CHAPTER-1

General Introduction

General Introduction:

Schiff bases are versatile organic compounds which are widely used and synthesized by condensation reaction of different amino compound with aldehydes or ketones. Schiff base ligands are considered as privileged ligands as they are simply synthesized by condensation and reacts with most of the metal ions.

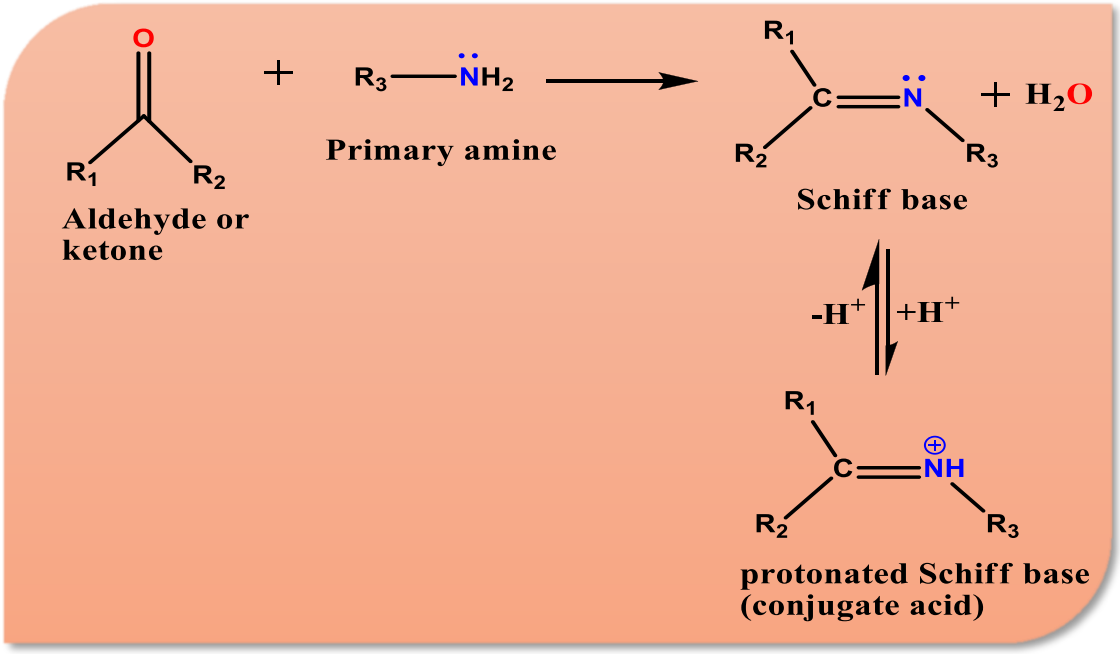


Figure 1.1. The general strategy for the synthesis of the Schiff base.

Hugo Schiff, who first reported the reversible acid-catalyzed condensation reaction between primary amine and carbonyl compounds is known as Schiff base [1,2]. Schiff base ligands are also known as imines [3]. Schiff bases are an important class of ligands for co-ordination chemistry because of their facile syntheses, easy availability and electronic properties and they coordinate to metal ions via azomethine nitrogen [4]. In recent times, coordination chemistry with Schiff base ligands have attracted much attention because of their application in analytical chemistry, refining of metals, metallurgy, electroplating, and photography [5-7]. Schiff bases have wide applications in dye industry, catalysis and agrochemical etc. [8-18]. Several Schiff bases are reported to possess remarkable antifungal, antibacterial, anticancer activities. It is reported that the C=N moiety in the Schiff base ligands is important for biological activity [19]. Many transition metal complexes have been studied using a variety of Schiff base ligands for anticancer, antimicrobial, antifungal and other

biological activities [20-37].

Metal complexes of Schiff bases have occupied a central role in the development of coordination chemistry. This situation is manifested by the huge number of publications ranging from the purely synthetic to modern physicochemical to biochemically relevant studies of these complexes. A tremendous variety of stable chemical species have been synthesized containing both transition and non-transition metals and multidentate Schiff base ligands.

Schiff bases are generally bidentate (1)[38], tridentate (2)[39], tetradentate (3)[40] or polydentate (4)[41] ligands and capable of forming very stable chelate complexes with transition metals. They can only act as coordinating ligands if they bear a functional group, usually the hydroxyl, sufficiently near the site of condensation in such a way that a five or six membered ring can be formed when reacting with a metal ion [Fig.1.2].

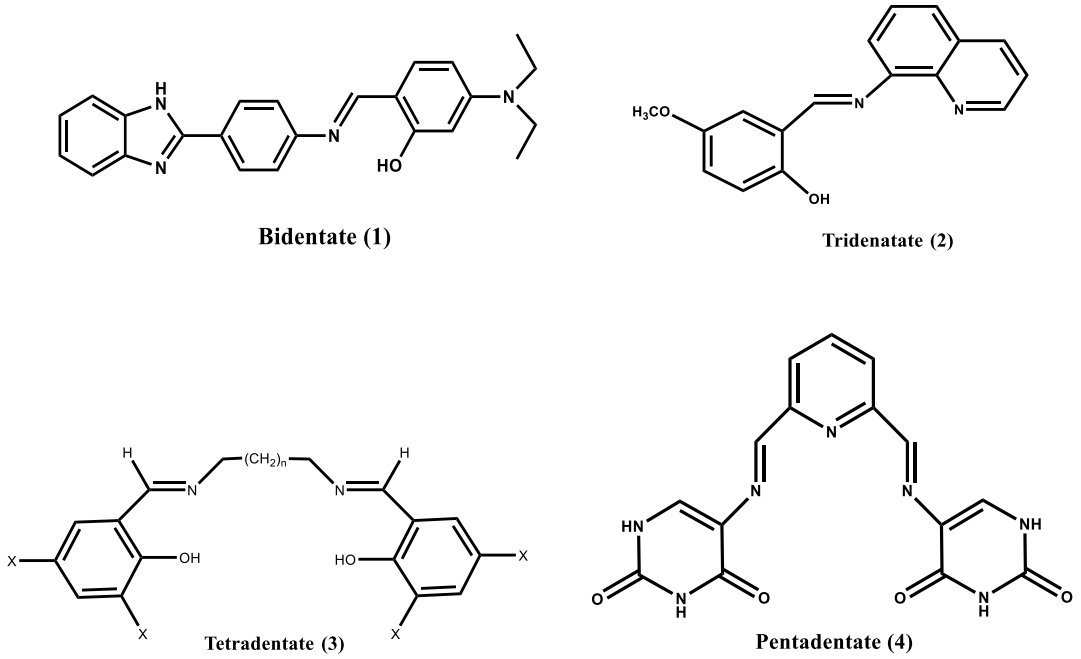
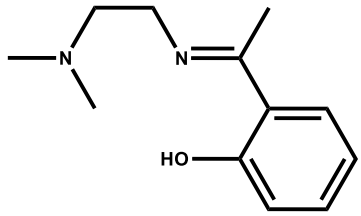


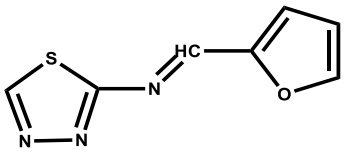
Figure 1.2. Structures of Schiff base ligands.

Metal complexes with heterocyclic containing Schiff bases are of special interest for the chemists because of their structural variability and tunable electronic properties due to the presence of hetero atoms. Hetero atoms like N, O containing Schiff base play a key role in the binding sites of metallobiomolecules. Transition metal ions are an integral part of biological system and become easily soluble in biological fluids, so they have been used in medicines for centuries [42,43].

