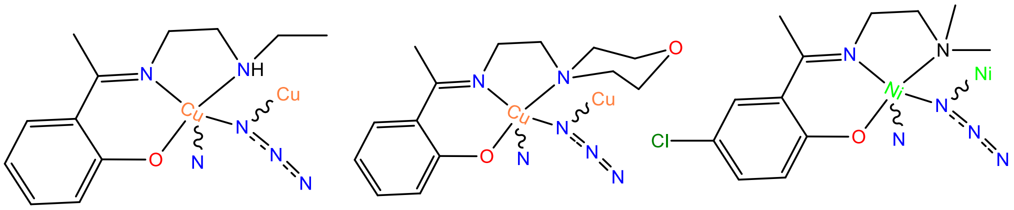
End to end pseudohalide bridged polynuclear complexes are common in literature.[42d,70a,70j,82,83] Variable temperature magnetic susceptibility measurements reveals that most of such complexes show antiferromagnetic interactions between copper(II) centers.[42d,82c,82d,82e] Structures of some selected complexes with tridentate Schiff bases are shown in **Scheme I.A.24.** No such nickel (II) and cobalt(III) complexes are found in literature.



$[Cu(L^a)(\mu_{1,3}\text{-}N_3)]_n$ **$[Cu(L^b)(\mu_{1,3}\text{-}N_3)]_n$** **$[Cu(L^c)(\mu_{1,3}\text{-}N_3)]_n$**

$[Cu(L^d)(\mu_{1,3}\text{-}NCS)]_n$ **$[Cu(L^e)(\mu_{1,3}\text{-}NCS)]_n$** **$[Cu(L^f)(\mu_{1,3}\text{-}NCS)]_n$**

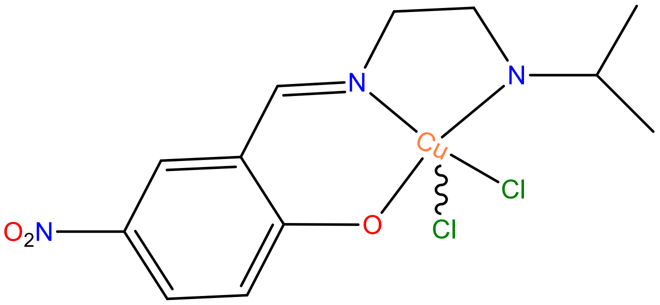
Scheme I.A.24. Schematic representation of end to end pseudohalide bridged polynuclear copper(II) complexes $[Cu(L^a)(\ \mu_{1,3\text{-}}N_3)]$.[70] $[Cu(L^b)(\mu_{1,3\text{-}}N_3)]$[??] $[Cu(L^c)(\mu_{1,3\text{-}}N_3)]_n$,[42d] $[Cu(L^d)(\mu_{1,3\text{-}}NCS)]$[83a] $[Cu(L^d)(\mu_{1,3\text{-}}NCS)]$.[83b] and $[Cu(L^f)(\ \mu_{1,3\text{-}}(NCS)]$[83] with N_20 donor salicylaldimine Schiff bases, HL^a = 2-((2- morpholinoethylimino) methyl) -5-methoxyphenol, HL^b = 1-((3- (dimethylamino) propylimino) methyl) naphthalen-2-ol, HL^c = 2-((2-(dimethylamino) ethylimino) methyl) phenol, HL^d = 2-((2-piperidinoethylimino) methyl) -4-nitrophenol, HL^e = 2-((2- (methylamino) ethylimino) methyl)-4-nitrophenol and HL^f = 2-((2- (dimethylamino) ethylimino) methyl)-4-bromophenol.



$[Cu(L^a)(\mu\text{-}N_3)]_n$ $[Cu(L^b)(\mu\text{-}N_3)]_n$ $[Ni(L^c)(\mu\text{-}N_3)]_n$

Scheme I.A.25. Schematic representation of end on azide bridged polynuclear copper(II) and nickel (II) complexes $[Cu(L^a)(\mu_{1,1}\text{-}N_3)]_n$,[84c] $[Cu(L^b)(\mu_{1,1}\text{-}N_3)]_m$[82d,82c] and $[Ni(L^c)(\mu_{1,1}\text{-}N_3)]_n$,[47f] with N_2O donor salicylaldimine Schiff bases, HL^a = 2-(1-(2- (ethylamino) ethylimino) ethyl) phenol, HL^b -2-((2-morpholinoethylimino) methyl)- phenol and HL^c-2-(1-(2-(dimethylamino) ethylimino) ethyl) -4-chlorophenol.

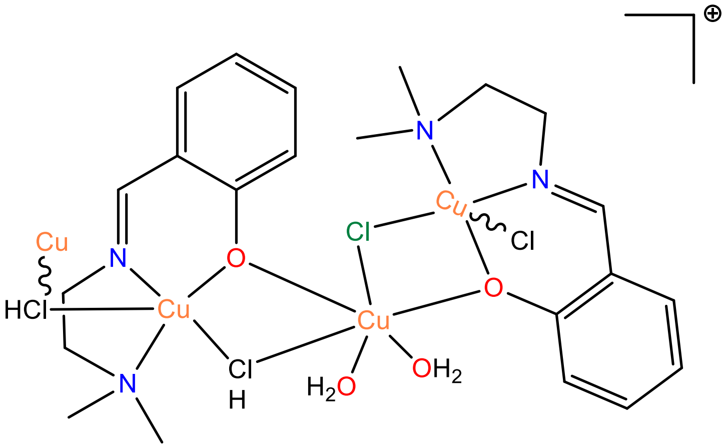
End on azide bridged polynuclear complexes have also been found in literature.[42e,47f,70h,70i,82d,82c,84] Structures of some copper(II) and nickel(II) complexes are shown in **Scheme I.A.25.** Variable temperature magnetic susceptibility measurements reveal antiferromagnetic interactions between end on azide bridged centers in most of the cases,[82c,70h] although ferromagnetic interactions may copper(II) also be possible.[82d] No such cobalt(III) complexes have been characterized by single crystal X-ray diffraction studies.



$[Cu(L^a)(\mu\text{-}Cl)]_n$

Scheme I.A.26. Schematic representation of chloride bridged polynuclear copper (II) complex $[Cu(L^a)\ (\mu\text{-}Cl)]_n$, with N_2O donor salicylaldimine Schiff base, HL^a = 2-((2-(isopropylamino)ethylimino)methyl)phenol.[85]

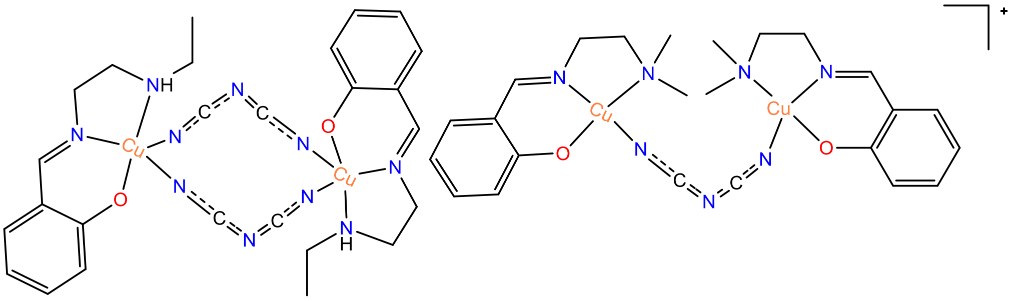
Halide bridged polynuclear copper (II) complex has also been found in literature (**Scheme 1.A.26.**) Report of similar type of nickel (II) and cobalt(III) complexes is once again not found in literature.



$[Cu_3(L^a)_2(H_2O)_2(\mu\text{-}Cl)_3]_n$

Scheme I.A.27. Schematic representation of combined phenoxo and halide bridged polynuclear copper (II) complexes $[Cu_3(L^a)_2(H_2O)_2(\mu\text{-}Cl)_3]$, with N_20 donor salicylaldimine Schiff bases, HL^a = 2-((2- (dimethylamino) ethylimino) methyl) phenol.

There is an example where phenoxo oxygen of Schiff base ligand supports to form chloride bridged polynuclear copper(II) complexes as shown in **Scheme I.A.27.**[83f] Report of similar type of nickel(II) and cobalt(III) complexes is once again not found in literature.

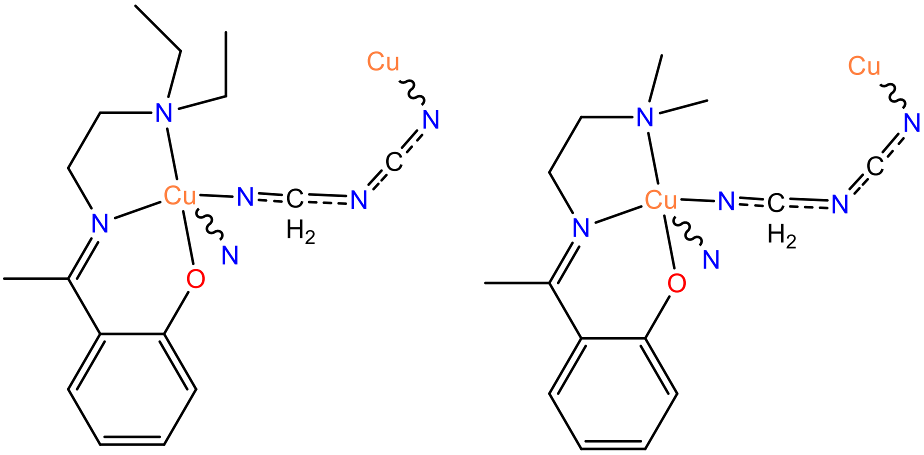


$[Cu_2(L^a)_2(\mu\text{-}NCNCN)_2]$

$[Cu_2(L^a)_2(\mu\text{-}NCNCN)_2]^+$

Scheme I.A.28. Schematic representation of dinuclear copper(II) complexes $[Cu_2(L^a)_2(\mu_{1,5}\text{-}NCNCN)_2]$,[87d] and $[Cu_2(L^d)_2(\mu_{1.5}\text{-}NCNCN)]^+$,[87b,87c] with N_2O donor salicylaldimine Schiff bases, HL^a = 2-((2-(ethylamino) ethylimino) methyl) phenol and HL^b-2-((2-(dimethylamino) ethylimino) methyl) phenol.

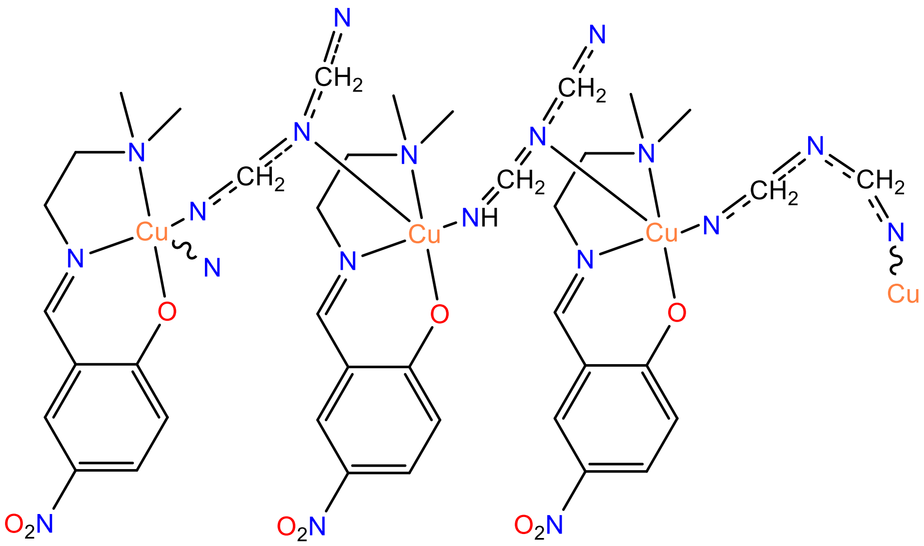
Di cyanamide is sometimes called bent pseudohalide and the coordination polymers based on dicyanamide have also attracted much attention in the past few years for their interesting extended architectures and magnetic properties as well.[86] Several research groups have reported the syntheses, and characterization of dicyanamide bridged di and polynuclear copper (II) complexes.[87,88] Structures of some di and polynuclear complexes have been gathered in **Schemes I.A.28** and **I.A.29** respectively. Magnetic property of dicyanamide bridged copper(II) centers are investigated and most of the cases, weak antiferromagnetic interactions have been found,[87b,87d,88a] although ferromagnetic interactions can also be possible.[87c]



$[Cu(L^a)(\mu_{1,5}\text{-NCNCN})]_n$ **$[Cu(L^b)(\mu_{1,5}\text{-NCNCN})]_n$**

Scheme I.A.29. Schematic representation of dicyanamide bridged polynuclear copper(II) complexes $[Cu(L^a)(\mu_{1,5}\text{-NCNCN})]$,[88c] with N_2O donor salicylaldimine Schiff bases, HL = 2-(1-(2-(diethylamino) ethylimino) ethyl) naphthalen-1-ol [Cu(L^b) ($\mu_{1,5}$-NCNCN)][88b] where, HL^b = 2-(1-(2-(dimethylamino) ethylimino) ethyl)phenol.

Although end to end bridging mode of dicyanamide ($\mu_{1,5}$-NCNCN) is most common, $\mu_{1,3}$-NCNCN bridging mode of dicyanamide have also been found in literature.[87] In this connection, may discussed the structure of mixed $\mu_{1,3}$- and $\mu_{1,5}$-dicyanamide bridged polynuclear copper(II) complex, [Cu_3(L^c)3($\mu_{1,3}$- NCNCN)$_2$($\mu_{1,5}$-NCNCN)]$_n$, synthesized and characterized by P. K. Bhaumik et al.[87a] Structural analyses reveal that two consecutive dicyanamide units are serving as 1,3- bridging ligand ($\mu_{1,3}$-NCNCN), while the third one exhibits end to end 1,5-bridging mode ($\mu_{1,5}$-NCNCN) as shown in **Scheme I.A.30.**



[Cu_3(L^a)($\mu_{1,3}$-NCNCN)$_2$(μ-NCNCN)]$_n$

Scheme I.A.30. Schematic representation of mixed $\mu_{1,3-}$ and $\mu_{1,5-}$ dicyanamide bridged polynuclear copper(II) complexes $[Cu_3(L^c)_3(\mu_{1.3-}NCNCN)_2(\mu_{1,5-}NCNCN)]$,[87a] where, HL^a = 2-((2-(dimethylamino) ethylimino) methyl)-4- nitrophenol.

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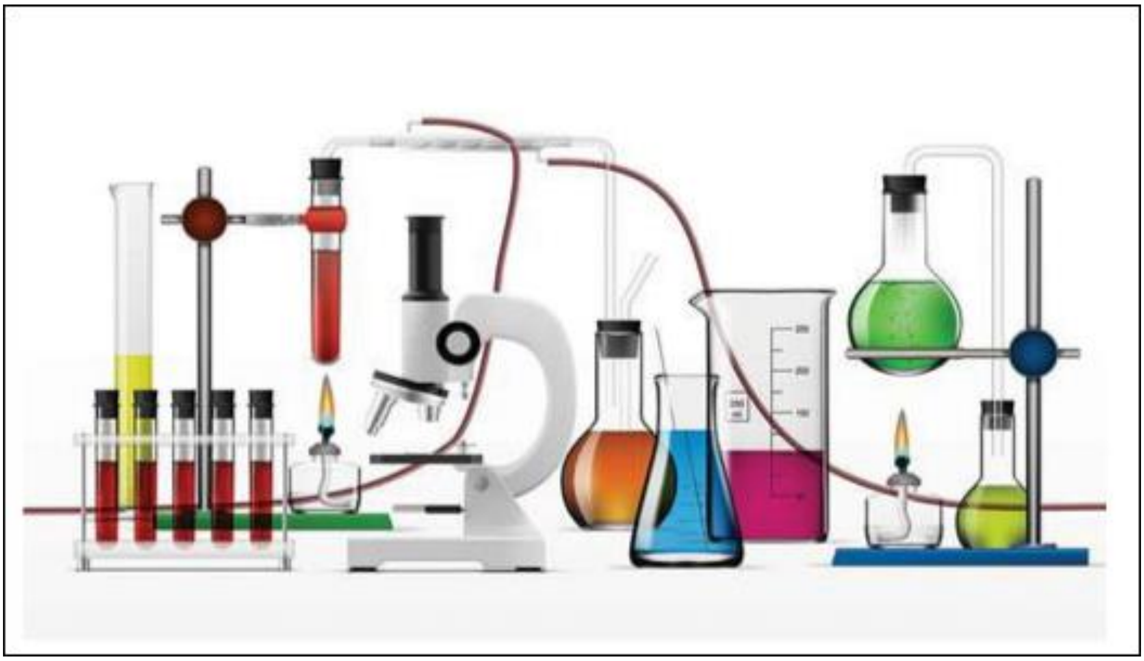
Section I.B

Materials and details of instrumentation



Starting materials

2, 3-Butanedione monoxime and N, N-dimethyl-1,2-ethanediamine were purchased from commercial sources and used as received. Copper (II) perchlorate hexahydrate was prepared by the standard laboratory method; solvents were of reagent grade and used without further purification.

Starting materials and solvents used in this work were purchased from Sigma-Aldrich, India (now Merck, India) and were of reagent grade. They were used as received, without any further purification. The entire syntheses were carried out under aerobic conditions.

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Physical Measurements

Elemental analysis (carbon, hydrogen and nitrogen) was performed using a Perkin-Elmer 240C elemental analyzer. IR spectrum in KBr (4500–500 cm^{-1}) were recorded with a Perkin-Elmer Spectrum Two spectrophotometer. Electronic spectrum of complex **1** was recorded on a JASCO J-630 spectrophotometer. Electronic spectra of other complexes in acetonitrile were recorded on a Perkin Elmer Lambda 35 UV–Visible spectrophotometer. Powder X-ray diffraction was performed on a Bruker D8 instrument with Cu-Ka (k = 1.5406 Å) radiation. In this process, the complex was ground with a mortar and pestle to prepare fine powders which were then dispersed with alcohol onto a zero background holder (ZBH). The alcohol was then allowed to evaporate to provide a nice, even coating of powder adhered to the sample holder. Mass spectrum was recorded on an XEVO G2QTof spectrometer (Waters) with an electrospray ionization source.

The variable temperature magnetization measurements of complexes **4** and **5** were carried out at 1 T in the 2–300 K range using a Quantum Design MPMSXL SQUID magnetometer and 51.11 mg of **4** and 54.42 mg of **5**. The data were corrected for the diamagnetic contribution of the sample holder and the intrinsic contributions on the basis of Pascal's constants.

X-ray crystallography

Suitable single crystals of complexes **1** and **5** were used for data collection using a 'Bruker D8 QUEST area detector' diffractometer equipped with graphite-monochromated Mo K_α radiation ($\lambda = 0.71073$ Å). Multi-scan empirical absorption corrections were applied to the data using the program SADABS [1] Other programs used included PLATON. In **5**, the solvent methanol molecule was disordered over three overlapping sites and refined accordingly. However, as it was not possible to see clear electron-density peaks in difference maps which would correspond with acceptable locations for the various disordered methanol H atoms, the refinement was completed with no allowance for these methanol H atoms in the model.

Suitable single crystal of the complexes (**2** – **4)** were picked, mounted on a glass fibre and diffraction intensities were measured with an Oxford

Diffraction X-Calibur diffractometer equipped with Mo-Ka radiation (k = 0.71073 Å, 50 kV, 40 mA) at an ambient temperature (150 K). Data collection and reduction were performed with the Crysalis software.[2] Absorption corrections were carried out using ABSPACK [3]

Suitable single crystals of all the four complexes **6**, **7**, **8** and **9** were used for data collection using a 'Bruker D8 QUEST area detector' diffractometer with graphite-monochromated Mo K_α radiation (λ = 0.71073 Å). Multi-scan empirical absorption corrections were applied to the data using the program SADABS.

The molecular structure was solved by direct method and refined by full-matrix least squares on F^2 using the SHELXL-18/1 package.[4] Non-hydrogen atoms were refined with anisotropic thermal parameters. All hydrogen atoms were placed in their geometrically idealized positions and constrained to ride on their parent atoms.

Catalytic oxidation of o-aminophenol to 2-aminophenoxazine-3-one

Phenoxazinone synthase mimicking activity of the complexes was conducted at room temperature under aerobic condition for ca. 2 h. During this experiment, 10^{-4} M acetonitrile solution of the complex in acetonitrile was added to solutions with varying concentrations (10^{-3} to 10^{-2}) of substrate (*o*-

aminophenol in acetonitrile. The kinetics of the reaction was followed spectrophotometrically by observing the increase in the absorbance maxima at around 425 nm, which is characteristic of phenoxazinone chromophore. In the above case, complex: substrate ratio were ≥ 1:10 to maintain pseudo-first order condition to determine the dependence of rate on substrate concentration and various kinetic parameters. The rate of the reaction was derived from the initial rate method.

Theoretical methods

The energies of the complex **3** included in this study were computed at the B3LYP-D/def2-SVP level of theory using the crystallographic coordinates. For the calculations we have used the GAUSSIAN-09 program [5] The same level of theory was used for the molecular electrostatic potential (MEP) surface calculations. We have also used Grimme's dispersion [6] correction since it is adequate for the evaluation of non-covalent interactions. The basis set superposition error for the calculation of interaction energies has been corrected using the counterpoise method [7] The NCI plot [8] isosurfaces have been used to characterize non-covalent interactions. They correspond to both favorable and unfavorable interactions, as differentiated by the sign of the second density Hessian Eigen value and defined by the isosurface color. The color scheme is a red-yellow-green–blue scale, with red for ρ^{+}cut (repulsive) and blue for ρ^{-} cut (attractive). The Gaussian-09 B3LYP-D/def2- SVP wave function has been used to generate the NCI plot.

The study of the magnetic behavior of the complexes **4** and **5** was performed at the B3LYP/6-31+G* level of theory[9] and using the crystallographic coordinates by means of the Gaussian-16 program.[10] To calculate the coupling constant (J) of the dinuclear nickel complexes, two energy levels are evaluated, corresponding to the high-spin (E_{hs}) and broken-symmetry (E_{bs}) states. Subsequently, the J values used in this work were obtained from the equation and methodology proposed by Ruiz et al.[11] The plots of the spin density and SOMOs were generated using Gauss View software v. 6.0.16 [12] for the HS configuration.

The fully optimized geometries and energies have been used to compute the homodesmotic reaction at the B3LYP-D/def2-SVP level of theory. In these complexes **6**, **7**, **8** and **9** the population analysis based on the electron density, i.e. natural population analysis (NPA) [13] has been performed. To compute the interaction energies in the solid state, the crystallographic coordinates have been used at the same level of theory. For the calculations, the GAUSSIAN-09 program has been used.[14] Grimme's dispersion correction [15] has also been used, as implemented in the GAUSSIAN-09 program, since it is adequate for the evaluation of non-covalent interactions where dispersion effects are relevant. The basis set superposition error for the calculation of interaction energies has been corrected using the counterpoise method.[16]

Hirshfeld surface analysis

Crystal Explorer[17] was used to calculate the Hirshfeld surfaces [18, 19] and associated 2D fingerprint plots [20–21] of the complex. Hirshfeld surface envelops that region of space surrounding a particular molecule in a crystal where the electron distribution of the promolecule exceeds that due to any other molecule. Generally, Hirshfeld surface is represented by thousands of surface points obtained by triangulation, and two parameters d_i (distance from the surface to the nearest atom interior to the surface) and d_e (distance from the surface to the nearest atom exterior to the surface) convey information about relevant contact distances from each point. In order to construct a 2D fingerprint plot the molecular Hirshfeld surface is first obtained using standard methods. These 2D plots are a novel visual representation of all the intermolecular interactions simultaneously, and are unique for a given crystal structure and polymorph. As described elsewhere, Hirshfeld surfaces and the associated two-dimensional (2D) finger print plots were calculated using Crystal Explorer, with bond lengths to hydrogen atoms set to standard values. The normalized contact distance (d_{norm}) based on d_{e} and d_{i} is given by the equation:

$$d_{norm} = \frac{(d_i - r_i^{vdw})}{r_i^{vdw}} + \frac{(d_e - r_e^{vdw})}{r_e^{vdw}}$$

Where, $\mathrm{r_i}^{vdW}$ and $\mathrm{r_e}^{vdW}$ are the van der Waals radii of the atoms. The value of d_{norm} is negative or positive depending on intermolecular contacts being shorter or longer than the van der Waals separations. The parameter d_{norm}

displays a surface with a red-white-blue colour scheme, where bright red spots highlight shorter contacts, white areas represent contacts around the van der Waals separation, and blue regions are devoid of close contacts.

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Section I.C

Summary of research work

Chapter II

A dinuclear copper (II) complex, $[(CH_3CN)Cu(L^1)_2Cu](ClO_4)_2$ **(1)** has been synthesized by reacting an oxime-based tridentate Schiff base ligand, 3-[2-(dimethylamino)-ethylimino] butan-2-one oxime (**HL^1**), with copper(II) perchlorate hexahydrate. The complex has beencharacterized by elemental and spectral analyses. Structure of the complex has been confirmed by single crystal X-ray diffraction technique. The complex may be used as moderate catalyst for the oxidation of *o*-aminophenol to 2-aminophenoxazine-3-one.

Chapter III

A dinuclear copper(II) complex $[LCu(\mu_{1,1}-N_3)_2CuL^2]$ **(2)** {where **HL^2** = (2-(3-aminopropylimino)methyl-6-methoxyphenol)} has been synthesized and characterized by several analytical techniques including single crystal X-ray diffraction analysis. Interesting supramolecular interactions are observed in the solid state of the complex. An unusual N-H···π interaction is observed where the chelate ring, $Cu(1)–N(1)–Cu(1)^b–N(1)^b$, [where ^{b} =1-x,-y,1-z] behaves as a π system. Supramolecular interactions have been related with

Hirshfeld surface calculations.The complex has been evaluated as functional model for phenoxazinone synthase enzyme by using *o*-aminophenol (OAPH) as a model substrate in acetonitrile medium. Kinetics of the reaction was followed spectrophotometrically, which confirm that catalytic reactions follow Michaelis–Menten enzymatic reaction kinetics.

Chapter IV

An ionic mixed valence cobalt(III/II) complex, $[Co^{III}(L)_2][Co^{II}(NCS)_3(H_2O)]$ **(3)**{where, $\mathbf{H_2L^2}$ = 2-((3-aminopropylimino)methyl)-6-methoxyphenol}, has been synthesized and characterized by several analytical techniques including single crystal X-ray diffraction analysis. The energetic features of solid state noncovalent interactions involved in the ionic coordination complex has been studied by means of DFT computation, which indicate that combination of strong $CH_3\cdots\pi$ and H-bonding interactions are the main reason behind stabilization this complex.

Chapter V

Two new dinuclear nickel(II) complexes, $[(H_2O)Ni(N_3)(L^3)(\mu\text{-}_{1,1}\text{-}N_3)Ni(L^3)]$ **(4)** and $[(H_2O)Ni(N_3)(L^4)(\mu\text{-}_{1,1}\text{-}N_3)Ni(L^4)]\cdot MeOH$ **(5)** derived from two isomeric Schiff base ligands, $\mathbf{HL^3}$ [2-{(2-(ethylamino)ethylimino)methyl}-6-ethoxyphenol] and $\mathbf{HL^4}$ [2-{(2-(dimethylamino)ethylimino)methyl}-6-ethoxy-phenol], have been synthesized and characterized. Variable temperature (2–300 K) magnetic susceptibility measurements indicate the presence of moderate ferromagnetic exchange coupling between nickel (II) centers. In each complex, antiferromagnetic exchange takes place through the phenoxido bridge and ferromagnetic through the $\mu_{1,1}$-azido bridge. The competitive interactions therefore reduce the overall magnetic coupling. In a theoretical complex, where the bridging azido ligand has been eliminated and the rest of the geometry is kept frozen, the magnetic coupling becomes antiferromagnetic which suggests that the ferromagnetic exchange occurs via the $\mu_{1,1}$-azido bridge. Mulliken population analysis and spin density plots clearly show that the spin distributed spherically in the Ni centers is due to the presence of one unpaired electron in both the $dx^2–y^2$ and dz^2 orbitals. The shape of the spin density at the bridging O-atom and azide evidences the participation of their p orbitals in the magnetic coupling. The SOMO is basically constituted by the dz^2 orbital of one nickel(II) center with the participation of the azide π-system. The SOMO−1 is constituted by the $dx^2–y^2$ orbital of the other nickel (II), an oxygen atom and the azide π-system.

Chapter VI

Two compartmental, N_2O_4 donor, Schiff bases, **H_2L^5** [N,N-bis(3-methoxysalicylidene)-2,2-dimethylpropane-1,3-diamine] and **H_2L^6** [N,N-bis(3-ethoxysalicylidene)-2,2-dimethylpropane-1,3-diamine], each having inner N_2O_2 and outer O_4 compartments have been used to prepare four heterotrinuclear nickel(II) complexes $[Ni(L^5)Na(L^5)Ni(NCS)]\cdot H_2O$ (**6**), $[Ni(L^5)Na(L^5)Ni(N_3)]$ (**7**), $[Ni(L^6)Na(L^6)Ni]NCS\cdot CH_3OH$ (**8**), $[Ni(L^6)Na(L^6)Ni]ClO_4$ (**9**) All complexes have been characterized by elemental and spectral analyses. Single crystal X-ray diffraction analyses have confirmed their structures. In each complex, nickel (II) is placed in inner N_2O_2 compartment and sodium is placed in outer O_4 compartment of the respective Schiff base ligand. In complexes **6** and **7,** one nickel (II) center is tetra-coordinated (square planar) and other is penta coordinated (square pyramidal), whereas in complexes **8** and **9,** both nickel (II) centres are tetra-coordinated. The geometries of complexes **6** and **8** have been optimized without a counterion (denoted as 1^+ and 3^+). The electrophilic nickel (II) centre is found to be accessible in complex 1^+ and, conversely, it is unreachable in complex 3^+, in agreement with the experimental result. Starting from the hypothetical 1+ complex where both nickel (II) centres are tetra-coordinated, the energy change for replacing four methyl groups with four ethyl groups has been computed using ethane and methane to complete the homodesmotic equation. The result is that the intra-molecular interaction of the four ethyl groups favours complex 3^+ by $\Delta E = -26.1$ kcal mol^{-1}

Chapter II

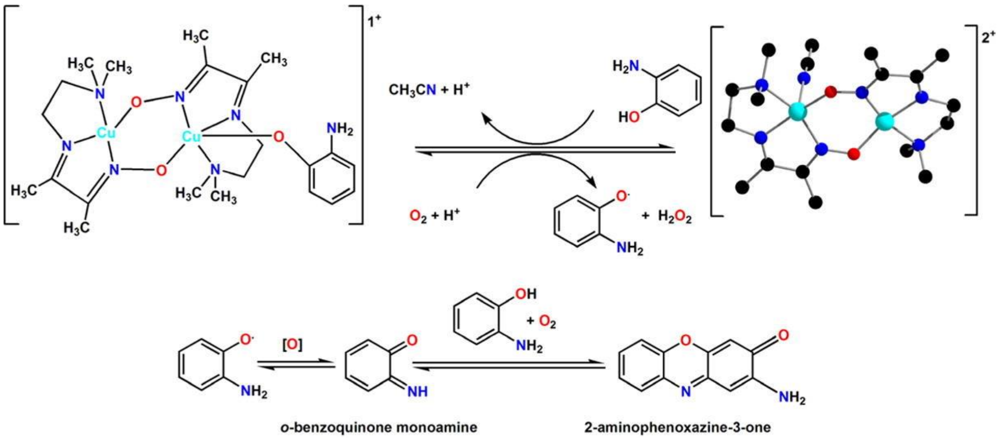
Synthesis and characterization of a double oximato bridged di nuclear copper (II) complex and exploration of its phenoxazinone synthase mimicking activity

"A goal should scare you a little and excite a lot"

-Joe Vitale

Chapter II

Synthesis and characterization of a double oximato bridged di nuclear copper (II) complex and exploration of its phenoxazinone synthase mimicking activity



Chapter II

Synthesis and characterization of a double oximato bridged di nuclear copper (II) complex and exploration of its phenoxazinone synthase mimicking activity

II.1 Introduction

Diverse catalytic activity [1–6] utility in modeling the multimetal active sites of metalloproteins[7] and potential use in material science [8–10] have attracted the attention of coordination chemists to design and synthesize homo- or hetero-polynuclear complexes of transition metals. Among them many copper(II) complexes have been synthesized to explore the involvement of copper active sites in several catalytic biological processes, to understand the magneto-structural correlations arising from the electronic exchange coupling among copper(II) centers, and to develop different molecular-based functional materials [11–15] Many complexing agents have been used to prepare such complexes.

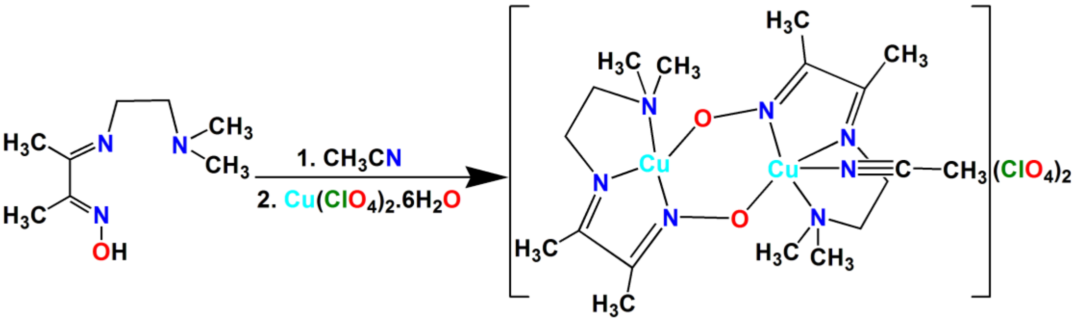
Oximes are very significant ligands in synthetic inorganic chemistry and coordination chemistry as well [16–21] Probably, dimethyl glyoxime

(H_2DMG) is the most famous in this family and is known to have the potential to detect nickel(II) in quantitative analysis by forming the rose red complex, Ni(DMG)$_2$ [22]. It is also used in gravimetric analysis of nickel since long [23]. Oxime ligands are once again topical in connection with the amazing capability of the deprotonated oximato groups to form bridges between metal ions thereby producing multinuclear complexes of various nuclearity [24–49]. Literature shows that many oximato Schiff bases have been used to prepare many copper (II) and mixed valence copper (II/I) complexes. Magnetic properties of many such complexes have been studied in detail [50–52] DNA binding and cleavage activity of few such complexes also studied[53]. However, best to our knowledge, there is no report of phenoxazinone syntheses mimicking activity of any such complexes. Phenoxazinone synthase is a copper-containing oxidase enzyme, which is found in the bacterium, Streptomyces antibioticus. The oxidative condensation of various derivatives of o-aminophenol (two molecules) into phenoxazinone chromophore is catalyzed by this enzyme [54]. In the present work, a dinuclear copper (II) complex has been synthesized with an oximato Schiff base, 3-[2-(dimethylamino) ethylimino]butan-2-one oxime (HL^1). The structure of the complex was confirmed by single crystal X-ray diffraction analysis. The complex has been found to be an efficient catalyst to perform the aerial oxidation of o-aminophenol to 2-aminophenoxazine-3-one and could be used as functional model for copper containing enzyme phenoxazinone synthase.

