General Introduction:

The chemistry of nitrogen containing heterocycle based ligands is of special interest because they constitute an important class of natural and synthetic products, many of which exhibit useful biological activities [1–3]. The coordination chemistry of transition metals and nitrogen containing heterocyclic ligand 2,2'-bipyridine was introduced by F. Blau [4]. Bidentate and tridentate nitrogen containing heterocyclic ligands such as 1,10-phenanthroline and 2,2':6',2''-terpyridine have been extensively used in the transition and non-transition metal complexes as they are excellent π-acceptors. Hence, they provide soft sites for metal coordination [5-6]. The development of coordination chemistry of nitrogenous ligands and their applications in the variety of fields like chemical, structural, catalysis etc. have encouraged us to design nitrogen containing multidentate ligand. Imidazole, pyrazole, and oxazole derivatives are in general well-known π-excessive five-member nitrogen-containing heterocyclic compounds and they are poorer π-acceptors, in fact, they are better π-donor and hence act as hard donor sites [7]. Among these heterocycles, we are currently interested in pyrazole and substituted pyrazole containing ligand due to their variety of applications.

Pyrazole is five-membered heterocyclic aromatic ring which consist of three carbon atoms and two nitrogen atoms at the positions 1 and 2 as shown in the Fig.1.1. The N(1)-H is acidic in nature due to the proton, whereas the N(2) is basic due to lone pair in the sp^2 orbital. Therefore, a basic character is present in the pyrazole molecule. Tautomerism exists in the case of symmetrical substitution, or non-substitution on the ring, unless the substituent is in position 1, because the rupture of the N-C bond is more difficult than that of the N-H bond.

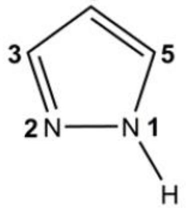


Fig.1.1. Structure of Pyrazole

The coordination chemistry of Pyrazole containing ligands started in 1889 with the report of a silver pyrazole complex, $[Ag(pz)]_n$ [8]. Much later, pyrazole containing anionic tripodal poly(pyrazole)borate ligand was introduced by Trofimenko in 1966 and it has been extensively employed to stabilize a variety of organometallic and coordination compounds [9-12]. Transition metal complexes with pyrazole based ligands have wide applications. At present, a number of review articles on pyrazole containing ligands and their complexes are available in the literature [7, 13-17]. A new method for the N-substituted pyrazole derivatives with different amines and their coordination behaviour towards first-row transition metal ions was reported by Driessen [18-24]. Many multidentate chelating ligands were synthesized by following this method. The spacer groups play a very important role in a designing of multidentate ligands. They are regulating the steric and electronic properties of the metal complexes by connecting the different coordination moieties at a desired distance from each other. When methylene group is incorporated between the rings, the electronic communication between these two heterocyclic is prevented and the complexes of such ligands give rise to significantly different electronic properties. The coordination chemistry of pyrazole-based chelating ligands, which consist of pyrazole heterocycles linked by NR (R = H or alkyl or benzyl or pyridine-CH_2) with incorporation of 'insulating spacer(s)' between the coordinating sites is also well-developed and the complexes of such ligands give rise to significantly different electronic properties. The design of such ligands will be the important factor influencing the stability and molecular geometry of the complexes.

Pseudohalides:

Pseudohalides like azide, thiocyanate, isocyanate and selenocyanate are ambidentate ligands. Transition metal complexes containing pseudohalides as co-ligand are very interesting because of their various modes of coordination and formation of mono, di- and polynuclear complexes [25-31]. Among these, azide and thiocyanate anion are versatile ligands. The azide ion bridges the metal center either by end-on ($\mu_{1,1}$) or end-to-end (μ-$_{1,3}$) coordination mode whereas the thiocyanate ion preferably adopts end-to-end (μ-$_{1,3}$) coordination mode [32-36]. Pseudohalides can also act as monodentate ligand and form mononuclear complex with transition elements (Fig.1.2.) [37-38]. But it is not possible to know whether they will act as monodentate or bridging ligand in the bi- and polynuclear complexes. The magnetic behaviour of Ni(II) and Cu(II) complexes with different modes of coordination of N_3^- and NCS^- ions are reported [26].

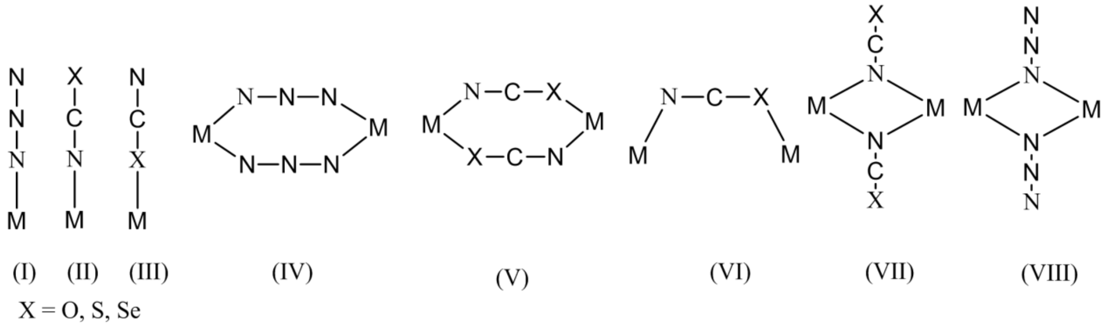


Fig.1.2. Different coordination mode of pseudohalides with metal ion.

Carboxylates and Nitrite ligands

Carboxylate ions are versatile ligands and can act as a monodentate ligand [39-41] (a) or bidentate ligand [42-43] (b) or bridging ligand (c and d) [44-45] and coordinate to metal centres and form mono, di- or polynuclear [46-47] complexes (Fig.1.3.).

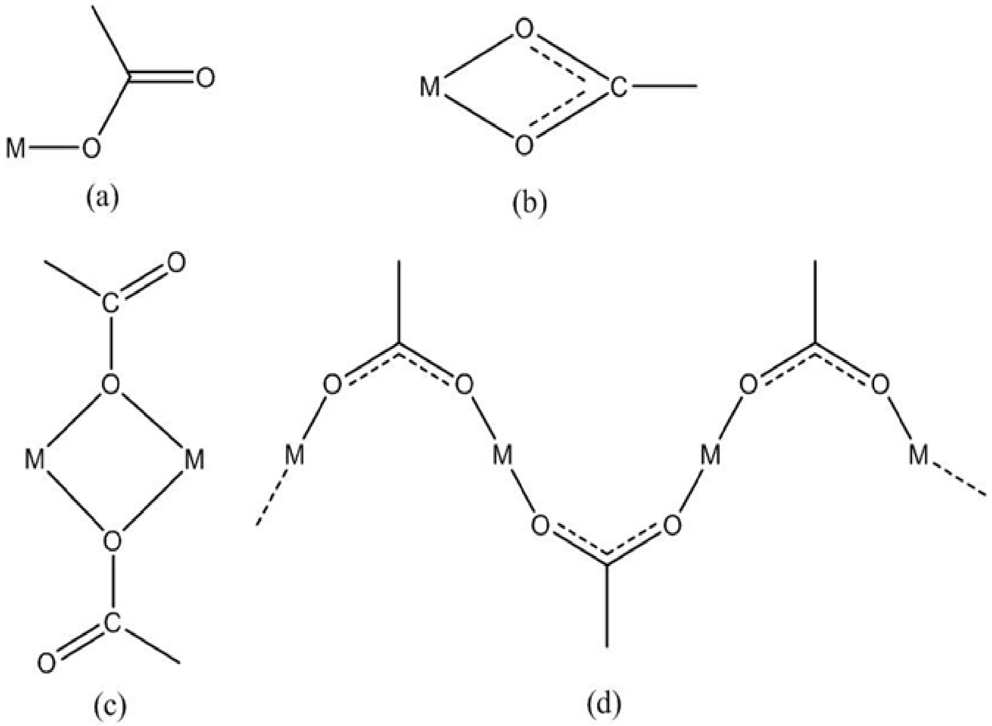


Fig.1.3. Different coordination mode of acetate ion.

Nitrito ion is also an ambidentate ligand and has different mode of coordination with metal ions (Fig.1.4.). It can act as a monodentate ligand either binding through nitrogen or through oxygen atom [48-49]. As a bidentate ligand, it can coordinate or bridge through nitrogen and oxygen atom or through both oxygen atoms or through single oxygen atom [48, 50-56]. There are few reports available in which nitrite act as a tridentate ligand [57-59]. The nitrite-bridged polynuclear complexes and their magnetic behaviour were also reported [60-66].

