Studies on the Chemistry of some Transition metal ion Complexes containing multidentate ligands.

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In

Chemistry

by

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Synopsis of the Thesis

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Title of the Thesis: "Studies on the Chemistry of some Transition metal ion Complexes containing multidentate ligands".

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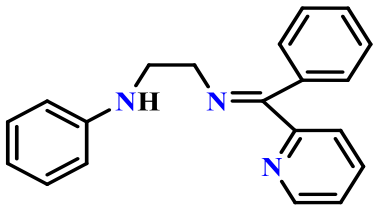
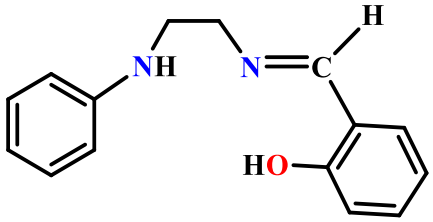
The studies presented in this thesis is to explore the reactivity of some transition metal ions with (i) tridentate N_2O and N_3-donor Schiff base ligands and (ii) pyrazole based tetradentate N_4 and N_3S coordinated tripodal ligands in presence of bridging dicyanamide ligand. Schiff base containing ligands have been the subject of research interest owing to their interesting coordination chemistry, a number of established and potential applications. Schiff based ligands form a variety of coordination complexes with a number of metal ions, providing varying coordination geometry and nuclearity. Dicyanamide is an ambidentate ligand and also acts as bridging ligand in many complexes and shows different modes of coordination in the polynuclear complexes. The objective of this work is to explore the different coordination modes of dicyanamide ligand in the polynuclear transition metal complexes in presence of N_4 and N_3S-donor pyazolyl based ligands.

To amplify the scope of Schiff base ligands and their transition metal complexes, we have focused on the synthesis and characterization of one N_3- donor ligand N′-Phenyl-N′′-(phenyl(pyridin-2-yl)methylene)ethane-1,2-diamine (L1) [Fig.1] and two new N_2O coordinated Schiff base ligands namely 2-(((2-(phenylamino)ethyl)imino)methyl)phenol (L2) [Fig.2] and 2,4-dichloro-6-(((2-(phenylamino)ethyl)imino)methyl)phenol (L3) [Fig.3] and their copper(II), nickel(II), cobalt(II), zinc(II), cadmium(II) and manganese(II) complexes. The ligands and complexes were characterized by microanalysis, spectroscopic techniques and single crystal X-ray diffraction studies.



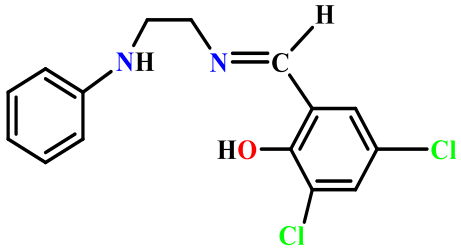
***N*-(2-((phenyl(pyridin-2-yl)methylene)amino)ethyl)aniline (L1)**

Fig.1



2-(((2-(phenylamino)ethyl)imino) methyl)phenol (L2)

Fig. 2



2,4-dichloro-6-(((2-(phenylamino)ethyl)imino) methyl)phenol (L3)

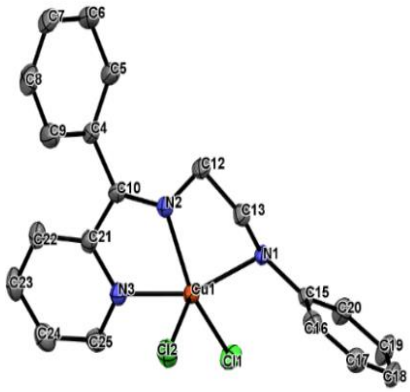
Fig.3

Chapter-I: The general introduction of the work has been described in Chapter I and bench work has been described in Chapter II to V.

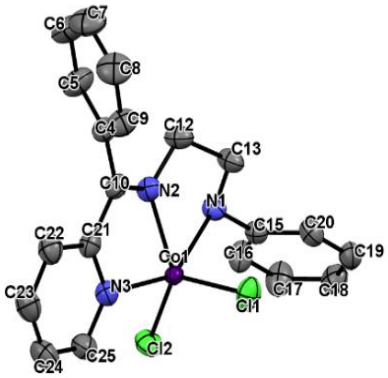
Chapter-II: The Chapter II is divided into two parts: Chapter-II(A) and Chapter-II(B)