The detailed kinetic study of the catalytic cycle was performed to evaluate various kinetic parameters, including the turnover number.

II.2.2 Preparation of $[(CH_3CN)Cu(L^1)_2Cu](ClO_4)_2$ (1)

Yield: 496 mg (~70%, based on copper (II)). Anal. Calc. for $C_{18}H_{35}$-$Cl_2Cu_2N_7O_{10}$ (FW: 707.53): C, 42.51; H, 6.94; N, 19.28. Found: C, 42.4; H, 6.8; N, 19.4%. FT-IR (KBr, cm^{-1}): 1661 (C═N); 1030–1075 cm^{-1}, 620 cm^{-1} (νClO_4), 1140 cm^{-1} (νNO), 464 cm^{-1} (νCu–N).UV–Vis, k_{max} (nm), [e_{max} (L mol^{-1} cm^{-1})] (solvent): 579 (0.30×10^2); 418 (0.87×10^2); 312 (6.84×10^2). Crystal data for the complex: $C_{18}H_{35}Cl_2Cu_2N_7O_{10}$, M.W. = 707.53, monoclinic, space group $P2_1/n$, a (Å) = 13.428(2), b (Å) = 12.639(2), c (Å) = 17.014(3), V (cm^3) = 2887.0(8), Z = 4, dcalc = 1.628 g cm^{-3}, l (mm^{-1}) = 1.719, F(000) = 1456, 57,855 total 5189 unique reflections [R(int) = 0.096], 353 no of parameters, Observed data 2r(I)] = 3822, R1 = 0.0898, wR2 = 0.2097 (all data), R1 = 0.0610, wR2 = 0.1713 [I > 2r(I)], Temperature = 273 K.



Scheme II.1. Synthetic route to the complex **1**

II.2.3. Catalytic oxidation of o-aminophenol to 2-aminophenoxazine-3-one

Phenoxazinone synthase mimicking activity of the present complex was conducted at room temperature under aerobic condition for ca. 2 h. During this experiment, 10^{-4} M acetonitrile solution of the complex in acetonitrile was added to solutions with varying concentrations (10^{-3} to 10^{-2}) of substrate (o-aminophenolin acetonitrile. The kinetics of the reaction was followed spectrophotometrically by observing the increase in the absorbance maxima at around 425 nm, which is characteristic of phenoxazinone chromophore. In the above case, complex: substrate ratio were $\geq$ 1:10 to maintain pseudo-first order condition to determine the dependence of rate on substrate concentration and various kinetic parameters. The rate of the reaction was derived from the initial rate method.

II.3. Results and discussion

II.3.1. Synthesis

N,N-dimethylethylenediamine was refluxed with 2,3-butanedione monoxime in a 1:1 ratio to form a N_3O donor compartmental Schiff base ligand, HL^1, following a literature method [16]. This Schiff base (HL^1) on reaction with copper(II) perchlorate hexahydrate in acetonitrile formed the complex. Formation of the complex has been shown in **Scheme II.1.**

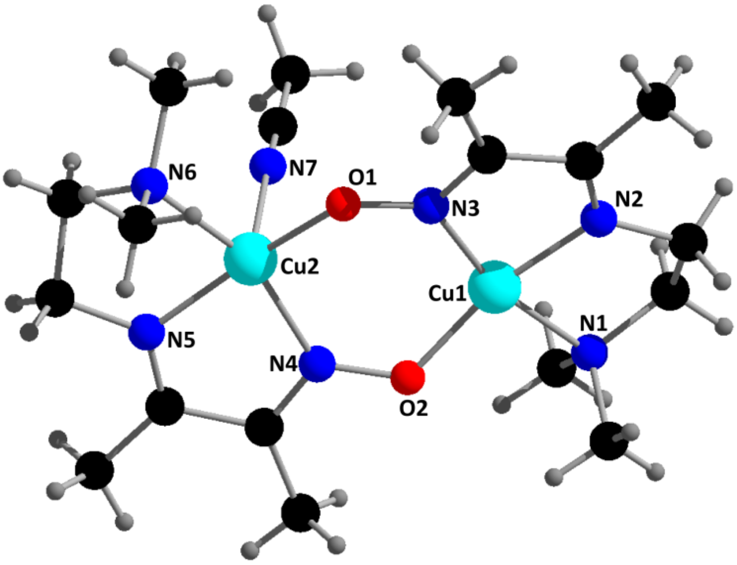


Fig.II.1. Perspective view of the complex with selective atom numbering scheme.

Formula	$C_{18} H_{35} Cu_2 N_7 O_2 2(ClO_4)$
Temperature	273 K
Space group	*P* 21/n
a	13.428(2)
b	12.639(2)

c	17.014(3)
α	90
β	91.091(5)
γ	90
μ [mm^{-1}]	1.719
F000	1456.0
N_{ref}	5189
R(reflections)	0.0610(3822)
wR2(reflections)	0.2097(5189)
No of parameter	253

Selected bond lengths (Å) of the complex

Cu(1)-O(1)	1.878(5)
Cu(1)-N(1)	2.051(5)
Cu(1)-N(1)	1.917(5)
Cu(1)-N(3)	1.992(5)
Cu(2)-O(1)	1.916(4)
Cu(2)-N(4)	2.006(5)
Cu(2)-N(5)	1.946(5)
Cu(2)-N(6)	2.057(5)
Cu(2)-N(7)	2.304(7)

Selected bond angles (°) of the complex

O(2)-Cu(1)-N(1)	89.6(2)
O(2)-Cu(1)-N(2)	166.2(2)
O(2)-Cu(1)-N(3)	104.9(2)
N(1)-Cu(1)-N(2)	84.08(19)
N(2)-Cu(1)-N(3)	165.2(2)
N(2)-Cu(1)-N(3)	81.08(19)
O(1)-Cu(2)-N(4)	103.06(19)
O(1)-Cu(2)-N(5)	162.3(2)
O(1)-Cu(2)-N(6)	90.98(18)
O(1)-Cu(2)-N(7)	97.9(2)
N(4)-Cu(2)-N(5)	79.8(2)
N(4)-Cu(2)-N(6)	160.3(2)
N(4)-Cu(2)N(7)	93.3(2)
N(5)-Cu(2)-N(6)	82.7(2)
N(5)-Cu(2)-N(7)	99.4(2)
N(6)-Cu(2)-N(7)	98.4(2)

II.3.2. Description of $[(CH_3CN)Cu(L^1)_2Cu](ClO_4)_2$

The molecular structure of the complex 1 has been established by X-ray single crystal diffraction measurement. It reveals that the complex 1 consists of cationic dinuclear unit of formula $[Cu_2L^1_2\ ]^{2+}$ along with two uncoordinated perchlorate anions and a coordinated acetonitrile molecule. The complex **1** crystallizes in monoclinic space group, $P2_1/n$, with Z = 4. The dinuclear unit has been shown in **Fig.II.1.** The dinuclear complex **1** contains two deprotonated Schiff bases, of which, both acts as a tridentate ligand. The coordination polyhedral around both metal centers are different: one copper centre, Cu (1), is a tetra-coordinated being bonded to N(3) (oxime nitrogen), N(2) (imine nitrogen), N(1) (amine nitrogen) of the tridentate ligand and the fourth position is occupied by O(2) (oxime oxygen) of the second ligand. The tetrahedral environment around Cu(1) is distorted as confirmed by the τ_4 index which is 1.172. The τ_4 index is defined as $\tau_4 = [360^{\circ}(\alpha+\beta)]/141^{\circ}$ with α and β (in°) being the two largest angles around the central metal in the complex with $\tau_4 = 0$ for a perfect square planar and $\tau_4 = 1$ for a perfect tetrahedron. [57] On the other hand, penta-coordinated Cu(2) is either square pyramidal or trigonal bipyramidal being bonded to N(4)(oxime nitrogen), N(5) (imine nitrogen), N(6) (amine nitrogen) of the tridentate ligand and the fourth position is occupied by O(1) (oxime oxygen) of the second ligand. However, one of the axial position of Cu (2) is occupied by the nitrogen atom, N(7) of an acetonitrile solvent at a distance of 2.303(7) Å. The distortion from the square pyramid to the trigonal bipyramid is calculated using the Addison parameter [58] The Addison parameter (s) value for Cu (2) is 0.032, confirming the actual geometry is distorted square pyramid (dsp). The basal planes around both the copper atoms are coordinated by the three nitrogen atoms of one ligand and oxygen of a second ligand from the tridentate Schiff base ligand. The deviations of the coordinating atoms, O(2), N(1), N(2) and N(3), in the basal plane from the mean plane passing through them are _0.104(5), 0.068(5), 0.118(5) and 0.060(5) Å, respectively, whereas deviations of the coordinating atoms, O(1), N(4), N(5) and N(6), in the basal plane from the mean plane passing through them are 0.093(5), 0.011(5), 0.089(5) and 0.003(5) Å, respectively in the complex. The deviation of Cu(1) and Cu(2) from the same plane is 0.0942(7) Å and 0.195(7) respectively.

A cooperative –NO– bridged dinuclear cluster usually contains a central six-membered [Cu(1)–N(3)–O(1)–Cu(2)–N(4)–O(2)] ring in the complex is close to planarity. The average ring angle is 118.26º. The main deviation from a regular hexagonal ring shape is due to the relatively large size of the copper atoms and to the difference in the Cu–O and Cu–N bonds. The Cu(1)–O(2) and Cu(1)–N(3) bond distances are 1.878(5) and 1.991(4) Å respectively, whereas the Cu(2)–O(1) and Cu(2)–N(4) bond distances are 1.916(5) and 2.006(4) Å respectively, as expected from electronegativity considerations. The coordinated CH_3CN group appears to have little effect. Thus, the six-membered rings may be considered as pseudoaromatic systems containing sp^2 oxygen and nitrogen atoms, with the p_z orbital of each oxygen and nitrogen atom contributing an electron pair and the copper atoms each contributing one unpaired electron to make a total of ten p electrons ring system. The average ligand–Cu (1)–ligand angle is 89.9º. The average ligand–Cu (2)–ligand angle (ignoring the acetonitrile) is 89.14º. The copper–copper separation is 3.613(1) Å which is within the range of the reported distance separation in $\mu_{1,2}$-N,O double oximato-bridged Cu_2 complexes [33,59]. No significant supramolecular interactions are observed.

II.3.3. Hirshfeld surfaces

The Hirshfeld surface emerged from an attempt to define the space occupied by a molecule in a crystal for the purpose of subdividing the crystal electron density into molecular fragments [60]. d_{norm} is a normalised contact distance [61]. Intermolecular contacts are highlighted in the dnorm surface (when atoms make intermolecular contacts closer than the sum of their van der Waals radii, thesecontacts will be highlighted in red whereas longer contacts are blue, and contacts around the sum of van der Waals radii are white). Hirshfeld surfaces of the complex mapped over dnorm (range of -0.1 to 1.5 Å). Red spots on these surfaces denote the dominant interactions [N...H/H...N, O...H/H...O and C...H/H...C]. As the Hirshfeld surface defines the shape of the molecule in terms of its surrounding crystalline environment, the local shape of the surface may provide some chemical insight whereas shape index is a qualitative measure of shape and can be sensitive to very subtle changes in surface shape, particularly in regions where the total curvature (or the curvedness) is very low [62] The 2D fingerprint plots, [63] which are used to analyze the intermolecular contacts at the same time, revealed that the main intermolecular interactions in the complex are N...H/H...N, O...H/H...O or

C...H/H...C. The Hirshfeld surfaces and the corresponding 2D fingerprint plots for the complex has been shown in **Fig.II.2.**

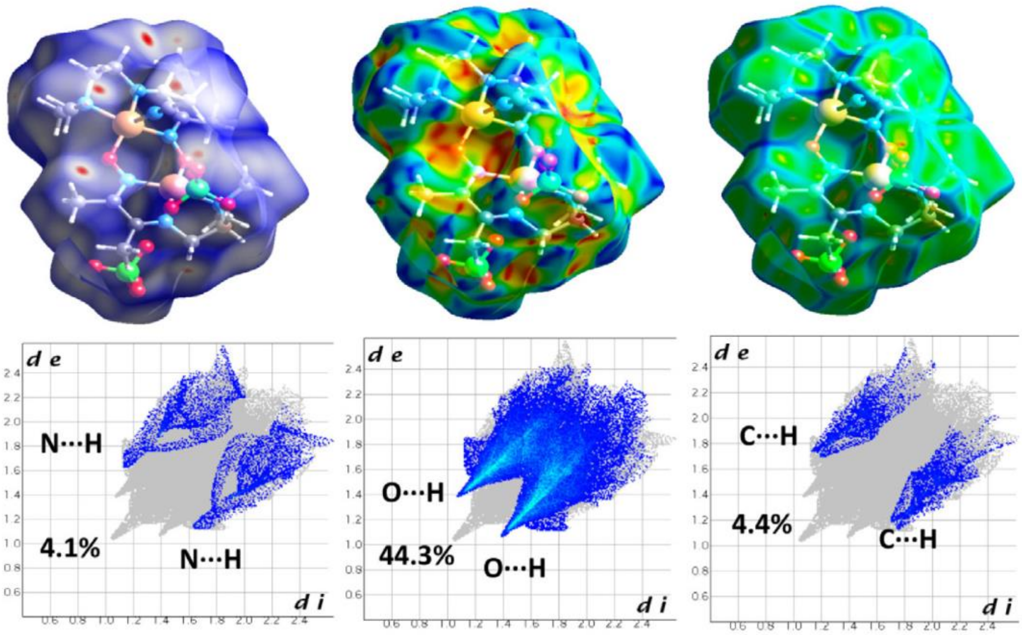


Fig. II.2. Hirshfeld surfaces and fingerprint plots of the complex **1**.

II.3.4. IR and electronic spectra

The IR spectrum of the complex 1 is in a good agreement with X-ray structural data. A weak and sharp absorption band at 1661 cm^{-1} assigned to the >C═N stretching frequency of the Schiff base ligand, HL^{1} [64]. The coordination of the ligand to the metal center is substantiated by a band appearing at 464

cm^{-1} for the complex mainly attributed to the Cu–N stretching, [65] while a band at 1140 cm^{-1} suggests the presence of N–O bonds [33] A characteristic band of the perchlorate anion around 1030–1075 cm^{-1} and 620 cm^{-1} in the spectrum of perchlorate complex assigned to the ionic perchlorate suggest the perchlorate group outside the coordination sphere in the complex [66]. The IR spectra of the ligand and the complex have been shown in **Fig.II.3.** and **Fig.II.4.** respectively.

Electronic spectrum of the complex 1 in acetonitrile displays one absorption band in the visible region at 579 nm which may be considered as $^2T_{2g}(D) \leftarrow {}^2E_g(D)$ transition for copper(II) in the square based environment [16] In addition, A band at 418 nm may be attributed to LMCT transition from the nitrogen donor centre of Schiff base to copper(II) [67]. Moreover, absorption band at 312 may be considered as intra-ligand charge transfer transitions [16, 67] The UV–V is spectrum of the complex has been shown in **Fig II.5.**

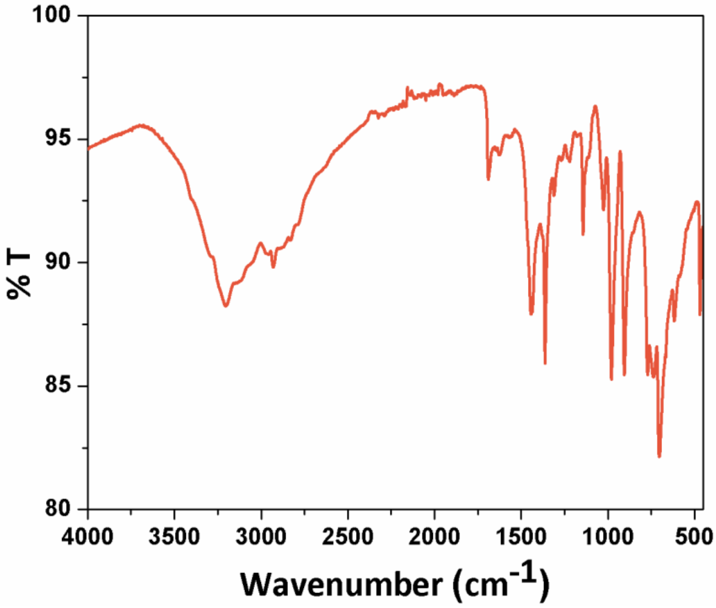


Fig.II.3. IR spectrum of the ligand

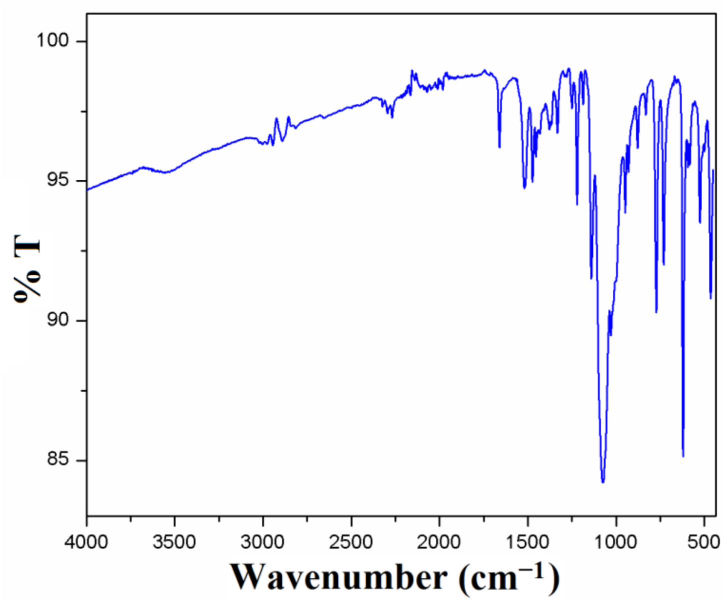


Fig.II.4. IR spectrum of the complex

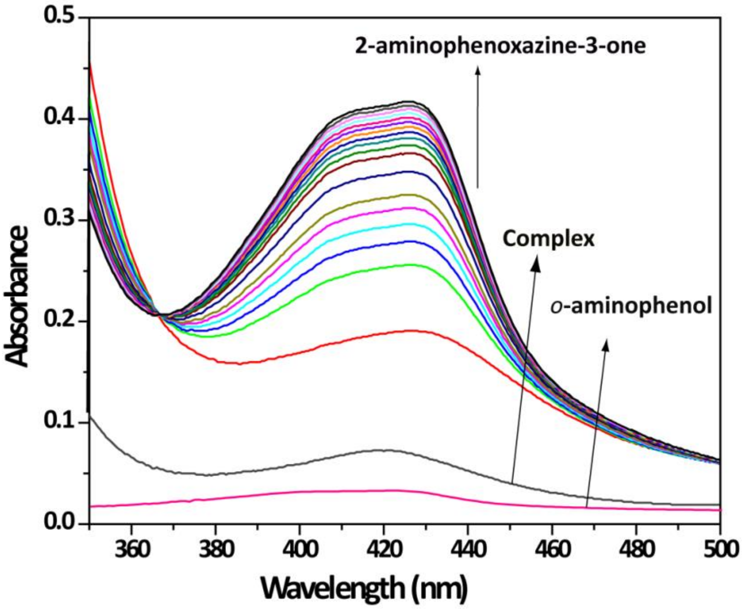


Fig.II.5. The UV–Vis spectral profiles indicating the increment of 2-aminophenoxazine-3-one at 425 nm upon gradual addition of 10^{-2} M *o*-aminophenol to the 10^{-4} M of the complex **1**.

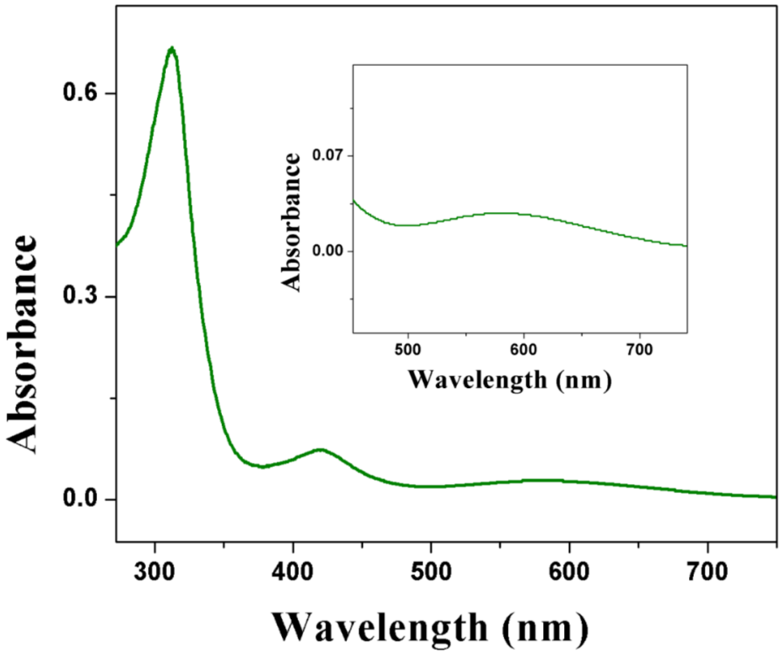
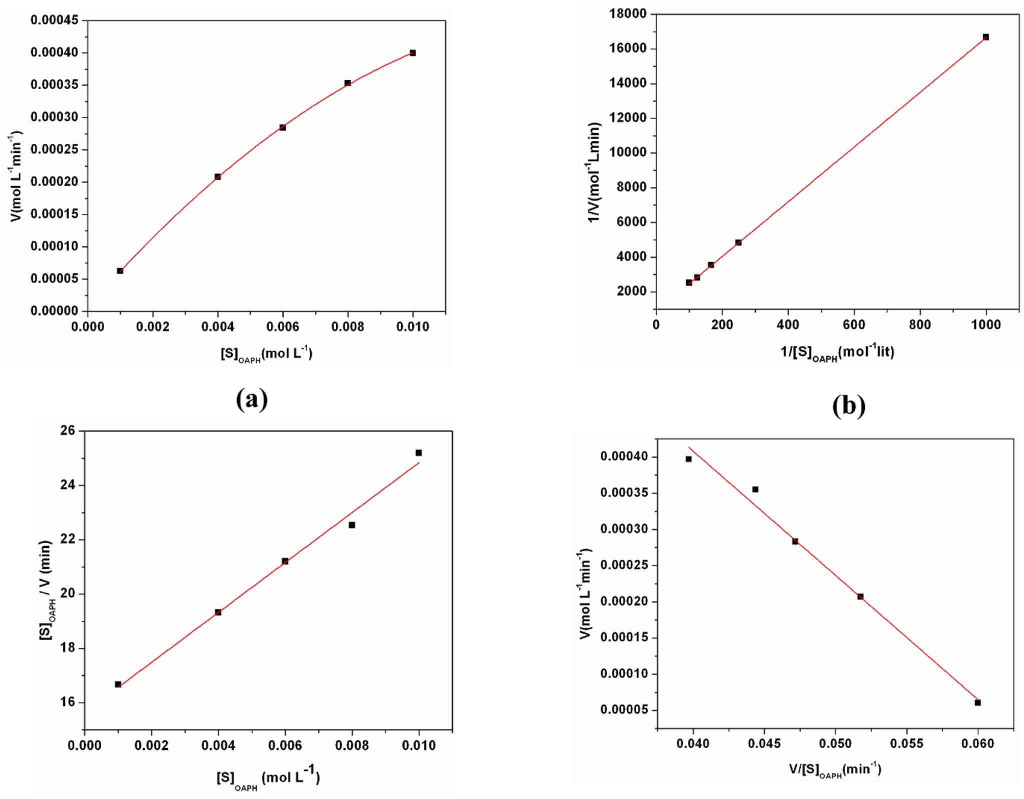


Fig.II.6. UV-vis spectrum of the complex. inset shows visible range spectrum



(a) (b)

(c) (d)

Fig.II.7. (a) Initial rate vs. substrate concentration plot, (b) Linear Lineweaver–Burk plot, (c) Hanes Wolf plot and (d) Eadie Hofstee plot for the oxidation of *o*-aminophenol in dioxygen-saturated acetonitrile catalyzed by the complex at room temperature.

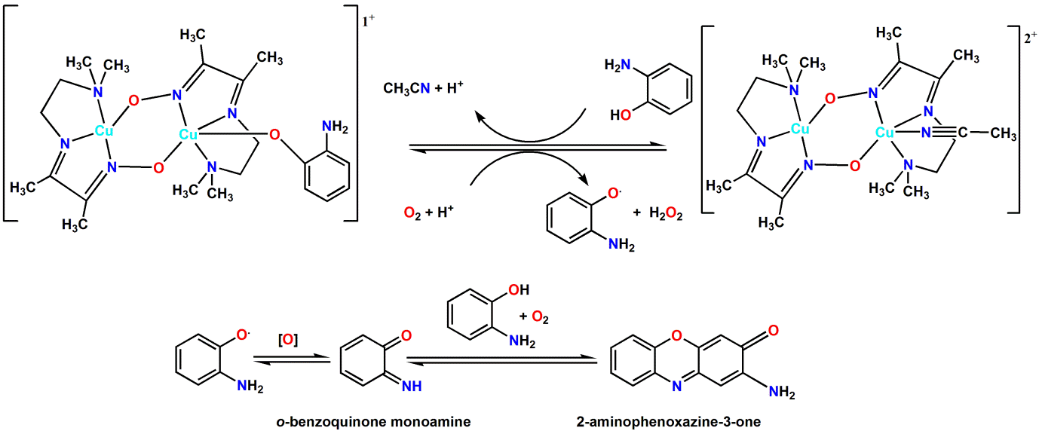
II.3.5. Phenoxazinone synthase mimicking activity

An acetonitrile solution (10^{-2} M) of o-aminophenol was mixed with 10^{-4} M acetonitrile solution of the complex to check the phenoxazinone synthase mimicking activity of the complex. Kinetics of the reaction was studied spectrophotometrically and the spectra were recorded for up to ~2 h in aerobic condition at room temperature. No additional base was added in the reaction medium to minimise the possibility of auto-oxidation of the substrate. The time dependent spectral scans of the complex **1** show gradual increase of the peak intensities at ~425 nm (typical for phenoxazi none chromophore), suggesting the catalytic areal oxidation of oaminophenol to 2-aminophenoxazine-3-one. To prove the phenoxazinone synthase mimicking activity of the complex, comparative experiments without catalyst under identical conditions has been performed, which showed no significant growth of the spectra at k_{max} ~ 425 nm. Also the spectral growth (corresponding to the formation of phenoxazinone) is negligible for (i) bare copper(II) perchlorate and (ii) bare copper(II) acetate compared to the spectral growth [at k_{max} ~ 425 nm] for the complex and hence it may be concluded that the complex 1 acts as better catalyst compared to the bare copper(II) salts. The time dependent spectral profile for a period of ~2 h in acetonitrile medium of the complex has been shown in **Fig.II.5.** The initial rate of the pseudo-first order reaction was easily calculated from the slope of the absorbance versus time plot. The same process was repeated for at least three times and the overall average value was taken. Initial rate of the reaction versus substrate concentration plot of the complex 1 indicates rate saturation kinetics of the complex **Fig.II.7.a** This observation clearly indicates that formation of 2-aminophenoxazine-3-one proceedsthrough a quite stable intermediate complex substrate adduct, which is formed at a pre-equilibrium stage and the irreversible substrate oxidation is the rate determining step of the catalytic cycle. K_M and V_{max} value for the complex is calculated 1.70×10^{-2} M and 1.11×10^{-3}, respectively. The turnover number (K_{cat}) value is obtained by dividing the V_{max} by the concentration of the complex used, and is found to be 11.1 h^{-1}.

It is clear that the copper (II) complex **1** is active towards the oxidation of o-aminophenol in aerobic condition at room temperature. A tentative catalytic cycle for the oxidation of o-aminophenol to 2-aminophenoxazine-3-one may be proposed. At the first step o-aminophenol forms adducts with the complex by replacing the acetonitrile molecule, which results an o-aminophenol radical by the reaction with molecular dioxygen regenerating the complex.

The o-aminophenol radical may generate o-benzoquinone monoamine, which may easily be converted to 2-aminophenoxazine-3-one by the reaction with dioxygen and o-aminophenol (**Scheme II.2.**)

In order to verify whether the complex is capable of maintaining its structural integrity during the phenoxazinone synthase mimicking activity, IR experiment for the complex was performed during the course of catalytic experiment. The IR experiment indicated that the pattern is nearly identical when compared with the pure complex. Hence the IR experiment imply that the complex maintains its structural integrity even after getting involved in the phenoxazinone synthase mimicking activity. IR spectra of the complex (before and after phenoxazinone synthase mimicking activity) have been shown in **Fig.II.8.**



Scheme II.2. Probable mechanistic pathway showing the formation of 2-aminophenoxazine-3-one.

II.4. Validation of kinetic parameters

Briggs-Haldane scheme [68] was used in the kinetic study to determine kinetic parameters. This scheme considers the formation and dissociation reactions of the enzyme-substrate complex1, ES and its decomposition reaction, forming the product (P) and regenerating the enzyme (E).

$$S + E \xrightarrow{k_1} ES$$

$$ES \xrightarrow{k_{-1}} S + E$$

$$ES \xrightarrow{k_2} P + E$$

Applying this kinetic scheme to the steady state approximation for the concentration of the enzyme-substrate adducts, the Michaelis-Menten equation for initial reaction rate was achieved (equation **1**).

$$V\ (\mathrm{time}^{-1}) = V_{max}[S]/([S] + K_M) \qquad \mathbf{(1)}$$

A double reciprocal Lineweaver–Burk plot is obtained upon linearization from Michaelis–Menten model, which is used to analyze a variety of parameters, viz. V_{max} (Maximum reaction velocity), K_M (Michaelis constant), and K_{cat} (Turnover number). The Lineweaver–Burk Equation as follows:

$$1/V = K_M/V_{max}.1/[S] + 1/V_{max} \qquad \mathbf{(2)}$$

Plot of Eq. (**1**) for kinetic studies of aerobic oxidations of *o*-aminophenol catalyzed by the complex 1 shows rectangular hyperbolic nature which finally leads to a saturation curve (**Fig.II.5.**) This confirms the first order rate kinetics followed by the substrates. Initial rate constants, V (min^{-1}) were obtained directly from the slope of the plot of $\log[(A_\infty{-}A_0)/(A_\infty{-}A_t)]$ vs. time which is a straight line passing through the origin. According to Eq. 1, the limiting rate at high substrate concentration, i.e. $[S]_0$, is designated as V_{max} ($V_{max} = k_{cat}[E]_0$)

Rearranging Eq. **1** gives Hanes equation (Eq. 3). In this case, [S]/V vs. [S] are plotted.

$$[S]/V = [S]/V_{max} + K_M/V_{max} \text{ - - - - - - - - - - } \mathbf{(3)}$$

Eadie-Hofstee equation (Eq. **4**) is sometimes used in biochemistry for graphical representation of enzyme kinetics. In this case, V/[S] vs. V is plotted.

$$V = V_{max} - K_M (V/[S]) \text{ - - - - - - - - - - - } (\mathbf{4})$$

Rate saturation kinetics was assessed by Eq. **1**. Significant kinetic parameters, like $\mathbf{V_{max}}$ i.e maximum reaction velocity, $\mathbf{K_M}$ i.e. Michaelis constant and $\boldsymbol{k_{cat}}$ i.e. turnover number, were obtained by utilizing Eqs. 3 and 4. Related plots of the catalytic activities of the complex 1 are shown in **Fig.II 7.**

The present complex **1** is the first copper (II) complex of any oxime based Schiff base exhibiting phenoxazinone synthase mimicking activity. It is therefore not possible to compare its catalytic activity other similar complexes. However, catalytic properties of some di and poly-nuclear copper(II) complexes [69–72] with N_2O donor Schiff base ligands have been gathered in gathered in **Table II.1.**

Table II.1.

CCDC	Complex	K_{cat} (h^{-1})	Refs.
1572023	$[L^1Cu(\mu\text{-}Cl)_2CuL^1]$	1065 (In CH_3OH) 213 (In CH_3CN) 2844 (In CH_2Cl_2)	69
		86.3 (In	

1507035	$[Cu_4(L^2)_4]$	CH_3OH)	70
1507036	$[Cu_4(L^3)_4]$	340.26 (In CH_3OH) 1028.9 (In DMSO)	70
1455999	$[Cu4(L^4)_4]$	1.21 × 10^5 (In CH_3OH)	71
1524680	$[Cu(\mu\text{-}Cl)(phen)Cl]_2$	1.69 × 104 (In CH_3OH)	72
1940162	$[(CH_3CN)Cu(L)_2Cu](ClO_4)_2$	11.1 (In CH_3CN)	This work

L^1 = 2-(a-Hydroxyethyl)benzimidazole (Hhebmz), L^2 = (E)-4-Chloro-2-((thiazol-2-ylimino)methyl)phenol, L^3 = (E)-4-Bromo-2-((thiazol-2-ylimino)methyl)phenol, L^4 = N-(2-hydroxyethyl)-3-methoxysalicylaldimine, L^5 = 2,20-bipyridine, L^6 = 1,10-phenanthroline, L^7 = N-(2-hydroxy-3,5-di-tert-butylphenyl)-2-aminobenzylalcohol.

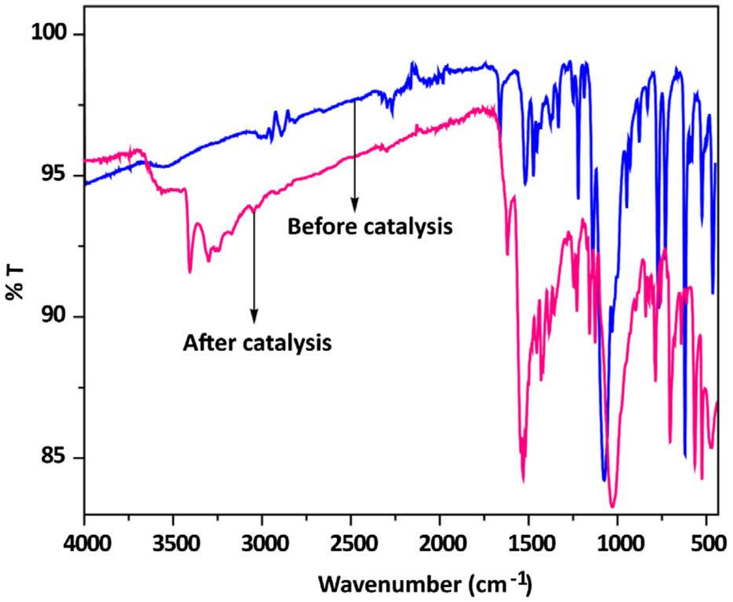


Fig.II.8. IR spectra of the complex before (blue) and after (pink) the catalytic experiment. (Colour online.)

