General Introduction:

Bearing of at least two different elements as a member of its ring called heterocyclic compounds. The chemistry of nitrogen containing heterocycle based ligands are attracted considerable attention because they constitute an important class of pharmacologically active molecules, natural and synthetic products, many of which exhibit useful biological activities [1-6]. The coordination chemistry of transition metal ions with nitrogen containing heterocyclic ligand was first discussed by F. Blau [7]. Nitrogen containing six member bidentate such as 2,2'-bypyridine, 1,10-phenanthroline and tridentate heterocyclic ligand such as 2,2':6',2''-terpyridine have been extensively used to synthesis transition and non-transition metal complexes as they provide soft sites for metal coordination because they are excellent π-acceptors [8-9]. The π-excessive nitrogen-containing five-member heterocyclic compounds such as imidazole, pyrazole, and oxazole derivatives are poorer π-acceptors, in fact, they are better π-donor and hence act as hard donor sites [10]. Among the heterocycles, pyrazole is one of the most versatile molecules in organic chemistry. So we are currently interested in pyrazole and substituted pyrazole containing ligands. As transition metal complexes with pyrazole containing heterocyclic compounds have various applications in the field of chemical, biological, catalysis etc., it has encouraged us to design new nitrogen and sulphur containing multidentate pyrazole containing ligands and to study their coordination behaviours towards 1st row transition metals [11-14]. There are many articles on the coordination and organometallic chemistry of pyrazolyl containing tripodal ligands and their various applications like as synthons in supramolecular chemistry and catalysis [15-18].

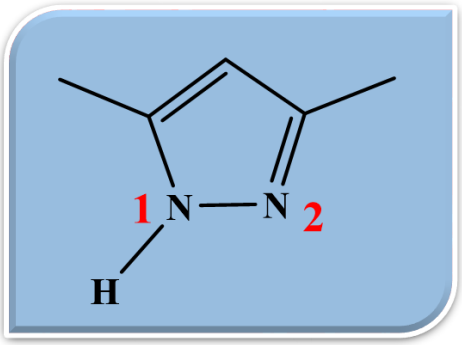


Fig.1.1. Structure of Pyrazole.

1.1. History and properties.

In 1883 German chemist Ludwig Knorr was first synthesized compounds containing this structure and given the name pyrazole [Fig.1.1] [19]. Pyrazoles rarely occur in nature and the first natural pyrazole(1-pyrazolyl-alanine) was isolated from seeds of watermelons in 1959 [20]. Pyrazole is an organic compound having a penta atomic heterocycle with a simple aromatic five member ring structure comprises three carbon and two nitrogen atoms at adjacent positions. The aromatic nature arises from the four π-electrons and the unshared pair of electrons on the –NH nitrogen take part in resonance and complete 6π electrons. The N(1)-H is acidic in nature due to the proton whereas another nitrogen atom N(2) is basic due to lone pair in the sp^2 orbital. Pyrazole is a tautomeric substance can be represented in three tautomeric forms [Fig.1.2]. In addition pyrazole and its derivatives exhibit broad spectrum of pharmacological and biological activities like antimicrobial [21-22], antifungal [23-24], antiviral [25-26], anticonvulsant [27-28], anticancer [29-30], analgesic [31], anti-inflammatory [32-33], antitubercular [34-35], cardiovascular [36], antidepressant [37-38], hypoglycaemic agent [39-40] etc.

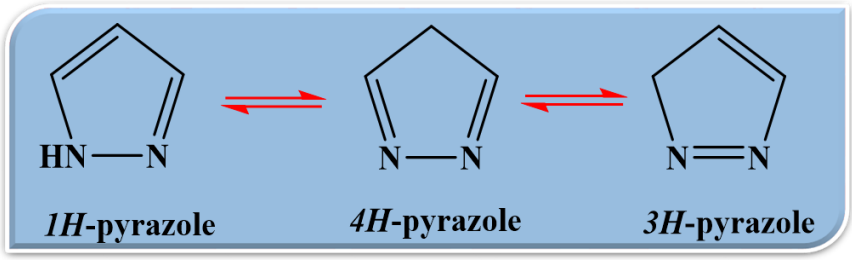


Fig.1.2. Tautomeric forms of Pyrazole.