Chapter-II-A focuses on synthesis and characterization new tridentate N_3-coordinate ligand *N′*-Phenyl-*N′′*-(phenyl(pyridin-2-yl)methylene)ethane-1,2-diamine (L1) [Fig.1]. The tridentate N_3-coordinate ligand (L1) has been used in the synthesis of three mononuclear complexes [M(L1)Cl_2] [M = Cu(II), Co(II), and Zn(II)] and one polynuclear Cd(II) complex [Cd(L1)Cl_2]$_n$ and these complexes were characterized by spectroscopic techniques. The structure of all the complexes have been solved by single crystal X-ray diffraction studies and the structural data reveals that all mononuclear complexes have distorted square pyramidal geometry. Cadmium(II) complex is polynuclear, bridged by two chloride ions with distorted octahedral geometry. The antimicrobial activity of all complexes were investigated against Gram positive (*Bacillus subtilis, Staphylococcus aureus*) and Gram negative (*Escherichia coli, Proteus vulgaris*) bacteria by disk diffusion method. All the compounds demonstrated significant antimicrobial activity while [Cd(L1)Cl_2]$_n$ exhibited the best antibacterial activity among all the synthesized complexes. Antimicrobial studies demonstrated the Cu(II) complex was found to effectively target both Gram positive and Gram

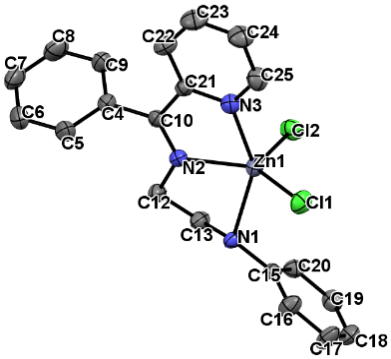
negative bacteria and it is therefore put forward as a promising antimicrobial agent.



[Cu(L1)Cl$_2$] (1)

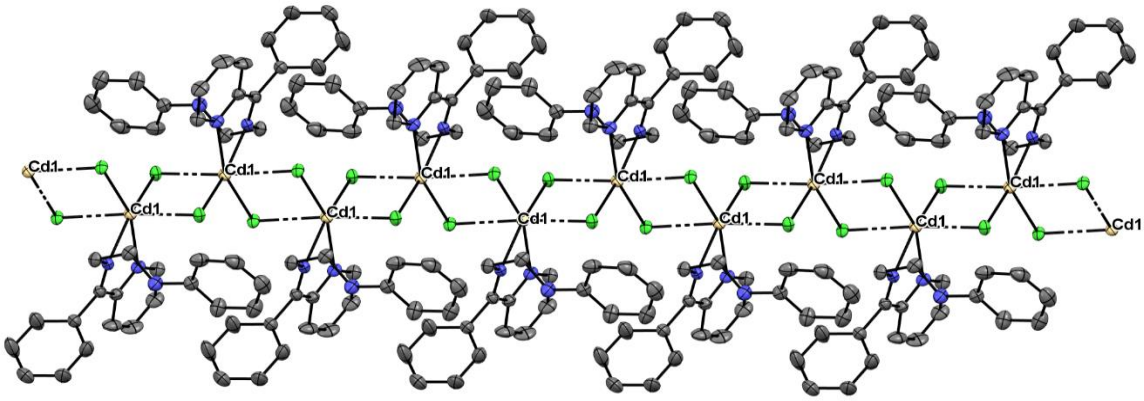


[Co(1)Cl$_2$] (2)



[Zn(L1)Cl$_2$] (3)

Fig. 4 ORTEP diagrams of the complexes **(1) - (3)**. (40% probability factor for the thermal ellipsoids, H-atoms are omitted for clarity).



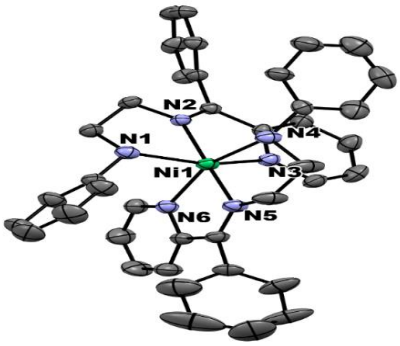
[Cd(L)Cl$_2$]$_n$(4)

Fig. 5. Polymeric 1D zig-zag chain of complex **4** with atom numbering scheme. (40% probability factor for the thermal ellipsoids, H-atoms are omitted for clarity).

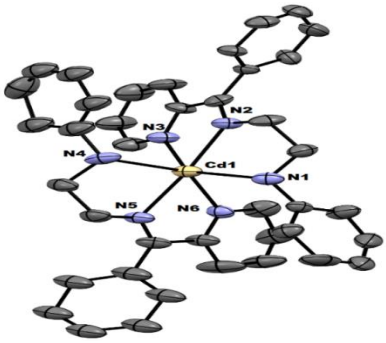
Table 1: Antimicrobial activity of the Schiff base ligand(L1) and its metal complexes.