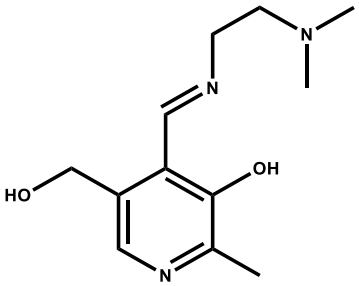
A large variety of NNO [44-56] and NNN [57-64] donor ligands have been synthesized till date and they find large applications due to their convenient preparation and structural varieties.



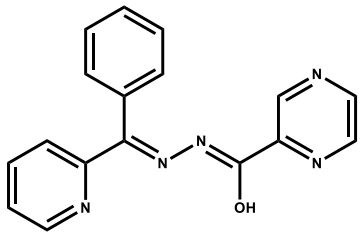
2-(1-((2-dimethylamino) ethyl)imino)ethyl)phenol



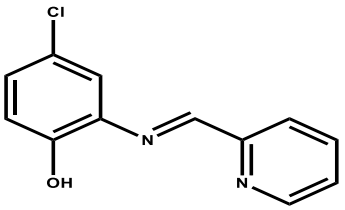
1-(furan-2-yl)-N-(1,3, 4-thiadiazol-2-yl) methanimine



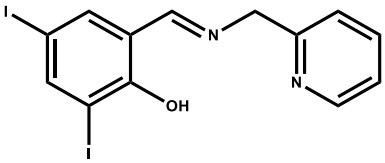
4-(((2-(dimethylamino) ethyl)imino)methyl)-5-(hydroxymethyl)-2-methylpyridin-3-ol



phenyl(pyridin-2-yl) methylene)pyrazine-2-carbohydrazonic acid

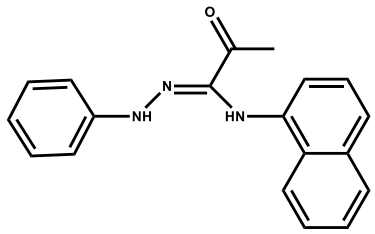


4-chloro-2-((pyridine 2-ylmethylene)amino) phenol

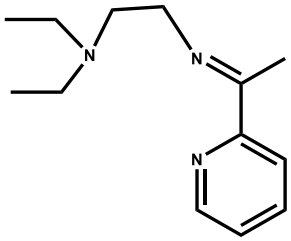


2,4-diiodo-6-(3-(pyridin-2-yl)Prop-1-en-1-yl) phenol

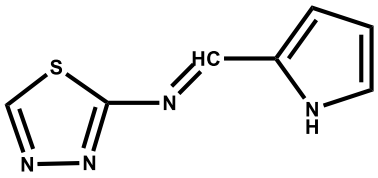
Figure 1.3. Structures of tridentate NNO donor Schiff base ligands.



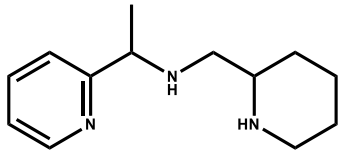
N-(naphthalen-1-yl)-2-oxo-N'-phenylpropane hydrazonamide



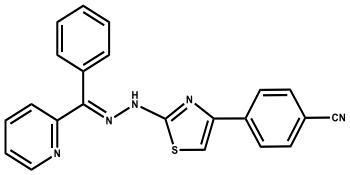
N,N-diethyl-2-((1-(pyridin-2-yl)ethyl idene)amino)ethan-1-amine



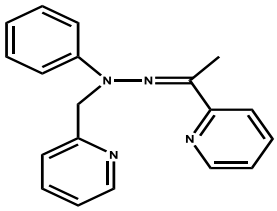
(1H-pyrrol-2-yl)-N-(1,3,4-thiadiazol-2-yl) methanimine



N-(piperidin-2-ylmethyl)-1-(pyridin-2-yl)ethan-1-amine, ammonia salt



4-(2-(2-(phenyl (pyridin-2-yl)meth ylene)hydrazinyl)-3H-pyrrol-5-yl)benzonit-rile



2-((1-phenyl-2-(1-(pyridin-2-yl)ethylidene) hydrazinyl)methyl) Pyridine

Figure 1.4. Structures of tridentate N_3- donor Schiff base ligands.

Importance of Transition metal ions

Transition metals occur in biological systems because they have multiple oxidation states separated by only modest potentials, which make them suitable candidates for electron-transfer processes. Transition metal complexes are subject of research interest for the development of new therapeutic and antimicrobial agents because the metal ions have structural diversity and reactivity and can bind with wide range of ligands. Among the transition metals, copper and cobalt are the most preferred as these are biocompatible and can bind and cleave DNA under physiological conditions. Traces of many transition metal ions are present for as metalloenzyme. Polynuclear, homo and heteronuclear complexes show interesting magnetic properties. Among the transition elements, mainly 3d-series elements and few 4d-elements will be used for complexation in our research works.

Sodium dicyanamide (dca):

Since a few decades in the field of metal-organic frameworks, scientist are more interested in the design and synthesis of new metal-organic framework due to their applications in various field [65]. These are obtained by integrating appropriate anionic/neutral bridging ligands with metal ions in presence of organic ligand acting as blocking ligand, varying the molar ratio and applying suitable reaction conditions [66].

Pseudohalides are ambidentate ligand and can also acts as bridging ligand in the transition metal complexes. Transition metal complexes containing pseudohalides are very interesting because pseudohalides such as N_3^-, NCS^-, $SeCN^-$, NCO^- shows various modes of coordination and form mono, di- and polynuclear complexes [67-80]. The versatile binding modes of pseudohalides made the molecules very interesting due to their interesting structures and magnetic behaviours. The larger pseudohalides like dicyanamide(dca) has attracted a lot of attention, partly due to the long-range magnetic ordering in the M-$(dca)_2$ compound [81,82]. Dicyanamide, like azide, is a flexible ligand that can display numerous coordination modes in transition metal complexes, such as μ-1, μ-1,3, μ-1,5, μ-1,3,5, μ-1,3,5,5 and μ-1,1,3,5,5.[Fig. 1.5]. Because of their different modes of coordination, they can form mono-, di-, and polynuclear complexes. Transition metal complexes containing bridging ligands like dca in presence of multidentate organic ligand will be very interesting. Therefore, we are interested to study the transition metal complexes with dca bridging ligand.

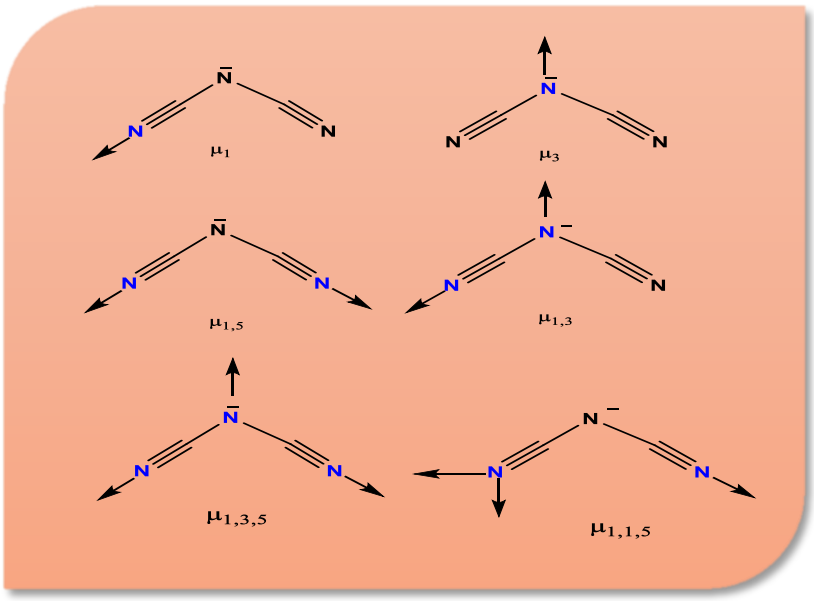


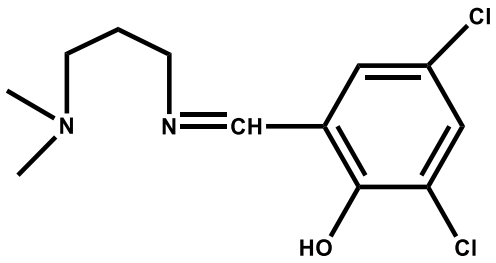
Figure 1.5. Coordination modes of dicyanamide ion $[N(CN)_2^-]$ (dca)