The study of the coordination chemistry with the pyrazole-based ligands was started in 1889. Buchner was first reported polymeric complexes $[Ag(pz)]_n$ in his paper on pyrazole [41]. Anticancer activity of synthesized pyrazoles based complex dichloro bis(pyrazole)platinum(II) first reported by Sakai et al on human colorectal cell lines (DLD-1, HCT15, HT29) and a human gastric cell line (AGS) and reported that the activity was similar to that of the cis-platin [42]. Metal complexes with pyrazole based ligand get more attention since 1960 and Trafimenko was first employed pyrazolyl containing scorpionet ligand hydrotris(pyrazolyl)borates [43] and published review articles on the coordination chemistry of pyrazole-derived ligands [44-46]. Transition

metal complexes with pyrazole based Schiff base ligands have wide applications and there are many articles on pyrazole containing schiff based ligands and their metal complexes [47-49]. Driessen et al was reported a new method for the synthesis of N-substituted pyrazolyl derivatives with different amines and their coordination behaviour towards first-row transition metal ions [50-56]. The coordination chemistry of main group transition metal complexes with pyrazole-based multidentate tripodal lidands and their wide application in chemical sciences is an interesting area of research in chemistry [57-60].

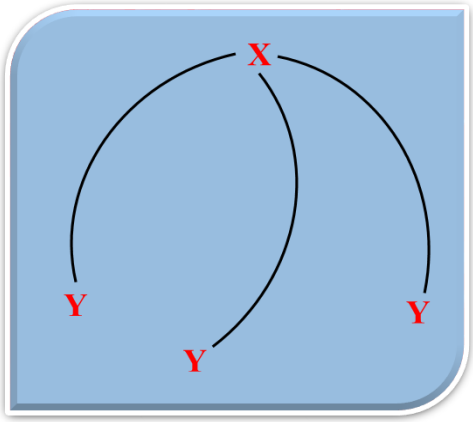


Fig.1.3. General structure of a tetradentate tripodal ligand.

The general structure of tetradentate tripodal ligands have depicted in Fig. 1.3 and consists of single tertiary N atom which is connected to three tripod arms, each arm also contains at least one methylene group and a donor atom Y, which can coordinate to a metal ion using their lone pair. The ease of synthesis of various tripodal ligands with pyrazoles is the most interesting in the design of new multidentate chelating ligands and hence offers the opportunity of both electronic and steric control of the properties of the metal complexes. 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 pyrazolyl-based chelating ligands, which consists of pyrazole heterocycles linked by NR (R = H or alkyl or benzyl), O or S group 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 [10].

1.2. Pseudohalides coligands

Transition metal complexes with pseudohalides as coligand are interesting area of research because pseudohalide ions such as N_3^-, NCS^-, $SeCN^-$ and NCO^- are ambidentate ligands and coordinate to the metal centers as terminal as well as bridging ligands using various coordination modes and form mono, di- and polynucler complexes and produce supramolecular network. In recent years, transition metal complexes with pseudohalides are used for synthesis of magnetic material and to study the magneto-structural correlation.