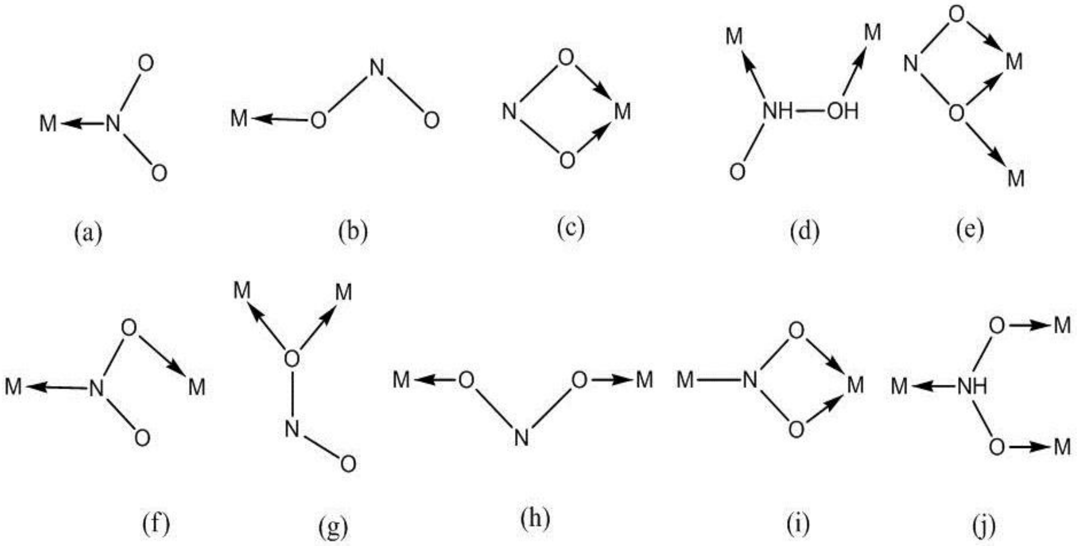
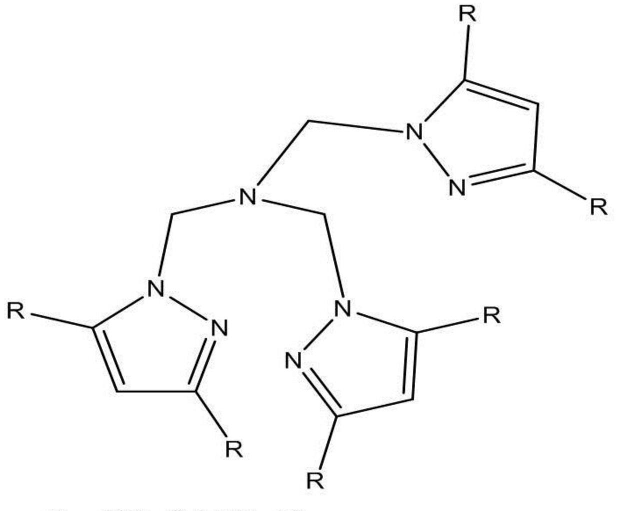


Fig.1.4. Different coordination mode of nitrite ion.

1.1. Review of the present status of the chemistry of pyrazolyl containing tetradentate ligands and their compounds.

It is clear that pyrazolyl containing multidonour ligand have rich coordination chemistry and form transition metal complexes with varying coordination number and geometry. In the present time many papers are reported dealing with the chemistry of pyrazolyl containing ligands and their metal complexes. Therefore we have restricted our discussion only to the nitrogen containing pyrazole based tetradentate ligands and their compounds as these are relevant to the chemistry are presented in the dissertation.

The tetradentate ligand tris(3,5-dimethyl-1-pyrazolylmethyl)amine (MeTPyA) was synthesized by F. Mani et al and its coordination behaviour was investigated by reaction with iron(II), cobalt(II), and nickel(II) ion [67]. The complexes have general formula [M(MeTPyA)X]BPh_4, (M = Fe, X = Cl, Br; M = Co, X = Cl, Br, I, NCS; M = Ni, X = Cl, Br), [Ni(MeTPyA)F]$BPh_4 \cdot CH_3COCH_3$, [Fe(MeTPyA)(NCS)I] and [Co(MeTPyA)]$(NO_3)_2$. The iron(II) complexes are penta- and hexa-coordinated whereas the coordination geometry of cobalt complexes are intermediate between trigonal bipyramidal and tetrahedral. The nickel complexes [Ni(MeTPyA)X]BPh_4 are dimeric, bridged through halide ion and has hexa-coordination with a ferromagnetic interaction between adjacent nickel ions. The zinc(II) isothiocyanate complex of ligand TPyA was synthesized and characterized by single crystal X-ray diffraction studies [68]. The remarkable feature of complex [Zn(TPyA)$(NCS)_2$] is that one pyrazole group of the ligand TPyA is not coordinated to the Zn(II) center and it has distorted tetrahedral geometry.

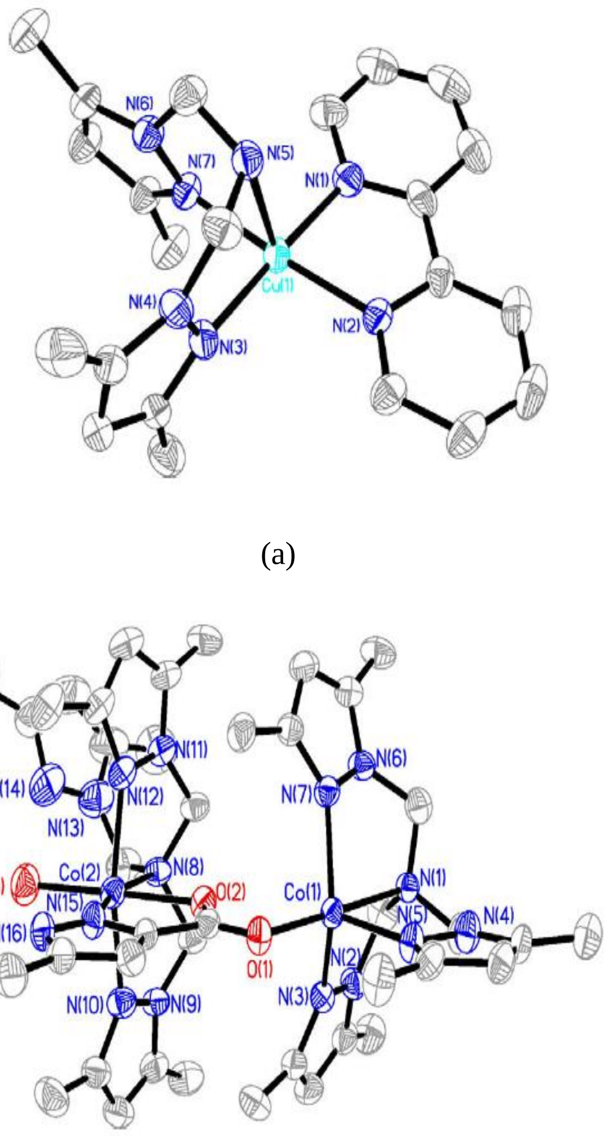


$R = CH_3$ (MeTPyA)
R = H (TPyA)

Fig.1.5. Structure of ligand MeTPyA and TPyA.

A series of mono and binuclear metal complexes of the type [Cu(DMPzA)(2,2′-bipy)] $(ClO_4)_2$, [(DMPzA)Cu(μ-4,4′-bipy)Cu(DMPzA)]$(ClO_4)_4$, [(MeTPyA) Cu (μ-H_2DPC)Cu(DMPzA)]$(ClO_4)_2$ and [(DMPzA) Co (μ-H_2DPC) Co (MeTPyA)] $(ClO_4)_2$ [bipy = bipyridine; H_2DPC = pyridyl-2,6-bicarboxylate; DMPzA = bis(3,5-bimethyl-pyrazolmethyl)amine] with ligand MeTPyA were synthesized and characterized [69]. The single crystal structure confirmed that when pyridyl derivatives were added as co-ligand to the reaction mixture, the tripodal ligand MeTPyA loses a pendant arm and coordinates with the metal center to form the complexes.

The effect of the pyridine ring on the cleavage of the pendant arm in the tripodal ligand was studied on the complex [(MeTPyA)Co(μ-HZPC) Co(MeTPyA) $(H_2O)_2](ClO_4)_3$. It was synthesized using pyrazole-carboxylate (HZPC) instead of pyridyl derivatives. The results confirmed that the complexes with MeTPyA have a strong ability to recognize pyridine compounds in methanol solvent.



(a)

(b)

Fig.1.6. Crystal structures of $[Cu(DMPzA)(2,2'\text{-bipy})](ClO_4)_2$ (a) and $[(MeTPyA)Co(\mu\text{-}HZPC)Co(MeTPyA)(H_2O)_2](ClO_4)_3$ (b) (adapted from Ref. 69).

Penta coordinate cobalt(II)-salicylate complex [(MeTPyA)Co(HSA)]ClO_4 of ligand MeTPyA was synthesized by B. Chakraborty et.al [70] and the cobalt atom adopted distorted trigonal bipyramidal geometry.