The number of dca-containing polynuclear complexes reported in the literature are less in comparison to other pseudohalides like azide or thiocyanate. That's why dca has been used as bridging ligand in the synthesis of coordination polymer.

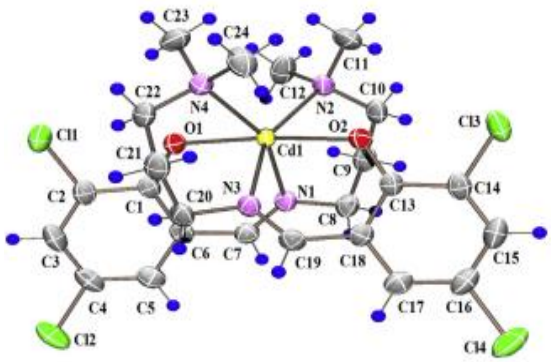
1.1. Review of the present status of the chemistry of tridentate Schiff base ligands and their compounds.

It is clear that Schiff base ligand have rich coordination chemistry and form transition metal complexes with different coordination number and geometry. There are many papers reported with Schiff base ligands and their metal complexes.

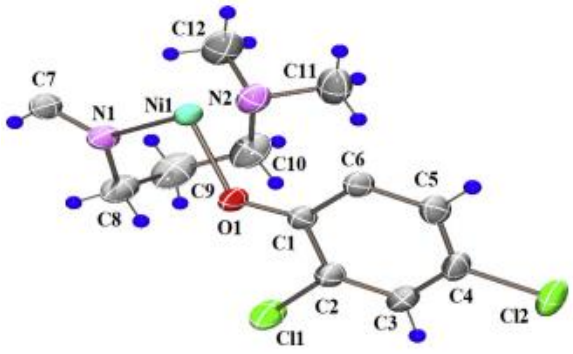
Mononuclear nickel(II) complex [NiL_2] and cadmium(II) complex [CdL_2].H_2O with tridentate Schiff base ligand 2,4-dichlorido-6-((3-(dimethylamino) propylimino)methyl) phenol (HL) was reported by M. Jayendran et. al [83].



(a)



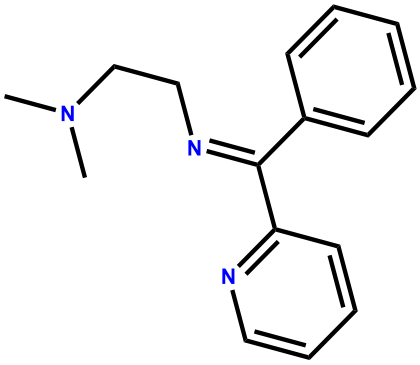
(b)



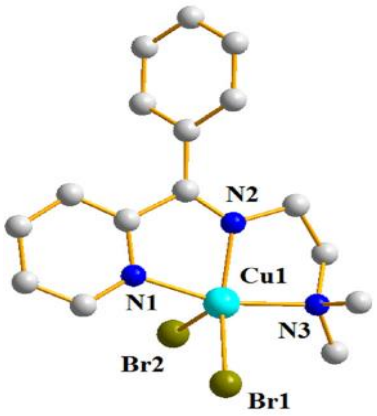
(c)

Figure. 1.6. The Crystal structure of (a) Ligand 2,4-dichlorido-6-((3-(dimethylamino) propylimino)methyl)phenol (HL) (b). [CdL_2].H_2O (c) [NiL_2] (adapted from Ref. (83)

Mononuclear copper complexes of the type $[Cu(L)(X)_2]$ (X = Cl, Br), $[Cu_3(L)_2(I)_5]$ and $[Cu(L)(Cl)(ClO_4)]$ were synthesized with tridentate N_3 donor Schiff base ligand (N,N-dimethyl-N'-[phenyl(2-pyridyl)methylene]ethane-1,2-diamine)(L) [Fig.1.7] and characterized with structures by Li et.al [84]



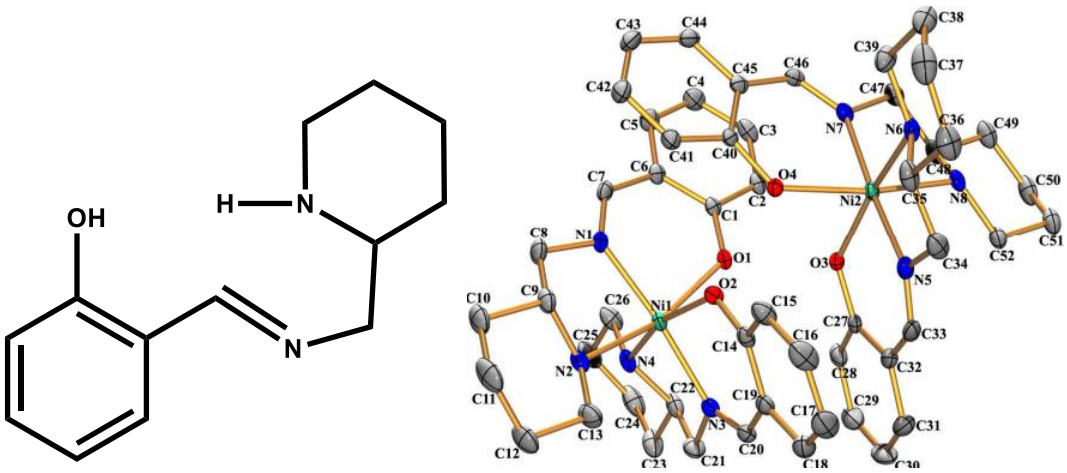
(a)



(b) **(c)**

Figure. 1.7. Structure of (a) tridentate Schiff base ligand (N,N-dimethyl-N'-[phenyl(2-pyridyl)methylene]et hane-1,2-diamine) (b) $[Cu(L)(Cl)_2]$ (c) $[Cu(L)(Br)_2]$. (adopted from m Ref. 84)

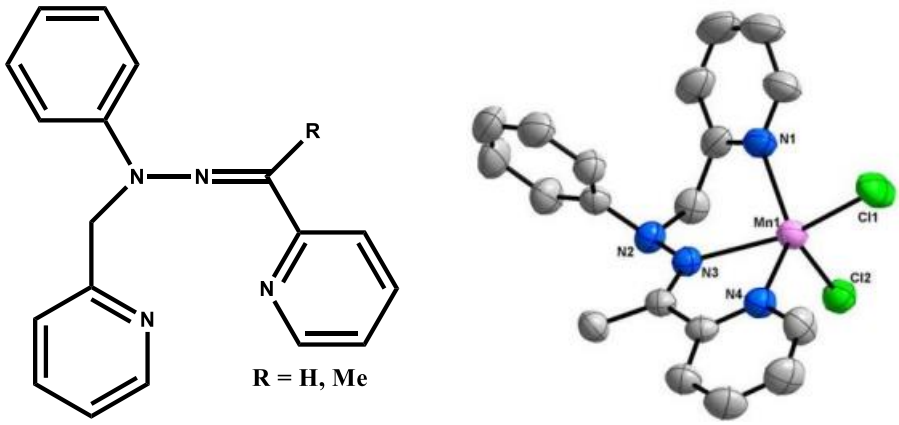
A NNO donor Schiff base ligand 2-[(piperidin-2- ylmethylimino)-methyl]-phenol)(HL) and mononuclear Ni(II) metal complex of the type $[Ni(L)_2]$ was synthesized and characterized by single crystal X-Ray diffraction studies by K. Jana et.al [85].