1.2.1. Azide ion

In 1948, Wilsdorf first report copper(I) complex using azide as ligand and the chemistry of azide complexes required little attention because of its explosive nature [61]. Azide is a linear anion and it has several resonance structures according to the valence bond theory [62]. The azide ion is the most versatile bridging ligand among the pseudohalides that can bridges metal centers in different coordination modes including symmetric and asymmetric double bridges $\mu_{1,3}$-N_3 (end-to-end, EE), $\mu_{1,1}$-N_3 (end-on, EO), $\mu_{1,1,3}$-N_3 and $\mu_{1,1,1}$-N_3 [63-69] as well as multi-bridges $\mu_{1,1,1,1}$-N_3, $\mu_{1,1,3,3}$-N_3, and $\mu_{1,1,1,3,3,3}$-N_3 are reported [Fig. 1.4] to yield dinuclear, tetranuclear, cubane, 1D, 2D and 3D compounds [70–73]. In general, transition metal complexes with end-to-end (EE or 1,3) azide bridge coordination mode gives antiferromagnetic interaction while the end-on (EO or 1,1) mode produce ferromagnetic coupling [74-75].

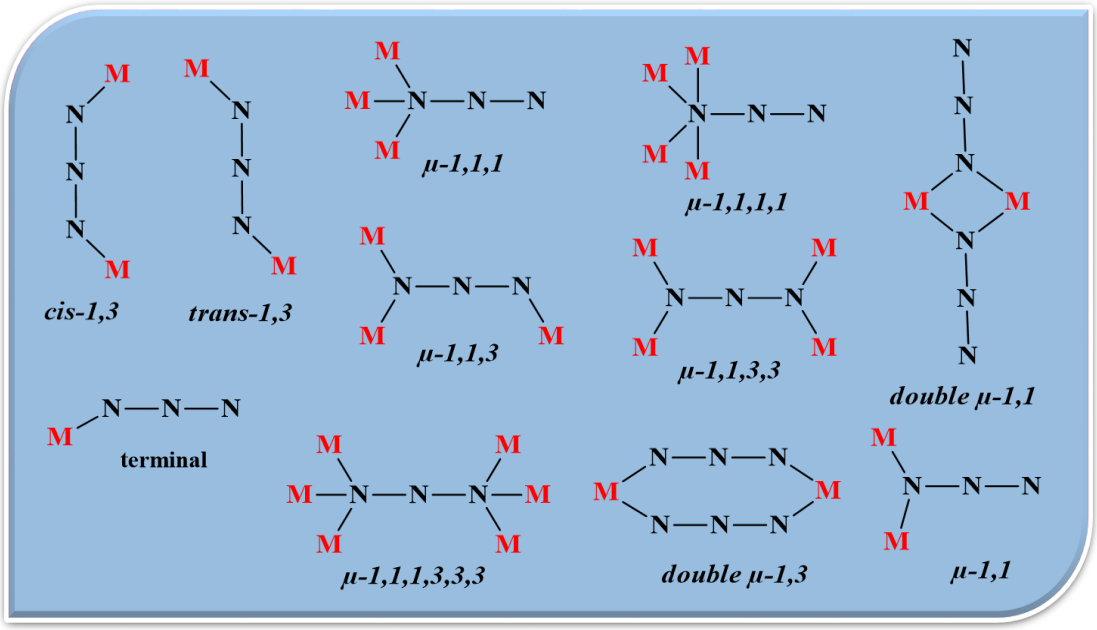


Fig.1.4. Bridging mods of azide ion.

1.2.2. XCN ions (X = O, S, Se)

The psudohalides XNC^- (NCS/ NCO/ NCSe) ions are ambidentate ligands that can bind metal ions as terminal as well as bridging ligand with various coordination modes such as $\mu_{N,N}$-(XCN), $\mu_{X,X}$-(XCN), $\mu_{N,X}$-(XCN) and form wide variety of multidimensional compounds such as mono-, di-, 1D single or double bridged polynuclear compounds and polymer-based super structures [76-82]. There are few examples reported with unique end-on (EE) bridging mode of psudohalides: SCN ($\mu_{S,S}$-NCS) [83-84], NCO ($\mu_{O,O}$-NCO) [85-87] and SeCN ($\mu_{Se,Se}$-NCSe) and their magnetic properties[88-91]. The XCN ligands with its bridging coordination modes with transition metal centres are expected to afford a number of binuclear and polynuclear structural assemblies with specific structural features and magnetic properties.