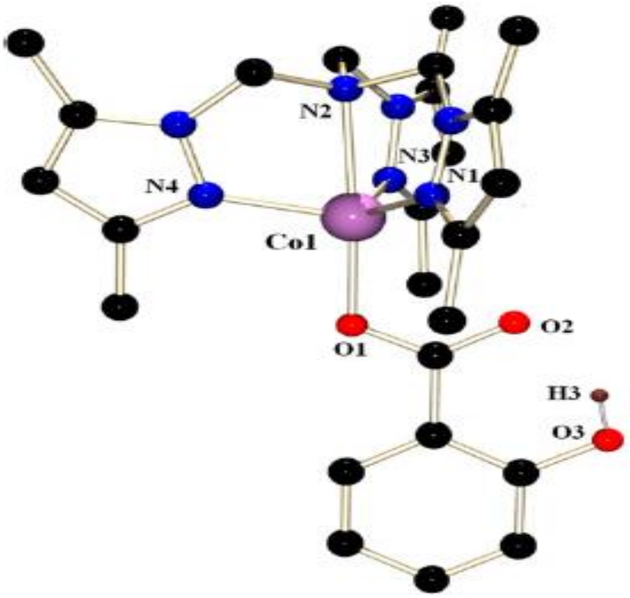


Fig.1.7. Crystal structure of [(MeTPyA)Co(HSA)]ClO_4 (adapted from Ref. 70).

A novel complex [Co(MeTPyA)Cl]$_2$[CdI_4] was prepared in situ from the redox reaction of Co^0, $CdCl_2$, NH_4I, 1-hydroxymethyl-3,5-dimethylpyrazole and was characterized by single crystal X-ray diffraction, IR, UV–VIS as well as magnetic and thermal investigations [71]. Ligand MeTPyA is formed in situ during the redox process of 1-hydroxymethyl-3,5-dimethylpyrazole and ammonia. There are two symmetry-independent cations present in the unit cell with C_3 point group symmetry. The overall symmetry of the complex [Co(MeTPyA)Cl]$_2$[CdI_4] was C_3V.

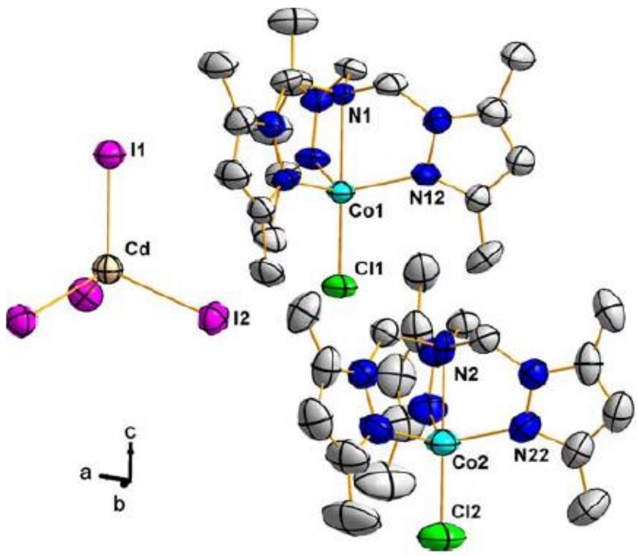


Fig.1.8. Crystal structure of [Co(MeTPyA)Cl]$_2$[CdI$_4$] (adapted from Ref. 71).

N,N′-dimethylethylenediamine based tetradentate ligand 2,5-bis(3,5-dimethyl pyrazol-l-ylmethyl)-2,5-diazahexane (debd) was synthesized by Driessen et.al [22]. A series of transition metal complexes of the type [M(debd)X] were synthesized from ligand debd in the presence of different coordinating anions Cl^- / Br^- / N_3^- / NCS^- (M = Mn, Fe, Co, Ni, Cu, Zn, Cd, X =NCS; M = Mn, Co, Ni, Co, Zn, Cd, X=N_3; M = Mn, Cd, X = Cl, Br). Single crystal X-ray structure of the complex [Ni(debd)(N$_3$)$_2$] confirmed octahedral geometry and two azide ions are in cis position with respect to nickel atom. The structure of [Cd(debd)Cl$_2$] are similar to [Ni(debd)(N$_3$)$_2$] and show that Cd octahedron are more distorted than the Ni octahedron [72]. The structure determinations of [Cu(debd)(NCS)$_2$] were carried out at 140 K and 298 K. It shows there is no change of the geometry of the complex although Cu-N bond lengths changes with temperature [73].

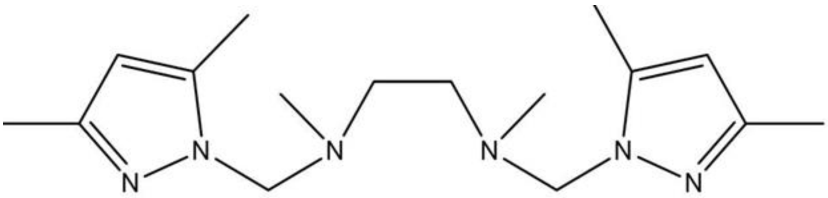
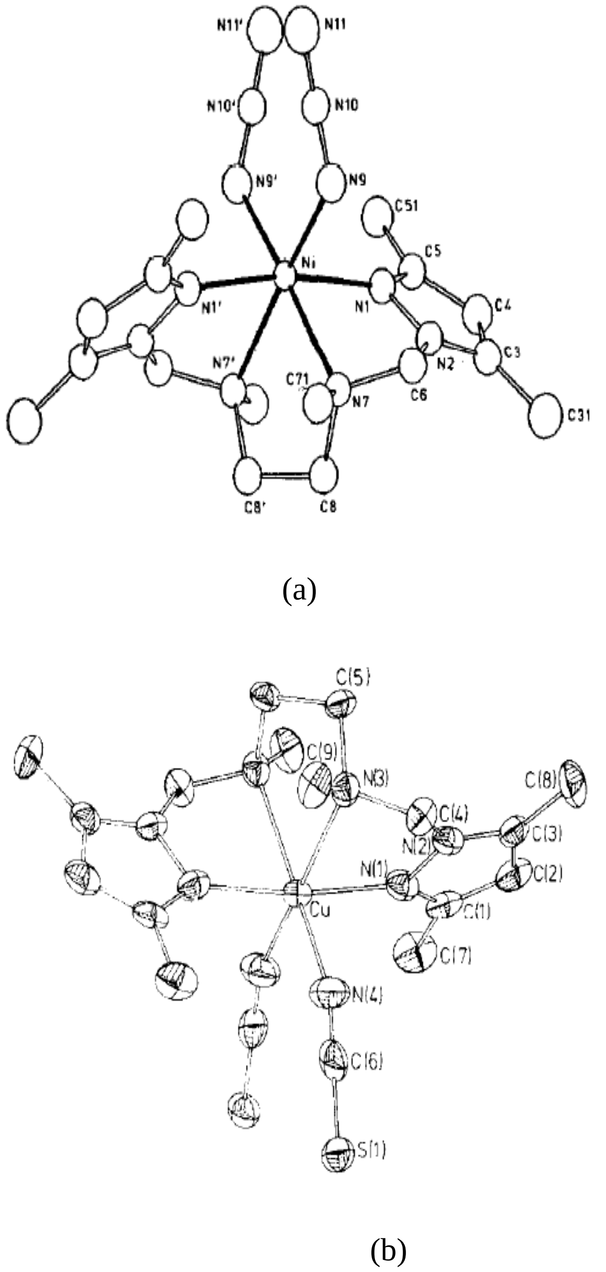


Fig.1.9. Structure of debd ligand.



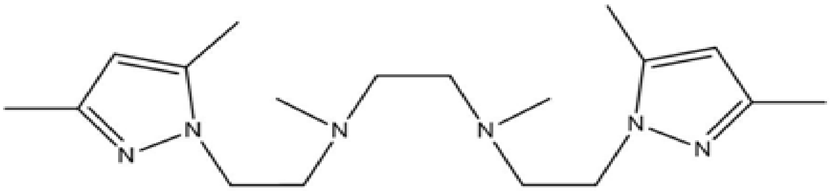
(a)

(b)

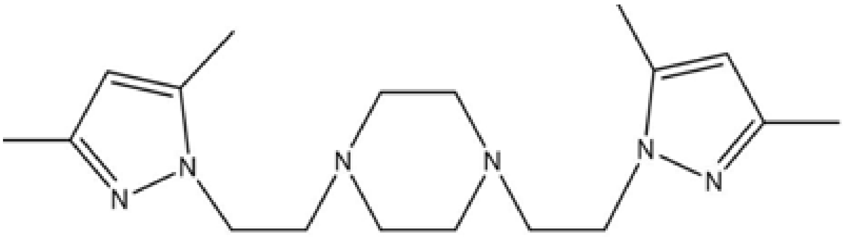
Fig.1.10. Crystal structures of $[Ni(debd)(N_3)_2]$ (a) and $[Cu(debd)(NCS)_2]$ (b) (adapted from Ref. 72 and 74).