(a) **(b)**

Figure. 1.8. Structure of (a) tridentate Schiff base ligand 2-[(piperidin-2- ylmethylimino)-methyl]-phenol)(HL) (b) $[Ni(L)_2]$ complex (adapted from Ref. 85) .

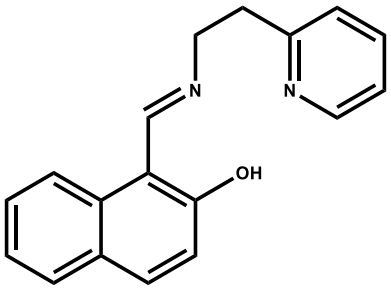
Synthesis and characterization of Mn(II) complexes using tridentate NNN donor ligands H─N3L (1-phenyl-1-(pyridine-2-ylmethyl)-2-(pyridine-2-ylmethylene) hydrazine) and Me─N3L (1-phenyl-2-(1-(pyridin-2-40yl)ethylidene)-1-(pyridin-2-ylmethyl) hydrazine) reported by S. Rathi et al.



(a) **(b)**

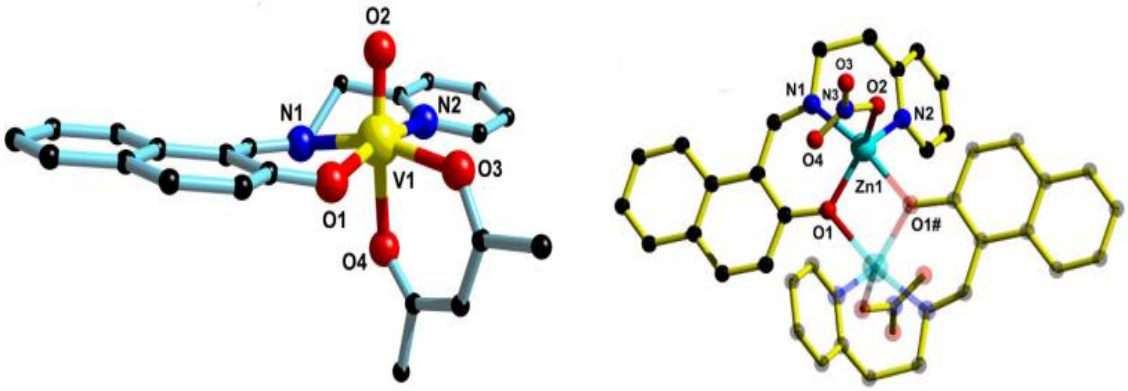
Figure. 1.10. Structure of tridentate Schiff base ligands (a). (H─N3L) or (Me─N3L) (b) $Mn(Me─N3L)Cl_2$ (adapted from Ref. 86)

Tridentate N_2O donor Schiff base ligand 1–[(2–pyridin–2–yl–ethylimino)–methyl]–naphthalen–2–ol, (HPEMN) and a series of mono and polynuclear complexes of Zn(II), Co(II), Cu(II) and VO(II) were synthesized by B. Naskar et. al. in order to study the various non–covalent interactions[87].



HPEMN

(a)



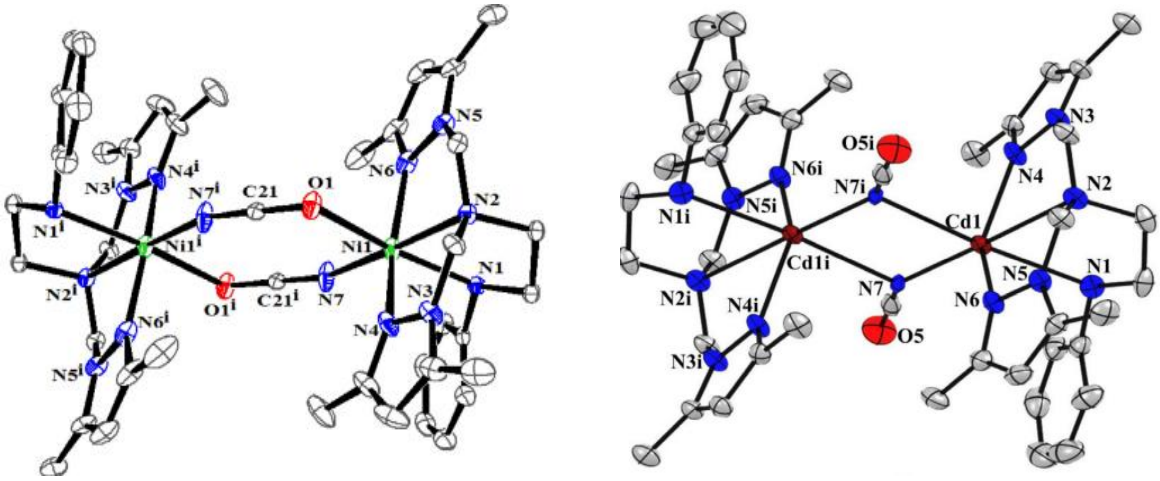
(b) **(c)**

Figure. 1.9. Structure of (a) tridentate Schiff base ligand 1–[(2–pyridin–2–yl–ethylimino)–methyl]–naphthalen–2–ol, (HPEMN) (b) VO(II) and (c) Zn(II) complexes (adapted from Ref. 87).

1.2. Chemistry of pyrazolyl containing tetradentate ligands and their compounds.

Pyrazolyl based tetradentate ligands are chelating ligand and form a variety of coordination complexes with M(II) ions in presence of bridging pseudohalides ligands like N_3^-, SCN^-, NCO^- etc and most of the reported complexes are either mono- or dinuclear complexes. There are only few polynuclear complexes are reported. Mononuclear complexes with square pyramidal geometry of the type [M(bdpab)(NCO)]X [M = Cu(II)