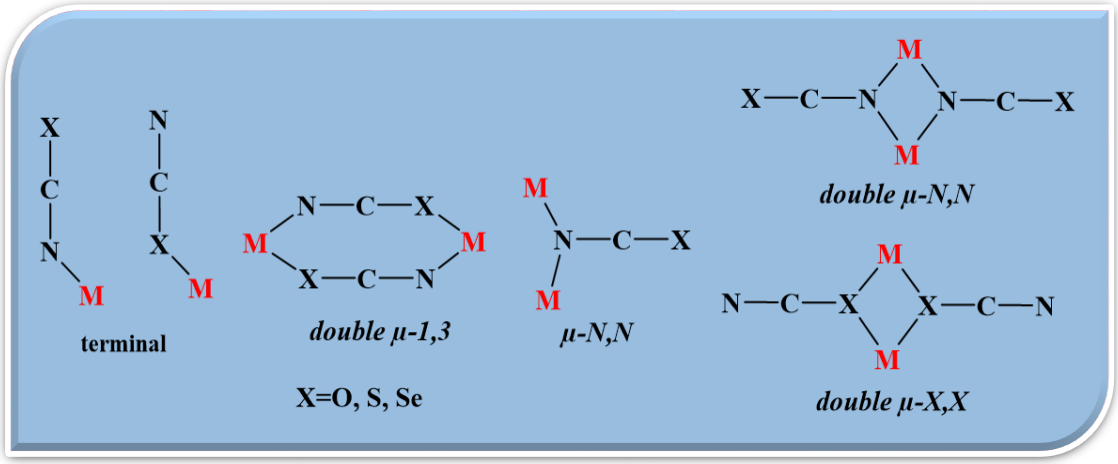


Fig. 1.5. Different bridging mode of XCN^- (X = O, S, Se)**.**

1.2.3. Carboxylates and Nitrite ligands

Carboxylate group has two oxygen atoms and it can utilize one as well as two oxygen atoms for bonding purpose and form mononuclear as well as multinuclear complexes. When two oxygen atoms of carboxylate acts as bridging ligand, it can bridged two metal ions in mono (μ-1,1) **(1)** or tri-atomic (μ-1,3) including *syn-syn* **(2)**, *syn-anti* **(3)** and *anti-anti* **(4)** and mono- and bi-dentate **(5)** coordination modes as shown in [Fig. 1.6] and form mono, di- or polynuclear complexes including metal clusters. In general, the mono- and tri-atomic (*syn-syn)* coordination mode usually promote to synthesis of binuclear complexes while the tri-atomic (*anti-anti* and *syn-anti*) conformations generally promote to synthesis of chain or layer compounds [92-93]. The magnetic properties of polynuclear systems are depended on the bridging conformation adopted by of the carboxylate group in it. Thus *syn-syn* bridge complexes shows antiferromagnetic interactions [94-95], *syn-anti* bridge complexes transmits weak antiferromagnetic or ferromagnetic interactions between metal ions [96-97], *anti-anti* bridged complexes exhibits weak antiferromagnetic exchange interactions [98].