Two N_4-coordinate tetradentate ligands 3,6-dimethyl-1,8-(3,5-dimethyl-1-pyrazolyl)-3,6-diazaoctane (ddad) and 1,4-bis(2-ethyl-(3,5-dimethyl-1-pyrazolyl))-pjperazine (bedp) were synthesized by Haanstra et.al [74]. A series of coordination complexes of M(II) ion and the ligand ddad are reported: $[M(ddad)](BF_4)_2$ (M = Cu, Ni), $Co(ddad)(H_2O)(BF_4)_2$, $[M_2(ddad)C1_4]$ (M = Co, Ni, Cu, Zn), $[Co_3(ddad)_2(NCS)_6]$ and $[Cu_2(ddad)(NCS)_3]$. The complexes $[Cu(ddad)][BF_4]_2$, $[Ni(ddad)][BF_4]_2$ and

[Ni(ddad)(NCS)$_2$] were characterized by single-crystal X-ray diffraction studies. The ligand ddad is coordinated with metal ion in square planar geometry but when two additional trans thiocyanate ions are coordinated to nickel centre, it forms octahedral [Ni(ddad)(NCS)$_2$] complex.



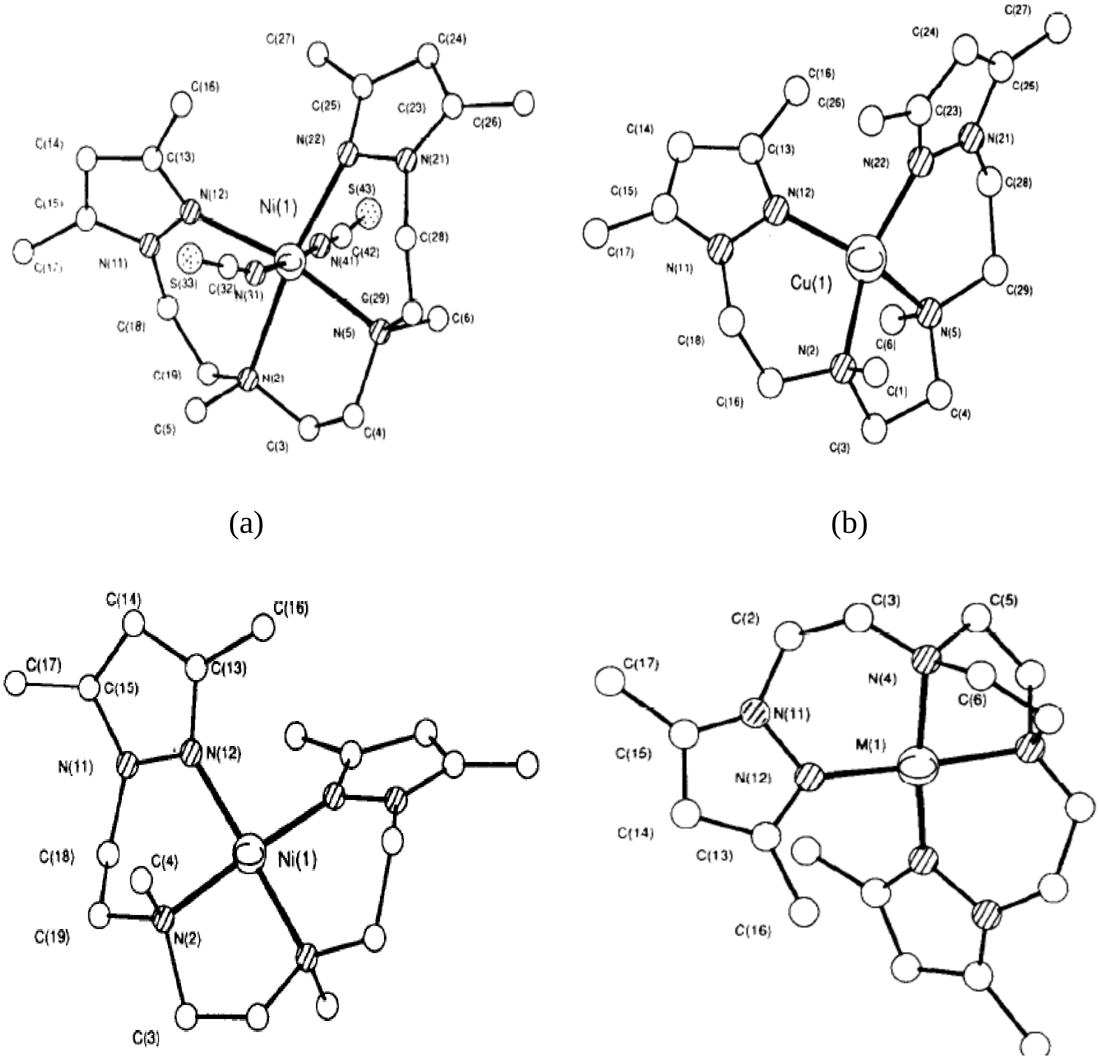
(a)



(b)

Fig.1.11. Structures of ligands ddad (a) and bedp (b).

For copper(II) complex there are two identical [Cu(ddad)]$^{2+}$ species are present in the asymmetric unit of [Cu(ddad)](BF$_4$)$_2$ and the geometry of the both copper centre is intermediate between tetrahedral and square planar. The main difference is in the conformation at chiral nitrogen atoms as expected from the chirality of the complex cation: one molecule has (*R*,*R*) diastereoisomer of the ligand and the other has (*S*,*S*) diastereoisomer. All the chloride complexes except nickel(II) are dinuclear with MN_2Cl_2 chromophores. A square planar [Ni(ddad)]$^{2+}$ and tetrahedral $NiCl_4^{2-}$ made the asymmetric unit of nickel(II) complex. The thiocyanate compound of Ni(II) and Zn(II) are isomorphous with octahedral $MN_2N'_2N''_2$ chromophores. The cobalt compound crystallizes as [Co(ddad)(NCS)]$_2$.Co(NCS)$_4$. The [Cu(ddad)]$^{2+}$ and [Cu(NCS)$_3$]$^{2-}$ ions form mixed valence compound [Cu$_2$(ddad)(NCS)$_3$].



(a) (b)

(c) (d)

Fig.1.12. Crystal structures of $[Ni(ddad)(NCS)_2]$ (a), $[Cu(ddad)]^{2+}$ (b), $[Ni(ddad)]_2^{+}$ (c) and $[M(bedp)]^{2+}$ (adapted from Ref. 74).

A series of mononuclear complexes of the type $[M(bedp)(H_2O)](BF_4)_2$ (M = Ni, Cu), $[M(bedp)(NCS)_2]$ (M = Ni, Co), $[Zn_2(bedp)(NCS)_4]$, $[M_2(bedp)Cl_4]$ and $[Cu_2(bedp)(NCS)_3]$ were prepared from ligand bedp. All the chloride complexes are dinuclear, similar to ddad, with MN_2C1_2 chromophores. A purple isomer of $[Ni_2(dedp)CI_4]$ with a tetrahedral NiN_2C1_2 chromophore is also obtained with the green form of $[Ni(bedp)][NiCI_4]$. $[M(bedp)(NCS)_2]$ (M = Ni, Co) are isomorphous with octahedral chromophores. The structure of mixed-valence compound $[Cu_2(bedp)(NCS)_3]$ is similar to the corresponding compound with ddad ligand.

Pyrazole and piperazine containing tetradentate ligands *N,N′*-bis(pyrazol-1-yl-methyl)piperazine (chbp) and *N,N′*-bis(3,5-dimethylpyrazol-l-yl-methyl)piperazine (chbd) were synthesized by Locher et al [75]. The transition metal complexes of the type [M(chbp)X] (M = Cu, X = Cl), [M(chbp)X_2] (M = Zn, X = Cl, Br) and [M_2(chbp)X_3] (M = Cu, Zn, X = Cl, Br) [M_2(chbd)X_4] (M = Cu, Zn, Mn, Cd, X = Cl; M = Cu, Zn, X = Br; and M = Cu, X = N_3, SCN) were synthesized from ligand chbp and chbd. The interesting point is that ligand chbd form only binuclear complexes probably due to the steric hindrance caused by the pyrazole methyl groups whereas ligand chbp formed both mono and binuclear complexes.

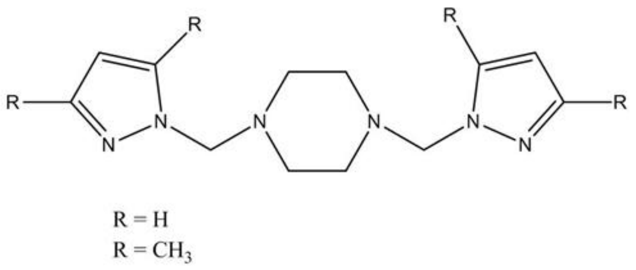


Fig.1.13. Structures of ligand chbp (R=H) and chbd (R=CH_3).

Two new low symmetry pyrazole containing tripodal ligands 2-(1H-pyrazol-1-yl)-*N*,*N*-bis(1H-pyrazol-1-yl-methyl)ethanamine (bmpz) and 2-(1H-pyrazol-1-yl)-*N*-[2-(1H-pyrazol-1-yl)ethyl]-*N*-(1Hpyrazol-1-ylmethyl)ethanamine (bepz) were reported by Cubenski et al [76].