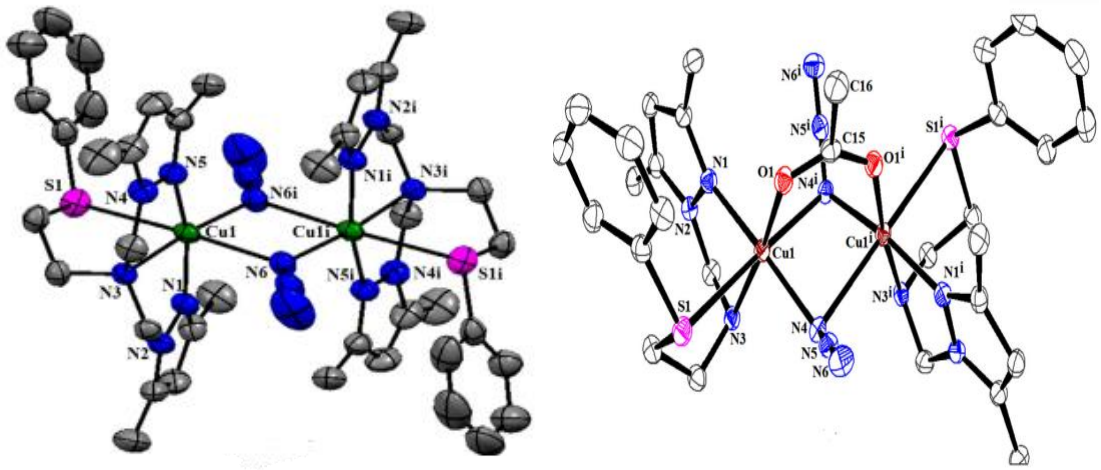
and Co(II), X = PF_6^- or ClO_4^-] and binuclear NCO^- bridged octahedral complexes of the formula [M` (bdpab)(μ-NCO)]$_2$(X)$_2$ [M` = Ni(II) and Cd(II)] with bdpab (N,N-bis(3,5-dimethyl -1 H-pyrazol-1-yl)methyl-N_2-phenylethane-1,2-diamine ligand were synthesized by sadhu et al[88].



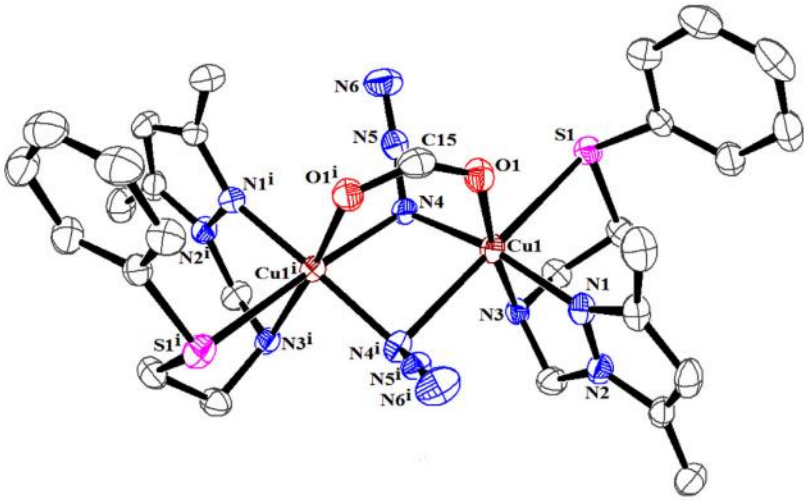
(a) **(b)**

Figure. 1.11. The Crystal structure of (a) [Ni(bdpab)($\mu_{1,3}$-NCO)]$_2$(ClO_4)$_2$ (b) [Cd(bdpab)($\mu_{1,1}$-NCO)]$_2$(ClO_4)$_2$ (adapted from Ref. 88)

Dinuclear triple bridged Cu(II) complexes of the type [Cu_2(dmpe)$_2$($\mu_{1,1}$-N_3)$_2$(CH_3COO)]PF_6 [dmpe = N-((3,5-dimethyl-1H-pyrazol-1-yl)methyl)- 2-(phenylthio) ethan-1-amine] and [Cu_2(dmpe)$_2$(μ1,1-N_3)$_2$(HCOO)]PF_6 were synthesized and characterized with structure and studied their magnetic properties by sadhu et al[Fig 12].



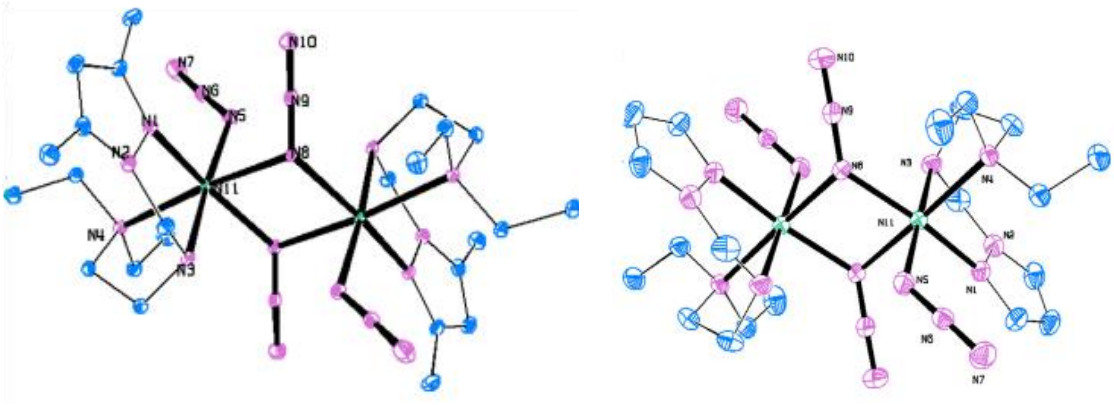
(a) **(b)**



(c)

Figure. 1.12. The Crystal structure of (a) $[Cu_2(bdmpe)_2(N_3)_2](ClO_4)_2$ (b) $[Cu_2(dmpe)_2(\mu_{1,1}\text{-}N_3)_2(CH_3COO)]PF_6$, and (c) $[Cu_2(dmpe)_2(\mu_{1,1}\text{-}N_3)_2(HCOO)]PF_6$ (adapted from Ref. 89)

Ankita et al. synthesized and characterized binuclear octahedral nickel(II) complexes with azide of the type $[Ni_2(L_1`)_2(N_3)_2(\mu\text{-}N_3)]$ and $[Ni_2(L_2`)_2(N_3)_2(\mu\text{-}N_3)]$, where L_1, L_2, $L_1`$ and $L_2`$ are N,N-diethyl-N`,N`-bis((3,5-dimethyl-1H-pyrazol-1-yl)methyl)-ethane-1,2-diamine (L_1), N,N-bis((1H-pyrazol-1-yl)methyl)-N`,N`-diethylethane-1,2-diamine (L_2), N,N-diethyl-N`-((3,5-dimethyl-1H-pyrazol-1-yl)methyl)ethane-1,2-diamine ($L_1`$) and N-((1H-pyrazol-1-yl)methyl)-N`,N`-diethylethane-1,2-diamine ($L_2`$).



(a) **(b)**

Figure. 1.13. The Crystal structure of (a) $[Ni_2(L_1`)_2(N_3)_2(\mu\text{-}N_3)]$ and (b) $[Ni_2(L_2`)_2(N_3)_2(\mu\text{-}N_3)]$ (adapted from Ref. 90)

A series of mononuclear Zn(II) complexes of the type [Zn(X)(dbdmp)]Y (where, X = N_3^-/NCO^-/ NCS^-, Y = ClO_4^-/PF_6) and binuclear octahedral Cd(II) complexes of the type [{Cd(dbdmp)}$_2$(μ-N_3)$_2$](ClO_4)$_2$ were synthesized and characterized with structures using ligand N,N-diethyl-N`,N`-bis((3,5-dimethyl-1H-pyrazol-1-yl)methyl)ethane-1,2-diamine (dbdmp) [Fig 1.14].