II.5. Concluding remarks

In this section the syntheses and structural characterization of one double oximato bridged dinuclear copper(II) complex 1 containing oxime-based tridentate Schiff base ligand was reported. Single crystal X-ray diffraction has confirmed the structure of the complex **1**. Both copper(II) centrers are not residing in identical environment, as one copper(II) is penta-coordinated and is additionally bound to an acetonitrile molecule. The complex was found to exhibit phenoxazinone synthase like activity (i.e. conversion of *o*-aminophenol to 2-aminophenoxazine-3-one). The loosely bound acetonitrile may be replaced by *o*-aminophenol to initiate catalytic cycle. The catalytic efficiency of the complex has been assessed following conventional Michaelis–Menten enzyme kinetics. The complex may be considered as the first copper(II) complex with oxime based Schiff base ligand, which is employed as catalyst for the oxidation of *o*-aminophenol to 2-aminophenoxazine-3-one, although the catalytic efficiency of the complex is moderate.

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Chapter III

Synthesis and characterization of a dinuclear copper (II) complex with a half salen type Schiff base ligand and exploration of its phenoxazinone synthase mimicking activity

“A person who never made a mistake never tried anything new”

-Albert Einstein

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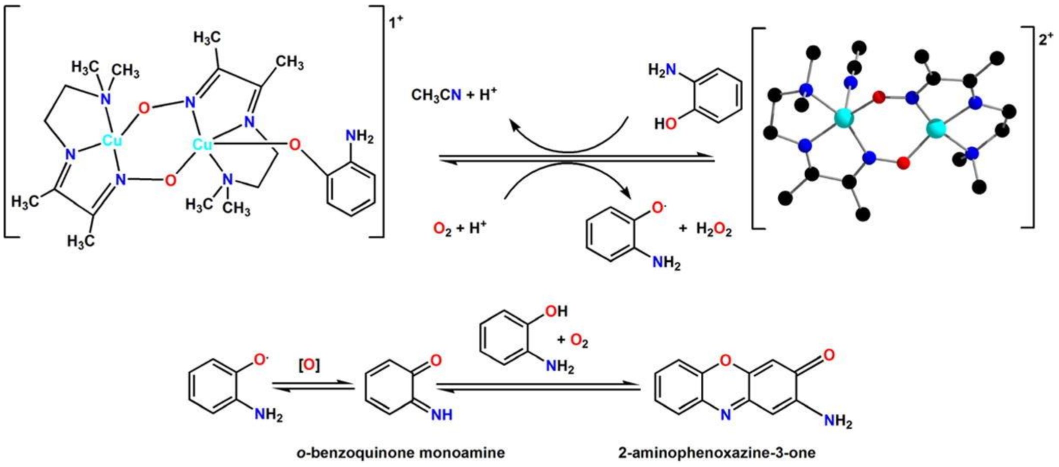

Chapter III

Synthesis and characterization of a dinuclear copper (II) complex with a half salen type Schiff base ligand and exploration of its phenoxazinone synthase mimicking activity

III.1. Introduction

Monocondensed N_2O donor Schiff base ligands are of special interest because of their usage as synthetic analogues of metal binding sites in copper proteins [1-2] Preparation of these unsymmetrical ligands by condensing diamines and salicyl aldehyde derivatives are difficult where one primary amine group forms an imine bond and the other is unchanged. These are termed as ‘half units’ and are used in preparing di/trinuclear complexes [3-13] These half units can be synthesized by several routes [14-17] Elder reported a very convenient way for template synthesis for nickel (II) complexes using these half ligands [18] Using similar ligands copper(II) complexes have been reported utilizing copper template effect [19-24] Several copper(II) complexes using half salen ligands have also been reported by our group [25-28] These complexes have mainly been prepared for magnetic studies as they have the abilities to mimic the magnetic properties of type-3 copper proteins which are well established experimentally [29-32] In recent years, use of metal complexes as efficient biomimetic catalysts is an active area of research at the interface of chemistry and biology [33-37] Our laboratory has also been actively engaged in designing, synthesis and investigation of bio-relevant catalytic activities, such as catechol oxidase, phenoxazinone synthase and phosphatase mimicking activities of several homo and heteronuclear transition metal complexes for the past few years [38-44]

A half salen type Schiff base ligand has been used to prepare a dinuclear copper (II) complex **2**. Supramolecular interactions along with Hirshfeld analyses have been explored. Phenoxazinone synthase mimicking activity of the complex has been studied using *o*-aminophenol (OAPH) as model substrate to evaluate the catalytic efficiency.

III.2. Experimental section

III.2.1. Synthesis of $[L^2Cu(\mu_{1,1}\text{-}N_3)_2CuL^2]$ (2)

Copper (II) acetate monohydrate (400 mg, 2 mmol) was added to a methanol solution (20 mL) of 3-methoxysalicylaldehyde (300 mg, 2 mmol) to produce a greenish coloured solution. A methanol-water (15 mL) solution of sodium azide (165 mg, 2.5 mmol) was then added to it and the resulting solution was stirred for ca. 30 min. 1, 3-diaminopropane (0.26 mL, 2 mmol) was then added slowly to the mixture with constant stirring. The mixture was then refluxed for ca. 45 min. X-ray diffraction quality dark green block shaped single crystals were obtained on slow evaporation of the reaction mixture in the open atmosphere.

Yield: 376 mg (60%). Anal. Calc. for $C_{22}H_{30}Cu_2N_{10}O_4$ (FW = 625.66): C, 42.10; H, 5.14; N, 22.32%. Found: C, 41.9; H, 4.9; N, 22.4%. FT-IR (KBr, cm^{-1}): 1628 ($\nu_{C=N}$); 2038 (ν_{N3}); 3274, 3211 (ν_{NH2}). UV-Vis [λ_{max} (nm)] [ε_{max} ($Lmol^{-1}cm^{-1}$)] (acetonitrile): 234 (5.6×10^4); 279 (3.1×10^4); 370 (8.8×10^3); 603 (1.9×10^2). ESI-MS (positive ion mode, CH_3CN) m/z: 426.09 [100%, $LCu(N_3)(CH_3OH)(CH_3CN)(H_2O)Na]^+$

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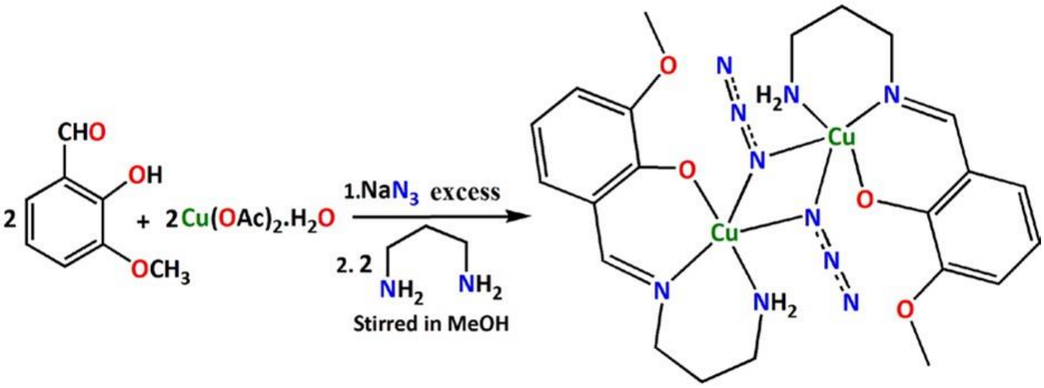


Scheme III.1. Synthetic route to the complex **2**

III.3. Results and discussion

III.3.1. Synthesis of the complex 2

The formation of the complex **2** can be rationalized in the light of the templating effect of copper (II) modulated by counter anions. The azide ligand, having approximately the same crystal field stabilization energy as that of Schiff base, occupies one coordination site of copper(II), leaving other three sites in the equatorial plane to be coordinated by the tridentate Schiff base and that can be achieved most efficiently by 'half-salen' type tridentate N_2O donor Schiff base ligands [25,55,56] In the present work, the 'half-salen' type mono-condensed Schiff base ligand HL^2 has been synthesized conveniently as the dinuclear copper (II) complex, $[L^2Cu(\mu_{1,1}\text{-}N_3)_2CuL^2]$ (2) by the reaction of 3-

methoxysalicylaldehyde, copper(II) acetate monohydrate and sodium azide, followed by the reaction with 1,3-diaminopropane. Formation of the complex **2** has been shown in **Scheme III.1.**

Table III.1. Crystal data and refinement details of the complex **2**

Formula	$C_{22}H_{30}Cu_2N_{10}O_4$
Formula Weight	625.66
Temparature (K)	150
Crystal System	Monoclinic
Space group	$P2_1/c$
a(Å)	9.6629(6)
b(Å)	11.2098(8)
c(Å)	11.4526(7)
β(°)	90.059(6)
D(calc) [g/cm^3]	1.675
μ [mm^{-1}]	1.767
F(000)	644

Total Reflections	4836
Unique Reflections	2726
Observed data [I > 2 σ(I)]	2052
No of parameters	181
R(int)	0.067
R1, wR2 (all data)	0.1038, 0.2204
R1, wR2 ([I > 2 σ(I)]	0.0882, 0.2042
Residual Electron Density(eÅ^{-3})	-1.94, 2.99
CCDC No:	1950898

III.3.2. Crystal structure of $[L^2Cu(\mu_{1,1}\text{-}N_3)_2CuL^2]$ (2)

Details of crystallographic data and refinement details are given in **Table III.1.** Single crystal X-ray structure determination reveals that the complex **2** is centrosymmetric where the asymmetric unit consists of discrete mononuclear unit, $[L^2Cu(N_3)]$. It crystallizes in monoclinic space group *P*2$_1$/*c*. Perspective view of the complex **2** with selective atom-numbering scheme is illustrated in **Fig.III.2.** Details of the crystallographic data and refinement details of the complex **2** are given in **Table III.1.** Selected bond lengths and bond angles of are gathered in **Tables III.2.** and **III.3.** respectively.

Table III.2. Selected bond lengths (Å) of the complex.

Cu(1)–O(11)	1.927(4)
Cu(1)–N(1)	2.042(5)
Cu(1)–N(19)	1.956(4)
Cu(1)–N(23)	2.024(5)
Cu(1)–N(1)a	2.459(5)

Symmetry transformations: ^{a} = 1-x,-y, 1-z.

Table III.3. Selected bond angles (°) of the complex

O(11)–Cu(1)–N(1)	87.88(17)
O(11)–Cu(1)–N(19)	93.46(15)
O(11)–Cu(1)–N(23)	171.68(18)

O(11)–Cu(1)–N(1)a	86.48(15)
N(1)–Cu(1)–N(19)	159.42(18)
N(1)–Cu(1)–N(23)	86.21(19)
N(1)–Cu(1)–N(1)a	88.90(17)
N(19)–Cu(1)–N(23)	94.14(17)
N(1)a–Cu(1)–N(19)	111.68(17)
N(1)a–Cu(1)–N(23)	87.57(17)

Symmetry transformations: a = 1-x, -y, 1-z.

Cu(1) is pentacoordinated, where an imine nitrogen atom, N (19), an amine nitrogen atom, N(23), one phenoxo oxygen atom, O(11), of a Schiff base ligand and a nitrogen atom, N(1), from a bridging azide constitute the equatorial plane. Another symmetry related nitrogen atom, N(1)^a, [a = 1 x, -y, 1-z] from another bridging azide coordinates in axial position to fulfill its coordination site. Both the metal centres, Cu(1) and Cu(1)^a, are joined by two nitrogen atoms, N(1) and N(1)^a of two $^{\mu}{}_{1,1}$ bridged azides. The geometry of any penta-coordinated metal centre may conveniently be measured using the Addison parameter, (τ) [τ = (Θ-Φ)/60, where Θ and Φ are the two largest ligand-metalligand angles of the coordination sphere] [56–58]. The copper (II) centre, Cu(1), adopts distorted square pyramidal geometry with s = 0.204. The trans angles, N(23)–Cu(1)–O(11) and N(1)–Cu(1)– N(19), are found to be

171.68(18)° and 159.42(18)° respectively. The distance between copper (II) centers is 3.226(8) Å. Saturated six membered chelate ring [Cu(1)–N(19)–C(20)–C(21)–C(22)–N (23)] has twist boat conformation with puckering parameters, q = 0.734(5) Å; h = 100.9(4); ϕ = 324.6(4) [59–61].

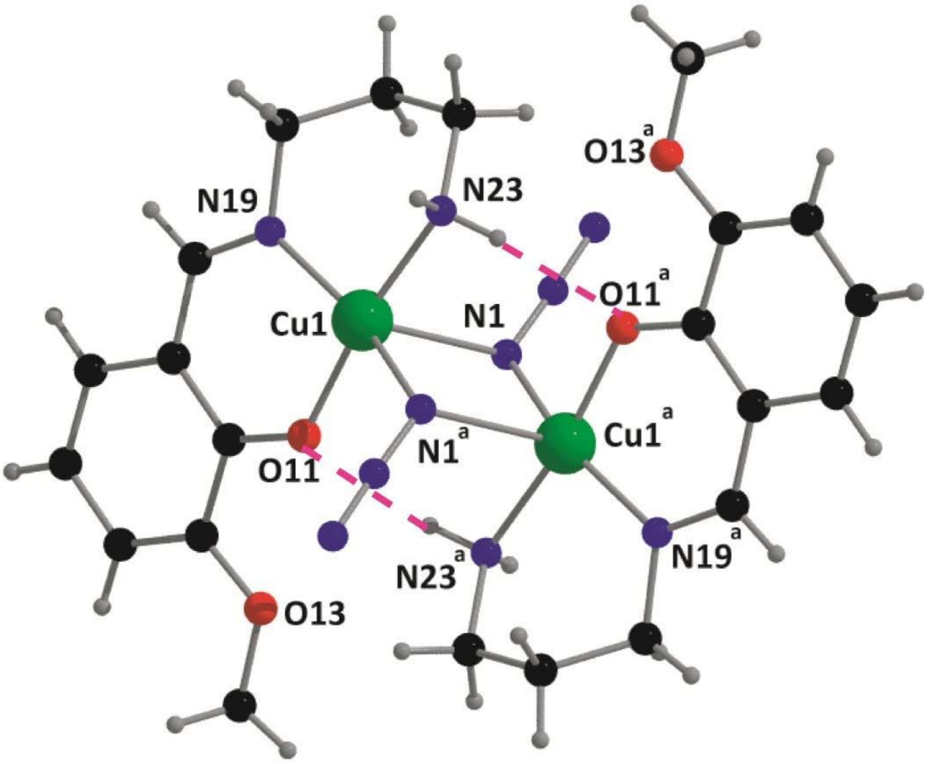


Fig.III.1. Perspective view of the complex **2** with selective atom numbering scheme. Dotted lines represent hydrogen bonds. Symmetry transformation a = 1-x, -y, 1-z

III.3.3. Supramolecular interactions

Interesting supramolecular interactions which lead to the formation of extended structures have been observed in the complex **2**.

The complex **2** shows two hydrogen bonding interactions. The hydrogen atoms, H(231) and H(232), attached with nitrogen atom, N(23), form hydrogen bonds with symmetry related nitrogen atom, N(3)^a of an azide and symmetry related phenoxy oxygen atom, O(11)^b [^{a} = x,-1/2y,-1/2+z; ^{b} = 1-x,-y,1-z] respectively. As a result of these interactions, a 2D structure has been formed and depicted in **Fig.III.2.** The details of the geometric features of the hydrogen bonding interactions have been given in **Table III.4.**

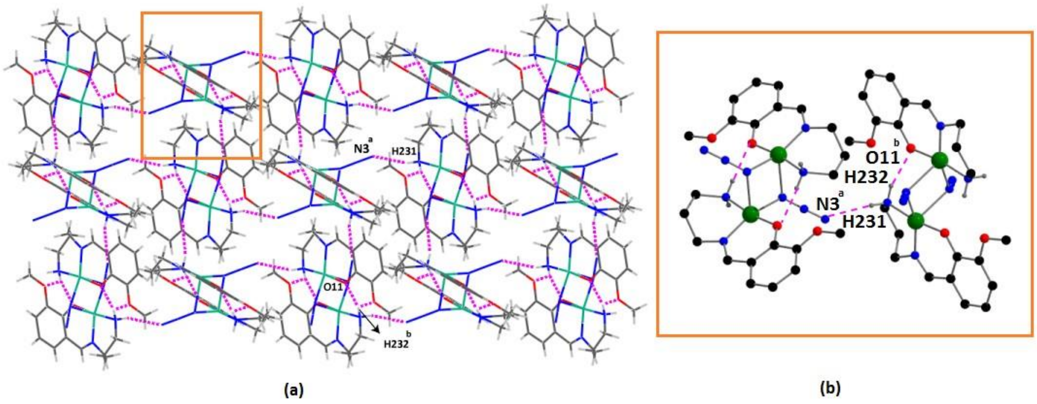


Fig.III.2. (a) 2D structure generated through hydrogen bonding interactions in the complex **2**. (b) The highlighted part has been shown. Only the relevant hydrogen atoms have been shown for clarity.

Table III.4. Geometric features of hydrogen bonding interactions in the complex.

D-H···A	**H···A (Å)**	**D-H (Å)**	**D-A (Å)**	**∠D−H···A**
N(23)-H(231)···N(3)[a]	2.37(5)	0.86(5)	3.200(6)	161(5)
N(23)-H(232)···O(11)[b]	2.11(4)	0.86(3)	2.942(6)	165(5)

Symmetry transformations: a = x,-1/2-y,-1/2+z; b = 1-x, -y, 1-z.

Table III.5. Geometric features (distances in Å and angles in °) of the C–H···π and N–H···π interactions obtained for the complex **2.**

C/N-H···Cg(Ring)	**H···Cg**	**C/N-H···Cg**	**C/N···Cg (Å)**
C(20) –H(20A)···Cg(4)[a]	2.63	155	3.536(6)
N(23)–H(232)···Cg(1)[b]	2.23(6)	98(4)	2.493(5)

Symmetry transformations: a = x, 1/2-y,1/2+z; b = 1-x,-y,1-z.

Cg(4) = Centre of gravity of the ring [C(12)–C(13)–C(14)–C(15)–C(16)–C(17)]; Cg(1) = Centre of gravity of the ring [Cu(1)–N(1)–Cu(1)^b–N(1)^b] for the complex **2**.

Methodologies have been used for describing the networks in crystal structures of metal ligand complexes that are based on intermolecular interactions such as hydrogen bond. Palin and Powell first described the crystal packing as a network where hydrogen bonds may be considered as linkers and molecules as nodes [62] This idea has been explored later by different groups describing inorganic solid state structures [63–67] In our case, each dinuclear unit is connected to four neighboring dinuclear units via four hydrogen bonds along crystallographic ab plane (**Fig. III.3.a).** Topology analysis reveals a (4, 4)-square grid topology (**Fig. III.3.b**) with copper (II) complex **2** is occupying the nodes and hydrogen bonds are behaving as linkers.

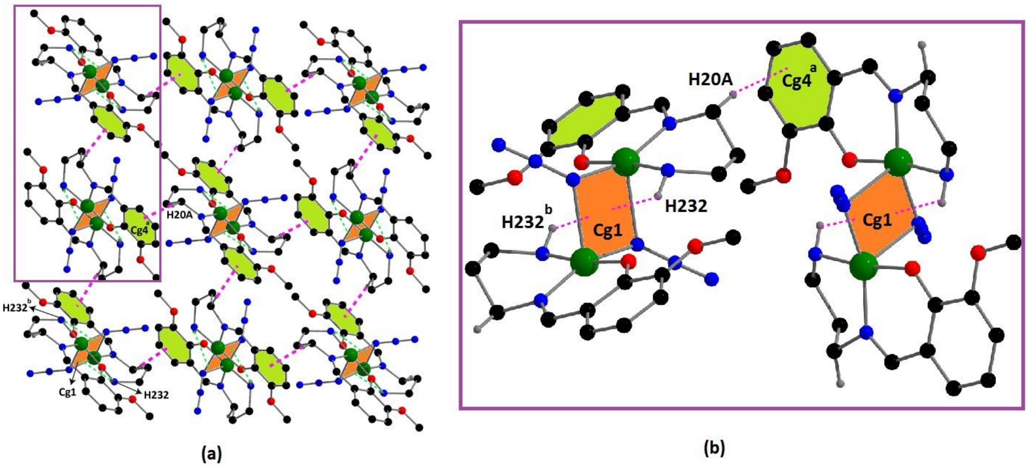


Fig. III.3. (a) 2D structure formed by C-H···π and N-H···π interactions in the complex **2**. (b) Highlighted part has been shown here. Only relevant hydrogen atoms have been shown for clarity.

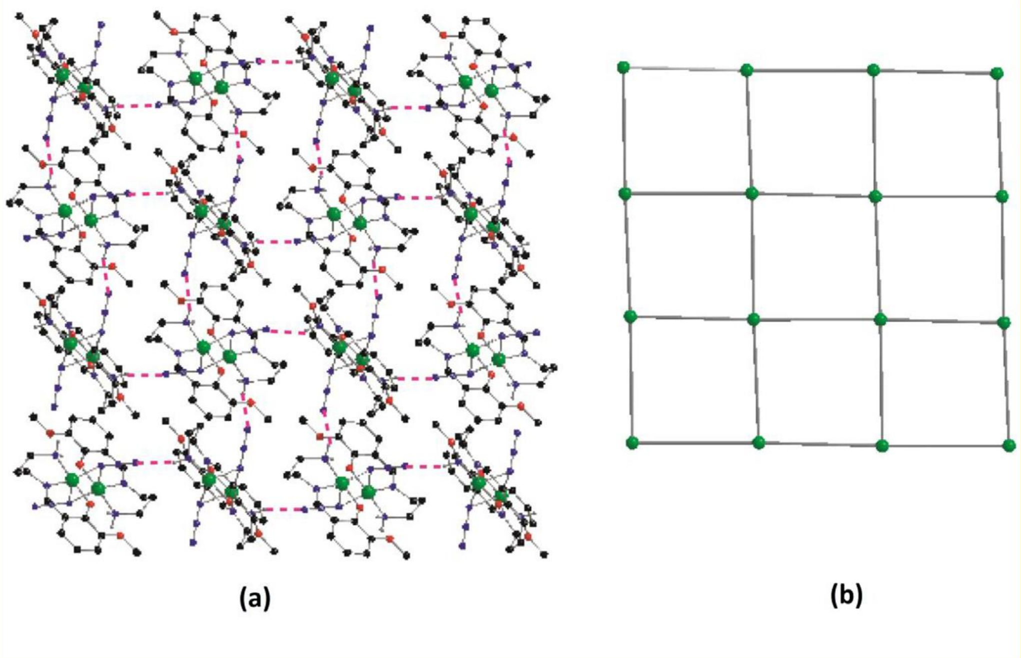


Fig. III.4. (a) Hydrogen bonded 2D layer structure of the complex **2**. Only the relevant atoms have been shown for clarity. (b) A perspective view of (4, 4) square grid topology of the complex.

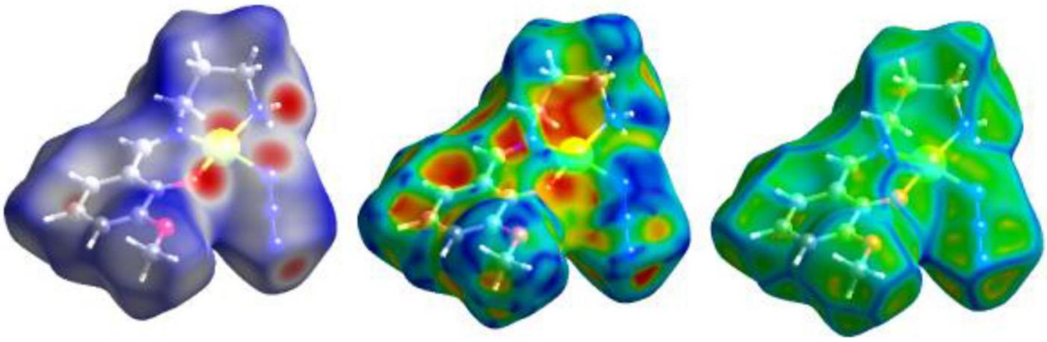


Fig. III.5. Hirshfeld surfaces mapped over dnorm (left-side), shape index (middle) and curvedness (right-side) of the complex **2**.

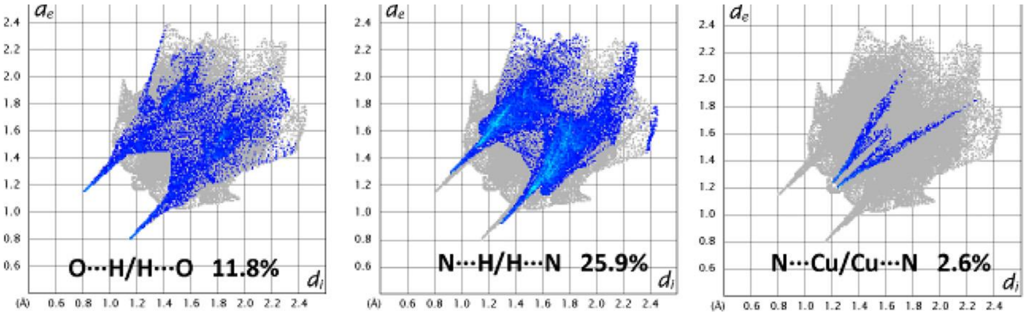


Fig. III.6. Fingerprint plot: Different contacts contributed to the total Hirshfeld Surface area of the complex **2**.

Solid state crystal structure of any complex **2** is stabilized through a number of supramolecular interactions and hence all these interactions should be considered. These lead to the finding of different unconventional interactions. Now, Hirshfeld surface analysis helps us to envisage and explore these important supramolecular interactions which could further be studied theoretically. Visualization and investigation of these major interactions using Hirshfeld surface based technique symbolize a vital progress in enabling supramolecular chemists and crystal engineers to gain insight into crystal packing [68] Hirshfeld surfaces of the complex **2** mapped over dnorm, shape index and curvedness is illustrated in **Fig III.5.** Red spots on these surfaces denote the dominant interactions [N…H/H…N and O…H/H…O].

The 2D fingerprint plot, which are used to analyze the intermolecular contacts at the same time, revealed that the main intermolecular interactions in the complex 2 are N…H/H…N and O…H/H…O shown in **Fig. III.6.** An interesting N…Cu/Cu…N contact is observed in the 2D fingerprint plot. This may be due to the formation of unusual [Cu(1)–N(1)–Cu(1)b–N(1)b] chelate ring. The N…H/H…N and O…H/H…O contacts are also in agreement with the hydrogen bonding and N–H…p interactions observed in the solid state of the complex.

III.3.4. IR, electronic spectra and PXRD

In the IR spectrum of the complex **2**, characteristic absorption band corresponding to azomethine (>C=N-) group has been observed at 1628 cm^{-1} [64-65] A sharp absorption band at 2038 cm^{-1} indicates the presence of azide which is also evident from crystal structure determination [66,67]. In addition, the IR spectrum of the complex also exhibits weak bands for the N–H stretching vibration frequencies in the region 3274-3211 cm^{-1} [68,69]

Electronic absorption spectrum of the complex **2** in acetonitrile shows a d-d transition band at 600 nm [70] A strong ligand to metal charge transfer transition at 370 nm has been observed which is characteristic of transition metal complexes with Schiff base ligands [71] Additionally, high energy absorption bands around 234 nm and 279 nm may be attributed to intra-ligand transitions i.e. $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions respectively [72]

The experimental PXRD patterns of the bulk products are in good agreement with the simulated XRD patterns from single crystal X-ray diffraction results, indicating consistency of the bulk sample. The simulated patterns of the complex **2** are calculated from the single crystal structural data (Cif files) using the CCDC Mercury software.

III.4. Phenoxazinone synthase mimicking activity

Phenoxazinone synthase mimicking activity for the complex has been assessed using OAPH as a model substrate. Mimicking activity studies have been performed in acetonitrile medium as complexes, substrates and their products are soluble in acetonitrile. Advancements of the reactions have been monitored spectrophotometrically. Spectrophotometric scans revealed a gradual increase in intensity of the absorption band 360 nm for phenoxazinone synthase mimicking activity **(Fig. III.7.)** The resulting solutions have also been monitored spectrophotometrically after 48 h, which show the formation of 2-aminophenoxazine-3-one respectively as the sole product. These results undoubtedly indicate that the synthesized complex is active towards phenoxazinone synthase mimicking activity. The spectral growth (corresponding to the formation of phenoxazinone) is negligible for bare copper (II) salts compared to the spectral growth for the complex which infers the catalytic property of the complex **2**.

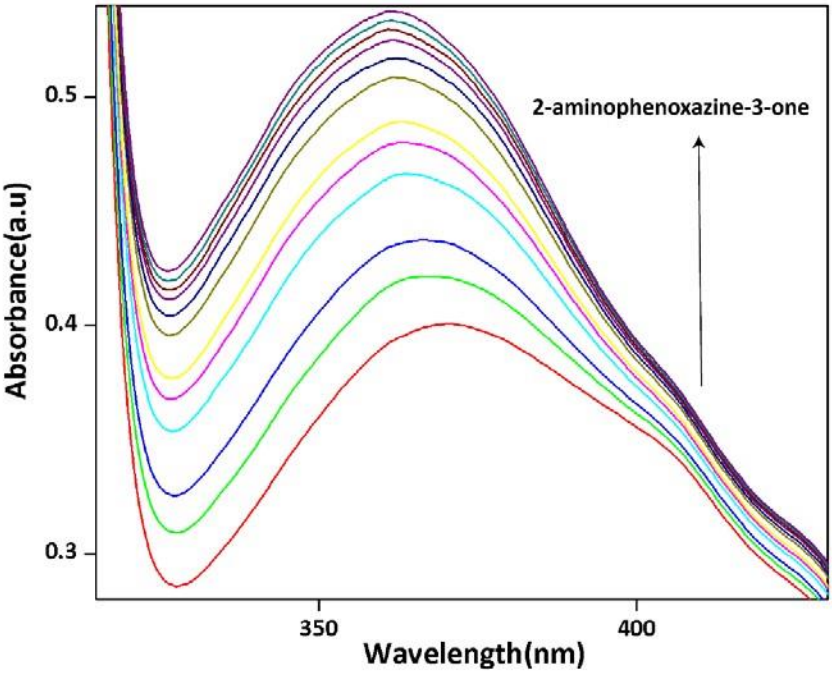


Fig. III.7. The spectral profile showing the growth of 2-aminophenoxazine-3-one at ~360 nm upon addition of 10^{-1} M Ortho-aminophenol to a solution containing the complex (10^{-5} M) in CH_3CN.

III.5. Kinetic investigations through a number of enzyme kinetic plots

The above mechanism is based upon the well-known Michaelis–Menten equation:

$$V = \frac{V_{max}\,[S]}{K_M + [S]}$$

Where, V = initial rate; [S] = concentration of the substrates; $K_M = (k_2 + k_3)/k_1$, Michaelis–Menten constant for the metal complex **2** and V_{max} = maximum initial rate attained for a particular concentration of the metal complex in the presence of a large excess of the substrate. One of the most widely used transformation of the above equation, is the well-known Lineweaver-Burk equation as follows:

$$\frac{\mathbf{1}}{\mathbf{V}} = \frac{\mathbf{K_M}}{\mathbf{V_{max}}}\frac{\mathbf{1}}{\mathbf{[S]}} + \frac{\mathbf{1}}{\mathbf{V_{max}}}$$

The Lineweaver-Burk plot has been used to analyze different parameters, viz. V_{max} (Maximum reaction velocity), K_M (Michaelis constant), and K_{cat} (Turnover number). The kinetic parameters of the complex for phenoxazinone synthase like activity are as follows; $V_{max} = 4.32\text{x}10^{-3}$ M min^{-1}, $K_M = 1.66\text{x}10^{-2}$ M, K$_{cat}$ = 432 min^{-1}. The initial rate has been determined from the slope of the absorbance vs time plot. First order dependence has been observed at low substrate concentrations, whereas saturation kinetics has been found at higher substrate concentrations. The initial rate versus substrate concentration and LineweaverBurk plots have been shown in **Fig. III.8.**

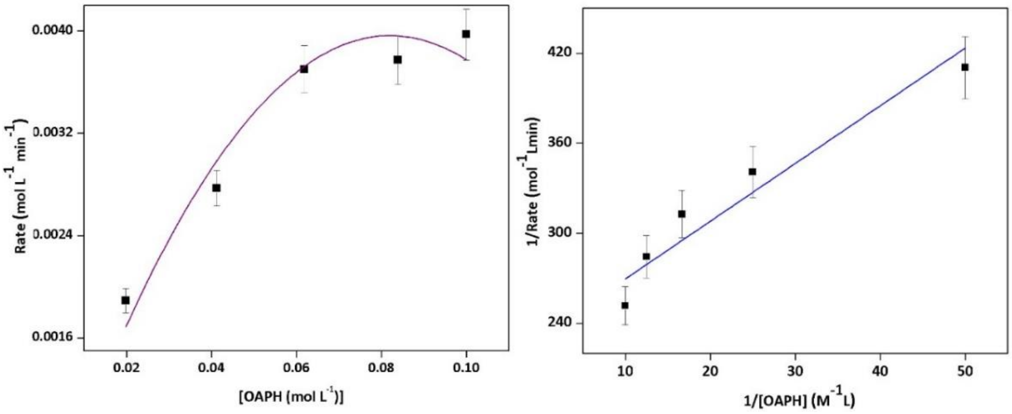
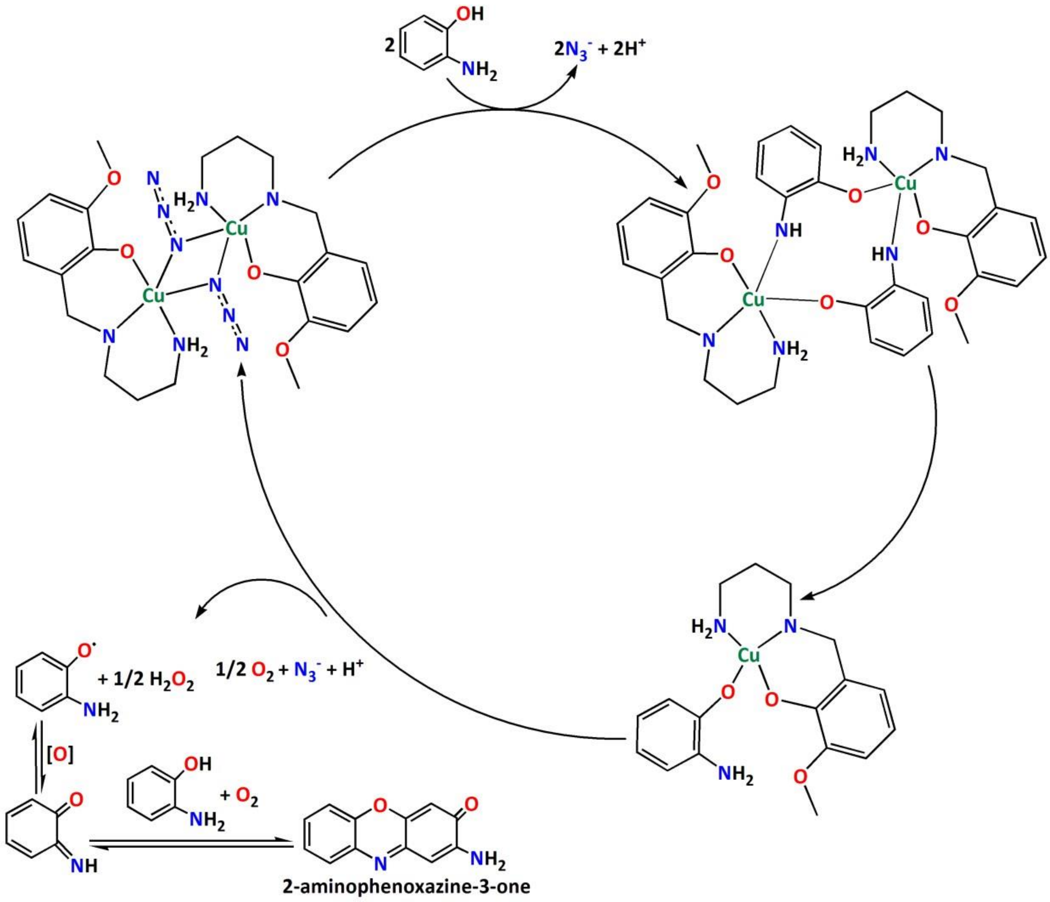


Fig. III.8. Initial lrate versus substrate concentration plot for the oxidation of oaminophenol catalyzed by the complex in CH_3CN (left). Representative Lineweaver-Burk plot for the oxidation of o-aminophenol catalyzed by the complex in CH_3CN (right).