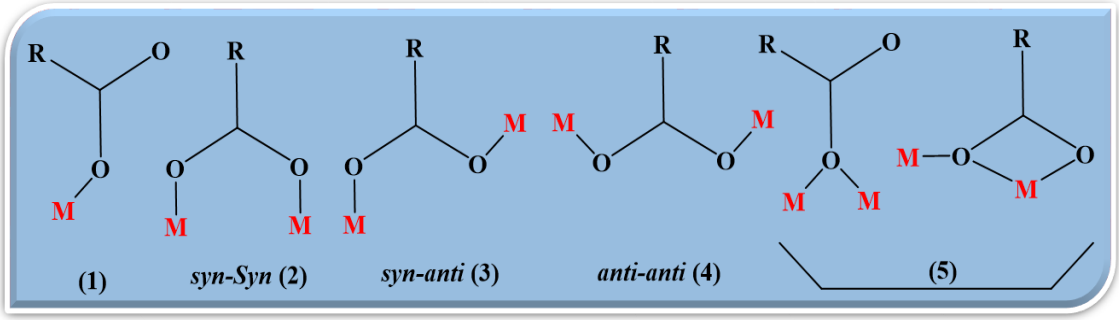


Fig.1.6. The various bridging modes of carboxylate ligand.

Nitrito (NO_2^-) is unique ligand which has three-atoms for coordination [Fig.1.7.] and acts as monodentate or bidentate or tridentate ligand and form mono-, di- and multinuclear complexes. The NO_2 group coordinated to the metal atom as a monodentate ligand using the nitrogen (as a nitro) or using an oxygen (a nitrito) and a chelating ligand using both oxygen atoms and form mononuclear complexes [99]. When it acts as a bidentate ligand, it can coordinate or bridge through two atoms O/N-bridging mode (a) is the most common one, through both oxygen atoms (*syn-syn* / *syn-anti* /*anti-anti*) (b) through single oxygen and nitrogen atoms [100]. There are few reports in which nitrite act as a tridentate ligand and coordinated to metal through the two oxygens and bridged to a second metal ion either through the nitrogen atom (c) or through (one of the chelating oxygen atoms (d)) [101].