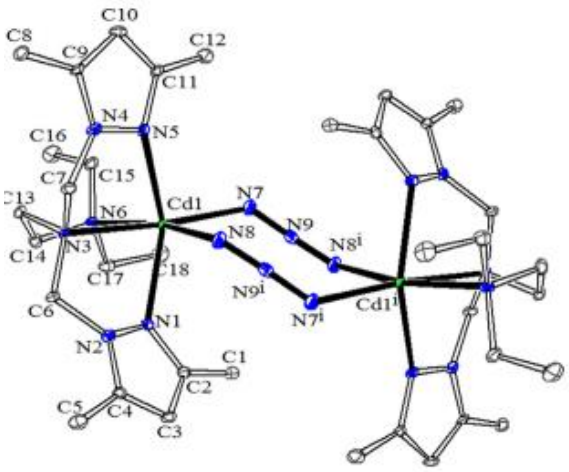


Figure. 1.14. The Crystal structure of [Cd(NCS)$_2$(dbdmp)]
(adapted from Ref. 91)

Polymeric 1D structures with SCN^- and $SeCN^-$ bridged octahedral cadmium(II) complexes [Cd(dpip)(μ$_{1,3}$-SCN)$_2$]$_n$ and [Cd(dpip)(μ$_{1,3}$-SeCN)$_2$]$_n$, [where dpip = 3,5-dimethyl-1-((3-phenylimidazolidin-1-yl)-methyl)-1H-pyrazole] were synthesized and characterized by Sadhu et al [Fig. 1.21].

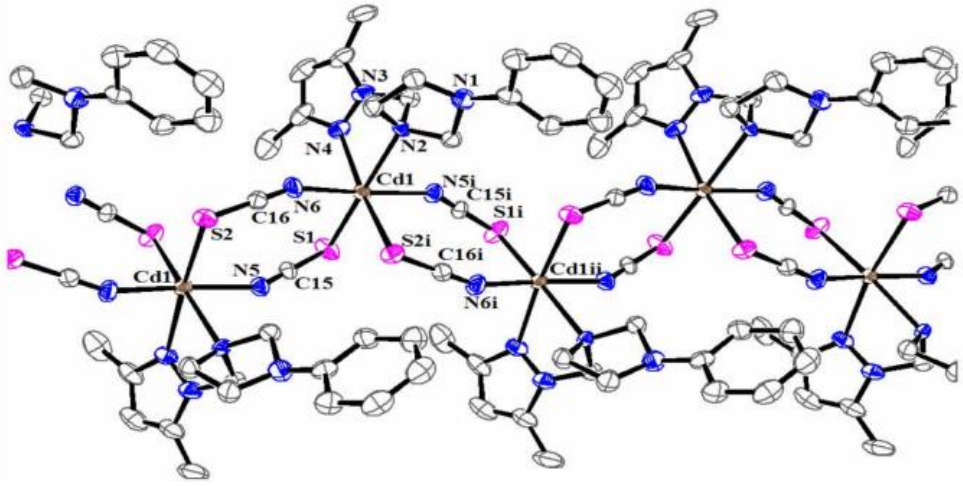
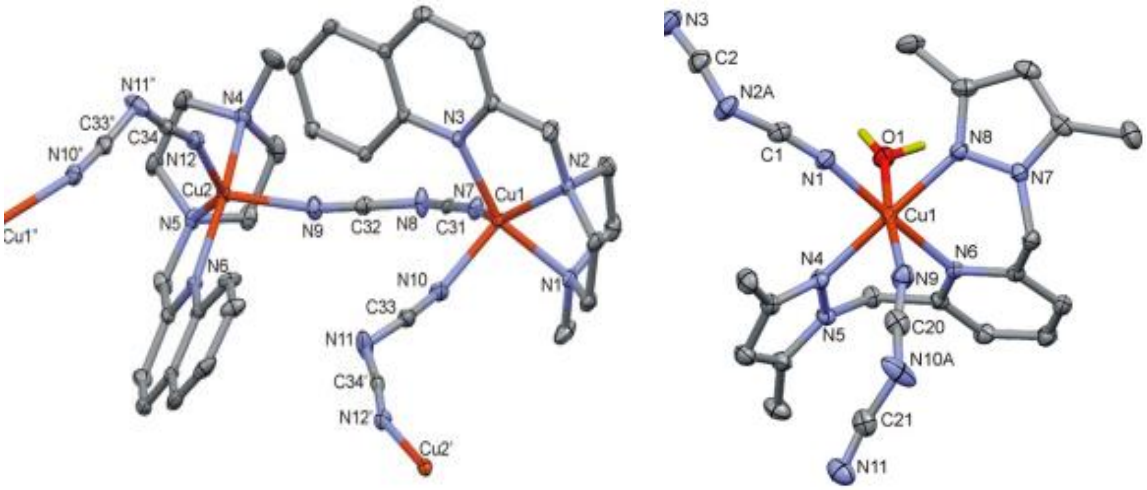


Figure. 1.15. The Crystal structure of [Cd(dpip)(μ$_{1,3}$-SCN)$_2$]$_n$.
(adapted from Ref. 92)

There are only few reports on the synthesis and structural characterization of mutinuclear M(II) ions complexes with pyrazolyl based ligand in presence of larger pseudohalide like dca.

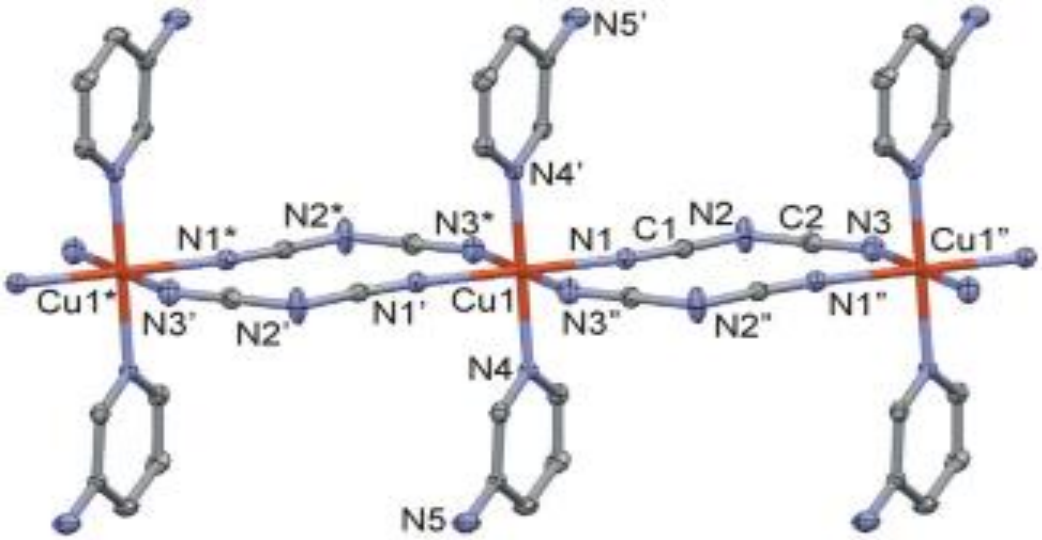
S. S. Massoud et al has synthesized mono-nuclear copper(II) complex $[Cu(bdmpzpy)(dca)_2(H_2O)]$ where bdmpzpy = 2,6-bis[(2,5-dimethyl-1H-pyrazolyl)methyl] pyridine and dca acts as monodentate ligand and polymeric $\{[Cu(mpiq)(\mu\text{-}_{1,5}\text{- dca})]ClO_4\}_n$ [mpiq = N-methyl-N-(2-quinolylmethyl)-piperazine)] and the coordination mode of dca is $\mu\text{-}_{1,5}$ in this complex [93].