III.6 Mechanistic pathway of catalytic activity

From the experimental results, it is clear that the complex **2** is able to mimic phenoxazinone synthase effectively. The catalytic activity depends on the interaction between the substrate and catalyst. More facile interaction leads to higher Kcat values. The formal oxidation state of copper in the complex is +2, which facilitate the approach of a negatively charged substrate to the metal centre. Catalytic activities depend upon the interaction between substrate and catalyst. Higher the interaction between substrate and catalyst, higher is the kcat value. It can be easily predicted that initially a catalyst-substrate adduct has been formed by replacing the monodentate azide co ligand, which leads to respective product formation regenerating catalyst molecule. Based on the several previously published reports, [73-75] tentative catalytic conversation for the mimicking activity has been given in **Scheme III.2.**

To elucidate active species present in catalytic pathway during mimicking activity, the electron spray ionization mass spectrum of the 1:50 mixture of the complex and o-aminophenol has been performed. The spectrum has been recorded separately after 5 min from mixing and the result has been depicted in **Fig. III.6.** Initially two molecules of the substrate *o*-aminophenol are proposed to replace two molecules of azide to initiate the catalytic cycle. The generated species, [(2-aminophenolate)$_2$(CuL)$_2$(H$_2$O)Li]+ correspeonds to the peak at m/z= 782.06 in the mass spectrum of the complex. In addition two peaks at m/z= 426.04 (100%) and 404.05, correspond to [(2-aminophenolate)CuL(CH$_3$CN)Li]+ and [(2-aminophenolate) CuL^2(H$_2$O)Li]+ respectively, which confirms the intermediate formation of the catalytic cycle. The mass spectrum shows peak around m/z ~ 215 corresponding to the formation of [phenoxazinone-H]$^+$, which implies the completion of the catalytic cycle. The catalytic pathway shown in **Scheme III.2.** is therefore justified by the mass spectrum analysis.



Scheme III.2. Tentative catalytic pathway for phenoxazinone synthase mimicking activity of the synthesized complex **2**.

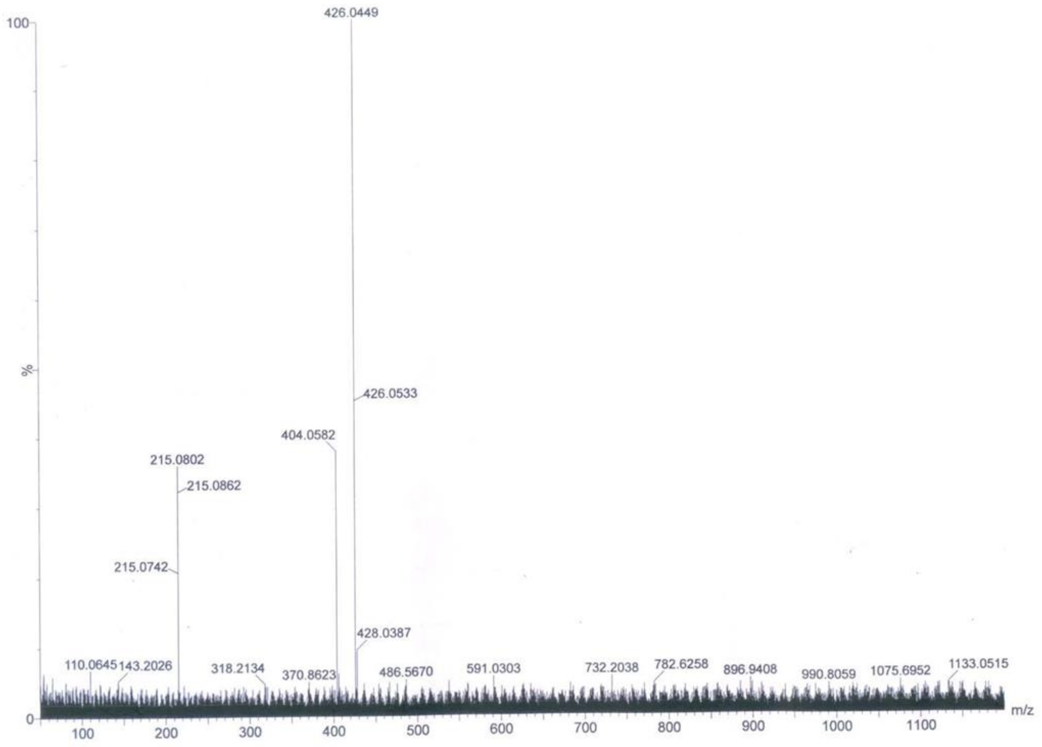


Fig. III.9. ESI-MS positive spectrum of 1:50 mixture of the complex and Ortho-aminophenol in acetonitrile at room temperature.

Several copper (II) complexes with different ligands have been reported in the literature, but very few of them have been reported on their catalytic properties. In **Table III.6.** complexes have been gathered where the coordination environment around both the copper (II) centres are similar to that of our complex [76-85] It has been found that none of the complexes has been found to show phenoxazinone synthase mimicking activity. Catalytic properties of dinuclear copper(II) complexes with half-salen type Schiff base ligands are interesting and needs to be explored.

Table III.6. X-ray characterized pseudohalide bridged dinuclear copper (II) complexes devoid of any catalytic properties reported in literature.

CCDC	**Complex**	**Kcat (min^{-1})**	**Ref**
AYIDAP	$[Cu_2(L^1)_2(N_3)_2]$	Not explored	[**76**]
JOPDUP	$[Cu_2(L^2)_2(N_3)_2]\cdot DMF$	Not explored	[**77**]
JOPFAX	$[Cu_2(L^3)_2(N_3)_2]$	Not explored	[**77**]
JOPFIF	$[Cu_2(L^4)_2(N_3)_2]$	Not explored	[**77**]
EZUTAV	$[Cu_2(L^5)_2(N_3)_2]$	Not explored	[**78**]
EZUTEZ	$[Cu_2(L^5)_2(N_3)_2]\cdot H_2O$	Not explored	[**78**]
XEDCAM	$[Cu_2(L^6)_2(N_3)_2]$	Not explored	[**79**]
NUNTOG	$[Cu_2(L^1)_2(NCS)_2]$	Not explored	[**80**]
IQUBIG	$[Cu_2(L^7)_2(\mu_{1,1}N_3)_2]\cdot CH_3OH$	Not explored	[**81**]
GUFCAM	$[Cu_2(dipn)_2(N_3)_2]$	Not explored	[**82**]
KOKBES	[Cu2(L82)(μ1,1–N3)2]	Not explored	[**83**]
KOKBIW	$[Cu_2(L^{82})(\mu_{1,1}–N_3)_2]\cdot H_2O$	Not explored	[**83**]

BODWUN	$[CuL^9(N3)]_2$	Not explored	[**2**]
YIDSAG	$[CuL^{10}(N_3)]_2$	Not explored	[**84**]
TEJPEF02	$[L^{11}CuN_3]_2\cdot(H_2O)_2$	Not explored	[**85**]
NIKLAW	$[CuL^{12}(\mu_{1,1}–N_3)]_2\cdot MeOH$	Not explored	[**86**]
NIKHOG	$[CuL^{13}(\mu_{1,1}–N_3)]_2$	Not explored	[**86**]
	$[LCu(\mu_{1,1}\text{-}N_3)_2LCu]$	432	This work

where, HL^1 = 2-[{3-(methylamino)propylimino}methyl]-6-methoxyphenol; HL^2 = 1-(2-aminopropylimino)methyl]naphthalen-2-ol); HL^3 = 1-[3-(dimethylamino)propylimino)ethyl]naphthalen-2-ol); HL^4 = 1-[2-(diethylamino)ethylimino)ethyl]naphthalen-2-ol); HL^5 = (2-[(3-methylaminopropylimino)-methyl]-phenol); HL^6 = (2-[(3-amino-2,2-dimethylpropylimino)-methyl]-6-methoxyphenol; HL^7 = 2-[(3-methylaminopropylimino)methyl]phenol; Hdipn = (4-[(3-aminopentylimino)-methyl]-benzene-1,3-diol); HL^8 = 1-[(3-dimethylaminopropylimino)methyl]naphthalen-2-ol); HL^9 = {2-[1-(3-

aminopentylimino)ethyl]phenol}; HL[10] = 4-nitro-2-[(3-dimethylaminopropylimino)methyl]phenol; HL[11] = 2-[{2(methylamino)ethylimino)methyl)-6-methoxyphenol; HL[12] = 2-[{2(methylamino)cyclohexylimino}methyl]-6-methoxyphenol; HL[13] = 2-[{2(methylamino)cyclohexylimino}methyl]phenol.

III.7. Concluding Remarks

In conclusion, the synthetic scheme and structural characterization of a pseudo halide bridged dinuclear copper (II) complex **2** has been discussed. Anion directed template synthesis method has been used to prepare the dinuclear copper (II) complex with a monocondensed, potential tetra-dentate, N_2O_2 donor Schiff base ligand. Structure of the complex has been confirmed by single crystal X-ray diffraction technique. Solid state supramolecular interactions in the complex have also been investigated. The complex is active towards catalytic conversation of OAPH to 2-aminophenoxazine-3-one (phenoxazinone synthase mimicking activity) in acetonitrile medium. Mimicking activity has been assessed by Michaelis-Menten enzymatic kinetics. Kinetic studies of the catalytic cycle have been performed in detail using a variety of enzyme kinetics plots to calculate a number of kinetic parameters, including k_{cat}

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Chapter IV

Synthesis and characterization of an ionic mixed valence cobalt (III/II) complex with a Schiff base ligand

“The only limit to our realization of tomorrow will be our doubts of today”

-Franlin.D.Roosevelt

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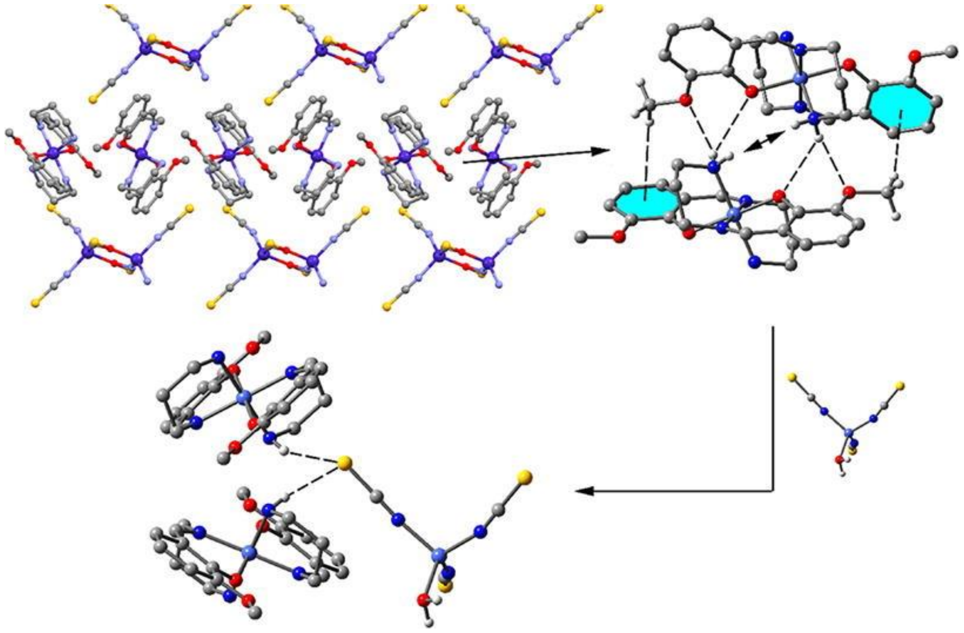
Synthesis and characterization of an ionic mixed valence cobalt (III/II) complex with a Schiff base ligand



Chapter IV

Synthesis and characterization of an ionic mixed valence cobalt (III/II) complex with a Schiff base ligand

IV.1. Introduction

Various di-/tri-/poly- nuclear transition metal complexes have attracted the inorganic chemists owing to the diversity of their structural features and potential application in the field of condensed physics and material chemistry [1-4] Another inherent potential of these complexes is the efficacy in modeling the multi-metal active sites of bio-molecules [5-7] Dinuclear cobalt complexes may function as mimics of the active biosites such as in methionine amino peptidase [8,9] and can show DNA cleavage activity 10 Alternatively, Schiff base ligands themselves have been widely used in coordination chemistry due to their facile syntheses, easily tunable steric and electronic properties and their applications in different branches of science [11-15] Transition metal complexes of Schiff base ligands are important stereochemical models in main group and transition metal coordination chemistry [11-16] These complexes have wide applications, including bioinorganic chemistry, material science and magnetism, bio-relevant catalytic activities, separation and encapsulation, hydrometallurgy, metal clusters, transport and activation of small molecules etc [16-24]

Herein, a new ionic mixed valence cobalt (III/II) complex, $[Co^{III}(L^2)_2][Co^{II}(NCS)_3(H_2O)]$, derived from mono-condensed Schiff base and thiocyanate co-ligands. Single crystal X-ray crystallography analysis confirms that the complex is an ionic mixed valence complex with one tetracoordinated cobalt (II) centre. To find out the reason behind such unique structure in solid state, complete DFT calculation has been performed which confirmed that the combination of $CH_3\cdots\pi$ and hydrogen bonding interactions plays a vital role in stabilization of ionic complex.

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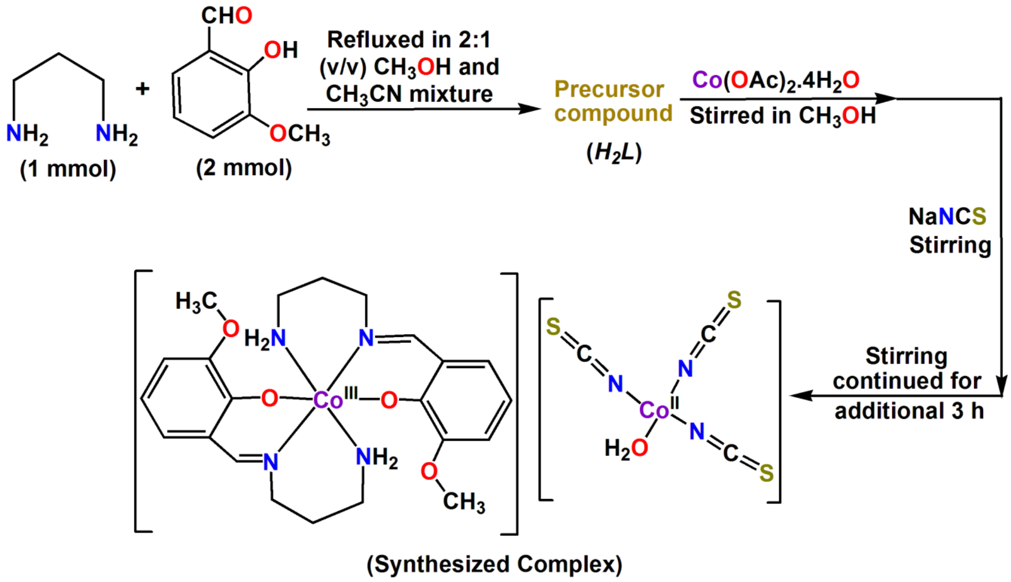
IV.2. Synthesis of $[Co^{III}(L^2)_2][Co^{II}(NCS)_3(H_2O)]$ (3)

0.10 mL (~1 mmol) of 1, 3-diaminopropane was mixed with 304 mg (~2 mmol) of *3-methoxysalicylaldehyde* in 25 mL 2:1 (v/v) methanol-acetonitrile mixture. The resulting mixture was refluxed for c.a. 1.5 h and allowed to cool. A methanol solution (10 ml) of cobalt(II) acetate tetrahydrate (500 mg, ~2 mmol) was then directly added to this yellow coloured solution of the Schiff base ligand, followed by the addition of a methanol solution (10 mL) of sodium thiocyanate (162 mg, ~2 mmol) with constant stirring. The stirring was continued for additional 1.5 h and then filtered in a beaker. The filtrate was then allowed to stand overnight till X-ray quality single crystals came into view at the bottom of the beaker. The crystals were dried in a desiccator containing anhydrous $CaCl_2$ and then characterized by single crystal X-ray diffraction, elemental analysis, and spectroscopic methods.

Yield: 685 mg (~54%); based on cobalt (III). Anal. Calc. for $C_{48}H_{64}Co_3N_{11}O_{12}S_3$ (FW = 1260.10): C, 45.75; H, 5.12; N, 12.23%. Found: C, 45.9; H, 5.0; N, 12.3%. **FT-IR (KBr, cm^{-1}):**3245-3214 ($\upsilon_{N\text{-}H}$), 2930-2910 ($\upsilon_{C\text{-}H}$), 2064 (υ_{NCS}), 1624 ($\upsilon_{C=N}$), 1439 ($\upsilon_{C=C}$). **UV-Vis:**λ_{max} (nm), [ε_{max} (dm^3 mol^{-1} cm^{-1})] (DMF), 540 (4.32×10^2), 396 (6.04×10^4), 273 (7.24×10^4). **Crystal data and refinement details*:*** Crystal System = Triclinic, Temperature (K) = 150(2), D(calc) [g/cm^3] = 1.360, Space group = $P\bar{1}$, a(Å) = 11.3567(7), b(Å) = 11.7058(8), c(Å) = 13.3789(8), α(°) = 66.228(6), β(°) = 89.455(5), γ(°) = 72.416(6), μ [mm^{-1}] = 0.963, F(000) = 654, Total Reflections = 7473, Unique Reflections = 5314, Observed data[I > 2 σ(I)] = 4819, No of parameters = 416, R(int) = 0.026, R1, wR2 (all data) = 0.1146, 0.2892, R1, wR2([I > 2 σ(I)] = 0.1081, 0.2861, Residual Electron Density (eÅ^{-3}) = 0.765, -0.701.



Scheme IV.1. Synthetic route to the complex **3**

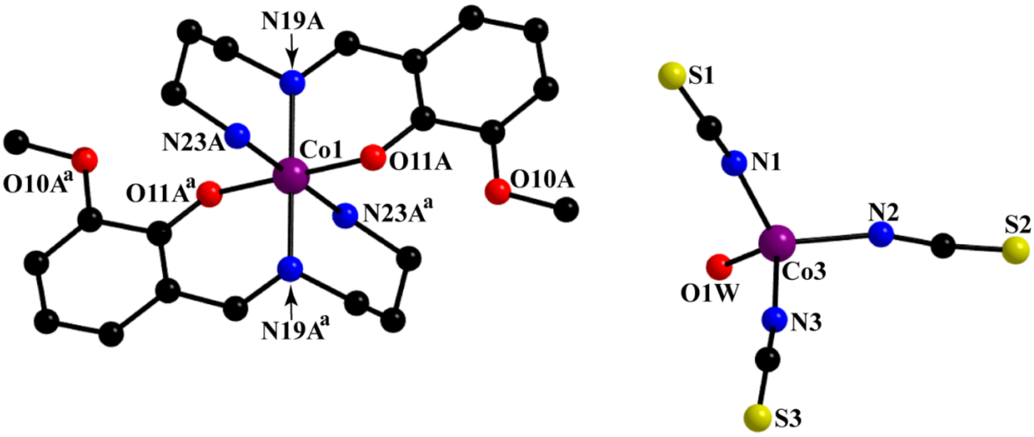


Fig.IV.1. Molecular structure of the complex with selective atom numbering scheme. Only the major component of the disorder has been shown. Hydrogen atoms have been omitted for clarity. Bond lengths in Å unit: Co(1)-O(11A) =

1.907(6), Co(1)-N(19A) = 1.931(7), Co(1)-N(23A) = 1.979(8), Co(1)-O(11A)a = 1.907(6), Co(1)-N(19A)a = 1.931(7), Co(1)-N(23A)a = 1.979(8), Co(3)-N(3) = 1.95(2), Co(3)-N(1) = 1.94(2), Co(3)-N(2) = 2.07(2), Co(3)-O(1W) = 2.03(2) (Symmetry transformation; a = -x,-y,-z).

Table IV.1. Crystal data and refinement details of the titled complex

Formula	$C_{48}H_{64}Co_3N_{11}O_{12}S_3$
Formula Weight	1260.10
Crystal System	Triclinic
Temperature (K)	150(2)
Space group	$P1$
a(Å)	11.3567(7)
b(Å)	11.7058(8)
c(Å)	13.3789(8)
α(°)	66.228(6)
β(°)	89.455(5)
γ(°)	72.416(6)
D(calc) [g/cm^3]	1.360
μ [mm^{-1}]	0.963
F(000)	654
Total Reflections	7473

Unique Reflections	5314
Observed data[I > 2 σ(I)]	4819
No of parameters	416
R(int)	0.026
R1, wR2(all data)	0.1146, 0.2892
R1, wR2([I > 2 σ(I)]	0.1081, 0.2861
Residual Electron Density (eÅ-3)	0.765, -0.701
CCDC No:	1970250

Table IV.2. Selected bond lengths (Å) of the titled complex.

Co(1)-O(11A)	1.907(6)
Co(1)-N(19A)	1.931(7)
Co(1)-N(23A)	1.979(8)
Co(1)-O(11A)a	1.907(6)
Co(1)-N(19A)a	1.931(7)
Co(1)-N(23A)a	1.979(8)
Co(3)-N(3)	1.95(2)
Co(3)-N(1)	1.94(2)

Co(3)-N(2)	2.07(2)
Co(3)-O(1)	2.03(2)

Symmetry transformation; a = -x,-y,-z.

Table IV.3. Selected bond angles (°) of the titled complex.

O(11A)-Co(1)-N(19A)	91.1(3)
O(11A)-Co(1)-N(23A)	87.6(3)
O(11A)-Co(1)-O(11A)^a	(180)
O(11A)-Co(1)-N(19A)^a	88.9(3)
O(11A)-Co(1)-N(23A)^a	92.4(3)
N(19A)-Co(1)-N(23A)	85.9(3)
O(11A)^a-Co(1)-N(19A)	88.9(3)
N(19A)-Co(1)-N(19A)^a	(180)
N(19A)-Co(1)-N(23A)^a	94.1(3)
O(11A)^a-Co(1)-N(23A)	92.4(3)
N(19A)^a-Co(1)-N(23A)	94.1(3)
N(23A)-Co(1)-N(23A)^a	(180)
O(11A)^a-Co(1)-N(19A)^a	91.1(3)
O(11A)^a-Co(1)-N(23A)^a	87.6(3)
N(19A)^a-Co(1)-N(23A)^a	85.9(3)
N(2)-Co(3)-N(3)	105.0(9)
O(1)-Co(3)-N(3)	110.0(9)

O(1)-Co(3)-N(1)	107.0(10)
O(1)-Co(3)-N(2)	109.9(9)
N(1)-Co(3)-N(2)	117.1(8)
N(1)-Co(3)-N(3)	107.8(10)

Symmetry transformation; a = -x,-y,-z.

IV.3. Results and discussion

IV.3.1. Synthesis of the complex 3

The formation of this complex can be rationalized in light of the one pot synthesis method. The Schiff base ligand was synthesized using previously reported synthetic route [35-38] The Schiff base ligand (HL^2), on reaction with cobalt (II) acetate tetra-hydrate and sodium thiocyanate, resulted in a mixed valence complex, $[Co^{III}(L^2)_2][Co^{II}(NCS)_3(H_2O)]$. It is obvious that initially a tetra-dentate Schiff base was formed which partially hydrolyzed at reaction condition to produce a tridentate Schiff base ligand (HL^2). As solvents were not dried, lots of water may be present in methanol. This increased concentration of water might be responsible to initiate hydrolysis. The synthetic route to both complexes has been shown in **Scheme IV.1.**

IV.3.2. Crystal structure description of the complex 3

Single crystal x-ray structure determination reveals that the synthesized complex consists of discrete di-nuclear unit, $[Co^{III}(L^2)_2][Co^{II}(NCS)_3(H_2O)]$. The complex crystallizes in triclinic system with P space group. A perspective view of the ionic coordination complex along with the metal centre coordinated atom numbering scheme is illustrated in **Fig.IV.1.** The complex consists of one cationic complex part, $[Co^{III}(L^2)_2]^+$, and one anionic complex part, $[Co^{II}(NCS)_3(H_2O)]^-$. In cationic part of the complex, there are two independent mononuclear subunits (A and B) with equivalent geometry. Subunit B has a very similar molecular structure; the structural details and relevant figures are provided in **Fig. IV.2.** Relevant bond angles are summarized in **Table IV.1.**

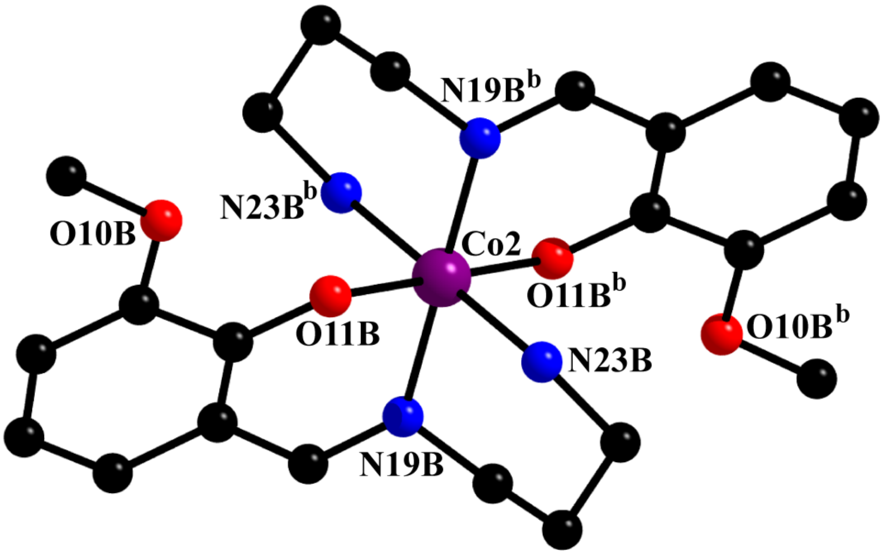


Fig. IV.2. Perspective view of cationic part subunit B of the synthesized complex with selective atom numbering scheme. Hydrogen atoms have been omitted for clarity.

In subunit A of the cationic part, cobalt(III) centre, Co(1), exhibits slightly distorted octahedral coordination geometry, with two imine nitrogen atoms, N(19A) and N(19A)^{a,} two amine nitrogen atoms, N(23A) and N(23A)^{a}, and two phenoxo oxygen atoms, O(11A) and O(11A)^{a}, from two deprotonated Schiff base ligands (L^3) to complete its octahedral geometry. The saturated six membered chelate rings, Co(1)-N(19A)-C(20A)-C(21A)-C(22A)-N(23A) and Co(1)-N(19A)^{a}-C(20A)^{a}-C(21A)^{a}-C(22A)^{a}-N(23A)^{a}, present in chair conformations, with puckering parameters [39,40] Q = 0.647(8) Å, θ = 11.3(7)°, and ϕ = 27(4)° and Q = 0.647(8) Å, θ = 168.7(7)°, and ϕ = 207(4)°, respectively (Symmetry transformation; ^{a} = -x,-y,-z). The Co (III)-N_{imine} distances are shorter than the Co (III)-N_{amine} ones, due to the diff erent hybridization of nitrogen atoms. This is a common phenomenon observed in many other cobalt (III) Schiff base complexes [35, 37]

In anionic complex part, cobalt (II) ion exhibits slightly distorted tetrahedral coordination sphere, in which cobalt (II) is coordinated by three thiocyanate nitrogen atoms, N(1), N(2) and N(3) and a water oxygen atom, O(1W). Although tetra-coordinated cobalt (II) is not routinely noticed, in many previously published papers presence of tetra-coordinated cobalt(II) complexes is observed [41-45] The bond angles (given in **Table IV.1.)** are highly deviate from perfectly tetrahedral geometry (~109.5°), which confirms distorted tetrahedral geometry around central cobalt(II).The N-C-S angles in terminal thiocyanate coligands are 180(3) {for N(1)-C(1)-S(1)}, 172(2) {for N(2)-C(2)-S(2)} and 179(3) {for N(3)-C(3)-S(3)}, which indicate more or less linear arrangements.

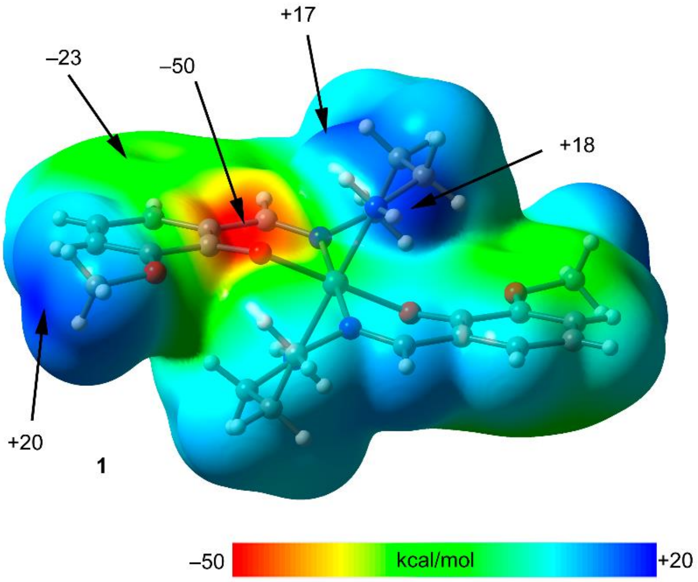


Fig.IV.3. MEP surface (isodensity = 0.001 a.u.) of cationic part of the synthesized complex, $[Co^{III}(L)_2]+$. The values are selected points of the surface are indicated. Negative and positive values are highlighted in red and blue colours, respectively.

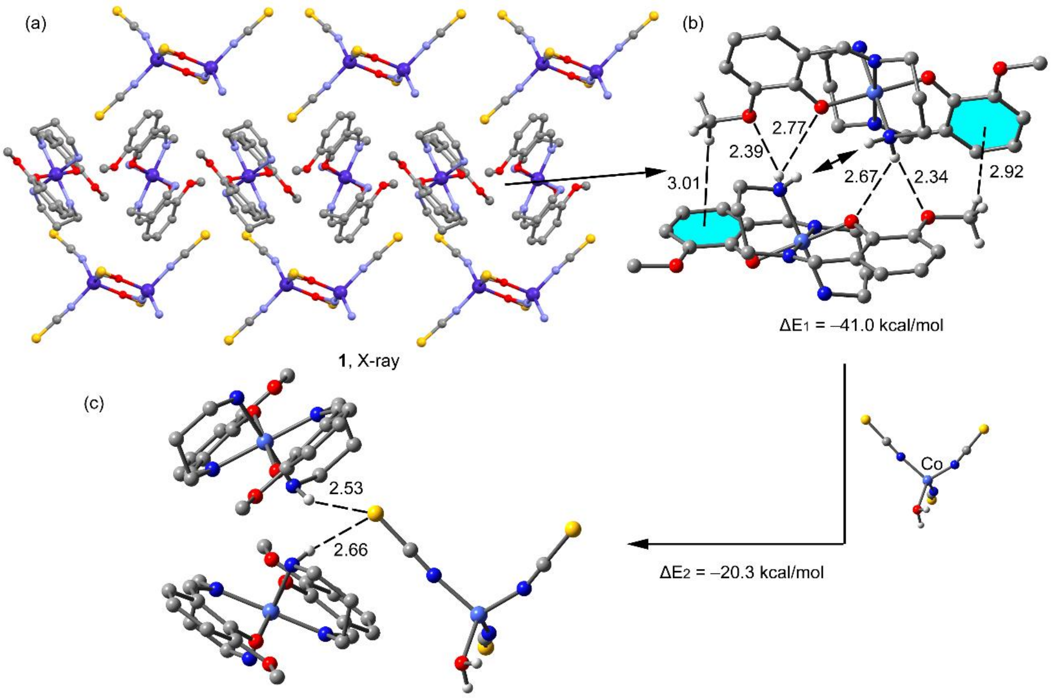


Fig.IV.4. (a) Partial view of the X-ray structure of the titled complex. Hydrogen atoms are omitted for clarity. (b) Theoretical model used to evaluate the noncovalent interactions (Distances are indicated in Å). Only the relevant hydrogen atoms are shown. (c) Theoretical model used to evaluate the interaction of the dimer with the $[Co^{II}(NCS)_3(H_2O)]^{-}$ anionic moiety.

IV.3.3. Theoretical calculations

The theoretical study is devoted to analyse the energy associated with the combination of $CH_3\cdots\Pi$ and hydrogen bonding interactions observed in the solid state of the titled complex and to characterize them using MEP and NCI plot computational tools. At first, the MEP was computed on surface of the $[Co^{III}(L^2)_2]+$ complex cation that is depicted in **Fig.IV.3.** The most negative MEP value is located between the oxygen atoms of the Schiff base ligands (–

50 kcal/mol). The most positive value is located at the hydrogen atoms of the methoxide group (+20 kcal/mol), that is unexpectedly more positive that the values of the MEP at the hydrogen atoms of the coordinated amino group. Finally, the MEP value over the aromatic ring is significantly negative, thus well suited for interacting with electron deficient regions.