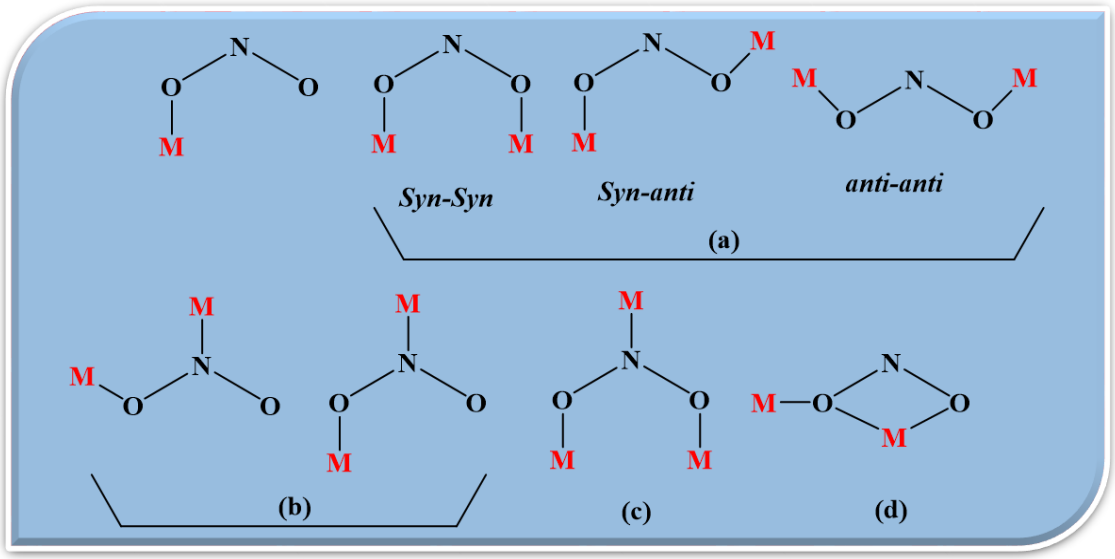


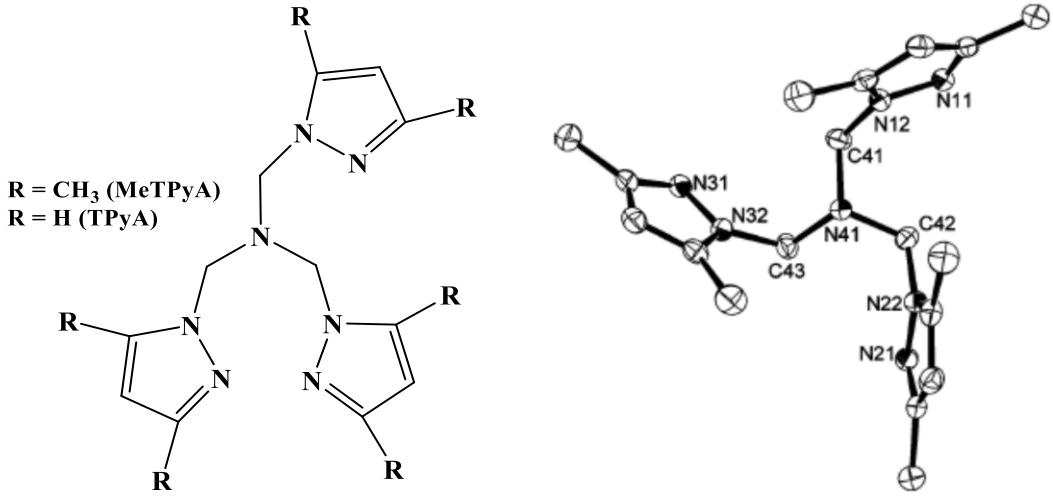
Fig. 1.7. Different coordination modes of nitrito ligand

1.3. Present status of the chemistry of pyrazolyl containing N_4-coordinate tetradentate ligands and their compounds

From the above discussion it is clearly concluded that pyrazole containing multidentate ligands are very interesting chelating ligand and form mono-, di- and polynuclear complexes with metal ions with various geometries. Recently, there are many articles dealing with metal complexes of pyrazolyl containing ligands and their applications in chemical sciences. There are many pyrazolyl containing multidentate ligands reported in the literature but our interest is in the two different types of tripodal

ligand with four coordination sites where one nitrogen from tertiary amine, two nitrogen from pyrazolyl groups and another position will be occupied by either secondary nitrogen or sulphur atom. In this section we have focused only on the tetradentate nitrogen containing ligands and their compounds which are relevant to the chemistry presented in the dissertation.

The coordination behaviour of tetradentate ligand tris(3,5-dimethyl-1-pyrazolylmethyl)amine (MeTPyA) was investigated with metal ions iron(II), cobalt(II), and nickel(II) ions by F. Mani et.al [109]. The general formula of synthesized complexes are $[M(MeTPyA)X]BPh_4$, (where, 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 $[Co(MeTPyA)](NO_3)_2$. Synthesized complexes shows ligand MeTPyA coordinated to the metal centres with different coordination numbers, six, five and intermediate between four and five with different coordination geometries, acting as tetra- and tridentate or intermediate between tetra- and tridentate. The zinc(II) isothiocyanate complex $[Zn(TPyA)(NCS)_2]$ with ligand TPyA was characterized by single crystal X-ray diffraction studies and structural data shows that Zn(II) has distorted tetrahedral geometry and one pyrazole group of the ligand TPyAis remain uncoordinated [110].