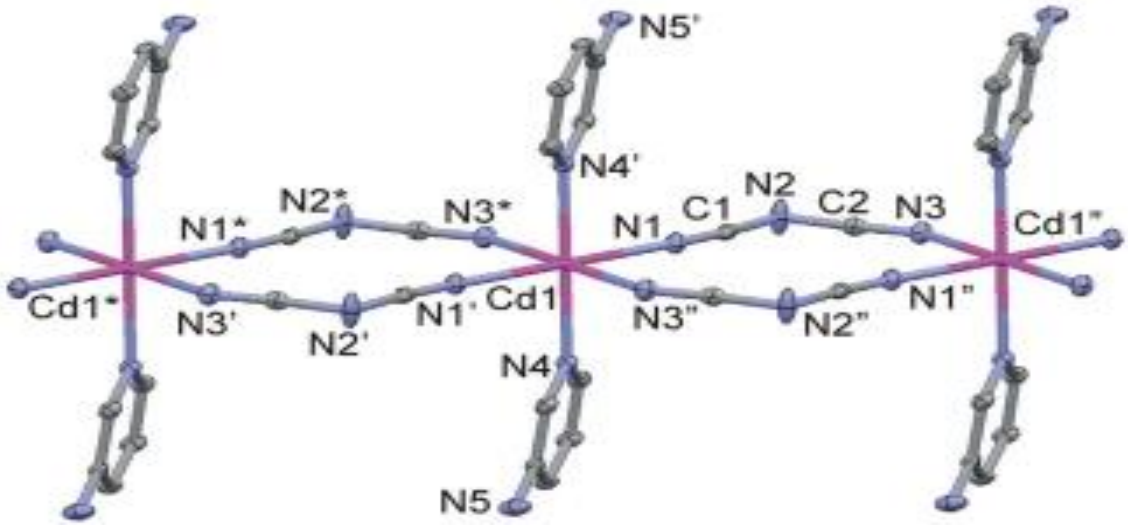
(a) **(b)**

Figure. 1.16. The Crystal Structure of (a) $[Cu(bdmpzpy)(dca)_2(H_2O)]$ and (b) $\{[Cu(mpiq)(\mu\text{-}_{1,5}\ dca)]ClO_4\}_n$ (adapted from Ref. 93)

Polymeric M(II) [Cu, Co, Zn and Cd] complexes were synthesized by Mautner et al using organic ligand 4-hydroxymethylpyridine (4-OMP) in presence of dicyanamide (dca) as bridging ligand. It shows the bridging mode of dca is $\mu\text{-}_{1,5}$ in all complexes. [94].



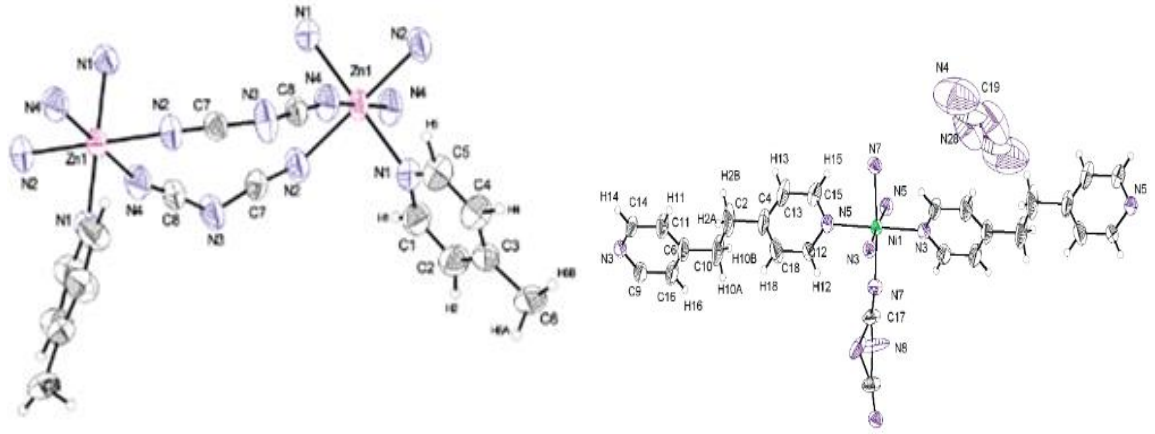
(a)



(b)

Figure 1.17. The crystal structure of (a) $[Cu(dca)_2(4\text{-}MOP)_2]_n$ and (b) $[Cd(dca)_2(4\text{-}MOP)_2]_n$ (adapted from Ref. 94)

New dca containing complexes $[M(dca)_2(bpa)]_n$ [M = Mn(II), Fe(II), Co(II) and Zn(II) and bpa = 1,2-bis(4-pyridyl)ethane] and $[Ni(dca)(bpa)_2]dca.6H_2O$ were synthesized and characterized by Noelia de la Pinta et al. [95].



(a) **(b)**

Figure 1.18. The Crystal Structure of (a) $[M(dca)_2(bpa)]_n$ and (b) $[Ni(dca)(bpa)_2]dca.6H_2O$ (adapted from Ref. 95)

It has been observed that bridging mode μ-$_{1,5}$ is the common mode of coordination for most of the synthesized complexes.

1.3. Present Work

The coordination chemistry of multidentate Schiff base ligands are very interesting as they can produce complexes with different coordination numbers (four to six) in the presence/absence of co-ligand and different geometry ranging from tetrahedral to square planar (for four coordination complexes), square pyramidal to trigonalbipyramidal (for five coordination) and octahedral for six coordination complexes. The variety of structures found in biological systems inspired us to prepare these complexes with different metal ions. It has been observed that Schiff base containing multidentate ligand forms mono and polynuclear complexes in the presence of halide and pseudohalides with various geometry. So we are interested to study the coordination behaviour of new tridentate N_3 or N_2O donor Schiff base ligands in presence of different M(II) ions. We are also interested in the synthesis of coordination polymer using multidentate organic ligand and pseudohalides as bridging ligands. As there are many report on polymeric complexes using bridging pseudohalides like azide, thicyanate and isocyanate, we are interested to use Schiff base or pyrazolyl based tetradentate ligand as organic blocking ligand and larger pseudohalide dca as bridging ligand.

Objectives of Present work

- Synthesis of new Schiff base tridentate ligands which can provide N_3 and N_2O coordination.
- Syntheses of transition metal complexes with different metal ions such as Cu(II), Ni(II), Co(II), Mn(II), Zn(II) and Cd(II) using the synthesized Schiff base ligands.
- Synthesis of multinuclear M(II) complexes with N_4-coordinate tetradentate pyrazolyl base ligands using bridging ligand dca.
- Characterization of the synthesized complexes by IR, NMR, microanalysis, UV-Vis, magnetism and EPR spectroscopy.
- To determine the structure of the synthesized complexes by single crystal X-ray diffraction studies and Hirshfeld surface analysis.
- To study the biological activities such as antimicrobial activity and cytotoxic activity of synthesized complexes.

The work has been carried out to complete the objectives and divided into following chapters.

In the **Chapter 1,** brief introduction about the coordination chemistry of multidentate Schiff base ligands and pyrazole containing tetradentate ligands is presented.

Chapter 2 is divided into two parts: **Chapter 2(A)** and **Chapter 2(B)**

In the chapter 2(A), synthesis and characterization of one new tridentate N-coordinate ligand N′-phenyl-N′′-(phenyl(pyridin-2-yl)methylene)ethane-1,2-diamine (L1) [Fig. 1.19] has been discussed. The tridentate N_3-coordinate ligand L1 has been used in the synthesis of a series 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 antimicrobial activity of all complexes was investigated against Gram-positive and Gram-negative bacteria by disk diffusion method.