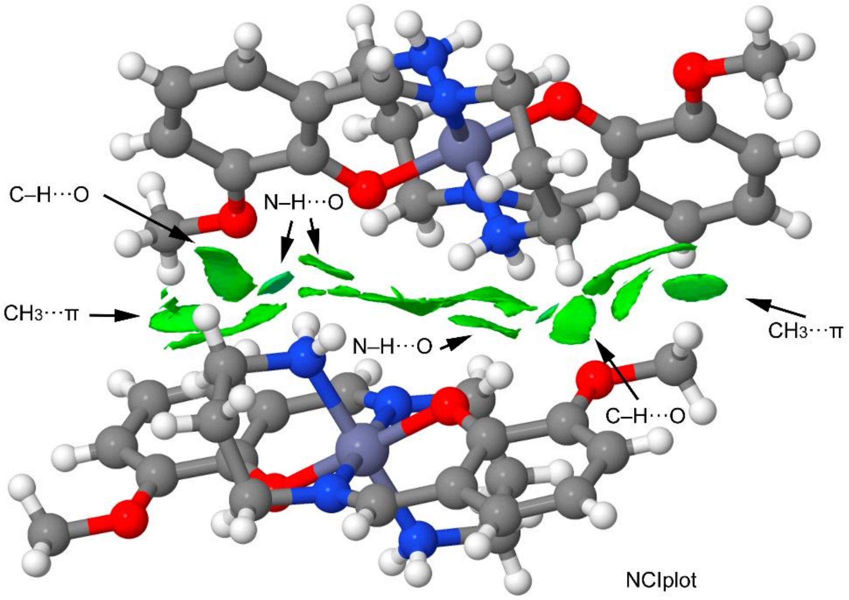


Fig.IV.5. NCI surface of the assembly in the synthesized complex. The gradient cut-off is s = 0.35 au, and the color scale is −0.04 <ρ< 0.04 au. Only intermolecular interactions are depicted for clarity.

In **Fig.IV.4. (a)** it has been found the X-ray structure of the titled complex, where $[Co^{III}(L^2)_2]^+$ cationic moieties form an infinite 1D tape in the solid state. Moreover, the tapes are sandwiched by the $[Co^{II}(NCS)_3(H_2O)]^-$ anionic counterparts, first analyzed one dimer of $[Co^{III}(L^2)_2]^+$ extracted from the infinite 1D chain **Fig.IV.4. (b)** It can be observed that its formation is governed by a combination of bifurcated hydrogen bonds between the N-H group and the oxygen atoms of the ligand, and quite short $CH_3 \cdots \pi$ interactions. The formation of latter interactions agrees well with the MEP surface analysis, since the most positive MEP value is located at the methyl group. Moreover, the MEP over the aromatic ring is large and negative likely due to the anionic nature of the ligand. As a consequence, the dimerization energy is large (ΔE_1 = –41.0 kcal/mol) due to the formation of two bifurcated hydrogen bonds and the electrostatically enhanced $CH_3 \cdots \pi$ interactions. In this dimer, there are two N-H groups {double arrow in **Fig.IV.4. (b)**} that converge to the same spatial region and thus adequate to interact with the electron rich thiocyanate ligand of the $[Co^{II}(NCS)_3(H_2O)]^-$ anionic counterpart. The interaction energy of the complex between the $[Co^{III}(L^2)_2]^+$ dimer and the $[Co^{II}(NCS)_3(H_2O)]^-$, which is also very large ΔE_2 = –20.3 kcal/mol.

Also computed the ‘‘non-covalent Interaction plot” (NCI plot) index in order to characterize the non-covalent interactions in the dimer of the titled complex. The NCI plot is a visualization index that can identify and characterize non-covalent. The presence of green isosurfaces located between the $–CH_3$ groups and the aromatic rings is observed, thus confirming the

$CH_3...\pi$ interactions. The NCI plot shows the existence of several smaller isosurfaces that characterize the bifurcated N–H...O hydrogen bonds and also reveals the existence of ancillary C–H...O interactions that also contribute to the stabilization of the assembly. Finally, this analysis also reveals the existence of long range van der Waals interactions due to the approximation of the bulk of both molecules.

IV.3.4. Hirshfeld surface analysis

Solid state crystal structure of any complex can be determined by an amalgamation of a number of important intermolecular and intramolecular interactions, and therefore all these interactions should be consider. Hirshfeld surface analysis helps us to visualize and investigate these important supramolecular interactions. Visualization and investigation of these major interactions using Hirshfeld surface based technique symbolize a vital progress in enabling supramolecular chemists and crystal engineers to gain insight into crystal packing. Hirshfeld surfaces of the titled complex mapped over none, di, de, dnorm, shape index and curvedness **(Fig.IV.6.)** The surfaces are shown as transparent so that molecular moieties around which Hirshfeld surfaces are calculated could be easily picturize. The predominant interactions in the complex are H···H, C···H/H···C, O···H/H···O, N···H/H···N and S···H/H···S. Bright red spots on the dnorm surface **(Fig.IV.6.)** indicate that these interactions are predominant. Additionally, 2D fingerprint plots

(Fig.IV.7.) exemplify various inter-molecular interaction patterns associated with the complex and their relative contributions are given in percentage scale. In 2D fingerprint plots inter-molecular interactions become visible as distinct spikes. Complementary regions are visible in the two dimensional fingerprint plots where one molecule act as donor (de>di) and the other as an acceptor (de<di). The fingerprint plots can also be decomposed to highlight preferred atoms pair close contacts. This decomposition enables separation of contributions from different interaction types, which overlap in the full fingerprint [23]

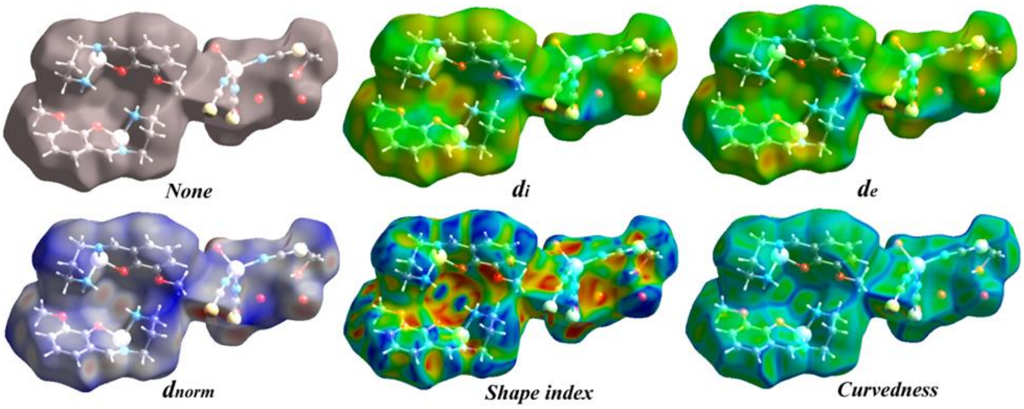


Fig.IV.6. Hirshfeld surfaces of the synthesized complex mapped over none, di, de, dnorm, shape index and curvedness.

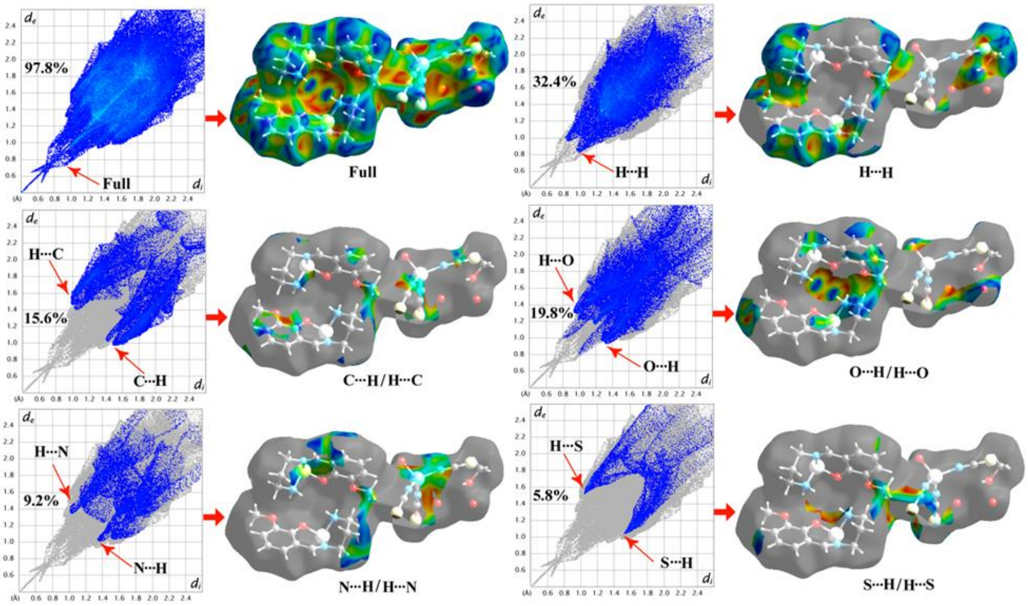


Fig.IV.7. Two dimensional fingerprint plots of the complex: Full and resolved into H···H, C···H / H···C, O···H / H···O, N···H / H···N and S···H / H···S contacts showing the percentages of contacts contributed to the total Hirshfeld Surface area of the complex. Surfaces in the right hand columns highlight the relevant surface patches associated with the specific contacts in the total Hirshfeld Surface area of the complex.

IV.3.5. IR and electronic spectroscopy

The IR and electronic spectra of the synthesized complex are in well agreement with its crystal structure. Some of the exceptionally informative infrared and electronic absorption picks which assist in the structural characterization of the complex are gathered in the Experimental section. Moderately strong bands in the range of 3245-3214 cm^{-1} (due to N-H starching) confirm the presence of free amine group in the titled complex [47, 48, 49, 55]. The band corresponding to azomethine (C=N) group is distinct and occur at 1624 cm^{-1} [35, 37, 50]. The appearance of a strong band at 2064 cm^{-1} indicates the presence of N-coordinated thiocyanate in the complex [35, 37] The bands in the range of 2930-29100 cm^{-1} due to alkyl C-H stretching vibrations are routinely noticed [35, 37].

The UV-Vis absorption spectrum of the complex in DMF shows low energy absorption bands at 540 nm, attributable to a transition in the visible region of a low-spin cobalt(III) in octahedral geometry, obscuring the transitions of the divalent metal ions [47, 51, 53, 54]. Bands from cobalt (II) are Laporte forbidden transitions and are assumed to be too weak to be visible. In addition to these low-energy d-d transition bands, low energy absorption band at 396 nm was observed in the electronic spectra of the complex, which may be assigned as ligand-to-metal charge transfer transitions [51, 52]. Moreover, high energy absorption band at 273 nm was observed in the electronic spectra of the complexes, which may be recognized as intra-ligand π-π*/n-π* transitions [51, 52]

IV.4. Concluding remarks

In conclusion, the synthetic stratagem and structural characterization of a new ionic cobalt (III/II) complex has been discussed. The structure of the complex was confirmed by the single crystal X-ray diffraction technique. The complex exhibits a combination of strong $CH_3\cdots\pi$ and H-bonding interactions in the solid state that have been rationalized using MEP surface analysis. The energies associated with the interactions have been computed using DFT calculations and further corroborated with the NCI plot index computational tool.

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Chapter V

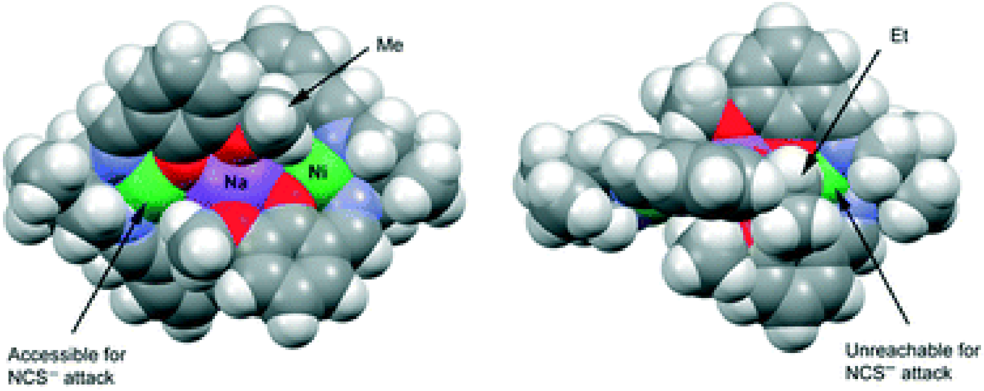
Synthesis and characterization of two dinuclear ferromagnetic nickel (II) complexes with isomeric Schiff bases and their magnetic studies

"The only one who can tell you 'you can't win is you and you don't have to listen"

-Jessica Ennis Hill

Chapter V

Synthesis and characterization of two dinuclear ferromagnetic nickel (II) complexes with isomeric Schiff bases and their magnetic studies



Chapter V

Synthesis and characterization of two dinuclear ferromagnetic nickel (II) complexes with isomeric Schiff bases and their magnetic studies

V.1. Introduction

The study of dinuclear coordination complexes of 3d metal ions has attained special interest for the last two decades due to their importance to bioinorganic chemistry and magnetochemistry.[1] The key aspect of molecular magnetism is understanding the mechanism of spin coupling and determination of magneto-structural correlations.[2] This can be done by studying discrete molecules, and large clusters or extended systems to obtain molecule-based magnetic materials.[3] The magnetic interactions in such complexes mainly occur due to super exchange coupling between the metal centers via bridging ligands, and the strength and nature of this interaction, whether ferromagnetic or antiferromagnetic, depend on the bridging moiety and its subtended angle.[4] Coordination complexes based on the nickel(II) ion could have potential applications in molecularbased ferromagnets, such as single molecule magnets (SMMs) and single chain magnets (SCMs), and these are used as data storage devices, nanoscale tools, and quantum computing systems.[5] Nickel(II) is a preferred spin carrier to prepare molecular ferromagnets due to its large single-ion zero-field splitting.[6] In this regard, tridentate N_2O donor Schiff base ligands obtained from diamines and salicylaldehyde derivatives are widely used for synthesizing oxido or phenoxido bridged nickel(II) complexes along with various bridging anionic coligands such as azide, thiocyanate, cyanate, etc.[7] However, dinuclear nickel(II) complexes with two dissimilar bridges of azide and phenoxido ligands are still relatively less explored.[8] Herein, the report that replacement of the Cu sites in $[(H_2O)Cu(L^1)(\mu_{1,1}\text{-}N_3)Cu(L^1)]ClO_4$ with Ni results in an isostructural complex $[(H_2O)Ni(N_3)(L^3)(\mu_{1,1}\text{-}N_3)Ni(L^3)]$ (**4**) that exhibits ferromagnetic coupling. It has been also replaced the HL^3 by a blocking ligand HL^4 to prepare $[(H_2O)Ni(N_3)(L^4)(\mu_{1,1}\text{-}N_3)Ni(L^4)]\cdot MeOH$ (**5**) to check its effect on the overall magnetic behaviour. Density functional theory (DFT) combined with the broken symmetry approach has also been reported to provide a qualitative theoretical interpretation on the overall magnetic behavior of complexes **4** and **5**.

V.1.1. Experimental section

All other chemicals were of reagent grade and used as purchased from Sigma-Aldrich without further purification.

Caution!! Although no problems were encountered in this work, organic ligands in the presence of azides are potentially explosive. Only a small amount of the material should be prepared and they should be handled with care.

V.1.2. Synthesis of complex $[(H_2O)Ni(N_3)(L^3)(\mu_{1,1}\text{-}N_3)Ni(L^3)]$ (4)

A methanol solution (10 mL) of 3-ethoxysalicylaldehyde (1 mmol, 0.166 g) and N-ethyl-1, 2-diaminoethane (1 mmol, 0.105 mL) was refluxed for 1 h to prepare a tetradentate N_2O_2 donor Schiff base, HL^3. The Schiff base was not isolated and was used directly for preparation of the complex. A methanol solution (10 mL) of nickel (II) acetate tetrahydrate (1 mmol, 0.250 g) was added to the methanol solution of the Schiff base followed by the addition of a methanol solution (5 mL) of sodium azide (1 mmol, 0.65 g) with constant stirring. The stirring was continued for 2h. Diffraction quality single crystals were obtained after a few days upon slow evaporation of a dark green solution of the compound in an open atmosphere.

Yield: 248 mg (72%). Anal. Calc. for $C_{26}H_{40}N_{10}Ni_2O_5$ (FW = 690.06): C, 45.25; H, 5.84; N, 20.30%. Found: C, 45.4; H, 5.6; N, 20.5%. FT-IR (KBr, cm−1): 1638 ($\nu_{C=N}$); 2064 (ν_{N3}); 3258 (ν_{NH2}). UV-VIS [λ_{max} (nm)] [εmax (L mol^{-1} cm^{-1})] (acetonitrile): 244 (1.73×10^4); 304 (4.76×10^3); 405 (1.14×10^3).

V.1.3. Synthesis of complex $[(H_2O)Ni(N_3)(L^4)(\mu_{1,1}-N_3)Ni(L^4)]\cdot MeOH$ (5)

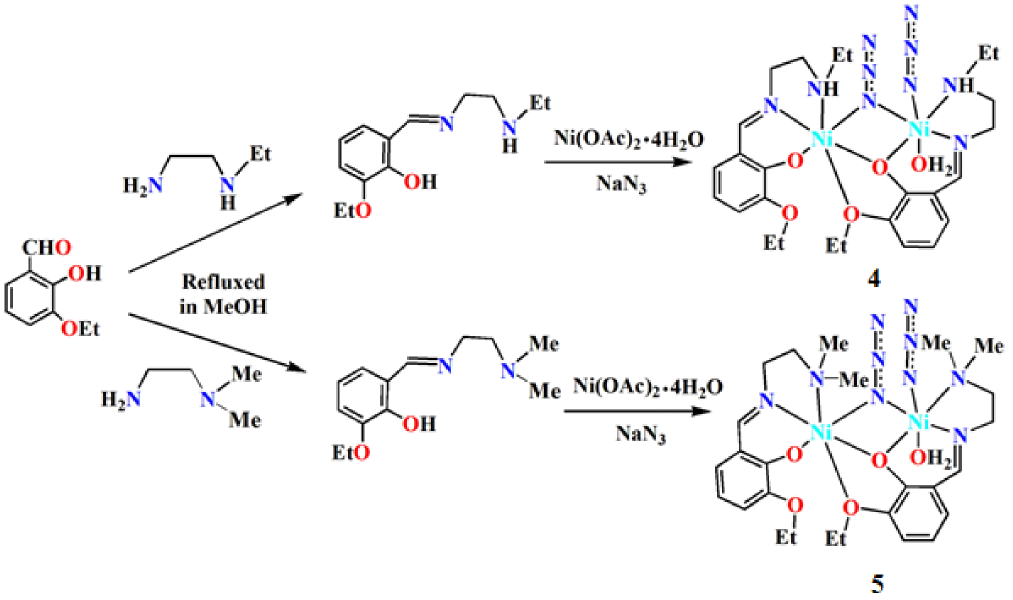
Complex **5** was prepared in similar method as that of complex **4**, except that N,N´-dimethyl-1,2-diaminoethane (1 mmol, 0.10 mL) was used instead of N-ethyl-1,2-diaminoethane. Single crystals, suitable for X-ray diffraction, were obtained on slow evaporation of the solution after 5 days.

Yield: 245 mg (68 %). Anal. Calc. for $C_{27}H_{44}N_{10}Ni_2O_6$ (FW = 722.10): C, 44.91; H, 6.14; N, 19.40%. Found: C, 44.7; H, 6.4; N, 19.2%. FT-IR (KBr, cm^{-1}): 1627 ($\nu_{C=N}$); 2061 (ν_{N3}); 3051, 3267 (ν_{NH2}); 3446 (ν_{OH}). UV-VIS [λ_{max} (nm)] [ε_{max} ($Lmol^{-1}cm^{-1}$)] (acetonitrile): 246 (1.73×10^4); 303 (5.4×10^3); 405 (1.4×10^2).

V.2. Results and discussion

V.2.1. Synthesis

The potential tetradentate Schiff base ligands HL^3 and HL^4 were prepared by the condensations of N-ethyl-1, 2-diaminoethane and N, N′-dimethyl-1, 2-diaminoethane with 3-ethoxysalicylaldehyde following a literature method.[25a] Methanol solutions of the Schiff base ligands, thus prepared, were added to methanol solutions of nickel(II) acetate tetrahydrate, and stirred for 2 h followed by the addition of sodium azide under constant stirring conditions for 2 h to produce complexes **4** and **5**. Formation of both complexes is shown in **Scheme V.1.** The phenoxido group has been known to have a tendency to bridge two or more metal centres for a long time.[25b] It is therefore used ‘salen’ or ‘half salen’ type ligands to prepare many di- and polynuclear complexes of different transition metals for the last decades.[25d–g] Pseudo-halides, e.g. azide, thiocyanate, cyanate, etc., also have the ability to bridge metal centres thereby producing multimetallic complexes.[25c,h,i] In the present study, it has been used two potential tetradentate (isomeric) half-salen type Schiff base ligands and the azide co-ligand to prepare two dinuclear nickel(II) complexes. In each complex, one Schiff base molecule shows a tetradentate coordination mode (where the amine, imine, phenoxido and alkoxy groups participate in coordination) and another molecule of the Schiff base shows a tridentate coordination mode (keeping the alkoxy part pendant). Similarly, one azide is used to bridge two nickel (II) centers and another azide acts as a terminal ligand [vide infra]. This synthetic procedure may be extended in the future to prepare a series of mixed bridged dinuclear nickel (II) complexes.



Scheme V.1. Synthetic route to complexes **4** and **5**.

V.2.2. Description of Structure

[$(H_2O)Ni(N_3)(L^3)(\mu_{1,1}-N_3)Ni(L^3)$] (4) Single crystal X-ray diffraction analysis reveals that complex **4** crystallizes in the orthorhombic space group $P2_12_12_1$ with Z = 4. The molecular structure is built from isolated dinuclear molecules of [(H_2O) $Ni(N_3)(L^3)(\mu_{1,1}-N_3)Ni(L^3)$], in which both nickel(II) centers are hexacoordinated. A perspective view of the complex is shown in **Fig.V.1.a** The dinuclear complex contains two deprotonated Schiff bases, one acting as a tetradentate ligand and the other as a tridentate one. Ni(1) has a distorted octahedral geometry, in which an amine nitrogen atom, N(22), one imine nitrogen atom, N(19), one phenoxido oxygen atom, O(11), of a Schiff base ligand and one nitrogen atom, N(1), of a bridged azide constitute the equatorial plane. One oxygen atom, O (1), of a water molecule and a nitrogen atom, N(4), of a terminal azide coordinate in the axial positions to complete the distorted octahedral geometry. The deviations of the coordinating atoms, N(1), O(11), N(19) and N(22), in the basal plane from their least-squares mean plane are −0.041(1), 0.051(1), −0.050(2), and 0.040(1) Å, respectively. The deviation of Ni (1) from the same plane is 0.068(2) Å.

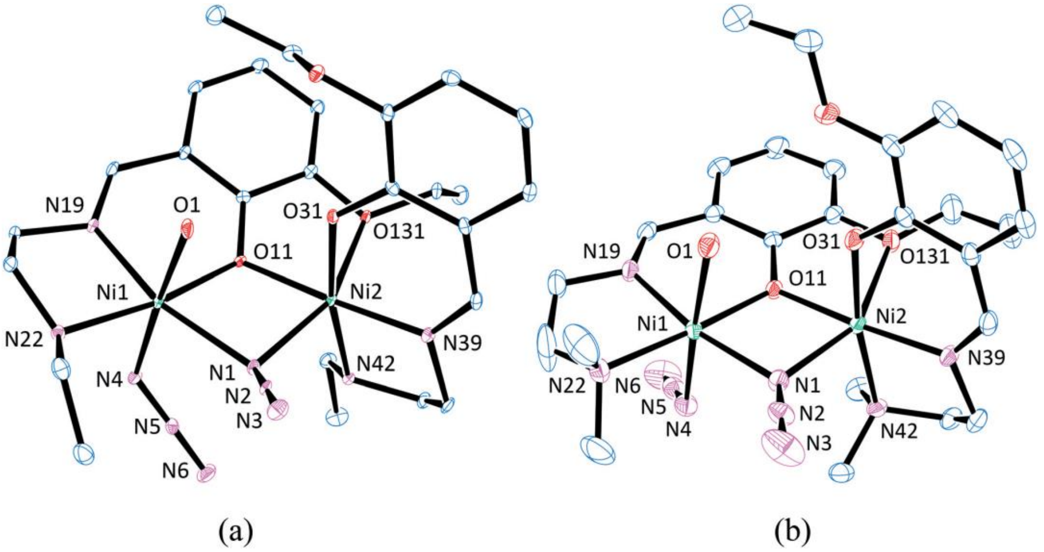


Fig.V.1. ORTEP views of complexes (a) **4** and (b) **5** with 30% thermal ellipsoid probability. Hydrogen atoms have been omitted for clarity. The lattice methanol molecule in **5** has also not been shown.

Similarly, Ni(2) also has a distorted octahedral geometry, where an imine nitrogen atom, N(39), of one Schiff base ligand, one phenoxido oxygen atom, O(11), one ethoxy oxygen atom, O(131), of the other Schiff base ligand and a nitrogen atom, N(1), from a bridging azide constitute the equatorial plane. One phenoxido oxygen atom, O (31), and an amine nitrogen atom, N(42), of one Schiff base ligand coordinate in the axial positions to complete the coordination. The deviations of the coordinating atoms, O(11), O(131), N(1) and N(39), in the basal plane from the mean plane passing through them are −0.011(2), 0.009(1), 0.009(1), and −0.007(1) Å, respectively. The deviation of Ni(2) from the same plane is 0.011(2) Å. The equatorial planes from the two metal centers intersect at an angle of 18.2(1)°.Selected bond lengths and bond angles are listed in **Tables V.4.** and **V.5.** respectively.

A nitrogen atom, N(1), of an azide ligand and a phenoxido oxygen atom, O(11), of a Schiff base ligand bridge two nickel(II) centers. The bridging angles Ni(1)–O(11)–Ni(2) and Ni(1)–N(1)–Ni(2) are 103.06(10)° and 94.82(11)° respectively. The distance between nickel(II) centers is 3.165(4) Å. Saturated five membered chelate rings [Ni(1)–N(19)–C(20)–C(21)–N(22)] and [Ni(2)–N(39)–C(40)–C(41)–N(42)] have envelope and half-chair conformations with puckering parameters q = 0.454(3) Å; ϕ = 106.5(3)° and q = 0.427(3) Å; ϕ= 90.7(3)° respectively.[26]

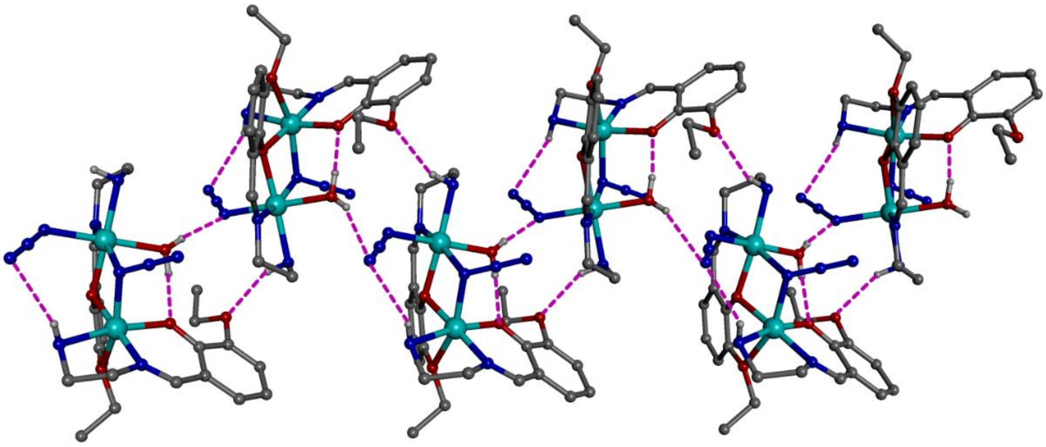


Fig.V.2. One-dimensional hydrogen bonded chain structure of complex **5**. Selected hydrogen atoms and ethyl group have been omitted for clarity.

The hydrogen atom, H(22), attached to the nitrogen atom,N(22), participates in hydrogen bonding interaction with the symmetry-related oxygen atom, O(331)[c] {symmetry transformation c = 1/2 + x, 3/2 − y,−z} (**Table V.6.**) The hydrogen atom, H(42), attached to the nitrogen atom, N(42), also participates in an intramolecular hydrogen bonding interaction with nitrogen atom N(6). Similarly, hydrogen atoms, H(1) and H(2), attached to the oxygen atom, O(1), participate in strong hydrogen bonding interaction with the oxygen atom, O(31), and symmetry-related nitrogen atom, N(4)[a] {symmetry transformation a = −1/2 + x, 3/2 − y,−z} (**Table V.6.**) All these hydrogen bonding interactions lead to the formation of a supramolecular chain **(Fig.V.2.)**

[$(H_2O)Ni(N_3)(L^2)(\mu_{1,1}$-$N_3)Ni(L^4)$]·MeOH (5). Complex **5** shows a similar dinuclear molecular structure to complex **1** but crystallizes in the monoclinic space group $P2_1/n$ with Z=4. The structure of [$(H_2O)Ni(N_3)(L^4)(\mu_{1,1}$-$N_3)Ni(L^4)$] also contains two hexacoordinated nickel(II) centers. A perspective view of complex **5** is shown in **Fig.V.1.b** It also contains two deprotonaed Schiff bases, one acting as a tetradentate ligand and the other as a tridentate one. Ni(1) adopts a distorted octahedral geometry, where an imine nitrogen atom N(19), an amine nitrogen atom, N(22), of one Schiff base ligand, one phenoxido oxygen atom, O(11), and a nitrogen atom, N(1), from a bridging azide constitute the equatorial plane. An oxygen atom of a water molecule, O(1), and a terminal azide nitrogen atom, N(4), coordinate in the axial positions to complete the distorted octahedron. The deviations of the coordinating atoms, N(1), O(11), N(19) and N(22), in the basal plane from the mean plane passing through them are −0.041(1), 0.049(1), −0.047(1), and 0.039(1) Å, respectively.

Thus the structure of **5** is basically the same as that found in complex **4**, although as is apparent from **Table V.2.** there are significant differences in the dimensions between the two structures. For example the Ni(2)-O(131) bond length is much longer in 5 at 2.472(2) Å, than in **4** at 2.238(2) Å but there is no obvious explanation for the differences.

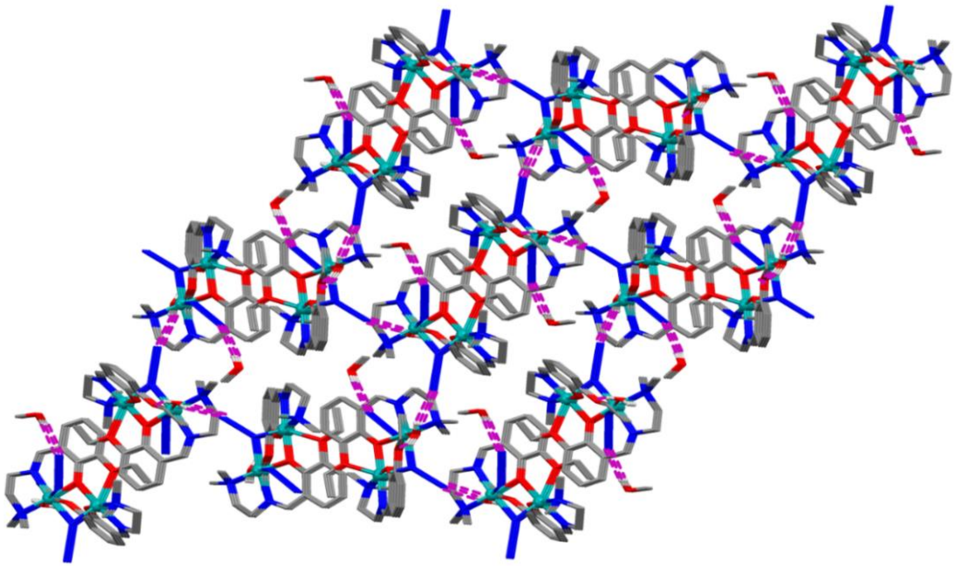


Fig.V.3. 3D supramolecular assembly via hydrogen bonding interactions in complex **5**. Selected hydrogen atoms have been omitted for clarity.

The water hydrogen atoms, H(1) and H(2), attached to O(1), participate in an intermolecular hydrogen bond with the terminal azide N(3)^c (^{c} =1/2-x,-1/2+y,1/2-z) and a strong intramolecular hydrogen bond with O(31). In addition, although their hydrogen atoms were not located, it seems clear that all three alternative oxygen positions for the disordered methanol solvent molecule form intermolecular hydrogen bonds with the terminal azide. All these hydrogen bonding interactions lead to the formation of a 3D supramolecular architecture **(Fig.V.3.)**

V.3. IR and electronic spectra

In the IR spectra of both complexes, distinct bands corresponding to the azomethine (C=N) stretching vibration appear around 1640 cm^{-1}.[27] Distinct bands around 2065 cm^{-1} is indicative of the presence of EO azido group in both the complexes.[28] The bands in the range of 2974-2878 cm^{-1} may be assigned to alkyl C-H bond stretching vibrations.[29] A moderately strong, sharp peak around 3251 cm^{-1}, may be attributed to the N–H stretching vibration.[30] Broad bands around 3450 cm^{-1} clearly indicate the presence of water molecule in the complex.[31]

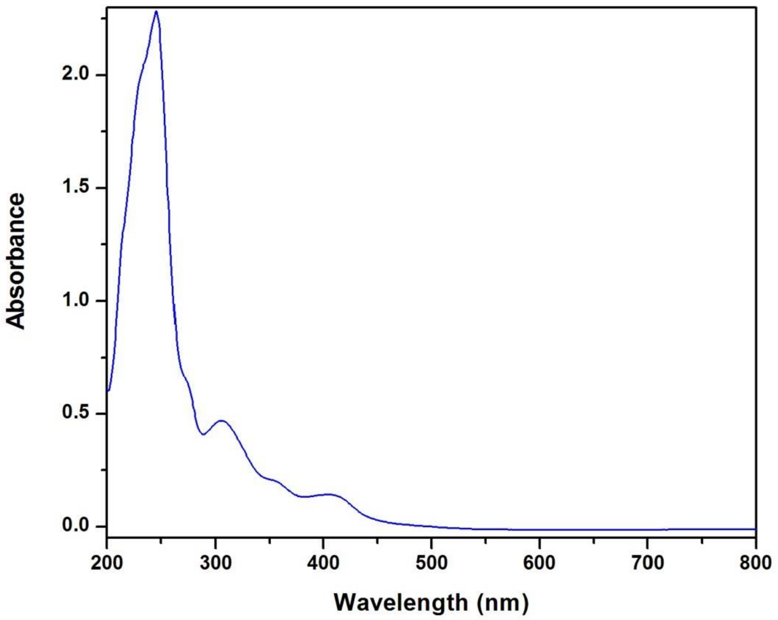


Fig.V.4. Electronic spectrum of complex **4**

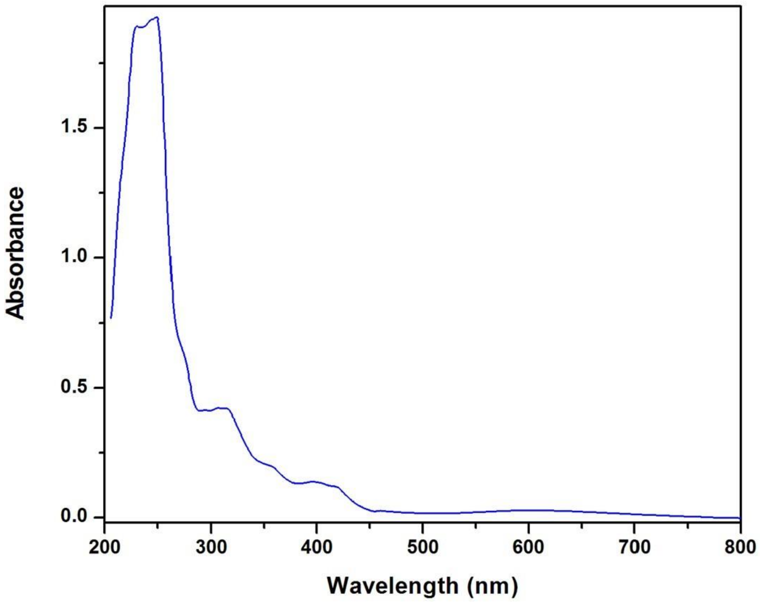


Fig.V.5. Electronic spectrum of complex **5**.