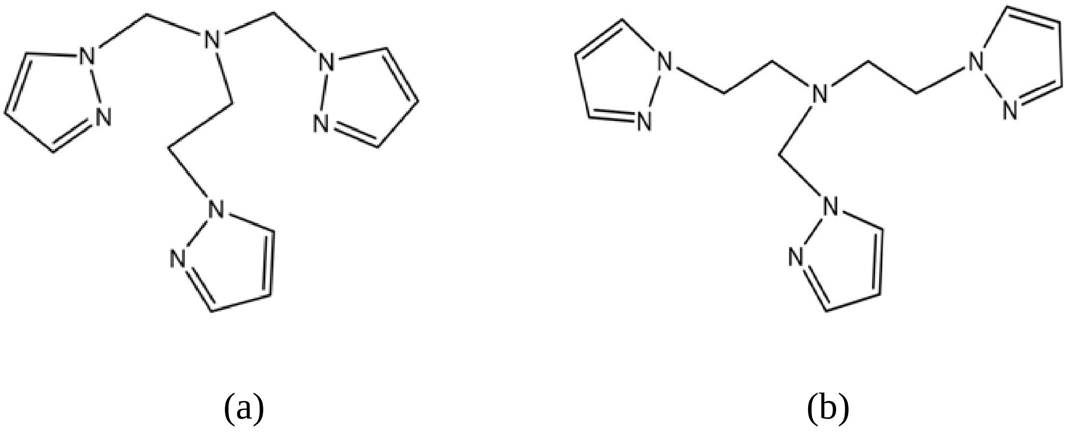
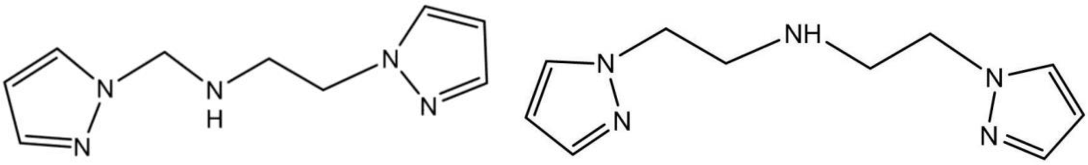

(a) (b)

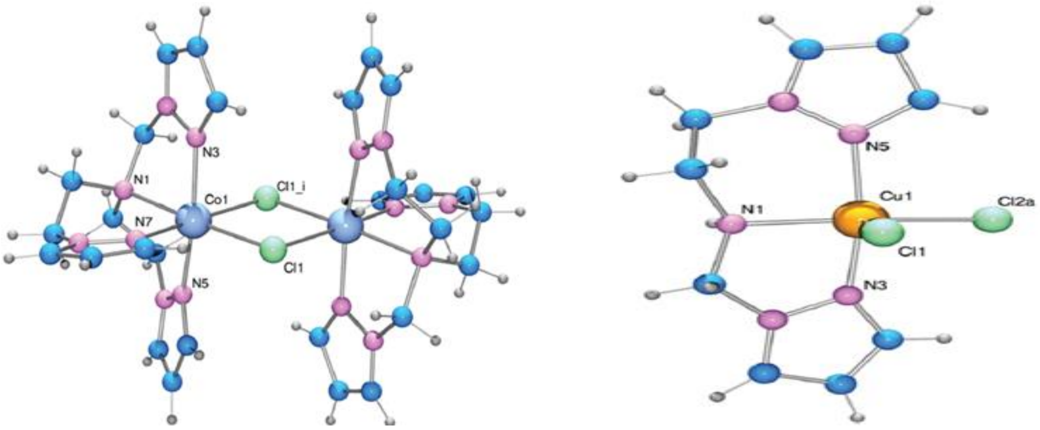
Fig.1.14. Structures of ligands bmpz (a) and bepz (b).

A series of metal complexes $[Co(bmpz)Cl]_2[CoCl_4]\cdot H_2O$, $[Co(bmpz) MeCN](ClO_4)_2\cdot 0.13H_2O$, $[Zn(bmpz)MeCN](ClO_4)_2\cdot 0.15H_2O$, $[Zn(bepz) OH_2](ClO4)_2\cdot 0.5 H_2O$ and $[(Co(bepz)Cl)_2]Cl_2\cdot 6H_2O$, $[Cu(L)Cl_2]\cdot 0.2H_2O$ and $[Cu(L')Cl_2]$ were prepared and characterized by single crystal X-ray diffraction studies and showed that there is no change of ligand structure in the cobalt(II) and zinc(II) complexes. However, in the case of copper(II) complexes, one pyrazole arm of ligand is removed and ligand transformed into tridentate ligand in protic solvent. The results suggest that aminal functionality was responsible for unstability of tripodal ligands.



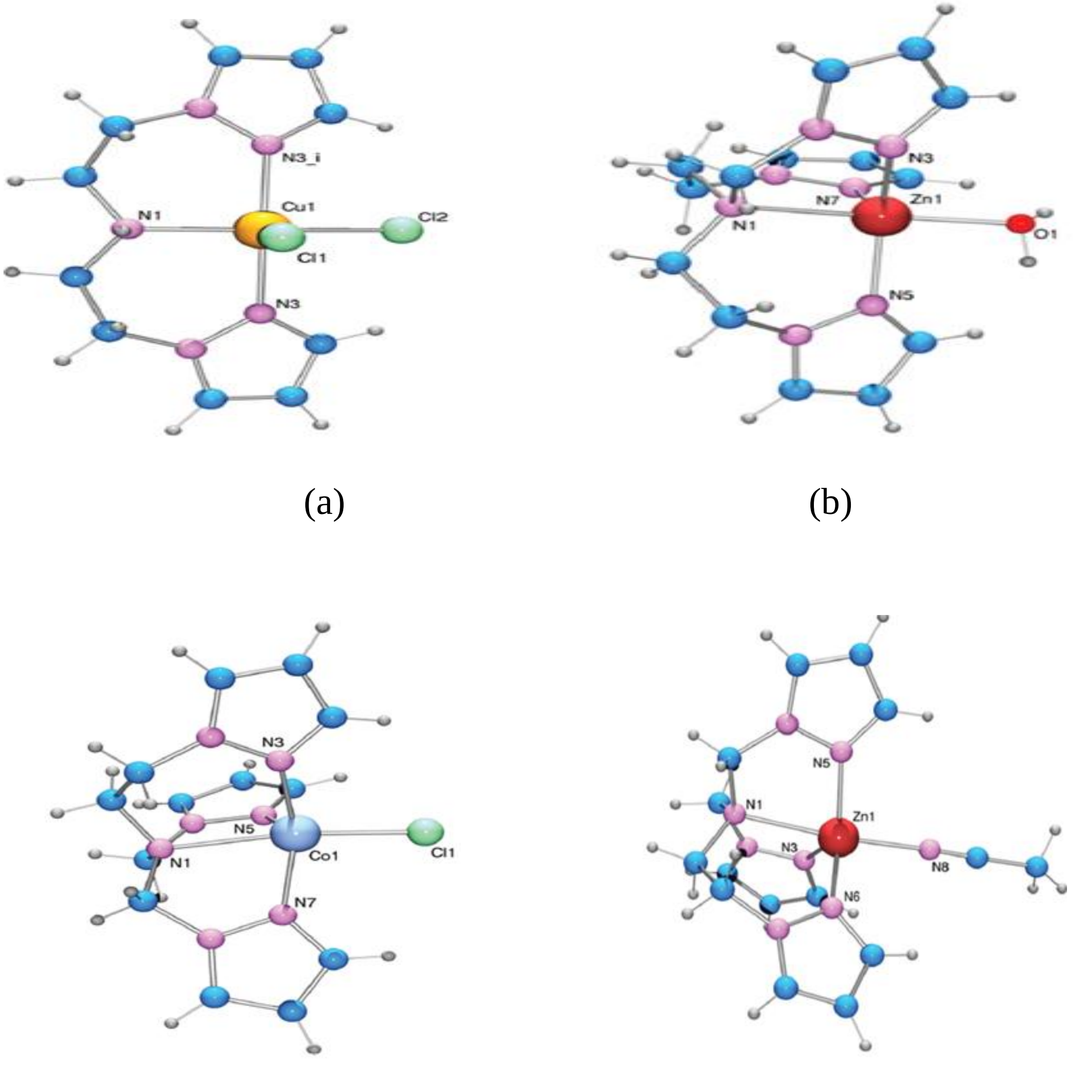
(a) (b)

Fig.1.15. Structures of ligands L (a) and L′(b).



(a) (b)

Fig.1.17. Crystal structures of $[(Co(bepz)Cl)_2]^+$ (a) and $[Cu(b)Cl_2]$ (b) (adapted from Ref. 76).