No.	Compound	MIC value in mM			
		E. coli	***P. vulgaris***	***S. aureus***	***B. subtilis***
1	Ligand(L-1)	10,000	>10,000	>10,000	>10,000
2	$[Cu(L)Cl_2]$	10,000	10,000	5,000	5,000
3	$[Co(L)Cl_2]$	>10,000	>10,000	10,000	>10,000
4	$[Zn(L)Cl_2]$	10,000	>10,000	5,000	5,000
5	$[Cd(L)Cl_2]_n$	>10,000	>10,000	500	5,000
Standard drug	Chloramphenicol	1.5	3	0.3	1.5

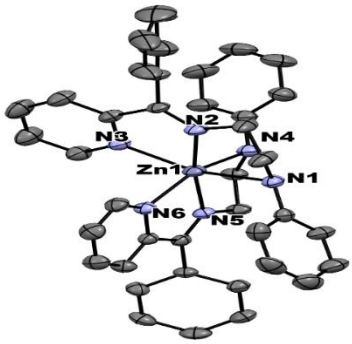
Chapter II-B deals with the syntheses and characterization of a series of metal perchlorate complexes of the type $[M(L1)_2](ClO_4)_2.2H_2O$ where M = Cu(II) Co(II), Ni(II), Mn(II), Zn(II) and Cd(II) and L1 = *N′*-Phenyl-*N′′*-(phenyl(pyridin-2-yl)methylene)ethane-1,2-diamine. All the complexes have been characterized by IR, UV-Visible, Mass spectra, Cyclic Voltammetry and single crystal X-ray diffraction studies. Structural data of the complexes $[Zn(L1)_2](ClO_4)_2.2H_2O$ and $[Ni(L1)_2](ClO_4)_2.2H_2O$ show they have distorted octahedral geometry. Cytotoxic activity of the ligand (L1) and its M(II) complexes were tested against neuroblastoma cancer cell line (SH-SY5Y) and analysis data demonstrated that all the complexes have different cytotoxic activities compared to ligand [Fig.7].



$[Ni(L1)_2](ClO_4)_2.2H_2O$ (3)



$[Cd(L1)_2](ClO_4)_2.2H_2O$ (5)



$[Zn(L1)_2](ClO_4)_2.2H_2O$ (6)

Fig. 6. ORTEP diagrams of the complexes **3, 5** and **6**. (40% probability factor for the thermal ellipsoids, H-atoms H_2O molecule and perchlorate ions are omitted for clarity).

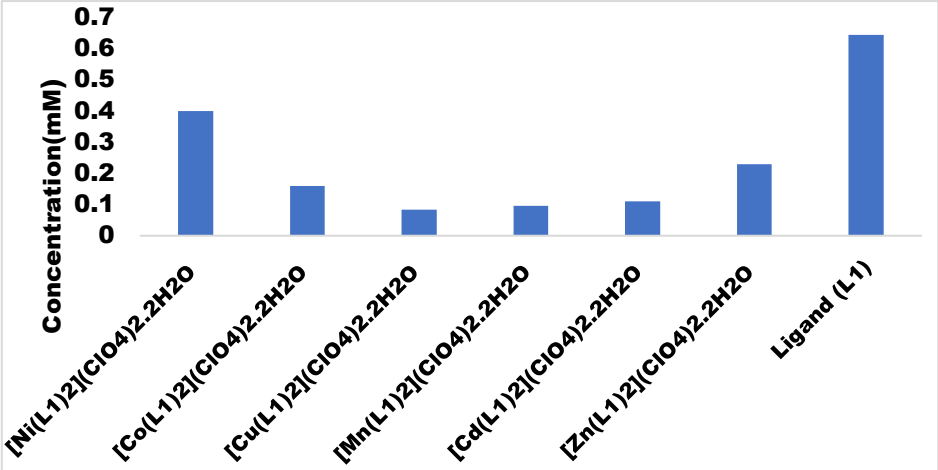


Fig. 7. Result of the cytotoxicity activity of the ligand (L1) and its M(II) complexes against neuroblastoma cancer cell line (SH-SY5Y).

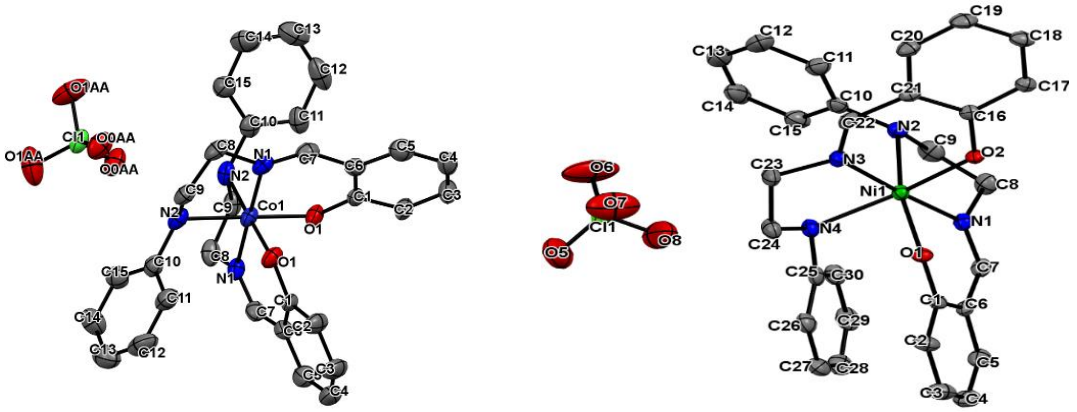
Table 2: IC50 Value of the Complexes

Compound	IC50 Concentration (mM)
$[Ni(L1)_2](ClO_4)_2.2H_2O$	0.4
$[Co(L1)_2](ClO_4)_2.2H_2O$	0.16
$[Cu(L1)_2](ClO_4)_2.2H_2O$	0.083
$[Mn(L1)_2](ClO_4)_2.2H_2O$	0.097
$[Cd(L1)_{2]}(ClO_4)_2.2H_2O$	0.11
$[Zn(L1)_2](ClO_4)_2.2H_2O$	0.23
Ligand (L1)	0.645