Electronic spectra of both complexes in acetonitrile display absorption bands around 405 nm.[32] Absorption bands around 305 nm are also observed and may be attributed to ligand to metal charge transfer transitions.[33] The intense absorption bands at wavelength 245 nm may be assigned as $\pi \rightarrow \pi^*$ transitions.[34] The electronic spectra of complexes **4** and **5** are shown in **Fig.V.4. and Fig.V.5.** respectively.

V.4. Hirshfeld surfaces analysis

Hirshfeld surfaces of both complexes, mapped over d_{norm} (range of -0.1 to 2.5 Å), shape index and curvedness, are illustrated in **Fig.V.6.** The fingerprint plots can be decomposed to highlight particular atoms pair close contacts. This decomposition enables separation of contributions from different interaction types, which overlap in the full fingerprint. The proportions of O···H and H···O interactions comprise 3.5% and 5.3% of the Hirshfeld surfaces for each molecule of complexes **4** and **5**, respectively. The C···H/H···C {12.9% (**1**) and 13.6% (**2**)} and N···H and H···N {21.4% (**1**) and 13.6% (**2**)} interactions also contribute to the overall Hirshfeld surfaces of both complexes **(Fig.V.7.)**

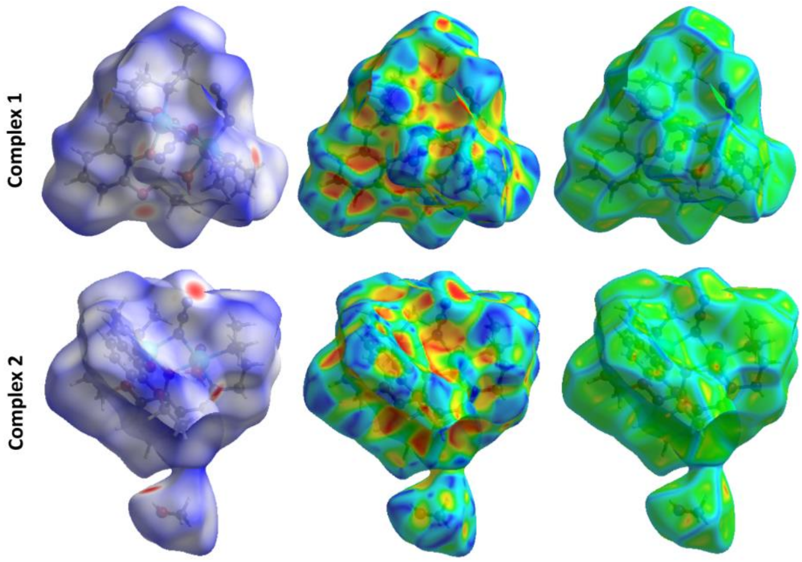


Fig.V.6. Hirshfeld surfaces mapped with dnorm (left), shape index (middle), curvedness (right bottom) for complexes **4** (above) and **5** (below).

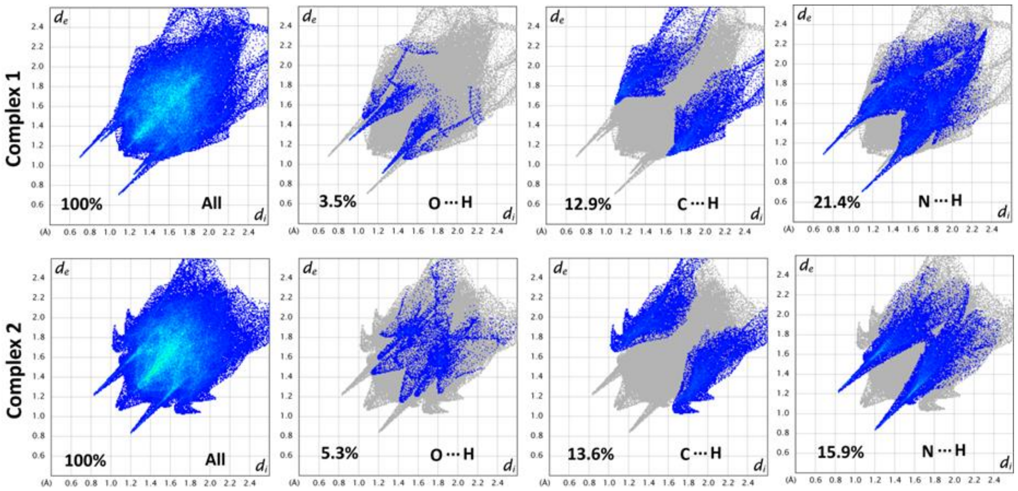


Fig.V.7. 2D fingerprint plots: Full; O···H/H···O, C···H/H···C and N···H/H···N interactions contributed to the total Hirshfeld surface area of complexes **4** (above) and **5** (below).

V.5. X-ray powder diffraction pattern

The experimental powder x-ray diffraction pattern of the bulk product agrees well with the simulated XRD pattern generated from cif. This indicates purity of the bulk samples **Fig.V.10.** shows the experimental and simulated XRD patterns for complexes **4** and **5**, respectively.

V.5.1. Magnetic properties of complex 4

The temperature dependence of both the molar magnetic susceptibility (χ_M) and the product of the molar magnetic susceptibility and the temperature ($\chi_M T$) of **4** is shown in **Fig.V.8.** The χ_M value increases continuously on cooling, as usually occurs for a paramagnetic compound. The value of the $\chi_M T$ product at room temperature is 2.68 cm^3 K mol^{-1}, which is slightly larger than the spin-only value (2.35 cm^3 K mol^{-1}) expected for a system with two isolated S = 1 ions assuming g = 2.17 (see below). An increase of the $\chi_M T$ product, which suggests the existence of predominant ferromagnetic interactions, is observed upon cooling. As a result, the $\chi_M T$ product reaches a maximum value of 4.26 cm^3 K mol^{-1} at 5.7 K. Further cooling of the sample, leads to a decrease of the $\chi_M T$ value, which is 3.44 cm^3 K mol^{-1} at 2.0 K. This decrease is probably due to existence of a zero-field splitting (D) which is typical of these type of Ni (II) complexes, and/or antiferromagnetic interactions. This behavior is similar to that found in other µ- phenoxido–$\mu_{1,1}$-azide dinickel(II) complexes.[8]

Experimental magnetic susceptibility data have been fitted using a modification of the model described by Prushan *et al.*[35] This model considers the existence of intramolecular interactions (J), and zero-field splitting (D) of the Ni(II) ions by applying the following Hamiltonian :

$$H = [-2J\hat{S}_1\hat{S}_2] + D[M_S^2 - \frac{1}{3}S(S+1)] \quad (1)$$

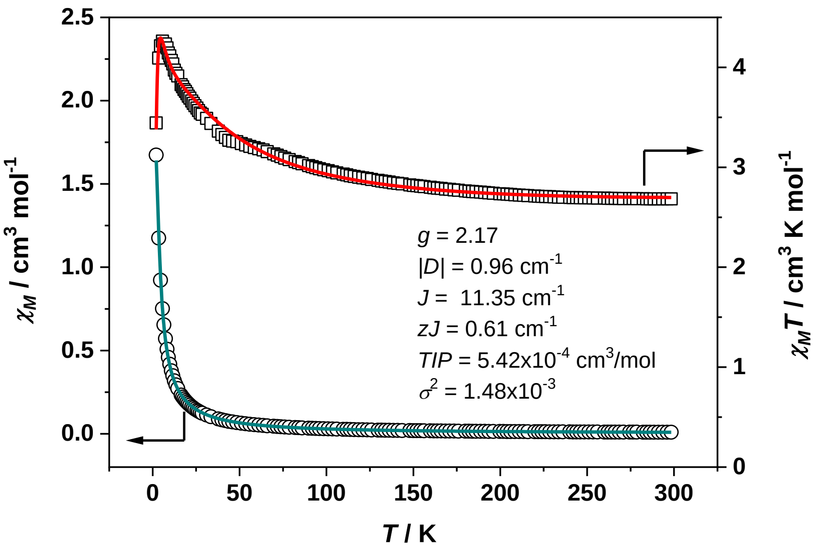


Fig.V.8. Temperature dependence of the molar susceptibility χ_M (circles) and χMT (squares) for complex **4**. Solid lines show the best fit to the data as described in the text.

Because the sign of D cannot be unequivocally determined from magnetization measurements of powder samples, the absolute value of this zero-field splitting parameter has been considered in the equation. A Temperature-Independent Paramagnetism (TIP) term is also included in this model. In addition, intermolecular interactions (*zJ*) have been also considered using the molecular field approximation.[36] Thus, the parameters obtained from the best fit of the magnetic data are $g = 2.17$, $|D| = 0.96$ cm^{-1}, $J = 11.35$ cm^{-1}, $zJ = 0.61$ cm^{-1}, TIP = 5.42×10^{-4} cm$^3\cdot$mol^{-1} with $\sigma^2 = 1.48\times10^{-3}$. **Fig.V.8.** shows the fit of the experimental data using this model. Comparable g[8, 35] and D[8b, 8g, 37, 38] values have been obtained for similar dinickel (II) complexes.

The small *zJ* value obtained in the fit of the data (0.61 cm^{-1}) indicates weak ferromagnetic intermolecular interactions. In spite of this small value, it has been necessary to include this parameter in the model in order to obtain good quality fit results. These interactions may take place through the hydrogen bonds that form the 1D supramolecular assembly, as shown in **Fig.V.2.** This kind of magnetic interaction through hydrogen bonds has been previously reported.[39]

V.5.2. Magnetic properties of complex 5

Fig.V.9. shows the variation with the temperature of the molar magnetic susceptibility (χ_M) and the product of the molar magnetic susceptibility and the temperature ($\chi_M T$) of **2**. There is a continuous increase of the χ_M value on decreasing temperature, showing the usual paramagnetic behaviour. The room temperature value of $\chi_M T$ (2.90 cm^3 K mol^{-1}), is slightly higher than the spin-only value (2.67 cm^3 K mol^{-1}) expected for a g = 2.31 system with two isolated S = 1 Ni (II) ions (see below).

The magnetic behaviour of this compound is analogous to that observed in complex **4**. Predominant ferromagnetic interactions are deduced due to the increase on cooling observed in the $\chi_M T$ value, which reaches a maximum value of 5.04 cm^3 K mol^{-1} at 7.5 K and then falls to a value of 3.45 cm^3 K mol^{-1} at 2.0 K caused by antiferromagnetic interactions and/or the presence of a zero-field splitting (*D*). Therefore, the magnetic data were fitted using the same model used for complex **4**. Applying this model, the best fit of the experimental data yielded the following results (**Fig.V.9.**); g = 2.31, $|D|$ = 1.26 cm^{-1}, J = 13.24 cm^{-1}, zJ = 0.84 cm^{-1}, TIP = 1.54×10^{-13} cm^3·mol^{-1} with σ^2 = 2.03×10^{-3}. The TIP value is negligible for this compound. Indeed, the fitting of the data without considering this parameter yields almost the same results (g = 2.30, $|D|$ = 1.28 cm^{-1}, J = 13.60 cm^{-1}, zJ = 0.85 cm^{-1}, σ^2 = 2.00×10^{-3}). The values of D[8b, 8g, 38] and g[8,35] are comparable to those observed in similar Ni(II) complexes. . The differences found in the coordination environments of the Ni(II) centres between complexes **4** and **5**, like the Ni(2)-O(131) bond length (mentioned above in the “Structure description” section) can explain the small variations in their values of g and D.

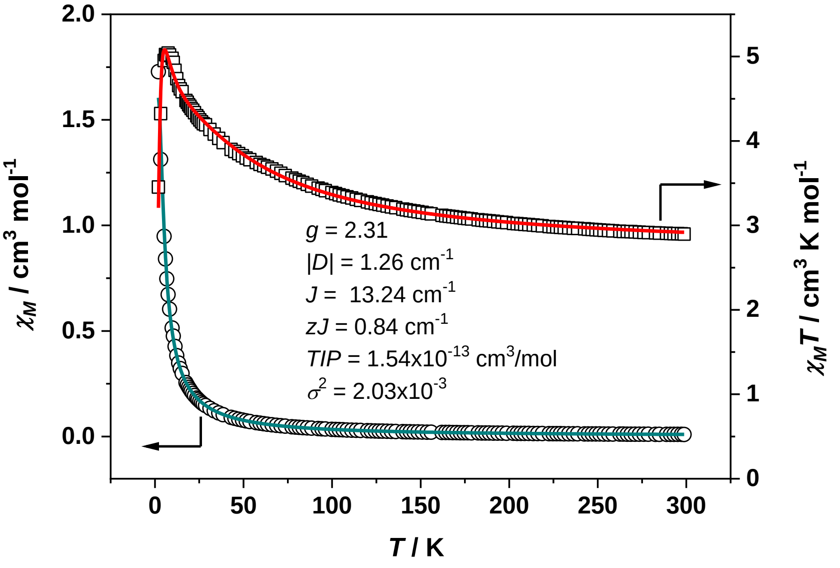


Fig.V.9. Temperature dependence of the molar susceptibility χ_M (circles) and χMT (squares) for complex **5**. Solid lines show the best fit to the data as described in the text.

Slight ferromagnetic intermolecular interactions are present in complex **5** as indicated by the low zJ value (0.84 cm^{-1}) obtained in the fit of the experimental data. Similarly to compound **4**, they may occur through the hydrogen bonds that form the 3D supramolecular structure shown in **Fig.V.3.**

V.5.3. Magneto-structural correlation

The J value of complex **4** is 11.35 cm^{-1}. Similar positive J values (2.8-25.6 cm^{-1}), indicating the existence of intramolecular ferromagnetic interactions between the two Ni(II) ions, have been obtained from the fit of the magnetic data of analogous heterobridged μ-phenoxido–$\mu_{1,1}$-azide dinickel(II) complexes.[8f] It has been described in the literature that the magnitude of J value in these compounds depends on different structural parameters such as the Ni-O-Ni and Ni-N-Ni angles, the Ni-O and Ni-N distances and the asymmetry of the two Ni-N bond lengths.[8d,8f] The high number of parameters that affect to the exchange coupling constant make it very difficult to predict the value of J only according to these structural parameters. However the comparison with analogous complexes with similar parameters is possible. For example, compounds $[Ni(L^3)_2(\mu_{1,1}-N_3)(N_3)]$[37] and $[Ni(L^4)_2(\mu_{1,1}-N_3)(N_3)(H_2O)]$[38] where L^3 and L^4 are Schiff base ligands, show very similar structural parameters to the title compounds, apart from the asymmetry in Ni-N bond lengths **(Table V.1.)** There is a difference of 0.028 Å between the two Ni-N bond lengths and a coupling constant of 15.6 cm-1 in the former compound, while the J in the latter is 5.84 cm^{-1}, for difference of 0.113 Å.

This is in accordance with the observed trend of stronger ferromagnetic interactions in compounds with two almost equal Ni-N distances.[8d,e] This difference in compound **4** is intermediate between these two extremes at 0.072 Å, which is consistent with a ferromagnetic interaction of intermediate strength (J = 11.35 cm^{-1}).

The J value of 13.24 cm^{-1} obtained for complex **5** is comparable with values observed in complexes with analogous structural parameters: $[Ni(L^3)_2(\mu_{1,1}-N_3)(N_3)]$ (J = 15.6 cm-1);35 $[Ni^{II}_2(L^3)_2(\mu_{1,1}-N_3)(CH_3CN)(H_2O)](ClO_4)\ H_2O\cdot CH_3CN$ (J = 16.9 cm-1)[;8d] and $[Ni^{II}_2(L^4)_2(\mu_{1,1}-N_3)(CH_3CN)(CH_3OH)](ClO_4)\cdot CH_3CN$ (J = 18.0 cm-1)[8f] where L^1, L^3, and L^4 are Schiff base ligands (**Table V.1.**) The difference between Ni-N bond lengths shown by these compounds is in the range 0.010-0.028 Å, but complex **5** exhibits two almost identical Ni-N distances. Their J values however do not exhibit the usual tendency for higher ferromagnetic coupling constants to be found in complexes with no Ni-N difference.[8d, e] However, it is obvious that other structural parameters also influence the magnitude of the ferromagnetic interaction, although the differences between those parameters in complex **5** and in the previously cited complexes do not seem very significant.[8, 37]

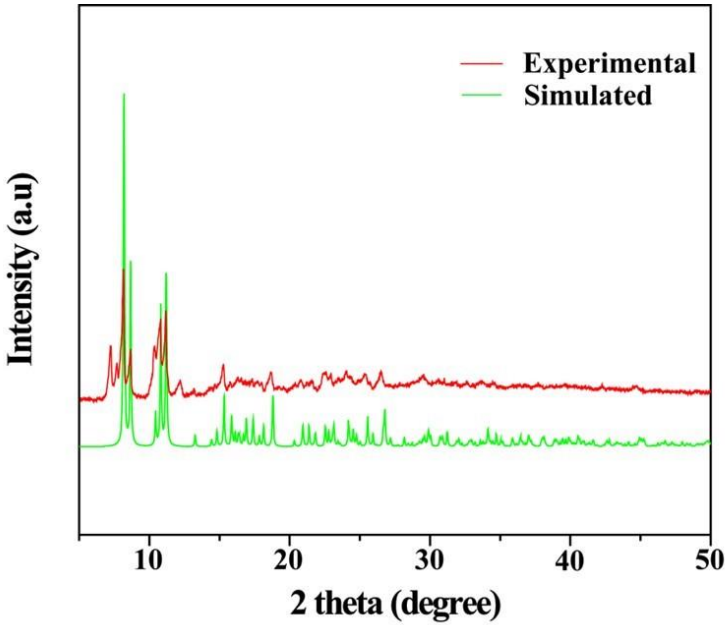


Fig.V.10. Experimental and simulated powder XRD patterns of complex **4** confirming the purity of the bulk material.

Table.V.1. Experimental magnetic coupling constant (Jexp) and structural parameters of **4, 5** and selected analogous μ- phenoxido–$\mu_{1,1}$-azide dinickel(II) complexes.

Complex	**Jexp[cm^{-1}]**	**Ni-O-Ni [°]**	**Ni-N-Ni [°]**	**Ni-O [Å]**	**Ni-N [Å]**	**Asymmetry Ni-N [Å]**	**Ref.**
1	11.35	103.1(1)	94.8(1)	2.037(2), 2.005(2)	2.185(3), 2.113(3)	0.072	This work
[Ni(L^1)$_2$(N_3)(N_3)]	15.60	102.67(6)	93.94(7)	2.013(1), 2.008(1)	2.161(2), 2.133(2)	0.028	37
[Ni(L^2)$_2$(N_3)(N_3)(H_2O)]	5.84	102.30(7)	95.43(9)	2.037(2), 2.052(1)	2.095(2), 2.208(2)	0.113	38
2	13.24	103.44 (8)	95.9(1)	2.003(2), 1.984(2)	2.105(2), 2.110(2)	0.003	This work
[Ni_2(L^3)$_2$(N_3)(CH_3CN)(H_2O)]	16.9	104.68(9)	97.02(11)	1.994(2),	2.125(3),	0.010	8d
(ClO_4) $H_2O \cdot CH_3CN$							

$Ni_2(L^4)_2(N_3)(CH_3CN)(CH_3OH)]$	18.0	104.55(12)	97.58(15)	2.004(3) 2.000(3)	2.119(3), 2.091(4)	0.028	8f
$(ClO_4)\cdot CH_3CN$							

L^1, L^2, L^3 and L^4 are the Schiff base ligands indicated in the correspondent reference.

V.6. DFT study

To better understand the magnetic behavior of the complexes, obtained the *J* values of complexes **4** and **5** theoretically, which are in good agreement with the experimental results and confirm the ferromagnetic nature of the intramolecular couplings. They are 11.70 cm^{-1} for **4** and 20.57 cm^{-1} for **5**, which are in acceptable agreement with the experimental finding (11.35 and 13.24 cm^{-1} for **4** and **5**, respectively). Since the theoretical *J* value for compound **5** seems overestimated, it is also computed it using a higher level of theory (B3LYP/def2-TZVP instead of B3LYP/6-31+G*) but the resulting *J* value (20.36 cm^{-1}) remains a poor fit to the experimental value of 13.24 cm^{-1}.

It has been previously demonstrated[8] that, in mixed bridged (μ-oxo, $\mu_{1,1}$-azido) dinuclear Ni(II) complexes, antiferromagnetic exchange takes place through the phenoxido bridge and ferromagnetic through the $\mu_{1,1}$-azido bridge. The competitive interaction in this type of complex reduces the overall magnetic coupling. The low experimental values of J in compounds **4** and **5** suggest the existence of this compensating effect. To further corroborate this explanation, the J was determined in compound **4** using a theoretical complex where the bridging azido ligand has been eliminated and the rest of the geometry kept frozen. As a result, the magnetic coupling changes to antiferromagnetic $J = -5.70\ \mathrm{cm}^{-1}$ thus evidencing that the ferromagnetic exchange occurs via the $\mu_{1,1}$-azido bridge.

To examine the magnetic coupling mechanism, the spin density distribution has been analyzed in both complexes **4** and **5** (see **Fig.V.8.** for compound **5**). The spin density of compound **4** in the high spin (HS) state is represented in **Fig.V.8.a** and the spin density values are summarized in **Table V.2.** for both (HS) and low spin (LS) states, where positive and negative signs denote α and β spin states, respectively. The Mulliken spin population analysis (HS) indicates that a significant spin (ca. 1.33 e) is delocalized through the ligands, and the rest (2.77 e) is carried by the central nickel atoms. The spin carried by the phenoxido oxygen atom is ca. 0.08 e in the high-spin state and only 0.005 e in the broken-symmetry state of complex **4** indicating a polarization competition between the two nickel atoms with α and β spin density, respectively. The spin carried by the bridging N-atom of azide is 0.059 e for the high spin and 0.011 e in the low spin, thus showing a similar behaviour.

Table V.2. The spin densities on the selected atoms for compound **4** at the UB3LYP/6-31G* level of theory. See **Fig.V.8.** for labelling.

Atom	**Spin density (HS)**	**Spin density (LS)**
Ni(1)	1.66	–1.68
Ni(2)	1.67	1.67
O(11)	0.08	0.005
N(1)	0.06	0.011
N(4)	0.04	–0.03
N(19)	0.08	–0.07
N(22)	0.07	–0.07
O(1)	0.01	–0.01
O(31)	0.05	0.05
O(131)	0.01	0.02
N(39)	0.07	0.08
N(42)	0.07	0.07

Table V.3. Crystal data and refinement details of complexes **4** and **5**.

Complex	**4**	**5**
Formula	$C_{26}H_{40}Ni_2N_{10}O_5$	$C_{26}H_{40}N_{10}Ni_2O_5$, CH_4O
Formula Weight	690.06	722.10
Temperature (K)	150	296
Crystal System	Orthorhombic	Monoclinic
Space group	$P2_12_12_1$	$P2_1/n$
a (Å)	11.5492(4)	11.7035(3)
b (Å)	12.4240(3)	11.3841(3)
c (Å)	21.6851(6)	25.2520(7)
β (˚)	(90)	94.194(1)
Z	4	4
dcal (g cm^{-3})	1.473	1.429
μ(mm^{-1})	1.263	1.176
F(000)	1448	1520.0
Flack Parameter	0.062(13)	n/a-
Total reflection	10054	25134
Unique Reflections	5144	5786
Observe data[I>2σ(I)]	4990	4626
R(int)	0.026	0.051
R1, wR2 (all data)	0.0276, 0.0560	0.0522, 0.1102

R1, wR2 [I>2σ(I)]	0.0261, 0.0555	0.0407, 0.1053
Residual electron density e/Å3	0.319, -0.375	0.715, -0.851

CCDC NO: 2049044 (4)
CCDC NO: 2036426 (5)

Table V.4. Selected bond lengths (Å) for complexes **4** and **5**.

	4	**5**
Ni(1)-O(1)	2.094(2)	2.178(2)
Ni(1)-O(11)	2.037(2)	2.003(2)
Ni(1)-N(1)	2.185(3)	2.105(2)
Ni(1)-N(19)	2.026(3)	1.989(2)
Ni(1)-N(22)	2.113(3)	2.117(3)
Ni(1)-N(4)	2.084(3)	2.106(3)
Ni(2)-O(11)	2.005(2)	1.984(2)
Ni(2)-O(31)	2.016(3)	1.994(2)
Ni(2)-O(131)	2.238(2)	2.472(2)
Ni(2)-N(1)	2.113(3)	2.109(3)
Ni(2)-N(39)	1.995(3)	1.986(2)
Ni(2)-N(42)	2.109(3)	2.160(2)

Table V.5. Selected bond angles (^{0}) for complexes **4** and **5**.

	4	**5**
N(4)-Ni(1)-O(1)	175.02(11)	177.03(10)
N(4)-Ni(1)-O(11)	91.35(10)	89.93(10)
N(4)-Ni(1)-N(1)	91.82(11)	94.63(11)
N(4)-Ni(1)-N(19)	94.62(12)	89.93(11)
N(4)-Ni(1)-N(22)	90.11(12)	89.51(11)
O(1)-Ni(1)-O(11)	90.14(10)	87.37(8)
O(1)-Ni(1)-N(1)	83.82(11)	83.68(9)
O(1)-Ni(1)-N(4)	175.02(11)	177.03(10)
O(1)-Ni(1)-N(19)	90.17(12)	91.34(9)
O(1)-Ni(1)-N(22)	89.15(12)	93.28(10)
O(11)-Ni(1)-N(1)	78.60(9)	79.93(9)
O(11)-Ni(1)-N(19)	88.22(10)	90.79(9)
O(11)-Ni(1)-N(22)	171.14(10)	175.65(9)

N(1)-Ni(1)-N(19)	165.47(10)	169.63(10)
N(1)-Ni(1)-N(22)	110.09(11)	104.42(9)
N(19)-Ni(1)-N(22)	82.95(11)	84.90(10)
O(11)-Ni(2)-O(31)	90.48(10)	88.71(8)
O(11)-Ni(2)-O(131)	75.23(9)	71.28(7)
O(11)-Ni(2)-N(1)	81.03(10)	80.25(9)
O(11)-Ni(2)-N(39)	176.97(10)	175.42(9)
O(11)-Ni(2)-N(42)	97.40(11)	97.61(9)
O(31)-Ni(2)-O(131)	85.31(9)	84.23(8)
O(31)-Ni(2)-N(1)	95.16(11)	93.12(9)
O(31)-Ni(2)-N(39)	88.15(12)	90.28(9)
O(31)-Ni(2)-N(42)	169.91(11)	171.20(9)
O(131)-Ni(2)-N(1)	156.26(10)	151.44(8)
O(131)-Ni(2)-N(39)	101.96(10)	104.18(9)
O(131)-Ni(2)-N(42)	90.60(9)	91.98(8)
N(1)-Ni(2)-N(39)	101.77(11)	104.26(10)
N(1)-Ni(2)-N(42)	92.29(11)	93.97(10)
N(39)-Ni(2)-N(42)	83.68(12)	82.93(9)

Table V.6. Geometric parameters for H-bonding interaction for complexes **4** and **5**

Complex	D–H···A	D–H (Å)	H···A (Å)	D···A (Å)	∠D–H···A (°)
1	O(1)–H(1)···O(31)	0.84(2)	1.80(2)	2.623(3)	163(4)
	O(1)–H(2)···N(4)[a]	0.87(2)	1.92(2)	2.771(4)	166(4)
	N(22)–H(22)···O(331)[b]	0.89(2)	2.29(3)	3.114(4)	155(3)
	N(42)–H(42)···N(6)	0.83(2)	2.55(3)	3.263(5)	145(3)
2					
	O(1)–H(1)···N(3)[c]	0.83(4)	2.34(4)	3.105(5)	155(4)
	O(1)–H(2)···O(31)	0.85(4)	1.91(4)	2.720(3)	160(4)

D, donor; H, hydrogen; A, acceptor. Symmetry transformation [a]= -1/2+x, 3/2-y,-z; [b]=1/2+x,3/2-y,-z; [c] = 1/2-x,-1/2+y,1/2-z.

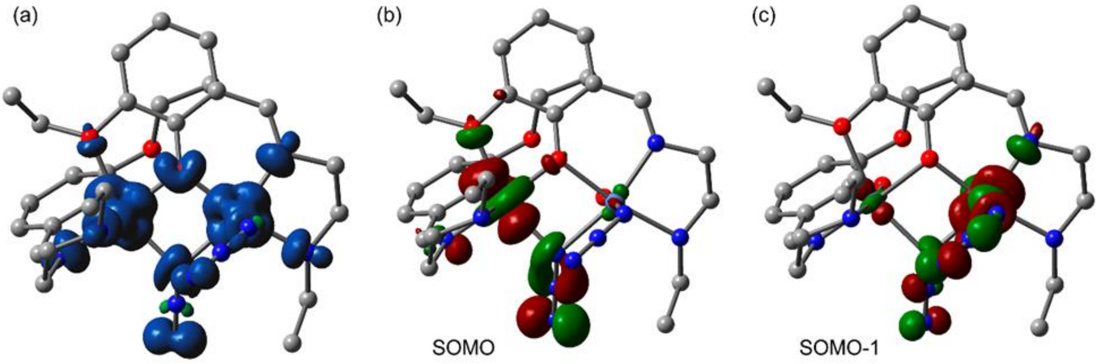


Fig.V.8. (a) Graphical representation of spin density (contour 0.004 a.u.) at the ground state (high spin) configuration. (**b** and **c**) Pictorial representation of the SOMO involving the d_{z2} and d_{x2-y2} orbitals of nickel (II) for the high spin state of complex **4**.

In octahedral Ni (II) complexes, d_{x2-y2} and d_{z2} orbitals contain the unpaired electrons. These orbitals along with the local orbitals of the bridging ligands are involved in the super-exchange pathway. This behavior is also observed in complex **5**. This is clearly evidenced by the Mulliken population analysis and the spin density plot that show the spin distributed spherically in the Ni centers due to the presence of one unpaired electron in both the d_{x2-y2} and d_{z2} orbitals. Moreover, the shape of the spin density at the bridging O-atom and azide evidences the participation of their p orbitals in the magnetic coupling. The SOMO and SOMO-1 are shown in **Fig.V.8.** as examples. The SOMO is basically constituted by the d_{z2} orbital of one nickel (II) metal center with the participation of the π-system of azide. The SOMO-1 is constituted by the d_{x2-y2} orbital of the other nickel (II) and the π-system of azide.

V.7. Conclusions

Reported here two relatively rare mixed phenoxido- and azide-bridged dinuclear nickel complexes (II). Both complexes show strong intermolecular hydrogen bonding interactions to form supramolecular chain structure in **4** and w3D network in **5**. Variable temperature (2–300 K) magnetic susceptibility measurements indicate the presence of ferromagnetic exchange coupling between copper (II) centers (J = 11.35 and 13.24 cm^{-1} for complexes **4** and **5**. The experimental findings were further checked and rationalized using the broken-symmetry DFT calculations, spin density and SOMO plots, which clearly support the presence of ferromagnetic coupling which is transmitted through the azide bridging ligand and compensates for the antiferromagnetic communication via the phen oxidobridge.

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Chapter VI

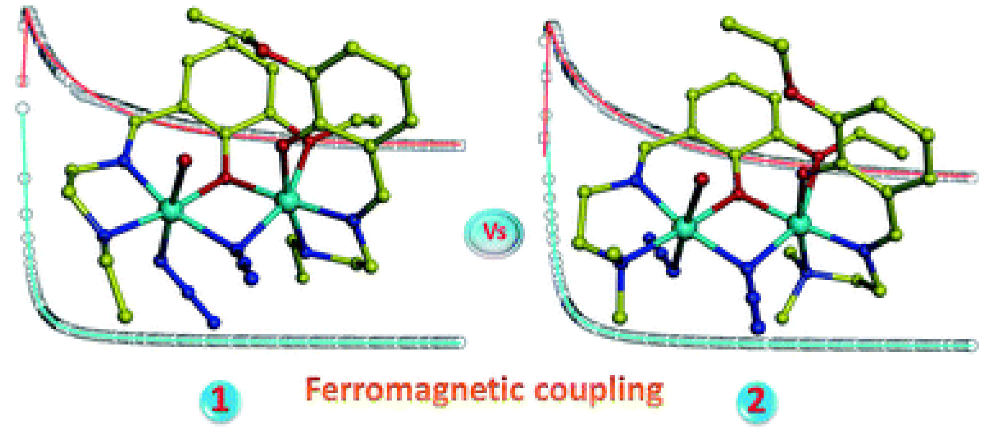
Synthesis and characterization of a series of hetero-trinuclear nickel (II)/sodium complexes

“It always seems impossible until it is done”

-Nelson Mandela

Chapter VI

Synthesis and characterization of a series of hetero-trinuclear nickel (II)/sodium complexes



Chapter VI

Synthesis and characterization of a series of hetero-trinuclear nickel (II)/sodium complexes

VI.1. Introduction

Nickel(II) may adopt tetrahedral, octahedral and square planar geometry depending on the electronic and steric effects of the ligands.[1-2] It may also have square pyramidal and trigonal bipyramidal geometries, with Addison parameter values close to zero for the former and close to one for the later.[3-5] Schiff base ligands were widely used to prepare varieties of nickel(II) complexes having different coordination numbers and different geometries.[6-9] Among various Schiff bases, salen-type ones are probably the most familiar for their easy synthetic procedure and also for their tendency to form multi-nuclear complexes as a result of the bridging ability of phenoxy oxygen atoms.[10-20] Salen type (N_2O_4 donor) compartmental Schiff bases can form multinuclear complexes more easily for having one inner (N_2O_2 donor) and one outer (O_4 donor) compartments, capable of entrapping two metal ions in two compartments.[21-26]

In the present work, two compartmental Schiff bases have been used to form four heterotrinuclear nickel(II)-sodium-nickel(II) complexes. In each complex, the central sodium ion is octa-coordinated with trigonal dodecahedral geometry. The geometry of nickel(II) is either square planar or square pyramidal. The variation of the geometry of nickel (II) may be correlated with the availability of the suitable orbital of nickel(II) towards the nucleophiles. Increase in the chain length of the alkoxy group allows it to encapsulate nickel (II) more tightly, leaving no space to be approached by the incoming nucleophiles. DFT calculations also support this proposition.