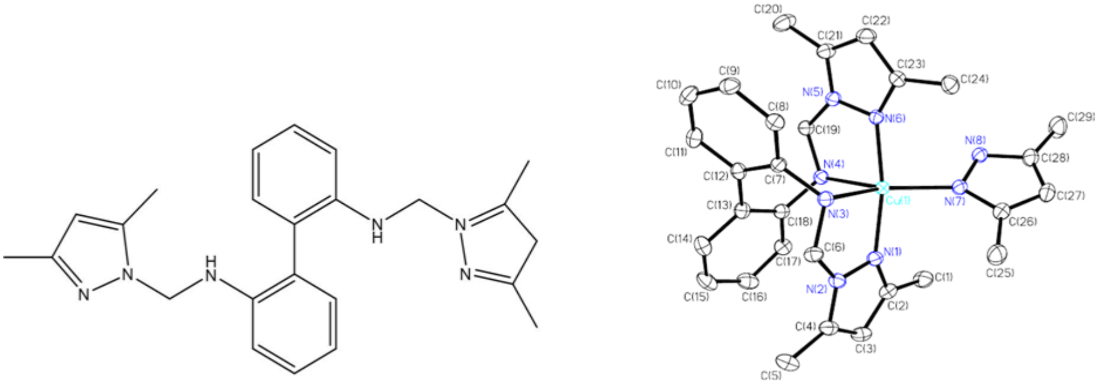


(a) (b)

(c) (d)

Fig.1.16. Crystal structures of $[Cu(L')Cl_2]$ (a), $[Zn(bepz)OH_2]^{2+}$ (b), $[Co(bmpz)Cl]^{+}$ (c) and $[Zn(bmpz)MeCN]^{2+}$ (d)

Biphenyl based pyrazole-containing tetradentate ligand 2,2′-bis[[(3,5-dimethylpyrazol-1-yl)methyl]amino]-1,10-biphenyl (N_4-mpz) and three Cu(II) complexes of the type $[Cu(N_4\text{-mpz})(Pz)]X_2$ where X = BF_4 or ClO_4 and $[Cu(N_4\text{-mpz})(Cl)]Cl$ were synthesized and characterized [77]. The X-ray structure of $[Cu(N_4\text{-mpz})(Pz)](ClO_4)_2.CH_3OH$ confirmed that Cu(II) coordinated by four nitrogen donors from ligand and fifth coordination site is filled up with an exogenous pyrazole donor that is extracted from another molecule of the ligand. The cyclic voltametry studies show that the complexes undergo quasi-reversible one-electron reductions in acetonitrile at potentials between 396 and 422 mV versus Ag/AgCl.



N_4-mpz (a)

Fig.1.18. Structure of ligand N_4-mpz and crystal structure of $[Cu(N_4\text{-mpz})(Pz)]^+$ (a) (adapted from Ref. 77).

A new series of tetradentate ligands [*N′*,*N′*-bis(pyrazol-1-ylmethyl)]-*N*,*N*-dimethylethylenediamine (L_1**)** and [*N′*,*N′*-bis(3,5-dimethylpyrazol-1-ylmethyl)]-*N*,*N*-dimethylethylenediamine (L_2) and their cobalt(II) complexes with tetraphenylborate were reported by Lee et al [78]. The X-ray diffraction study of the complex $[CoCl(L_2)]BPh_4$ confirms the trigonal bipyramidal geometry of the complex.

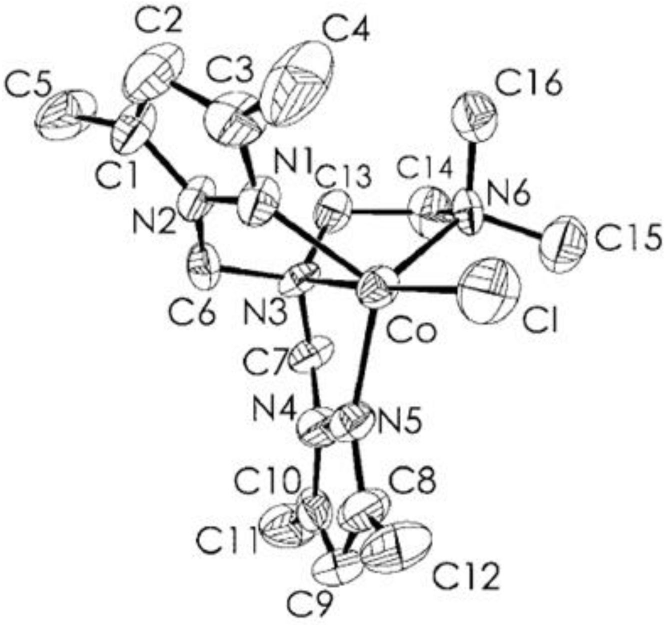
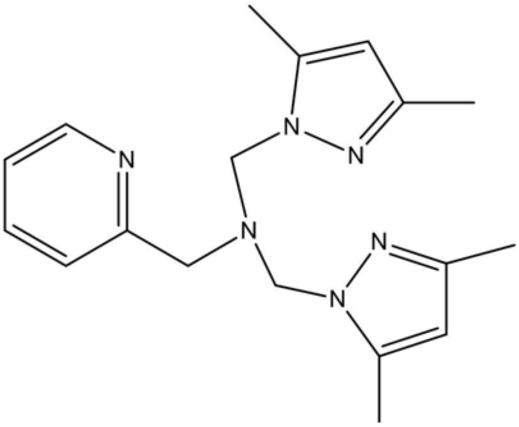
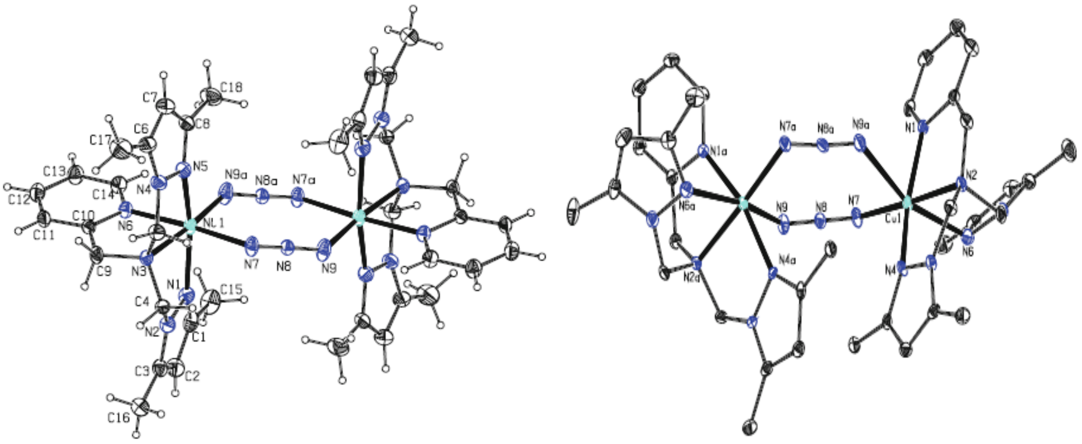


Fig.1.19. Crystal structure of $[CoCl(L_2)]^+$ (adapted from Ref. 78).

Pyridylpyrazole base tetradentate ligand *N*,*N*-bis(3,5-dimethylpyrazol-1-ylmethyl)aminomethylpyridine (L_3) and a series of halides or pseudohalide containing transition metal complexes were reported by Zala et al [79]. The ligand L_3 shows a wide range of structural variety with different metal ions in the presence of pseudohalides. In the case of $[Ni_2(L_3)_2(N_3)_2](ClO_4)_2.2EtOH$ (1) and $[Cu_2(L_3)_2(N_3)_2](ClO_4)_2$ (2), two azide ions are coordinated to metal centres in end-to-end coordination mode and geometry of the metal centres are distorted octahedral. The variable temperature magnetic susceptibility results show antiferromagnatic behaviour for complex 1 whereas no magnetic interactions was observed in the complex 2 as the distance between copper centres and end-to-end bridged azide ion is very high.



L_3

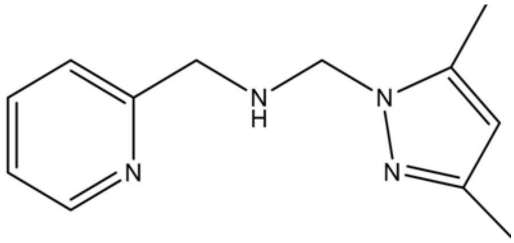


(a) (b)

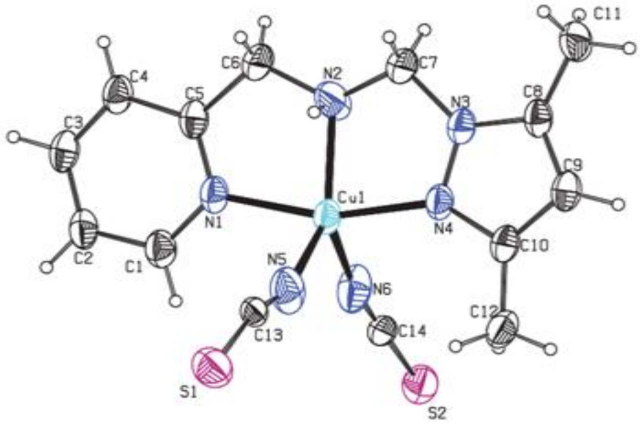
Fig.1.20. Structure of ligand L_3 and crystal structures of $[Ni_2(L_3)_2(N_3)_2]^{2+}$ (a), $[Cu_2(L_3)_2(N_3)_2]^{2+}$ (b) (adapted from Ref. 79).