Chapter-III: The Chapter III is divided into two parts: Chapter-III(A) and Chapter-III(B).

Chapter-IIIA contains the synthesis and characterization of N_2O donor Schiff base ligand {((2-(phenylamino)ethyl)imino)methyl}phenol (HL2) and its two octahedral complexes $[Ni(L2)(HL2)]ClO_4.0.5CH_3OH$ and $[Co(L2)_2]ClO_4$. The ligand and the complexes were characterized by spectroscopic techniques such as ^1H NMR, IR and UV-Visible spectroscopy etc and single crystal X-ray diffraction studies. The molar conductivities data of the two complexes show both the complexes are 1:1 electrolyte. Single crystal X-ray diffraction data shows both Ni (II) and Co (III) complexes have distorted octahedral geometry and two ligands are coordinated to the metal centers and one ClO_4^- ion outside the coordination sphere. Ligand (L2) acts as tridentate ligand and formed octahedral complexes with Ni(II) and Co(III). The intermolecular interactions in the complexes were evaluated by Hirshfeld surface analysis and revealed a significant contribution of non- or weakly polar interactions to the packing forces for both molecules, with crystal structure of **2** featuring short H/H contacts. The antimicrobial

activity of the Ni(II) and Co(II) complexes were tested against Gram positive (*Bacillus subtilis*, *Streptococcus aureus*) and Gram negative (*Escherichia Coli*, *Proteus Vulgaris*) bacteria by using disk diffusion method and the result demonstrated Ni(II) complex is inactive against all bacteria while Co(III) complex was found to effectively target gram positive bacteria and it is therefore put forward as a promising antimicrobial agent.



[Ni(L2)(HL2)](ClO$_4$) (1) **[Co(L2)$_2$](ClO$_4$) (2)**

Fig. 8 ORTEP diagrams of the Ni(II) and Co(III) complexes. (40% probability factor for the thermal ellipsoids, H-atoms are omitted for clarity).

Table 3: Antimicrobial activity of the Schiff base ligand (L2) and its Ni(II) and Co(III) complexes.

No.	Compound	MIC value in mM			
		E. coli	***P. vulgaris***	***S. aureus***	***B. subtilis***
1	Ligand (L2)	>10,000	>10,000	>10,000	>10,000
2	[Co(L2)$_2$] (ClO$_4$)	>10,000	>10,000	5,000	5,000
3	[Ni(L2)(HL2)](ClO$_4$).2H$_2$O	>10,000	>10,000	>10,000	>10,000
Standard drug	Chloramphenicol	1.5	3	1.5	0.3

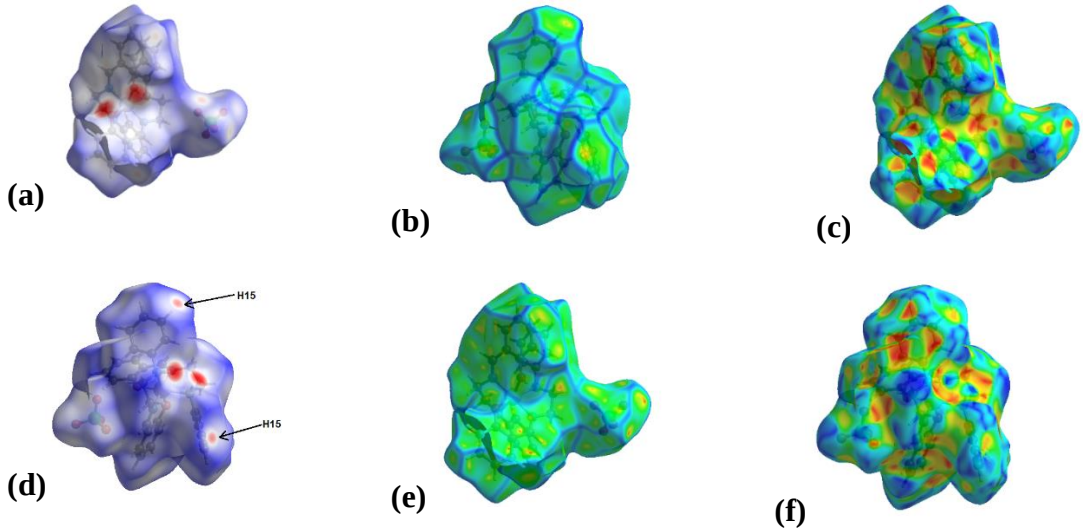
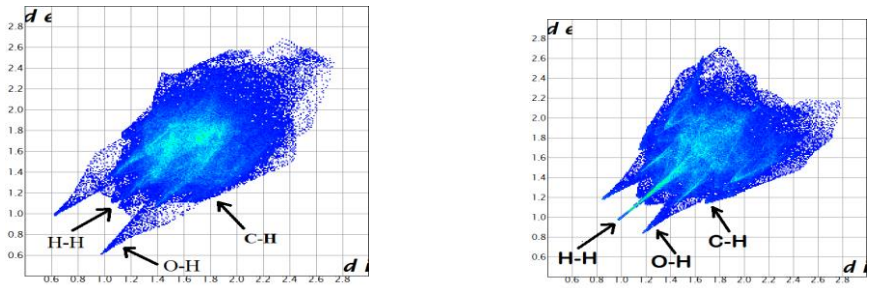