Herein, the synthesis and structures of a series of heterotrinuclear nickel(II)-sodium-nickel(II) complexes with salen type compartmental Schiff bases has been reported. The accessibility of nickel(II) in these complexes for the attack by pseudo-halides has been explained by DFT calculations using homodesmotic equation.

VI.2. Synthesis

VI.2.1. Synthesis of Schiff base ligands

VI.2.2. Synthesis of H_2L^5 [N,N-bis(3-methoxysalicylidene)-2,2-dimethylpropane-1,3-diamine] and H_2L^6 [N,N-bis(3-ethoxysalicylidene)-2,2-dimethylpropane-1,3-diamine]

A methanol solution of 2,2-dimethyl-1,3-propanediamine (102 mg, 1 mmol) was refluxed separately with 3-methoxysalicyldehyde (152 mg, 1 mmol) and 3-ethoxysalicyldehyde (166 mg, 1 mmol) in 1:2 molar ratio for ca. 1 h to prepare two N_2O_4 donor Schiff base ligands, H_2L^5 and H_2L^6 respectively.

VI.2.3. Synthesis of complexes

VI.2.3.1. Synthesis of [Ni(L^5)Na(L^5)Ni(NCS)]·H_2O (6)

10 ml methanol solution of nickel thiocyanate tetrahydrate (1 mmol, 250 mg) was added into the methanol solution of the Schiff base, **H_2L^5**, and the solution was kept stirring for 2 hr. A solution of sodium thiocyanate (1 mmol, 81mg) in methanol was added into it and the resulting solution was further stirred further for 1h more. Dark green coloured crystalline complex, suitable for X-ray diffraction, started to separate from the solution after ca. 3-4 days on standing at room temperature and was collected by filtration.

Yield: 252 mg (~52.86% based on Ni) Anal. Calc. For $C_{43}H_{50}N_5NaNi_2O_9S$ (FW = 953.31): C, 54.1; H, 5.2; N, 7.3; %. Found: C, 53.9; H, 5.1; N, 7.4%. FT-IR (KBr, cm^{-1}): 2946-2825 (ν_{C-H}), 1607 ($\nu_{C=N}$), 2052 and 2088 (ν_{NCS}); UV-Vis, [λ_{max} (nm)], [ε_{max} ($Lmol^{-1}cm^{-1}$)] (methanol) 595 (244); 353 ($5.3x10^4$); 271 ($11.8x10^4$). Magnetic moment: Diamagnetic.

VI.2.3.2. Synthesis of [Ni(L^5)Na(L^5)Ni(N_3)] (7)

10 methanol solution of nickel(II) perchlorate hexahydrate (1 mmol, 365 mg) was added into the methanol solution of the same Schiff base ligand, **H_2L^5**, with constant stirring for 2 hr and colour of the solution turned into dark green. 10 mL, methanol/water solution of sodium azide (1 mmol, 65 mg) is added to it and the resulting solution was continued further for ca.1 h. Single crystal, suitable for X-ray diffraction, were obtained after 5-6 days on slow evaporation of the solution in open atmosphere.

Yield: 275 mg (~59.90% based on Ni). Anal. Calc. for $C_{42}H_{48}N_7NaNi_2O_8$ (FW = 919.24): C, 54.8; H, 5.2; N, 10.6 %. Found: C, 54.7; H, 5.1; N, 10.7%. FT-IR (KBr, cm^{-1}) 2965-2868 (ν_{C-H}), 1604 ($\nu_{C=N}$), 2030 (ν_{N3}); UV-Vis, [λ_{max} (nm)], [ε_{max} ($Lmol^{-1}cm^{-1}$)] (methanol) 592 (140); 352 (10^3); 272 ($2.4x10^5$). Magnetic moment: Diamagnetic.

VI.2.3.3. Synthesis of $[Ni(L^6)Na(L^6)Ni]NCS\cdot CH_3OH$ (8)

It was synthesized following the similar procedure as that for complex **6** except that the Schiff base ligand, $\mathbf{H_2L^6}$, was used instead of $\mathbf{H_2L^5}$. Dark green coloured crystalline complex suitable for X-ray diffraction, started to separate from the solution after ca. 2-3 days on standing at room temperature and was collected by filtration.

Yield: 287.25 mg (~56.60% based on Ni). Anal. Calc. For $C_{48}H_{52}N_5NaNi_2O_9S$ (FW = 1023.44): C, 56.33; H, 5.91; N, 6.84 %. Found: C, 56.2; H, 5.8; N, 6.9%. FT-IR (KBr, cm^{-1}): 2950-2860 (ν_{C-H}), 1620 ($\nu_{C=N}$), 2053 (ν_{NCS}); UV-Vis, [λ_{max} (nm)], [ε_{max} ($Lmol^{-1}cm^{-1}$)] (methanol) 597 (120); 353 (10^3); 270 ($1.6x10^5$). Magnetic moment: Diamagnetic.

VI.2.3.4. Synthesis of $[Ni(L^6)Na(L^6)Ni]ClO_4$ (9)

It was synthesized following the similar procedure as that for complex **7** except that the Schiff base ligand, $\mathbf{H_2L^6}$, was used instead of $\mathbf{H_2L^5}$. Dark green coloured crystalline complex suitable for X-ray diffraction, started to separate from the solution after ca. 3-4 days on standing at room temperature and was collected by filtration.

Yield: 293.85 mg (~56.91% based on Ni). Anal. Calc. for $C_{46}H_{56}N_4NaNi_2O_{12}Cl$ (FW = 1032.77): C, 53.50; H, 5.47; N, 5.42 %. Found: C, 50.4; H, 5.3; N, 5.5 %. FT-IR (KBr, cm^{-1}2973-2865 (ν_{C-H}), 1611 ($\nu_{C=N}$); UV-Vis, [λ_{max} (nm)], [ε_{max} ($Lmol^{-1}cm^{-1}$)] (methanol) 597 (10^2); 355 ($7.6x10^3$); 269 ($20.7x10^3$); 231 ($4.5x10^4$). Magnetic moment: Diamagnetic.

VI.2.5. Results and discussion

VI.2.5.1. Synthesis and spectral characterization

The facile condensation of 2, 2-dimethyl-1, 3-propanediamine separately from 3-methoxysalicylaldehyde and 3-ethoxysalicylaldehyde (in a 1:2 molar ratio) in methanol produced two hexadentate compartmental Schiff bases, H_2L^5 and H_2L^6, respectively. Both these Schiff bases on further reaction with different nickel(I) precursors under ambient conditions produced four novel heterotrinuclear nickel(II)–sodium–nickel(II) complexes, **6**–**9**. The synthetic procedure for all the four complexes has been shown in **Scheme VI.1.** The nickel (II) centres were well surrounded by alkoxy groups in complexes **8** and **9** and therefore pseudo-halides (azide/thiocyanate) were unable to coordinate with the nickel (II) centre (vide infra).

VI.2.5.2. Description of structures

Complexes 6 and 7. X-ray crystal structure determination reveals that both these complexes crystallize in the monoclinic space group $P2_1/c$. The molecular structure of each complex is built from isolated heterotrinuclear $[(L^5Ni)Na\{L^5Ni(X)\}]$ moieties; X = thiocyanate in **6** and azide in **7**. Each complex consists of two terminal 'metalloligands' (NiL^5 and L^5NiX) and one central sodium, as shown in **Fig.VI.1.** One nickel(II) centre, Ni(1), is penta coordinated and the second nickel(II) centre, Ni(2), is tetracoordinated in each complex. The trans angles {O(2)–Ni(1)–N(1)}, {O(6)–Ni(2)–N(3)} are 171.71(4)° and 172.48(4)° in complex 6 and 153.60° and 167.20(2)° in complex **7**.

Ni(1) is a distorted square pyramid, as confirmed by its trigonality index (vide infra). The basal plane is coordinated by two imine nitrogen atoms [N(1) and N(2)] and two phenoxo oxygen atoms [O(1) and O(2)] of the deprotonated Schiff base. The apical position is coordinated by a nitrogen atom, N(5), from a thiocyanate co-ligand. The geometry of any penta-coordinated structure may be confirmed from its trigonality index, which is popularly known as the Addison parameter[39] (τ), named after A. W. Addison. The value of τ is defined as the difference between the two largest donor–metal–donor angles divided by 60; τ is 0 for the ideal square pyramid and 1 for the trigonal bipyramid. The τ value of Ni(1) is 0.221 in complex **6** and 0.041 in complex **7**, indicating that the geometry around the Ni(1) centre in complex 6 is slightly more distorted from the ideal square pyramidal geometry. The deviation of Ni(1) from the basal plane passing through O(1), O(2), N(2) and N(1) is 0.179(11) Å in complex **6** and 0.257(10) Å in complex **7**. On the other hand, Ni(2) has a slightly distorted square planar geometry and is coordinated by two imine nitrogen atoms, N(3) and N(4), and two phenoxo oxygen atoms, O(5) and O(6) of one deprotonated Schiff base ligand.

The central sodium is octa-coordinated by four phenoxy oxygen atoms and four ethoxy oxygen atoms of two deprotonated Schiff base ligands and assumes a trigonaldodecahedral geometry (**Fig.VI.2.**) The dihedral angles between the mean planes passing through [O(1)–O(2)– O(3)–O(4)] and [O(5)–O(6)–O(7)–O(8)] are 85.54(3)° (in complex **6**) and 84.35(3)° (in complex **7**), suggesting that the Schiff base ligands are almost orthogonal to one another. Na(1)– Ni(1) and Na(1)–Ni(2) distances are 3.500(2) Å and 3.571(2) Å in complex **6**, 3.612(2) Å and 3.649(2) Å are in complex **7**. The saturated six membered chelate rings, Ni(1)–N(1)–C(9)–C(10)–C(13)–N(2) and Ni(2)–N(3)–C(30)–C(31)–C(34)–N(4), have chair conformations in both complexes with puckering parameters,40 q = 0.551(7) Å; θ = 157.50IJ6)°; φ = 338.90(2) and q = 0.524(7) Å; θ = 156.50IJ7)°; φ = 178.40(2) (for complex **6**) and q = 0.533(7) Å; θ = 163.50IJ6)°; φ = 15.00(3) and q = 0.543(8) Å; θ = 145.00IJ7)°; φ = 21.50(13) (for complex **7**) respectively.

Complexes 8 and 9. X-ray crystal structure determination reveals that complexes **8** and **9** crystallize in the monoclinic space group $P2_1$/n and C2/c, respectively. The molecular structures of complexes **8** and **9** are built from isolated heterotrinuclear $[(L^6Ni)_2Na]^+$ moieties along with noncoordinating counteranions, thiocyanate in **8** and perchlorate in **9**. One lattice methanol molecule is also present in the asymmetric unit of complex **8**.

Each of the trinuclear structures of **8** and **9**, as shown in **Fig.VI.3.** respectively, contain a sodium and two nickel(II) centers in an approximately linear arrangement. The central Na^+ core is linked to two neutral NiL^6 units via four phenolate O atoms and four methoxy O atoms from the salen-type Schiff base ligand (H_2L^6). The Na^+ in each complex is eight-coordinated and exhibiting trigonal-dodecahedron geometry (**Fig.VI.4.**) In complex **8** the Na-O (phenolate) distances are 2.411(3), 2.424(4), 2.417(4), and 2.419(4) Å. In complex **9** the Na-O (phenolate) distances are 2.442(5), 2.423(5), 2.435(5), and 2.419(5) Å and the distances of Na-O (methoxy) are larger than that of Na-O (phenolate) distances. The dihedral angle between the mean planes passing through [O(1)–O(2)–O(3)–O(4)] and [O(5)–O(6)–O(7)–O(8)] is 86.32° suggesting that the two sets of salen-type Schiff base ligands are almost orthogonal. Both the nickel (II) centers are four-coordinated in an approximately square-planar geometry constructed by two imine nitrogen atoms and two phenolate oxygen atoms. Sum of the different angles around the nickel(II) centers is almost 360° [362.07^0 for Ni(1) and 362.10^0 for Ni(2) in complex **8,** whereas 361.80^0 for Ni(1) and 361.60^0 for Ni(2) in complex **9**] indicating only very slightly distorted square-planar geometry around the nickel(II). The distortion may conveniently be measured by the trans angles that are ideally 180° for a square-planar compound and 109.5° in a tetrahedral compound. The trans angles are found to be 166.47(2)° {O(1)–Ni(1)–N(2)}, 167.63(17)°{O(2)–Ni(1)–N(1)}, 167.9(2)°{O(5)–Ni(2)–N(4)} and 168.74(3)°{O(6)–Ni(2)–N(3)} for complex **8**. For complex **8,** deviations of the coordinating atoms, O(1), O(2), N(2) and N(1), from the least-square mean plane through them are 0.211(3), -0.206(3), 0.195(4), -0.192(4), Å respectively and that of Ni(1) from the same plane is -0.008(8). Deviations of the coordinating atoms, O(5), O(6), N(4) and N(3), from the least-square mean plane through them are -O.186(3), 0.186(3), -0.175(6) and 0.171 (5), Å respectively and that of Ni(2) from the same plane is 0.003(7). For complex **9,** deviations of the coordinating atoms, O(1), O(2), N(2) and N(1), from the least-square mean plane through them are -0.176(4), 0.174(4), -0.160(4), 0.161(5) Å respectively and that of Ni(1) from the same plane is 0.001(6). Deviations of the coordinating atoms, O(5), O(6), N(4) and N(3), from the least-square mean plane through them are O.166(4), -0.165(4), 0.152(5), -0.153(6), Å respectively and that of Ni(2) from the same plane is 0.001(7). In the complex **8,** intramolecular separations between Ni(1) and Ni(2) is 6.889(1) Å, whereas Ni(1)···Na(1) and Ni(2)···Na(1) separations are 3.442(2) Å and 3.450(2) Å respectively. In complex **9,** intramolecular separations between Ni(1) and Ni(2) is 6.932(5) Å, whereas Ni(1)···Na(1) and Ni(2)···Na(1) separations are 3.474(4) Å and 3.463(3) Å respectively. None of these distances are sufficiently short to imply any metal–metal bonding or to allow intra-metal spin exchange through mutual interaction. The O(1)–Ni(1)–N(2), O(2)–Ni(1)–N(1), O(5)–Ni(2)–N(4) and O(6)–Ni(2)–N(3) angles are 169.12(4)°, 168.72(4)°, 169.4(2)° and 169.5(2)° respectively.

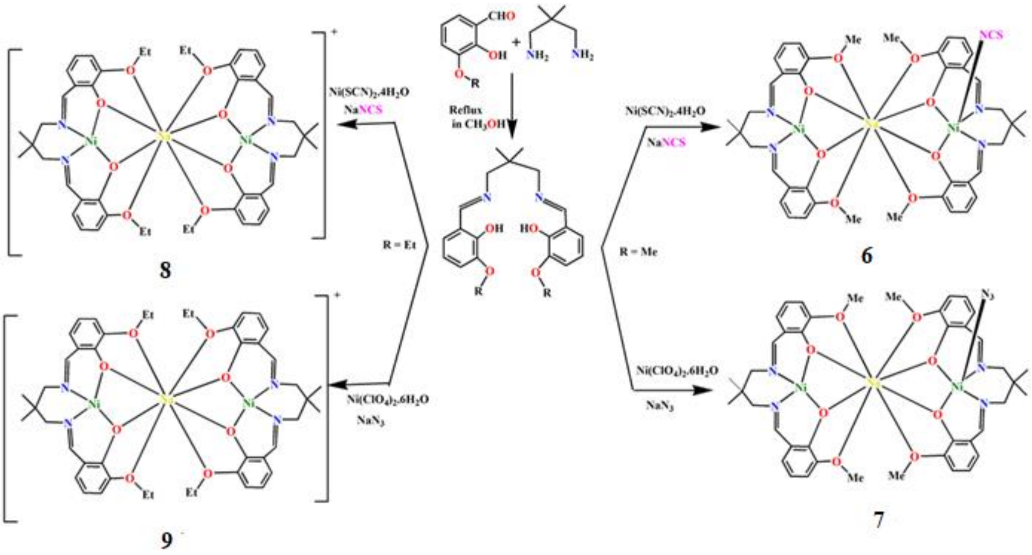
The saturated six membered chelate rings [Ni(1)-N(3)-C(33)-C(34)-C(37)-N(4)] and [Ni(2)-N(1)-C(10)-C(11)-C(14)-N(2)] have twist boat conformations with puckering parameters, q = 0.821(7) Å; φ = 87.50(5) and q = 0.779(6); φ = 86.10(4), respectively (for complex **8**). The saturated six membered chelate rings [Ni(1)-N(3)-C(33)-C(34)-C(37)-N(4)] and [Ni(2)-N(1)-C(10)-C(11)-C(14)-N(2)] have twist boat conformations with puckering parameters, q = 0.802(8) Å; φ = 87.5(5) and q = 0.779(6); θ = 86.10(6)°; φ = 86.2(5), respectively (for complex **9**).

Table VI.1. Crystal data and refinement details of complexes **6-9**

Complex	**6**	**7**	**8**	**9**
Formula	$C_{43}H_{50}N_5S$	$C_{42}H_{48}N_7NaNi_2O_8$	$C_{48}H_{60}N_5NaNi_2O_9SO_9S$	$C_{46}H_{56}ClN_4NaNi_2O_{12}$
Formula Weight	953.31	919.24	1023.44	1032.77
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	P21/c	$P2_1/c$	$P2_1/n$	$C2/c$
a(Å)	10.574(8)	20.524(3)	15.267 (2)	37.440(3)
b(Å)	17.731(1)	10.413(11)	17.882(4)	9.494(8)
c(Å)	23.316(2)	22.375(3)	19.158(2)	34.860(3)
β	94.18(3)	117.25(3)	106.96(3)	114.19(4)
Z	4	4	4	8
$d_{calc}(gcm^{-3})$	1.452	1.436	1.359	1.214
μ (mm^{-1})	0.982	0.957	0.861	0.776
F(000)	1992	1920	2152	4320
Total	89466	30804	66154	67869

Reflections				
Unique Reflections	9600	7494	11291	10031
Observed data [I >2 σ (I)]	6179	4686	5915	6755
R(int)	0.068	0.082	0.082	0.065
R1,wR2 (all data)	0.1273,0.2618	0.1203,0.2238	0.1388,0.2284	0.1077,0.2254
R1,wR2 [I > 2 σ(I)]	0.0819,0.2226	0.0697, 0.1846	0.0680,0.1713	0.0745,0.2011

CCDC NO: 1952446–1952449 (6-9)



Scheme VI.1. Synthetic route to complexes **6-9** Non-coordinated molecules and counter anions have been omitted for clarity.

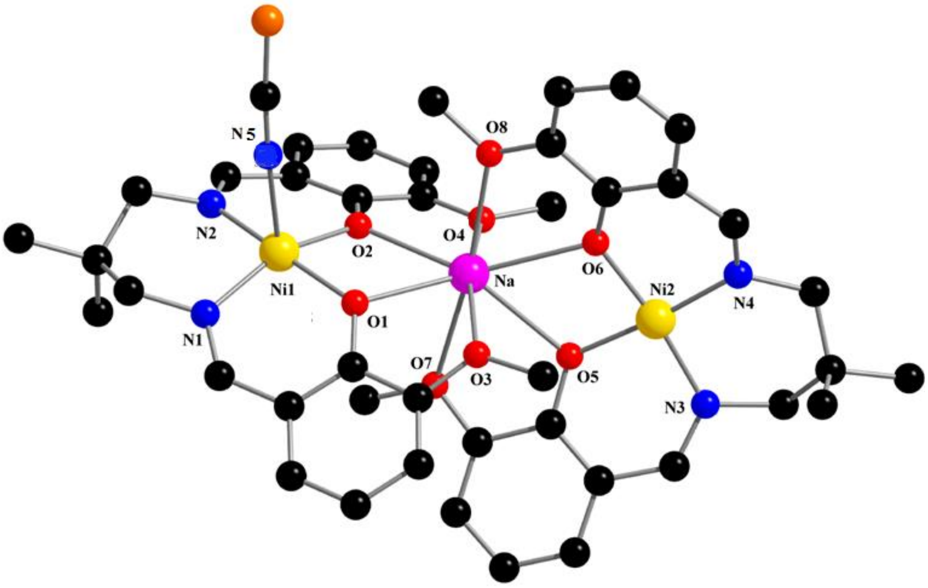


Fig.VI.1. Perspective view of the complex 6 with selective atom-numbering scheme. Non coordinated water molecule has been omitted for clarity

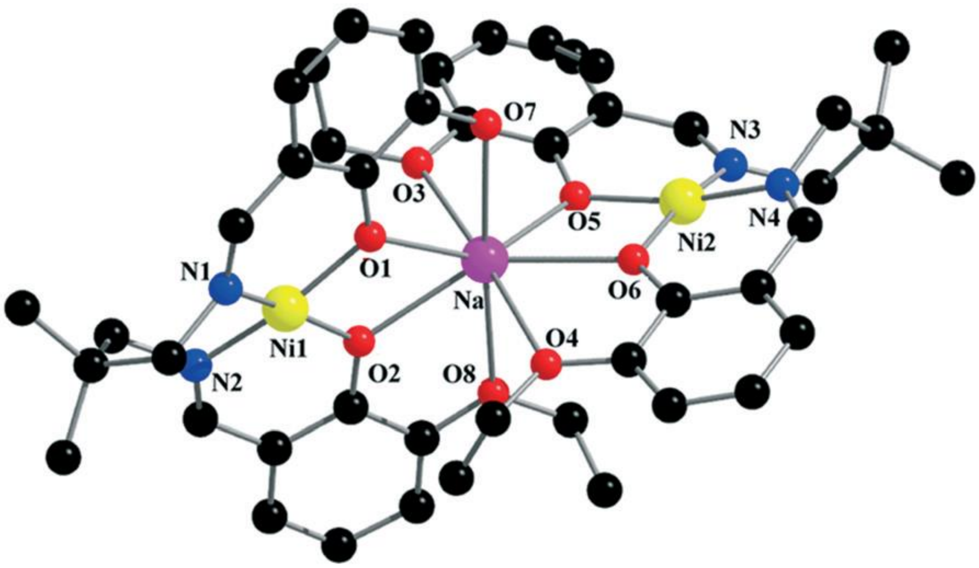


Fig.VI.3. Perspective view of complex **8** with a selective atom numbering scheme. Noncoordinated methanol solvent molecules and thiocyanate counteranions have been omitted for clarity.

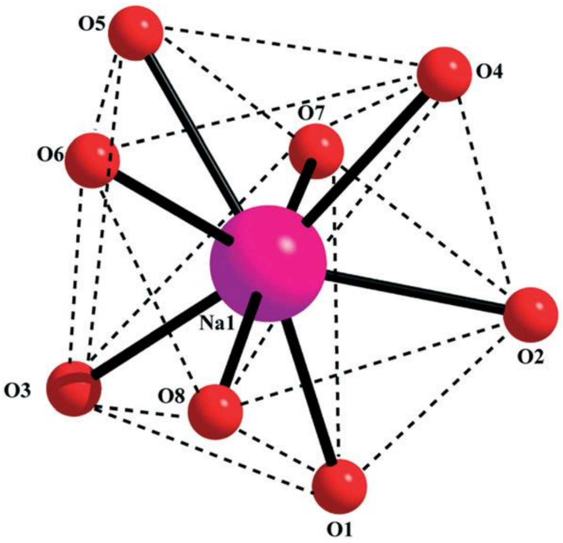


Fig.VI.2. Trigonal dodecahedral geometry of sodium (I) in complex **6**.

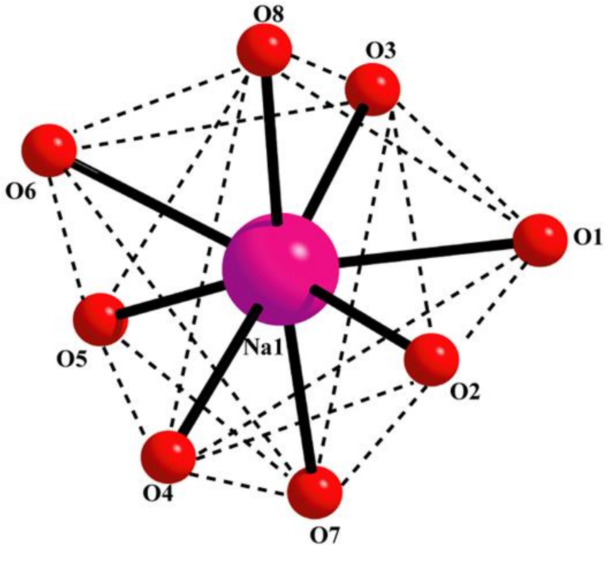


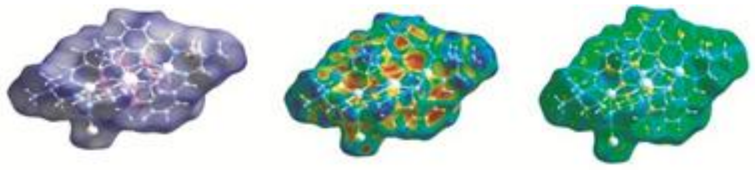
Fig.VI.4. Trigonal dodecahedral geometry of sodium (I) in complex **8**

Table VI.2. Selected bond lengths (Å) of complexes **6-9**.

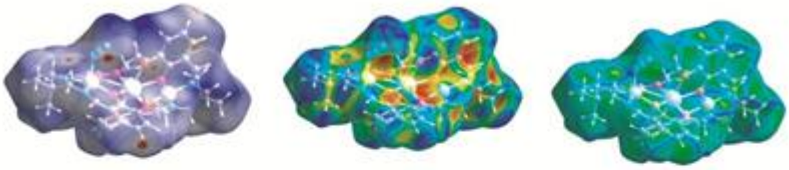
Bond length	**6**	**7**	**8**	**9**
Ni(1)–O(1)	1.912(3)	1.988(4)	1.841(3)	1.857(4)
Ni(1)–O(2)	1.948(4)	1.977(4)	1.847(3)	1.851(4)
Ni(1)–N(1)	1.944(5)	2.016(6)	1.859(4)	1.869(5)
Ni(1)-N(2)	1.989(5)	2.029(4)	1.864(4)	1.885(5)
Ni(1)–N(5)	2.240(10)	2.072(8)	---	---
Ni(2)–O(5)	1.877(4)	1.870(4)	1.845(3)	1.851(4)
Ni(2)–O(6)	1.872(5)	1.860(5)	1.847(3)	1.855(4)
Ni(2)–N(3)	1.888(5)	1.912(6)	1.863(4)	1.863(6)
Ni(2)–N(4)	1.897(5)	1.893(6)	1.860(6)	1.876(5)
Na(1)–O(1)	2.415(4)	2.502(5)	2.411(3)	2.442(5)
Na(1)–O(2)	2.476(4)	2.464(5)	2.424(4)	2.423(5)
Na(1)–O(3)	2.399(6)	2.588(5)	2.539(4)	2.591(6)
Na(1)–O(4)	2.555(6)	2.447(5)	2.669(6)	2.541(5)
Na(1)–O(5)	2.507(4)	2.547(5)	2.417(4)	2.435(5)
Na(1) –O(6)	2.474(4)	2.527(6)	2.419(4)	2.419(5)
Na(1)–O(7)	2.508(5)	2.494(5)	2.589(5)	2.533(6)
Na(1)–O(8)	2.458(5)	2.425(7)	2.565(5)	2.612(5)

VI.3. Hirshfeld surfaces

The Hirshfeld surfaces of four complexes are mapped over d_{norm} (range -0.1 Å to 1.5 Å), shape index and curvedness (**Fig.VI.5.**) Red spots on the Hirshfeld surfaces mapped with dnorm denote the dominant interactions (**Fig.VI.5.**) In complexes, **6-9**, the dominant interactions are C···H/H···C. Other visible spots in the Hirshfeld surfaces correspond to O···H contacts, N···H contacts and S···H contacts. The intermolecular interactions are summarized effectively in the spots with the large circular depressions (deep red) visible on the dnorm surfaces indicative of hydrogen bonding interactions and other weak interactions. The 2D fingerprint plot of Hirshfeld surfaces for all complexes and the comparative contributions of different interactions overlapping in full fingerprint plots have been shown in **Fig.VI.6.** In the 2D fingerprint plot intermolecular interactions appear as distinct spikes. Complementary regions are observable in the 2D fingerprint plots where one molecule act as donor (de > di) and the other as an acceptor (de < di). The relative percentages of intermolecular interactions of four complexes have been shown in **Fig.VI.6.**



Complex 6



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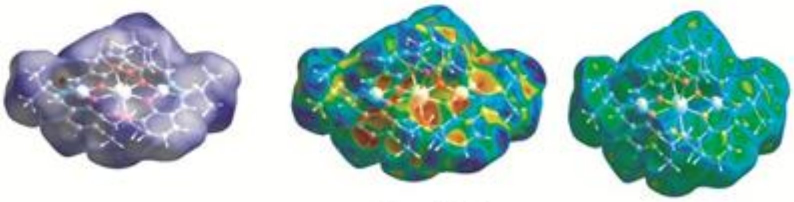
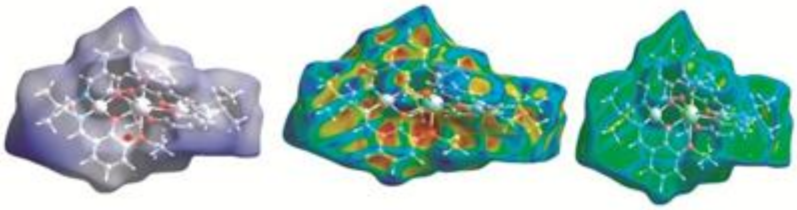
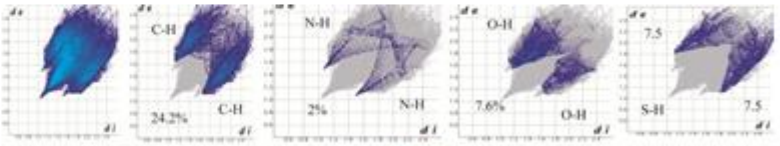


Complex 8

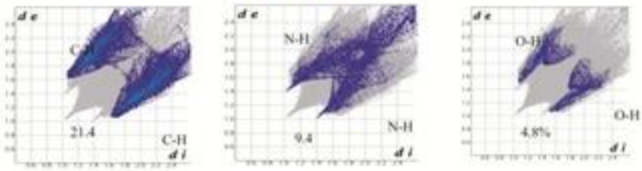


Complex 9

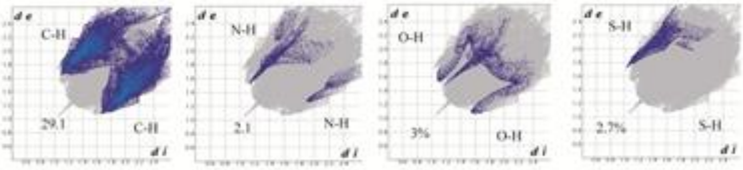
Fig.VI.5. Hirshfeld surfaces mapped with d_{norm} (left column), shape index (middle) and curvedness (right column) of complexes **6-9**



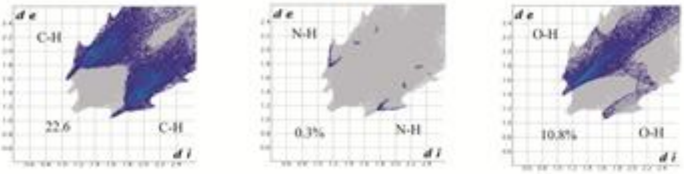
Complex 6



Complex 7



Complex 8



Complex 9

Fig.VI.6. Fingerprint plot: Full (extreme left), resolved into H···C/C···H (second from the left), H···N/N···H (second from the right) and H···O/O···H (extreme right) contacts contributed to the total Hirshfeld Surface area of complexes **6-9**.

VI.4. IR and electronic spectra

A distinct band for azomethine, (C=N) groups of Schiff base moiety around 1600 cm^{-1} has been noticed in all the complexes.[15] Broad bands in the range of 2950-2825 cm^{-1} has been observed in the IR spectrum of each complex which may be routinely assigned to the C–H stretching vibration.[16]

Very strong band at a range 2088-2052 cm^{-1} is obtained in complexes **6** and **8** for thiocyanate group, while in case of complex **7**, a sharp band at 2030cm^{-1} is obtained azide group. IR spectra of all complexes (**6-9**) have been jointly given in **Fig.VI.7.**

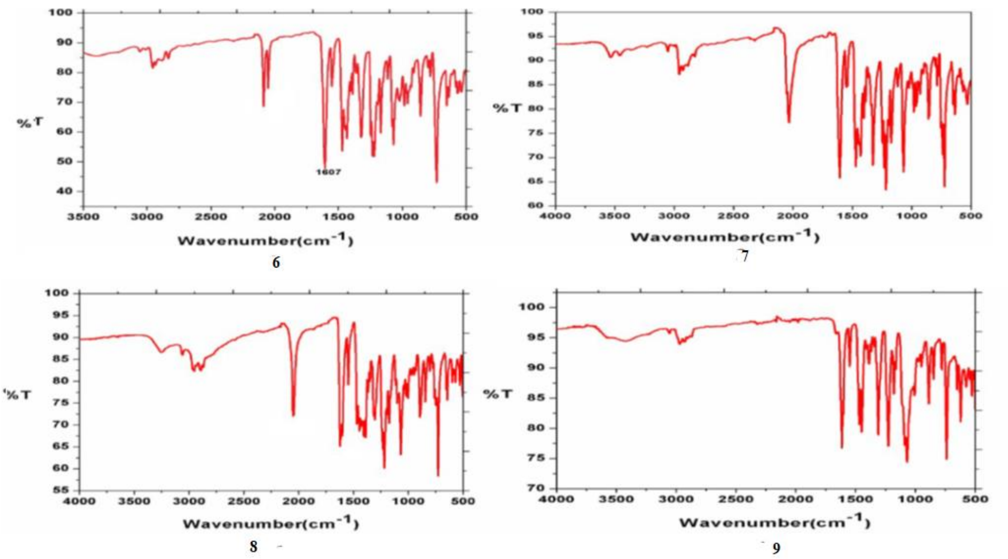


Fig.VI.7. IR spectra of all complexes (**6-9**)

Electronic spectrum of each complex in methanol displays an absorption band around 600 nm corresponds to d-d transition of nickel.[5a] An intense absorption band at shorter wavelength ∼355 nm is observed which may be attributed to ligand to metal charge transfer transition. In addition high energy absorption bands around wavelength 270 nm may be assigned as $\pi^*\leftarrow\pi$ transition.