Mononuclear NCS^- containing complexes of the type $[M(NCS)_2L_3]$, $[Cu(NCS)_2L_3']$ and $NCSe^-$containing complexes $[ML(NCSe)(H_2O)]ClO_4$ [M = Ni(II) and Co(II)] also reported with ligand L_3[80]. Single crystal X-ray structure of

$[Cu(NCS)_2L_3']$ confirmed that copper is five coordinate with distorted trigonal bipyramidal geometry and two NCS^- ion are in cis position. The tetradentate ligand L_3 is converted into tridentate ligand *N*-(3,5-dimethylpyrazol-1-ylmethyl) aminomethylpyridine (L_3') during the reaction. The geometry of complexes $[M(NCS)_2L_3]$ and $[ML_3(NCSe)(H_2O)]ClO_4$ [M = Ni(II) and Co(II)] are expected to be octahedral.



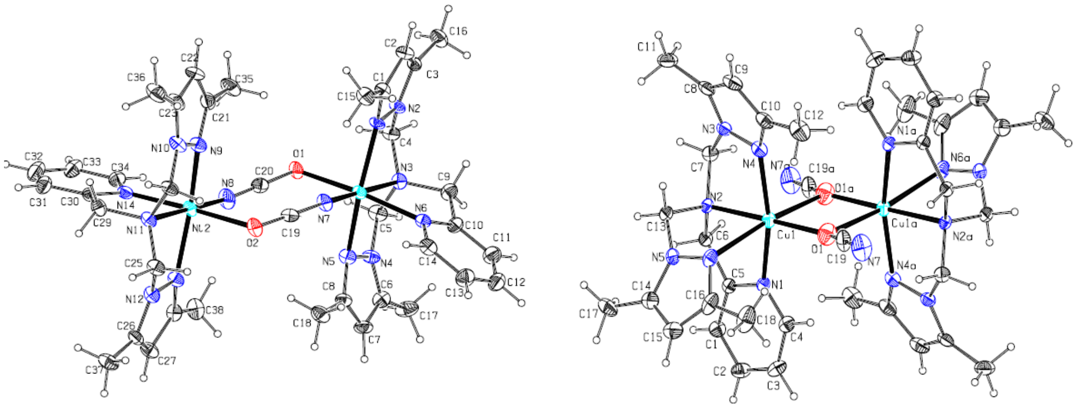
L_3'



(a)

Fig.1.21. Structure of ligand L_3' and crystal structure of $[Cu(NCS)_2L_3']$ (adapted from Ref. 80).

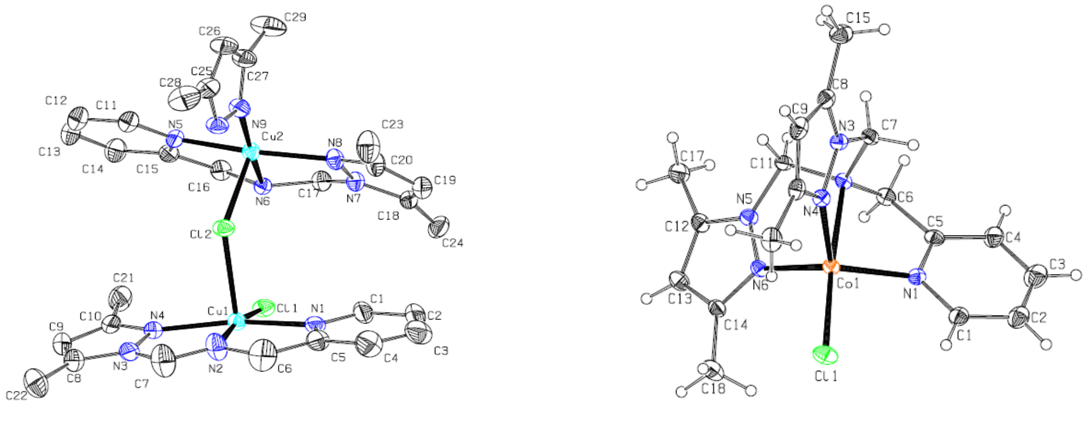
Two new cyanato bridged binuclear complexes of the type $[Ni(L_3)(NCO)]_2(PF_6)_2$ and $[Cu(L_3)(NCO)]_2(PF_6)_2$ with ligand L_3 were synthesized and characterized by physicochemical methods [81]. The single crystal X-ray diffraction analysis confirmed that cyanate ligand is coordinated to the nickel(II) centre in double end-to-end (μ-1,3) mode and in double end-on (μ -1,1) mode for copper(II) complex. The geometry of both the complexes is distorted octahedral. The variable temperature magnetic susceptibility data show that nickel(II) complex has weak antiferromagnetic interaction whereas copper(II) complex has very weak ferromagnetic interaction.



(a) (b)

Fig.1.22. Crystal structures of $[Ni(L_3)(NCO)]_2^{2+}$ (a), $[Cu(L_3)(NCO)]_2^{2+}$ (b) (adapted from Ref. 81).

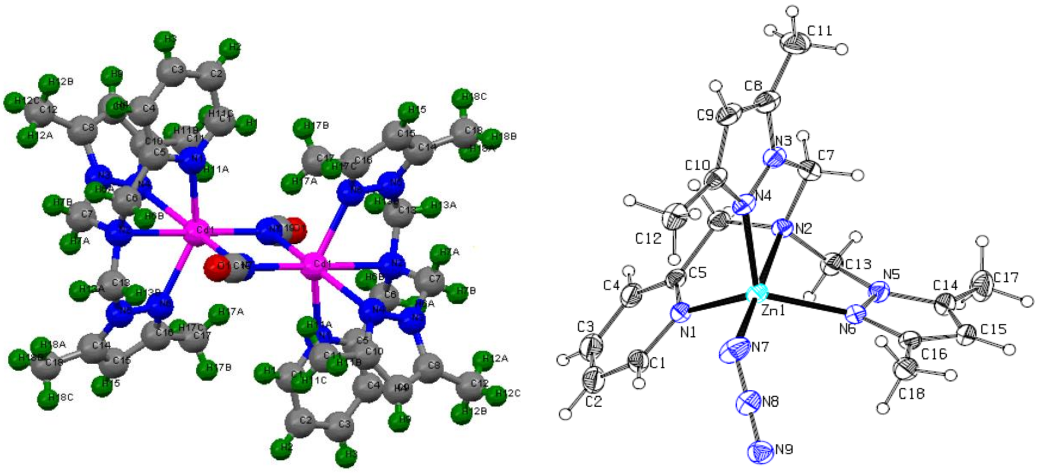
A new chloride bridged binuclear copper(II) complex $[L_3'(Cl)Cu\text{-}(\mu\text{-}Cl)\text{-}Cu(pz)L_3'](PF_6)_2$ (where pz = 3,5-dimethyl-pyrazole) and two mononuclear cobalt(II) complexes $[Co(Cl)L_3]BF_4.½CH_3OH$ and $[Co(Cl)L_3]PF_6$ were synthesized and characterized by single crystal X-ray diffraction studies [82]. In the complex $[L_3'(Cl)Cu\text{-}(\mu\text{-}Cl)\text{-}Cu(pz)L_3'](PF_6)_2$, two square planner copper(II) centres are connected through a single chloride (μ-Cl) bridge and coordination environment around both copper are different. The ligand L_3 is transformed into tridentate ligand L_3' during the reaction. The geometry of $[Co(Cl)L_3]BF_4.½CH_3OH$ is trigonal bipyramidal which is confirmed by X-ray diffraction studies. The ligand and complexes show cytotoxic activity against human lymphocyte HL-60 cell line.



(a) (b)

Fig.1.23. Crystal structures of $[L_3'(Cl)Cu\text{-}(\mu\text{-}Cl)\text{-}Cu(pz)L_3']^{2+}$ (a) and $[Co(Cl)L_3]^+$ (b) (adapted from Ref. 82).

A series of zinc(II) and cadmium(II) complexes of the type $[M(L_3)(NCS)_2]$, $[M(L_3)(N_3)]PF_6$, $[M_2(L_3)_2(NCO)_2](PF_6)_2$ of ligand L_3 were also reported [83]. X-ray diffraction studies confirmed that two NCO^- ions are coordinated to the cadmium centres through end-on coordination mode in $[Cd_2(L_3)_2(NCO)_2](PF_6)_2$ and geometry of the complex is distorted octahedral. The structure of $[Zn(L_3)(N_3)]^+$ showed that zinc(II) is penta coordinated with distorted square pyramidal geometry.



(a) (b)

Fig.1.24. Crystal structures of $[Cd_2(L_3)_2(NCO)_2]^{2+}$ (a) and $[Zn(L_3)(N_3)]^+$ (b) (adapted from Ref. 83).

Iron(II) chloride complexes of ligand L_3 was reported by Xeu et al and used in the cross-coupling of aryl Grignard with alkyl halides [84].