Fig. 9. Hirshfeld surfaces mapped for *d*norm surfaces (a), shape index (b) and curvature (c) of Ni(II) complex and *d*norm surfaces (d), shape index (e) and curvature (f) of Co(III) complex.

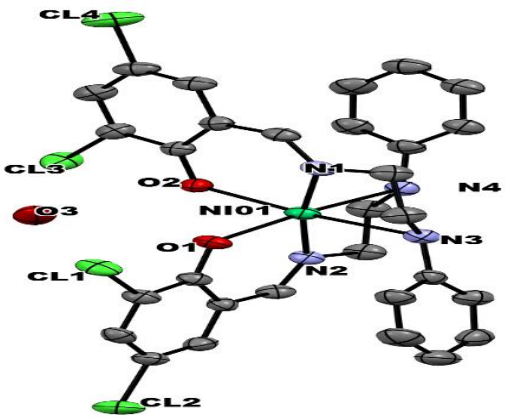


(a) **(b)**

Fig. 10. Finger print plot of (a) Ni(II) and (b) Co(III) complexes: full and resolved into H⋯H, C⋯H and O⋯H contacts.

<u>Chapter-IIIB</u> focuses on synthesis and characterization of new tridentate ligand 2,4-dichloro-6-(((2-(phenylamino)ethyl)imino)methyl)phenol (L3) [Fig.3]. The tridentate N_2O-coordinate ligand (L3) has been used in the synthesis of two mononuclear complexes $[Ni(L3)_2].H_2O$ and $[Co(L3)(HL3)]ClO_4$ and these complexes were characterized by IR and UV-Visible spectroscopy and single X-ray diffraction studies. The molar conductivity data of the Co(II) complex shows that the complex is 1:1 electrolyte due to the presence of one perchlorate ion outside the coordination sphere. Single crystal X-ray diffraction data shows

Ni(II) complex has distorted octahedral geometry and two ligands are coordinated to the metal centers. The antimicrobial activity of the complexes was tested against Gram positive (*Streptococcus pyogenes*, *Streptococcus aureus*) and Gram negative (*Escherichia Coli*, *Pseudomonas Aeruginosa*) bacteria using Broth Dilution Method and the result demonstrated Co (II) complex was found to effectively target both gram positive as well as gram negative bacteria and it is therefore put forward as a promising antimicrobial agent.



[Ni(L3)$_2$)].H$_2$O

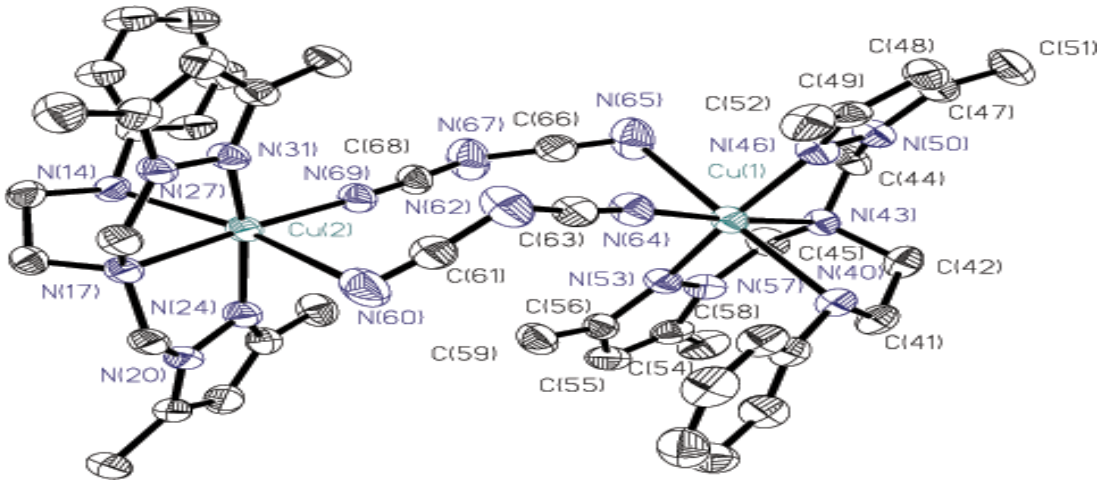
Fig. 11. ORTEP diagram of the Ni(II) complex. (40% probability factor for the thermal ellipsoids, H-atoms are omitted for clarity).