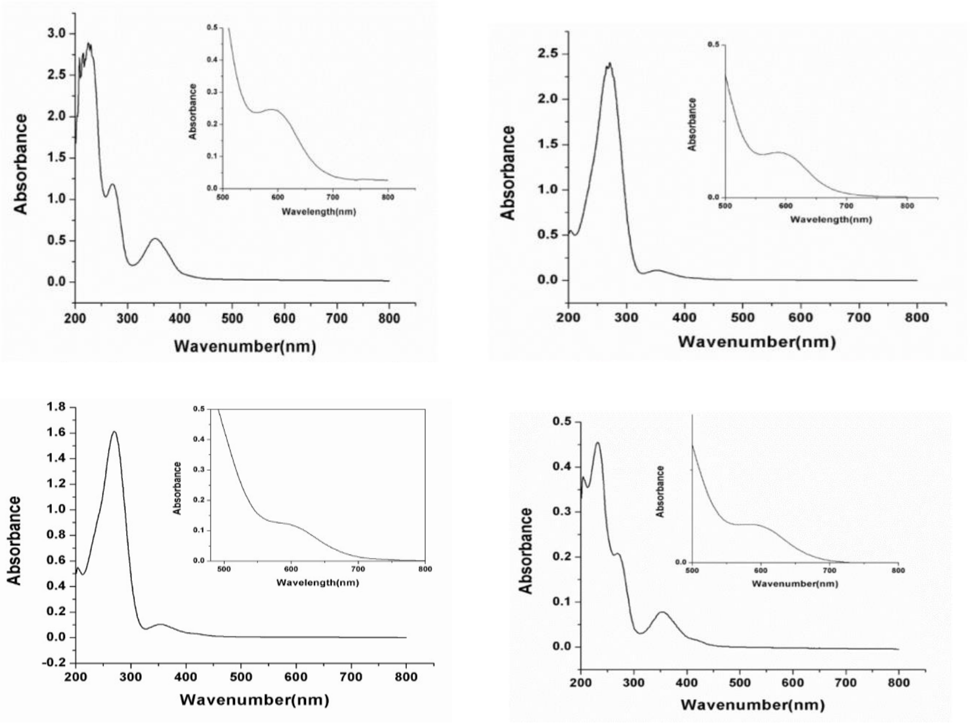


Fig.VI.8. Electronic spectrum of complexes **6, 7, 8, 9** shows the selected small range (500-800 nm) electronic spectrum of the complex**.**

VI.5. Theoretical study

The theoretical analysis has been focused to explain the different coordination environment in the nickel ions depending on the substitution (3-methoxy or 3-ethoxy) of ligand used in the synthesis. The study has been performed using compound **6** and **7** for the theoretical analysis because both present SCN^- in the structure. The geometry of complexes **6** and **8** have been optimised first without the counter ion (denoted as **6**$^+$ and **8**$^+$), which are represented in **Fig.VI.9.** using the CPK model. It has been observed that the electrophilic nickel (II) metal centre is accessible in compound **6**$^+$ and, conversely, it is unreachable in compound **8**$^+$ in agreement with the experimental result.

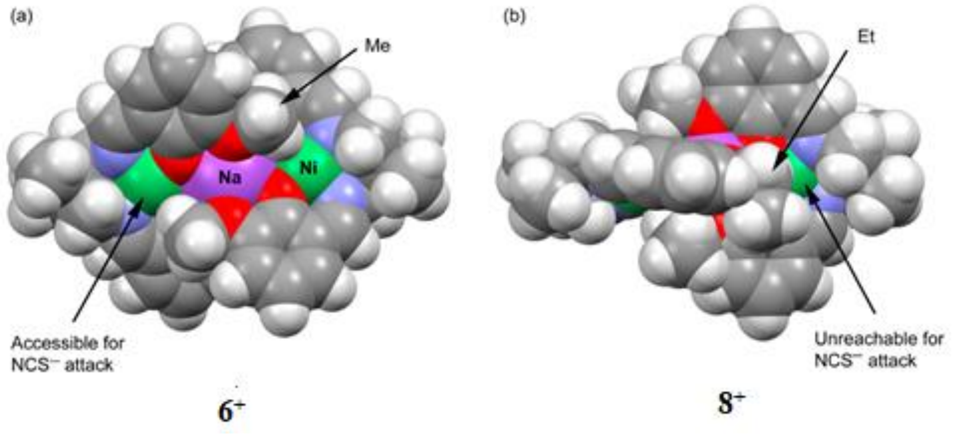
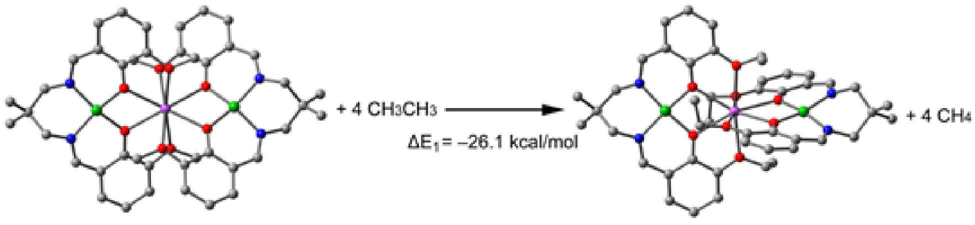


Fig.VI.9. B3LYP-D/def2-SVP optimized complexes **6**$^+$ (a) and **8**$^+$ (b).

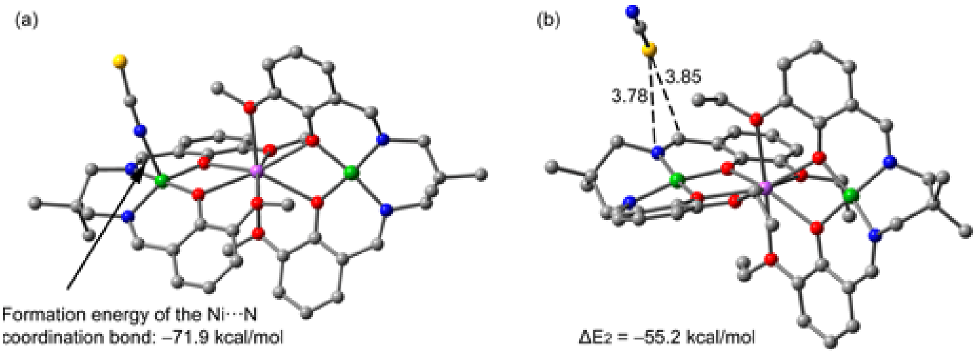
An additional explanation for the different coordination environment of nickel (II) in complexes **6** and **7** can be also related to the energy balance between stabilization energy of Ni–NCS coordination bond in **6**$^+$ and the non-covalent interaction between **8**$^+$ and the SCN$^-$ anion in conjunction with the inter-molecular interaction of the ethyl group with the aromatic surface (see **Fig.VI.9.** (**b**). For evaluating the inter-molecular interaction of the ethyl group in **8**$^+$ compared to that of the methyl group in **6**$^+$, homodesmotic equation[18] have been used, as shown in **Fig.VI.10.** Starting from the hypothetical **6**$^+$ compound where both nickel(II) centers are tetra-coordinated, energy change of replacing four methyl groups by four ethyl groups have been computed using ethane and methane to complete the homodesmotic equation. The result is that the intra-molecular interaction of the four ethyl groups favours compound **8**$^+$ is $\Delta E_1 = –26.1$ kcal/mol.



6$^+$ **8**$^+$

Fig.VI.10. Homodesmotic equation used to evaluate the extra estabilization energy provided by the four ethyl groups in **8**$^+$ compared to the methyl group in **6**$^+$.

Finally, the covalent and noncovalent interactions of the counter ion with complexes **6**$^+$ and **8**$^+$ have been evaluated. As expected the Ni–NCS coordination bond is energetically more favourable (–71.9 kcal/mol) than the noncovalent interaction, $\Delta E_2 = –55.2$ kcal/mol, that is established between the SCN anion and the imidic double bond. Altogether, the results gathered in Figures **6** and **7** indicate that the Ni–NCS coordination bond in compound **6** is compensated in compound **8** by the combination of the noncovalent interaction SCN$^-\cdots$**8**$^+$ and the four intramolecular ethyl$\cdots\pi$ interactions, that is $\Delta E_1 + \Delta E_2 = –81.3$ kcal/mol. This further explains that in compound **8** both Ni atoms are tetra-coordinated and square planar due to the influence of the ethyl group, which on one hand hinders the attack of the SCN$^-$ anion and on the other hand establishes intramolecular interactions with the Schiff-base co-ligand.



6

8

Fig.VI.11. Theoretical models used to evaluate the coordination bond in **6** and the anion···π(C=N) noncovalent interaction in **8**. Distances in Å.

VI.6. Conclusion

In this paper, four hetero-trinuclear complexes have been prepared and X-ray characterized where the nickel (II) is placed in inner N_2O_2 compartment and sodium is placed in outer O_4 compartment of the respective Schiff base ligand. Depending on the substituent (methoxy or ethoxy) of the salicyl ring, one nickel (II) centre is tetra-coordinated (square planar) and the other one is penta coordinated (square pyramidal) or both are tetra-coordinated. The DFT calculations have been used to rationalize this finding. The ethoxy group has a dual effect since it hinders the attack of the SCN^- to the nickel (II) metal centre and also contributes to the stabilization of the complex by intramolecular interactions, which have been evaluated using a homodesmotic equation.

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Chapter VII

Highlights of thesis

"If opportunity doesn't knock, build a door"

-Milton Berle

Chapter VII

Highlights of thesis

The entire dissertation deals with synthesis and characterization of several new copper(II), nickel(II) and cobalt(III) complexes with various polydentate ligands. The interesting observations are highlighted here in the following paragraphs. The studies of noncovalent interactions in solid state of different complexes have been investigated in details. In several occasions, density functional theory (DFT) calculations and NCI plot have been employed to understand and estimate the energetic contribution of each interaction in the formation of supra-molecular assemblies. In terms of applications, some complexes have shown good catalytic efficiency, intriguing magnetic property and formation of electronic devices. The most attention-grabbing observations are highlighted below.

Synthesis and characterization of a new dinuclear copper(II) complex containing oxime-based tridentate Schiff base ligand has been reported in **chapter II**. The phenoxazinone synthase mimicking activity of the complex has been explored.

Chapter III reports the synthesis and characterization of a pseudohalide bridged dinuclear copper(II) complex with a half salen type

Schiff base ligand. Phenoxazinone synthase mimicking activity of the complex has been investigated.

Synthesis and characterization of an ionic cobalt(III/II) complex has been reported in **Chapter IV**. DFT calculations have been performed in detail to understand the main reason behind the stabilization of this ionic cobalt(III/II) complex. DFT calculations indicate that a combination of strong CH3···π and H-bonding interactions play a crucial role in the stabilization of this complex.

Synthesis and characterization of two relatively rare mixed phenoxo and azide bridged dinuclear nickel(II) complexes have been discussed in **chapter V**. Both complexes show strong intermolecular hydrogen bonding interactions and exhibit ferromagnetic exchange coupling.

The dual effect of the ethoxy groups in hindering the attack of pseudo-halides on the nickel(II) centre and in stabilizing a nickel(II) complex by intra-molecular interactions is depicted in detail in **Chapter VI**.

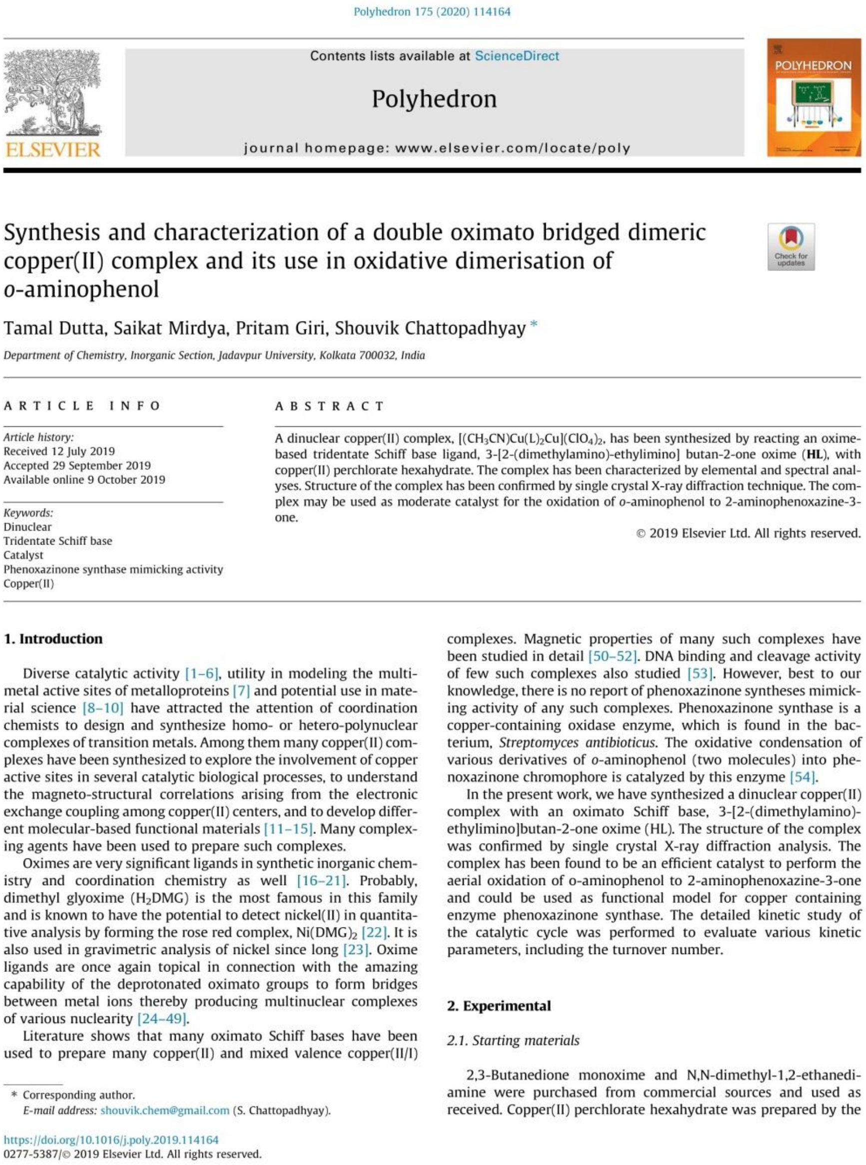
Tamal Dutta.

Appendix

List of Publications

Appendix

List of Publications



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Synthesis and characterization of a double oximato bridged dimeric copper(II) complex and its use in oxidative dimerisation of *o*-aminophenol

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ABSTRACT

A dinuclear copper(II) complex, $[(CH_3CN)Cu(L)_2Cu](ClO_4)_2$, has been synthesized by reacting an oxime-based tridentate Schiff base ligand, 3-[2-(dimethylamino)-ethylimino] butan-2-one oxime (**HL**), with copper(II) perchlorate hexahydrate. The complex has been characterized by elemental and spectral analyses. Structure of the complex has been confirmed by single crystal X-ray diffraction technique. The complex may be used as moderate catalyst for the oxidation of *o*-aminophenol to 2-aminophenoxazine-3-one.

1. Introduction

Diverse catalytic activity [1–6], utility in modeling the multimetal active sites of metalloproteins [7] and potential use in material science [8–10] have attracted the attention of coordination chemists to design and synthesize homo- or hetero-polynuclear complexes of transition metals. Among them many copper(II) complexes have been synthesized to explore the involvement of copper active sites in several catalytic biological processes, to understand the magneto-structural correlations arising from the electronic exchange coupling among copper(II) centers, and to develop different molecular-based functional materials [11–15]. Many complexing agents have been used to prepare such complexes.

Oximes are very significant ligands in synthetic inorganic chemistry and coordination chemistry as well [16–21]. Probably, dimethyl glyoxime (H_2DMG) is the most famous in this family and is known to have the potential to detect nickel(II) in quantitative analysis by forming the rose red complex, $Ni(DMG)_2$ [22]. It is also used in gravimetric analysis of nickel since long [23]. Oxime ligands are once again topical in connection with the amazing capability of the deprotonated oximato groups to form bridges between metal ions thereby producing multinuclear complexes of various nuclearity [24–49].

Literature shows that many oximato Schiff bases have been used to prepare many copper(II) and mixed valence copper(II/I) complexes. Magnetic properties of many such complexes have been studied in detail [50–52]. DNA binding and cleavage activity of few such complexes also studied [53]. However, best to our knowledge, there is no report of phenoxazinone syntheses mimicking activity of any such complexes. Phenoxazinone synthase is a copper-containing oxidase enzyme, which is found in the bacterium, *Streptomyces antibioticus*. The oxidative condensation of various derivatives of *o*-aminophenol (two molecules) into phenoxazinone chromophore is catalyzed by this enzyme [54].

In the present work, we have synthesized a dinuclear copper(II) complex with an oximato Schiff base, 3-[2-(dimethylamino)-ethylimino]butan-2-one oxime (HL). The structure of the complex was confirmed by single crystal X-ray diffraction analysis. The complex has been found to be an efficient catalyst to perform the aerial oxidation of o-aminophenol to 2-aminophenoxazine-3-one and could be used as functional model for copper containing enzyme phenoxazinone synthase. The detailed kinetic study of the catalytic cycle was performed to evaluate various kinetic parameters, including the turnover number.

2. Experimental

2.1. Starting materials

2,3-Butanedione monoxime and N,N-dimethyl-1,2-ethanediamine were purchased from commercial sources and used as received. Copper(II) perchlorate hexahydrate was prepared by the

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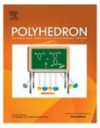

Phenoxazinone synthase mimicking activity of a dinuclear copper(II) complex with a half salen type Schiff base ligand

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ABSTRACT

A dinuclear copper(II) complex *[LCu($\mu_{1,1}$-N_3)$_2$CuL]* {where *HL = (2-(3-aminopropylimino)methyl-6-methoxyphenol)*} has been synthesized and characterized by several analytical techniques including single crystal X-ray diffraction analysis. Interesting supramolecular interactions are observed in the solid state of the complex. An unusual N–H···π interaction is observed where the chelate ring, Cu(1)–N(1)–Cu(1)^b–N(1)^b, [where ^{b} = 1 − x, −y, 1 − z] behaves as a π system. Supramolecular interactions have been related with Hirshfeld surface calculations. The complex has been evaluated as functional model for phenoxazinone synthase enzyme by using *o*-aminophenol (OAPH) as a model substrate in acetonitrile medium. Kinetics of the reaction was followed spectrophotometrically, which confirm that catalytic reactions follow Michaelis–Menten enzymatic reaction kinetics.

1. Introduction

Monocondensed N_2O donor Schiff base ligands are of special interest because of their usage as synthetic analogues of metal binding sites in copper proteins [1,2]. Preparation of these unsymmetrical ligands by condensing diamines and salicylaldehyde derivatives are difficult where one primary amine group forms an imine bond and the other is unchanged. These are termed as 'half units' and are used in preparing di/trinuclear complexes [3–13]. These half units can be synthesized by several routes [14–17]. Elder reported a very convenient way for template synthesis for nickel(II) complexes using these half ligands [18]. Using similar ligands copper(II) complexes have been reported utilizing copper template effect [19–24]. Several copper(II) complexes using half salen ligands have also been reported by our group [25–28]. These complexes have mainly been prepared for magnetic studies as they have the abilities to mimic the magnetic properties of type-3 copper proteins which are well established experimentally [29–32]. In recent years, use of metal complexes as efficient biomimetic catalysts is an active area of research at the interface of chemistry and biology [33–37]. Our laboratory has also been actively engaged in designing, synthesis and investigation of bio-relevant catalytic activities, such as catechol oxidase, phenoxazinone synthase and phosphatase mimicking activities of several homo and heteronuclear transition metal complexes for the past few years [38–44].

In the present work, a half salen type Schiff base ligand has been used to prepare a dinuclear copper(II) complex. Supramolecular interactions along with Hirshfeld analyses have been explored. Phenoxazinone synthase mimicking activity of the complex has been studied using *o*-aminophenol (OAPH) as model substrate to evaluate the catalytic efficiency.

2. Material and methods

2.1. Starting materials and solvents

Starting materials and solvents used in this work were purchased from Sigma-Aldrich, India (now Merck, India) and were of reagent grade. They were used as received, without any further purification. The entire syntheses were carried out under aerobic conditions.

Caution!!! *Even though no troubles were experienced in this work, metal complexes containing azide salts and organic ligands are potentially explosive. Only a small amount of material should be prepared, and it should be handled with care.*

2.2. Preparation of *[LCu($\mu_{1,1}$-N_3)$_2$CuL]*

Copper(II) acetate monohydrate (400 mg, 2 mmol) was added to a methanol solution (20 mL) of 3-methoxysalicylaldehyde (300 mg,

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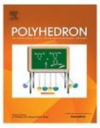

A combined experimental and theoretical study on an ionic cobalt(III/II) complex with a Schiff base ligand

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ABSTRACT

An ionic cobalt(III/II) complex, $[Co^{III}(L)_2][Co^{II}(NCS)_3(H_2O)]$, where H_2L = 2-((3-aminopropylimino)methyl)-6-methoxyphenol, has been synthesized and characterized by several analytical techniques, including single crystal X-ray diffraction analysis. The energetic features of the solid state non-covalent interactions involved in the titled ionic coordination complex have been studied by means of DFT computations, which indicate that a combination of strong $CH_3 \cdots \pi$ and H-bonding interactions is the main reason behind the stabilization of this complex.

1. Introduction

Various di-/tri-/poly-nuclear transition metal complexes have attracted interest of inorganic chemists for the diversity of their structural features and potential applications in the field of condensed physics and material chemistry [1–4]. Another inherent potential of these complexes is their efficacy in modelling the multi-metal active sites of biomolecules [5–7]. Dinuclear cobalt complexes may function as mimics of active biosites, such as in methionine amino peptidase [8,9], and can show DNA cleavage activity [10]. Alternatively, Schiff base ligands themselves have been widely used in coordination chemistry due to their facile syntheses, easily tunable steric and electronic properties, and their applications in different branches of science [11–14,55]. Transition metal complexes of Schiff base ligands are important stereochemical models in main group and transition metal coordination chemistry [11–14,15,55]. These complexes have wide applications, in different fields such as bioinorganic chemistry, material science and magnetism, bio-relevant catalytic activities, separation and encapsulation, hydrometallurgy, metal clusters, transport and activation of small molecules etc [16–23].

Herein, we report a new ionic cobalt(III/II) complex, $[Co^{III}(L)_2][Co^{II}(NCS)_3(H_2O)]$, derived from a mono-condensed Schiff base and thiocyanate co-ligands. Single crystal X-ray crystallography analysis confirms that the complex is an ionic cobalt(III/II) complex with one tetracoordinated cobalt(II) centre. To find out the reason behind such a unique structure in the solid state, complete DFT calculations have been performed, which confirmed that a combination of $CH_3 \cdots \pi$ and hydrogen bonding interactions plays a vital role in the stabilization of the ionic cobalt(III/II) complex.

2. Material and methods

2.1. Starting materials and solvents

The starting materials and solvents used in this work were purchased from Sigma-Aldrich, India (now Merck, India) and were of reagent grade. They were used as received, without any further purification. The entire syntheses and manipulations were carried out under aerobic conditions.

2.2. Preparation of $[Co^{III}(L)_2][Co^{II}(NCS)_3(H_2O)]$

0.10 mL (~1 mmol) of 1,3-diaminopropane was mixed with 304 mg (~2 mmol) of 3-methoxysalicylaldehyde in 25 mL of a 2:1 (v/v) methanol–acetonitrile mixture. The resulting mixture was refluxed for c.a. 1.5 h and allowed to cool. A methanol solution (10 mL) of cobalt(II) acetate tetrahydrate (500 mg, ~2 mmol) was then directly added to this yellow coloured solution of the Schiff base ligand, followed by the addition of a methanol solution (10 mL) of sodium thiocyanate (162 mg, ~2 mmol) with constant stirring. The stirring was continued for an additional 1.5 h and then the reaction mixture was filtered into a beaker. The filtrate was allowed to stand overnight until X-ray quality single crystals were

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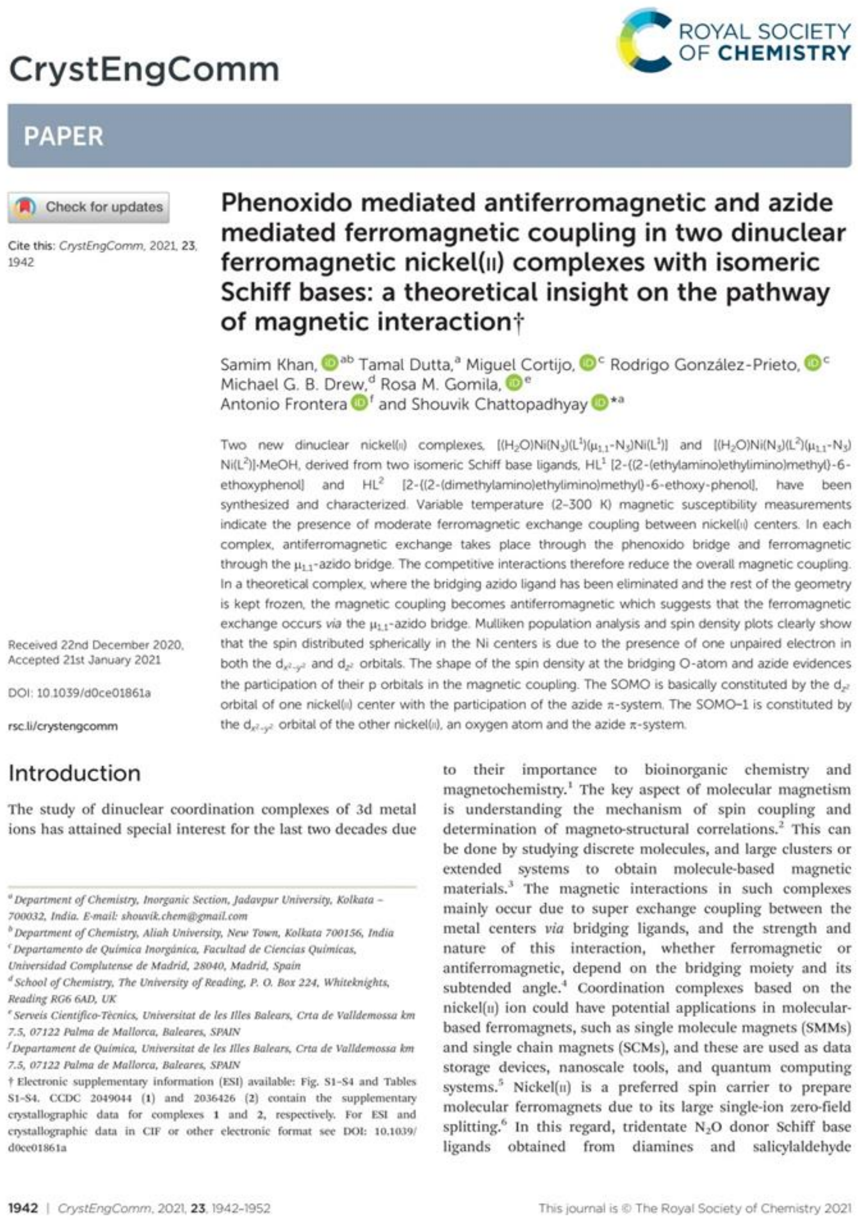

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Phenoxido mediated antiferromagnetic and azide mediated ferromagnetic coupling in two dinuclear ferromagnetic nickel(II) complexes with isomeric Schiff bases: a theoretical insight on the pathway of magnetic interaction†

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Two new dinuclear nickel(II) complexes, $[(H_2O)Ni(N_3)(L^1)(\mu_{1,1}\text{-}N_3)Ni(L^1)]$ and $[(H_2O)Ni(N_3)(L^2)(\mu_{1,1}\text{-}N_3)Ni(L^2)]\cdot MeOH$, derived from two isomeric Schiff base ligands, HL^1 [2-((2-(ethylamino)ethylimino)methyl)-6-ethoxyphenol] and HL^2 [2-((2-(dimethylamino)ethylimino)methyl)-6-ethoxy-phenol], have been synthesized and characterized. Variable temperature (2–300 K) magnetic susceptibility measurements indicate the presence of moderate ferromagnetic exchange coupling between nickel(II) centers. In each complex, antiferromagnetic exchange takes place through the phenoxido bridge and ferromagnetic through the $\mu_{1,1}$-azido bridge. The competitive interactions therefore reduce the overall magnetic coupling. In a theoretical complex, where the bridging azido ligand has been eliminated and the rest of the geometry is kept frozen, the magnetic coupling becomes antiferromagnetic which suggests that the ferromagnetic exchange occurs *via* the $\mu_{1,1}$-azido bridge. Mulliken population analysis and spin density plots clearly show that the spin distributed spherically in the Ni centers is due to the presence of one unpaired electron in both the $d_{x^2-y^2}$ and d_{z^2} orbitals. The shape of the spin density at the bridging O-atom and azide evidences the participation of their p orbitals in the magnetic coupling. The SOMO is basically constituted by the d_{z^2} orbital of one nickel(II) center with the participation of the azide π-system. The SOMO−1 is constituted by the $d_{x^2-y^2}$ orbital of the other nickel(II), an oxygen atom and the azide π-system.

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Introduction

The study of dinuclear coordination complexes of 3d metal ions has attained special interest for the last two decades due to their importance to bioinorganic chemistry and magnetochemistry.[1] The key aspect of molecular magnetism is understanding the mechanism of spin coupling and determination of magneto-structural correlations.[2] This can be done by studying discrete molecules, and large clusters or extended systems to obtain molecule-based magnetic materials.[3] The magnetic interactions in such complexes mainly occur due to super exchange coupling between the metal centers *via* bridging ligands, and the strength and nature of this interaction, whether ferromagnetic or antiferromagnetic, depend on the bridging moiety and its subtended angle.[4] Coordination complexes based on the nickel(II) ion could have potential applications in molecular-based ferromagnets, such as single molecule magnets (SMMs) and single chain magnets (SCMs), and these are used as data storage devices, nanoscale tools, and quantum computing systems.[5] Nickel(II) is a preferred spin carrier to prepare molecular ferromagnets due to its large single-ion zero-field splitting.[6] In this regard, tridentate N_2O donor Schiff base ligands obtained from diamines and salicylaldehyde

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† Electronic supplementary information (ESI) available: Fig. S1–S4 and Tables S1–S4. CCDC 2049044 (**1**) and 2036426 (**2**) contain the supplementary crystallographic data for complexes **1** and **2**, respectively. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/d0ce01861a

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Diminishing accessibility of electrophilic nickel(II) centres due to incorporation of a methylene spacer in the pendant side arm of a series of heterotrinuclear nickel(II)/sodium complexes: a DFT study using a homodesmotic equation†

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Sudipta Chatterjee,[c] Antonio Frontera*[d] and Shouvik Chattopadhyay*[b]

Two compartmental N_2O_4 donor Schiff bases, $\mathbf{H_2L^1}$ [*N*,*N*-bis(3-methoxysalicylidene)-2,2-dimethylpropane-1,3-diamine] and $\mathbf{H_2L^2}$ [*N*,*N*-bis(3-ethoxysalicylidene)-2,2-dimethylpropane-1,3-diamine], each having inner N_2O_2 and outer O_4 compartments, have been used to prepare four heterotrinuclear nickel(II) complexes $[Ni(L^1)Na(L^1)Ni(NCS)]\cdot H_2O$ (**1**), $[Ni(L^1)Na(L^1)Ni(N_3)]$ (**2**), $[Ni(L^2)Na(L^2)Ni]NCS\cdot CH_3OH$ (**3**), and $[Ni(L^2)Na(L^2)Ni]ClO_4$ (**4**). All the complexes have been characterized by elemental and spectral analyses. Single crystal X-ray diffraction analyses have confirmed their structures. In each complex, nickel(II) is placed in the inner N_2O_2 compartment and sodium is placed in the outer O_4 compartment of the respective Schiff base ligand. In complexes **1** and **2**, one nickel(II) centre is tetra-coordinated (square planar) and the other is penta coordinated (square pyramidal), whereas in complexes **3** and **4**, both nickel(II) centres are tetra-coordinated. The geometries of complexes **1** and **3** have been optimized without a counterion (denoted as $\mathbf{1}^+$ and $\mathbf{3}^+$). The electrophilic nickel(II) centre is found to be accessible in complex $\mathbf{1}^+$ and, conversely, it is unreachable in complex $\mathbf{3}^+$, in agreement with the experimental result. Starting from the hypothetical $\mathbf{1}^+$ complex where both nickel(II) centres are tetra-coordinated, the energy change for replacing four methyl groups with four ethyl groups has been computed using ethane and methane to complete the homodesmotic equation. The result is that the intra-molecular interaction of the four ethyl groups favours complex $\mathbf{3}^+$ by $\Delta E = -26.1$ kcal mol^{-1}.

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Introduction

Nickel(II) may adopt tetrahedral, octahedral and square planar geometries depending on the electronic and steric effects of the ligands.[1,2] It may also have square pyramidal and trigonal bipyramidal geometries, with the Addison parameter values close to zero for the former and close to one for the latter.[3–5] Schiff base ligands were widely used to prepare a variety of nickel(II) complexes having different coordination numbers and different geometries.[6–9] Among various Schiff bases, salen-type ones are probably the most familiar due to their easy synthetic procedure and also their tendency to form multi-nuclear complexes as a result of the bridging ability of phenoxy oxygen atoms.[10–20] Salen type (N_2O_4 donor) compartmental Schiff bases can form multinuclear complexes more easily for having one inner (N_2O_2 donor) and one outer (O_4 donor) compartments, capable of entrapping two metal ions in the two compartments.[21–26]

In the present work, two compartmental Schiff bases have been used to form four heterotrinuclear nickel(II)–sodium–nickel(II) complexes. In each complex, the central sodium ion is octa-coordinated with trigonal dodecahedral geometry. The geometry of nickel(II) is either square planar or square pyramidal. The variation of the geometry of nickel(II) may be correlated with the availability of the suitable orbital of nickel(II) towards nucleophiles. Increase in the chain length of alkoxy groups allows it to encapsulate nickel(II) more tightly, leaving no space to be approached by incoming nucleophiles. DFT calculations also support this proposition.

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