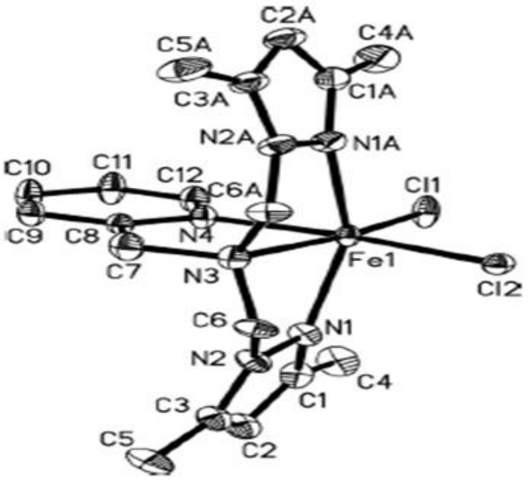
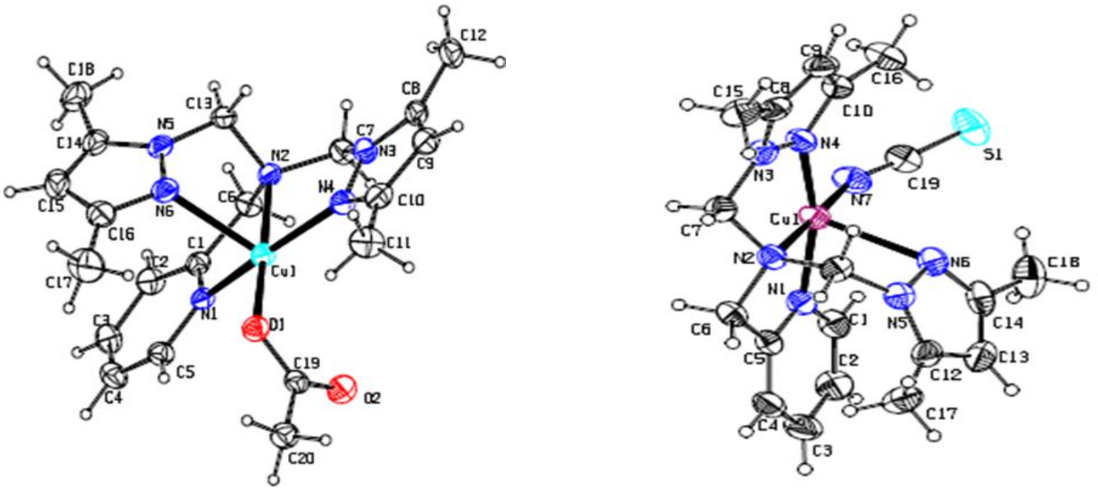


Fig.1.25. Crystal structure of $[FeL_3Cl_2]$ (adapted from Ref. 84).

Mononuclear copper(II) complexes with acetate and thiocyanate ions and nickel(II) chloride complex of ligand L_3 were reported recently [85]. The molecular structure of the complexes $[Cu(L_3)(CH_3COO)]PF_6.H_2O$ and $[Cu(L_3)(NCS)]PF_6$ confirmed by single crystal X-ray diffraction studies and showed that copper atom in both the complexes have distorted square pyramidal geometry. The proposed structure of nickel complex is octahedral.



(a) (b)

Fig.1.26. Crystal structures of $[Cu(L_3)(CH_3COO)]^+$ (a) and $[Cu(L_3)(NCS)]^+$ (b) (adapted from Ref. 85).

1.2. Present Work

The coordination chemistry of pyrazole based tetradentate ligands are very interesting as they can produce complexes with different coordination numbers (four to six) in the presence of co-ligand and different geometry ranging from tetrahedral to square planar (for four coordination complexes), square pyramidal to trigonal bipyramidal (for five coordination) and octahedral for six coordination complex. The variety of structures found in biological systems inspired us to prepare these complexes with different metal ions. We have observed that pyridylpyrazole containing tetradentate ligand forms mono and binuclear complexes in the presence of halide and pseudohalides with various geometry. So we are interested to study the coordination behaviour of two new tetradentate ligands where pyridine group is replaced by alkyl amine group and reactivity of the metal complexes synthesized from these two ligands. A number of new tetradentate ligands and their transition metal complexes are reported in the literature but synthesis, structure and bioactivity of transition metal complexes of tetradentate ligand in present of different co-ligands such as halides, pseudohalides, alkyl or aryl carboxylate, nitrite and pyrazole are limited.

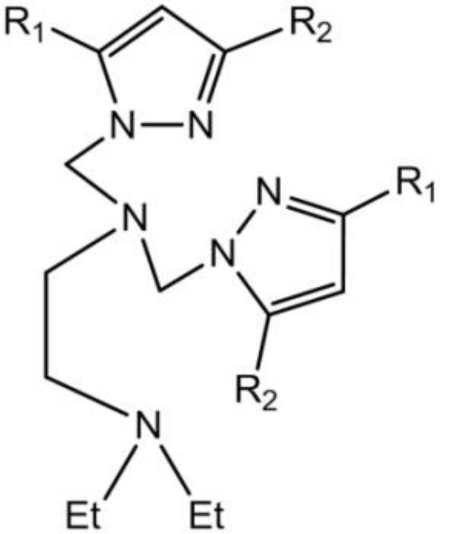
Objectives of Present work

- To synthesis new pyrazole based tetradentate ligands which can provide N_4 coordination.
- To study the coordination behaviour of synthesized ligands with different metal ions such as Cu(II), Ni(II), Co(II), Zn(II) and Cd(II) in presence of halides / pseudohalides / and alkyl or aryl carboxylate / nitrite / 3,5-dimethylpyrazole.
- To characterize the synthesized complexes by spectroscopic methods such as IR, NMR, microanalysis, UV-Vis etc., magnetism, cyclic voltammetry and EPR spectroscopy.
- To determine the structure of the synthesized complexes by single crystal X-ray diffraction studies.
- To study the magneto structural correlation of binuclear pseudohalide bridge complexes.
- To study the biological activities of synthesized complexes like antimicrobial activity, DNA and BSA binding and cyctotoxic activity.

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 tetradentate ligand is presented.

In the chapter 2, synthesis and characterization of two new tetradentate N_4-coordinated pyrazole based ligands namely *N,N*-diethyl-*N',N'*-bis((3,5-dimethyl-*1H*-pyrazol-1-yl)methyl)ethane-1,2-diamine (dbdmp) and *N',N'*-bis((*1H*-pyrazol-1-yl)methyl)-*N,N*-diethylethane-1,2-diamine (dbp) have been described. Syntheses, structures and magnetic properties of mononuclear thiocyanate containing nickel(II) and binuclear azido bridged nickel(II) complexes of both the ligands were discussed in detail.



For dbdmp R_1, R_2 = CH_3
For dbp R_1, R_2 = H

Fig.27. Structure of ligands *N,N*-diethyl-*N',N'*-bis((3,5-dimethyl-*1H*-pyrazol-1-yl)methyl)ethane-1,2- diamine (dbdmp) and *N',N'*-bis((*1H*-pyrazol-1-yl)methyl)-*N,N*-diethylethane-1,2-diamine (dbp).

Chapter 3 describes the syntheses, structure, DNA binding study and antimicrobial activity of mononuclear copper(II) complexes with ligand dbdmp and pseudohalides. A series of mononuclear copper(II) complexes were characterized using different spectroscopic techniques. The crystal structure determination of four complexes was carried out by single crystal X-ray crystallography. Electochemical properties of the complexes also studied in detail. DNA binding study of synthesized complexes was carried out by electronic absorption titration and ethidium bromide displacement by fluorescence spectroscopically. The synthesized compounds were screened for their antimicrobial activity against *Gram positive* and *Gram negative* bacteria.

Chapter 4 consists of the syntheses, structures and DNA and BSA binding activity of mononuclear cobalt(II) complexes with pseudohalides. The synthesized complexes were well characterized using microanalysis, IR, electronic spectra studies, magnetic studies including single crystal X-ray diffraction studies. DNA and BSA binding study were performed using electronic absorption titration and fluorescence spectroscopy.

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

Chapter 5(A) describes the syntheses, characterization and structures of cobalt(II), nickel(II), zinc(II) and cadmium(II) selenocyanide complexes of tetradentate ligand dbdmp. The ligand dbdmp has two different isomeric form in the complexes [Ni(dbdmp)(NCSe)$_2$] and [Cd(dbdmp)(SeCN)$_2$]. The binding mode of SeCN$^-$ ion with metal ions was described in details.

Chapter 5(B) consists of the syntheses, characterization and structures of mono- and dinuclear zinc(II) and cadmium(II) complexes of ligand dbdmp in the presence of pseudohalides and different counter anions. Four complexes were characterized by single crystal structure X-ray diffraction studies.

Chapter 6 consists of ternary complexes of copper(II) and cobalt(II) ions with tetradentate ligand dbdmp in the presence of carboxylate / nitrite / 3,5-dimethylpyrazole / chloride as a co-ligand. The coordination behaviour of above synthesized complexes was determined by single crystal X-ray diffraction studies. The electrochemical behaviour of copper(II) complexes were carried out by cyclic voltammetry. The cytotoxic activity of two copper(II) complexes with this ligand in the presence of benzoic acid / salicylic acid were screened against A549 lung carcinoma cell line. The antimicrobial activity against Gram positive and Gram negative bacteria was studied using diffusion method.

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