Table 4. Antimicrobial activity of the Schiff base ligand (L3) and its Ni(II) and Co(II) complexes.

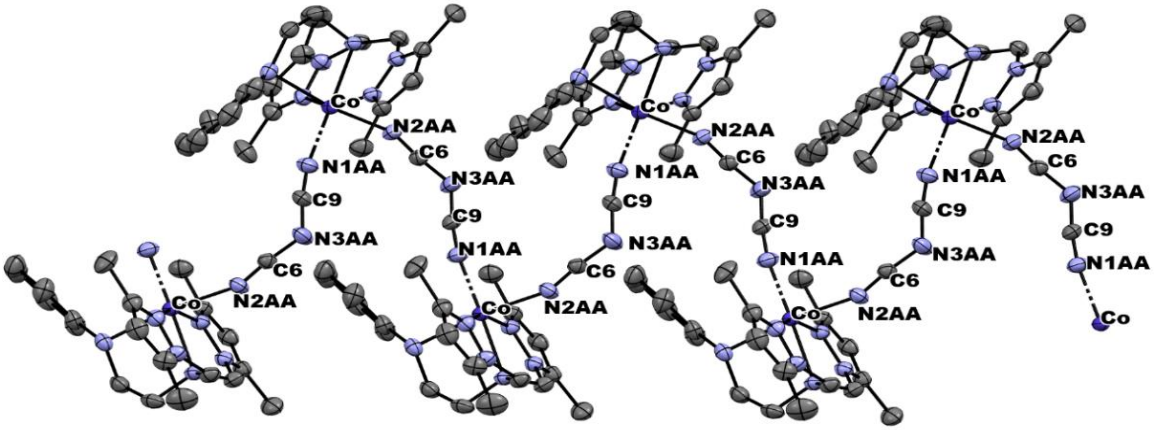
No.	**Compound**	**MIC value in µM**			
		E. coli	***P. aeruginosa***	***S. aureus***	***S. Pyogenes***
1	L-3	100	125	250	125
2	[Co(HL3)(L3)].ClO_4	125	62.5	100	50
3	[Ni(L3)]$_2$.H_2O	250	250	125	100
Standard Drug	Gentamycin	0.05	1	0.25	0.5

Chapter-IV: The Chapter IV is divided into two parts: Chapter-IV(A) and Chapter-IV(B).

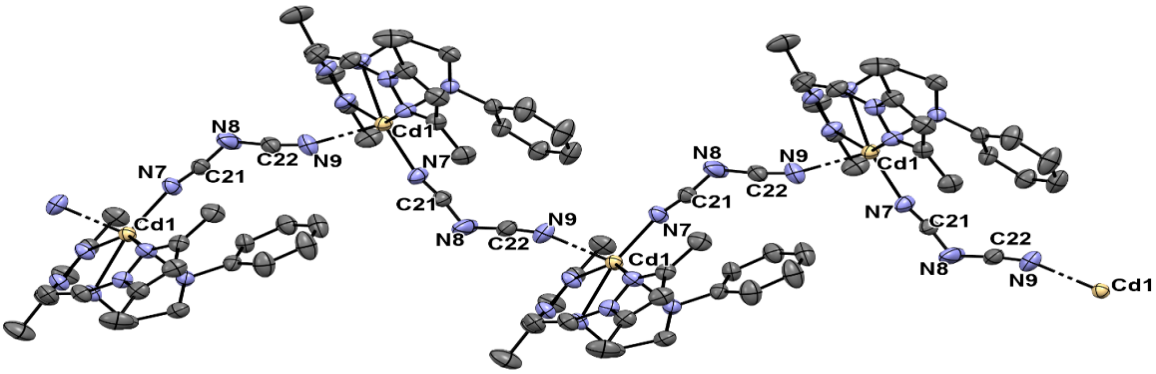
Chapter-IVA is devoted to the synthesis of binuclear copper(II) complex $[Cu(bdpab)(\mu\text{-}_{1,5}dca)]_2(ClO_4)_2$ and polynuclear complexes $[M(bdpab)(\mu\text{-}_{1,5}dca)]_n(ClO_4)_n$ [M = Ni(II), Co(II) and Cd(II) and dca = dicyanamide anion $\{N(CN)_2^-\}$] using pyrazolyl containing tetredentate N_4- coordinate ligand bdpab and bridging ligand dca and characterized by spectral data and single crystal X-ray diffraction studies. Structural characterization by single crystal X-ray diffraction studies show copper complex is binuclear and two copper centers are bridged by two $\mu\text{-}_{1,5}$ dca ligands whereas Co(II) and Cd(II) complexes are polynuclear and two metal centers are bridged by one $\mu\text{-}_{1,5}$ dca ligand in zig-zag pattern and all metal centers have octahedral geometry.