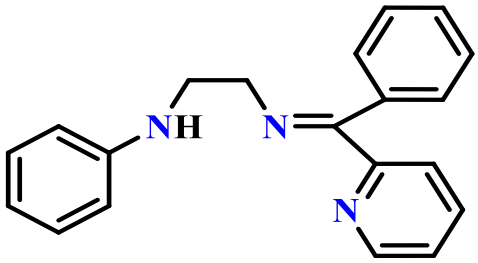


Figure. 1.19. Structure of ligand N′-phenyl-N′′-(phenyl (pyridin-2-yl)methylene)ethane-1,2-diamine (L1)

Chapter 2(B), consists of the syntheses, characterization and structures of mononuclear octahedral M(II) [M = Cu(II), Mn(II), Co(II), Ni(II), Zn(II) and Cd(II)] complexes using the ligand L1 [Fig. 1.19]. The synthesized complexes were characterized by microanalysis, IR, electronic spectra, single crystal X-ray diffraction studies. Cytotoxic activity of the all the complexes was investigated against neuroblastoma cancer cell lines SHSY5Y.

Chapter 3 is divided into two parts: **Chapter 3(A)** and **Chapter 3(B)**

Chapter-3(A) consists of synthesis and characterization of Ni(II) and Co(III) complexes using tridentate N_2O donor Schiff based ligand namely {((2-(phenylamino) ethyl)imino)methyl}phenol (HL2) [Fig. 1.20]. The complexes were characterized by different spectroscopic techniques and single crystal X-ray diffraction studies. The intermolecular interactions of both the complexes were evaluated by Hirshfeld surface analysis. The antimicrobial activity of the complexes was screened against *Gram positive* and *Gram-negative* bacteria using disk diffusion method.

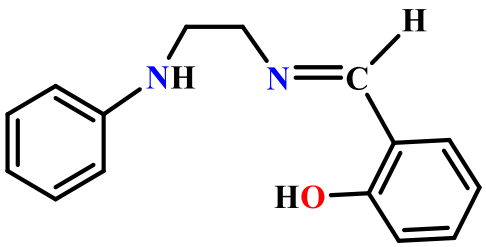


Figure. 1.20. Structure of ligand 2-(((2-phenylamino)ethyl)imino)methyl)phenol (HL2)

In the chapter 3(B), Synthesis and characterization of mononuclear Ni(II), Co(III) and trinuclear Cd(II) complexes with new tridentate N_2O donor Schiff based namely 2,4-dichloro-6-(((2-(phenylamino)ethyl)imino)methyl)phenol (HL3) have been described [Fig. 1.21]. The synthesized compounds were screened for their antimicrobial activity against *Gram positive* and *Gram-negative* bacteria.

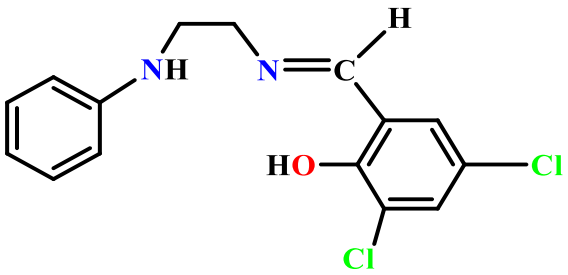


Figure. 1.21. Structure of ligand 2,4-dichloro-6-(((2-(phenylamino)ethyl)imino) methyl)phenol (HL3)

Chapter 4 is divided into two parts: **Chapter 4(A)** and **Chapter 4(B)**.

Chapter 4(A) described synthesis and characterization of multinuclear M(II) [M = Cu(II), Co(II), Ni(II) and Cd(II)] complexes with pyrazolyl containing tetradentate N_4-coordinated ligand N,N-bis(3,5-dimethyl-1H-pyrazol-1-yl) methyl-N2-phenylethane-1,2-diamine(bdpab) in presence of dca as co-ligand [Fig. 1.22]. Structural data shows copper(II) complex is binuclear and two copper centres are bridged by two dca with μ-$_{1,5}$ coordination mode and cobalt(II) and cadmium(II) complexes are polynuclear and two metal centres are bridged by one $\mu_{1,5}$-dca and all the metal centres have octahedral geometry.

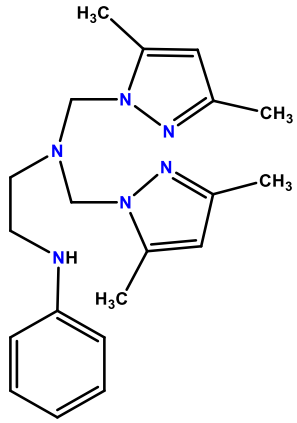


Figure. 1.22. Structure of ligand N,N-bis(3,5-dimethyl-1H-pyrazol-1-yl) methyl-N_2-phenylethane-1,2-diamine(bdpab)

Chapter 4(B) consists of synthesis of polynuclear Cu(II) complex with tridentate HL2 ligand in presence of bridging ligand dca and characterized by elemental analysis, IR spectra,

electronic spectra, EPR spectra and single-crystal X-ray diffraction studies. Structural data confirmed that Cu(II) complex is polynuclear and two copper(II) centres are bridged by dca using μ-1,5 coordination mode.

Chapter 5 is divided into two parts: **Chapter 5(A)** and **Chapter 5(B).**

In the chapter 5(A), synthesis, characterization with structure and Hirshfeld surface analysis of polymeric Cd(II) complex $\{[Cd(bdmpe)(\mu\text{-}_{1,5}dca)]ClO_4.CH_3OH\}_n$ with tetradentate pyrazolyl containing N_3S donor ligand N,N-bis((3,5-dimethyl-1H-pyrazol-1-yl)methyl)-2-(phenylthio) ethan-1-amine (bdmpe) [Fig. 1.23] in presence of bridging ligand dicyanamide has been described.

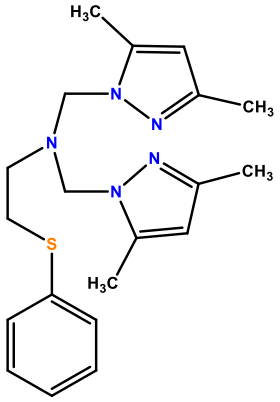


Figure. 1.23. Structure of ligand N, N-bis((3,5-dimethyl-1H-pyrazol-1-yl)methyl)-2-(phenylthio)ethan-1-amine (bdmpe)

Chapter 5(B) described synthesis and characterization with structures of binuclear Ni(II) and Cd(II) complexes of the type $[M(dbdmp)(\mu\text{-}_{1,5}dca)]_2(ClO_4)_2$ using N_4-coordinated pyrazole based tetradentate ligand N,N-diethyl-N′,N′-bis((3,5-dimethyl-1H-pyrazol-1-yl)methyl)ethane-1,2-diamine) (dbdmp) [Fig. 1.24] as blocking ligand in presence of bridging ligand dca.

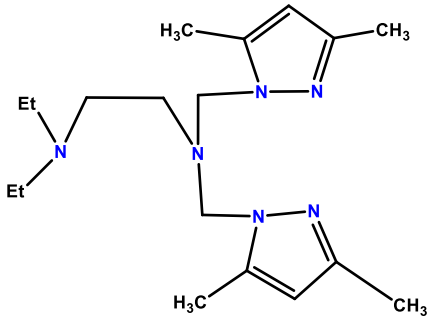


Figure. 1.24. Structure of ligand N,N-diethyl-N′,N′-bis((3,5-dimethyl-1H-pyrazol-1-yl)methyl)ethane-1,2-diamine) (dbdmp).

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