$[Cu(bdpab)\{N(CN)_2\}]_2(ClO_4)_2$ (1)



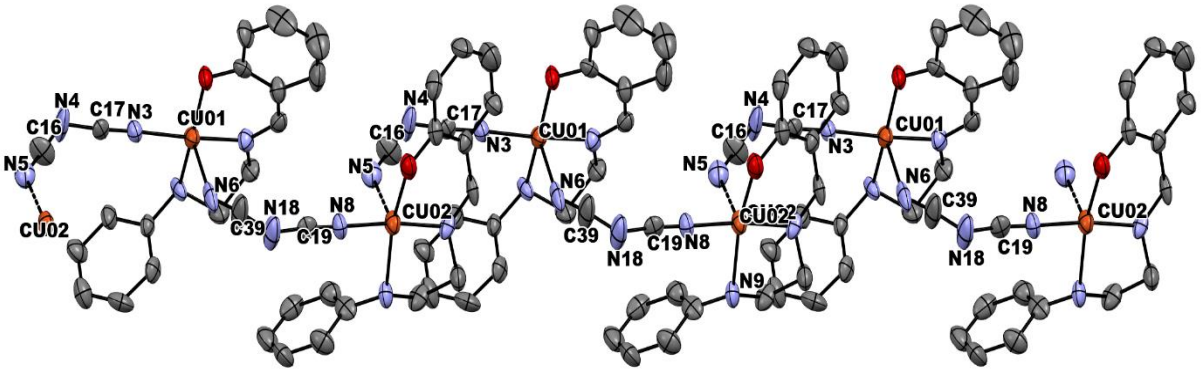
[Co(bdpab){N(CN)$_2$}]$_n$(ClO$_4$)$_n$ (2)



[Cd(bdpab){N(CN)$_2$}]$_n$(ClO$_4$)$_n$ (3)

Fig. 12. ORTEP diagrams depicting cation part of the dimeric complex **1** and polymeric complexes **2** and **3** with atom numbering scheme (40% probability factor for the thermal ellipsoids, H-atoms were omitted for clarity).

<u>Chapter-IV-B</u> focuses on synthesis and characterization a polynuclear copper(II) complex {[Cu(L2)(μ-$_{1,5}$dca)].CH$_3$CN}$_n$, (dca = dicyanamide anion) {N(CN)$_2^-$}] using N$_2$O- donor Schiff base ligand {((2-(phenylamino)ethyl)imino)methyl}phenol (L2) [Fig.2] in presence of bridging ligand dca and characterized by IR and UV-Visible spectroscopy and single X-ray diffraction studies. Structural data shows the complex is polynuclear and two copper centres is bonded through two terminal nitrile group of the $\mu_{1,5}$ dca ligand and each copper centres have distorted square pyramidal geometry.

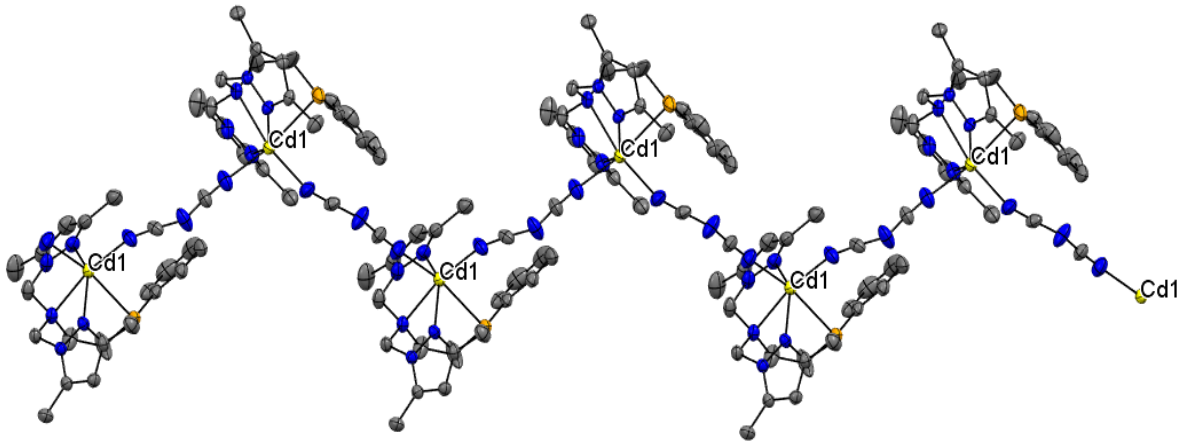


[Cu(L2){N(CN)$_2$}]$_n$(CH$_3$ CN)$_n$

Fig. 13. ORTEP diagram depicting cation part of the polymeric Cu(II) complex with atom numbering scheme (40% probability factor for the thermal ellipsoids, H-atoms were omitted for clarity).

Chapter-V: The Chapter V is divided into two parts: Chapter-V-(A) and Chapter-V(B).

Chapter-V-A outline the synthesis of one new polymeric cadmium(II) complex {[Cd(bdmpe)($\mu_{1,5}$-dca)]ClO_4.CH_3OH}$_n$ by the reaction of cadmium perchlorate with ligand *N,N*-bis((3,5-dimethyl-*1H*-pyrazol-1-yl)methyl)-2-(phenylthio)ethan-1-amine (bdmpe) in presence of dca (dicyanamide, $N(CN)_2^-$) as bridging ligand in methanol and characterized by spectroscopic techniques. Single crystal X-ray diffraction study of the complex confirmed the complex has polymeric 1D chain and each cadmium centers has distorted octahedral geometry with N_5S coordination and is bonded through two terminal nitrile group of the $\mu_{1,5}$ dca ligand. Intermolecular interactions and packing modes of the compound are described by Hirshfeld surface analysis and two-dimensional finger print plots.



$[Cd(bdmpe)\{N(CN)_2\}]_n(ClO_4)_n$

Fig. 14. ORTEP diagram depicting cation part of the polymeric Cd(II) complex with atom numbering scheme (40% probability factor for the thermal ellipsoids, H-atoms were omitted for clarity).

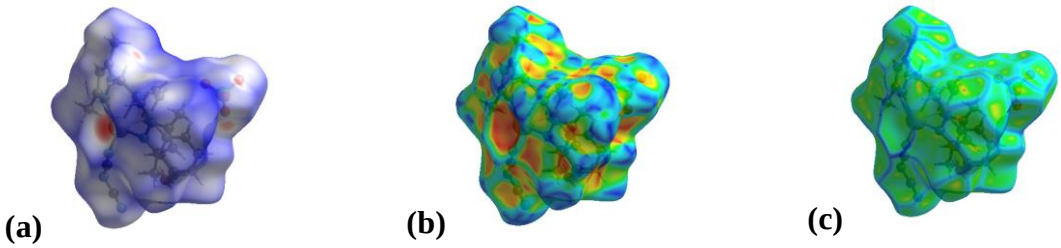
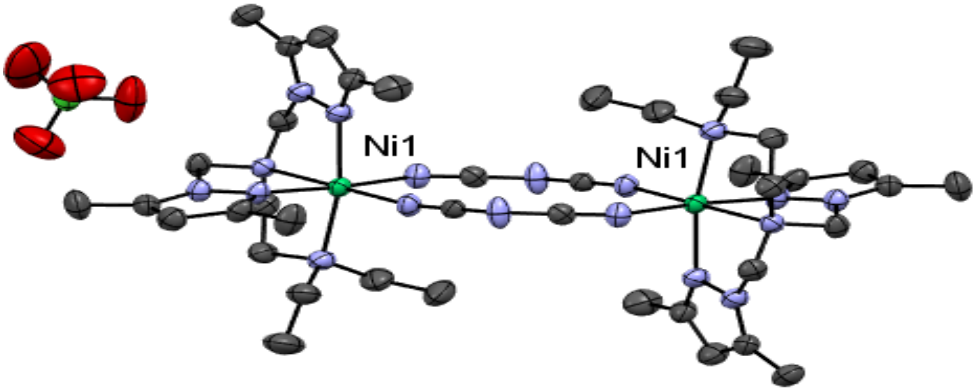


Fig. 15 Hirshfeld surfaces mapped for *d*norm surfaces (a), shape index (b) and curvature (c) of Cd(II) Complex.

(a) **(b)**

Fig. 16. (a) The intermolecular interactions in the polymeric Cd(II) complex. (b) Finger print plot Cd(II) complex indicating relative contributions to the percentage of Hirshfeld surface area for the various intermolecular contacts in Cd(II) complexe.

Chapter-VB describes the synthesis of binuclear transition metal complexes $[Ni(dbdmp)(\mu\text{-}_{1,5}\ dca)]_2(ClO_4)_2$ using tetradentate N_4- coordinate ligand N,N-diethyl-N′,N′-bis((3,5-dimethyl-1H-pyrazol-1-yl)methyl)ethane-1,2-diamine) (dbdmp) and bridging ligand dca [dca = dicyanamide anion $N(CN)_2^-$] and characterized by spectroscopic techniques such as IR, UV-Visible and single crystal X-ray diffraction studies. Structural characterization by single crystal X-ray diffraction studies shows nickel(II) complex is binuclear, each nickel centers has octahedral geometry with N_6-coordination mode and two nickel centers are bridged by two dca ligands with $\mu\text{-}_{1,5}$ coordination mode.



[Ni(dbdmp)**(μ-$_{1,5}$dca)]$_2$(ClO$_4$)$_2$**

Fig. 17. ORTEP diagram of the dimeric Ni(II) complex with atom numbering scheme (40% probability factor for the thermal ellipsoids, H-atoms were omitted for clarity).

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