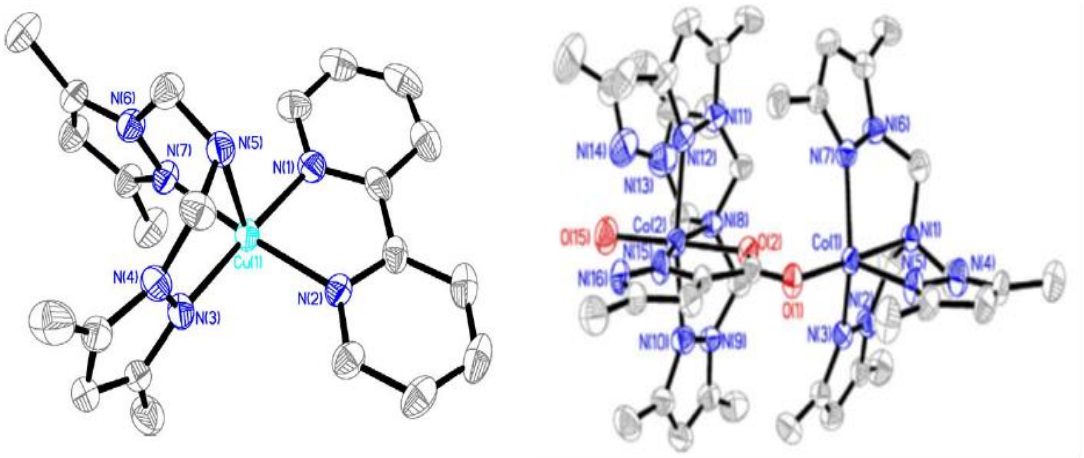
(a) (b)

Fig.1.8. Structure of ligands MeTPyA and HTPyA. (adapted from the Ref. 109).

Tripodal ligand MeTPyA containing mononuclear $[Cu(DMPzA)(2,2'\text{-bipy})](ClO_4)_2$ and a series of binuclear metal complexes of the type [(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)]$(ClO_4)_2$ [where bipy = bipyridine; H_2DPC = pyridyl-2,6-bicarboxylate; DMPzA = bis(3,5-bimethyl-pyrazolmethyl)amine] were synthesized and characterized by X-ray diffraction techniques [111]. When pyridyl derivatives were added as auxiliary ligands to the complex formation reaction in the presence of ligand MeTPyA, the tripodal ligand MeTPyA loses a pendant arm during in situ reaction. The cleavage of one arm confirmed by crystal structure and mechanism also studied by DFT calculations and ESI-MS spectra.

To examine the effect of the pyridine ring on the cleavage of the pendant arm, the complex [(MeTPyA)Co(μ-HZPC)Co(MeTPyA)$(H_2O)_2$]$(ClO_4)_3$ was synthesized using pyrazole-carboxylate (HZPC) instead of pyridyl derivatives. Crystal structure confirmed that the pendant arm in MeTPyA ligand has not been removed and the complexes have a strong ability to recognize pyridine compounds in methanol solvent.



(a) (b)

Fig.1.9. X-ray crystal structures of (a) [Cu(DMPzA)(2,2′-bipy)]$(ClO_4)_2$ and (b) [(MeTPyA)Co(μ-HZPC)Co(MeTPyA)$(H_2O)_2$]$(ClO_4)_3$. (adapted from Ref. 111).

A series of copper (I)/(II) complexes were synthesized with ligand MeTPyA and N1L4 namely [Cu^{II}(MeTPyA)Cl_2] (**1**) and [Cu^{II}(L1N4)Cl_2] (**2**), the copper(II) nitrato complexes [Cu^{II}(MeTPyA)(NO_3)](NO_3) (**3**) and [Cu^{II}(L1N4)(NO_3)](NO_3) (**4**) and the copper(II) sulfato complexes [Cu^{II}(MeTPyA)(SO_4)] (**5**) and [Cu^{II}(L1N4)(SO_4)] (**6**), and the copper(I) complexes [Cu^{I}(MeTPyA)](PF_6) (**7**) and

$[Cu^{I}(MeTPyA)(PPh_3)](ClO_4)$ (**8**), have been synthesized and characterized by X-ray crystallography [112]. The structural data shows that the coligands such as chloride/ nitrate / sulphate and triphenyl phosphate forced to change the geometry of the complexes. Moreover, the structures and physicochemical properties of these complexes are compared with related complexes containing the neutral tridentate tris(pyrazolyl)methane ligand and the neutral bidentate bis-(pyrazolyl)methane ligand.

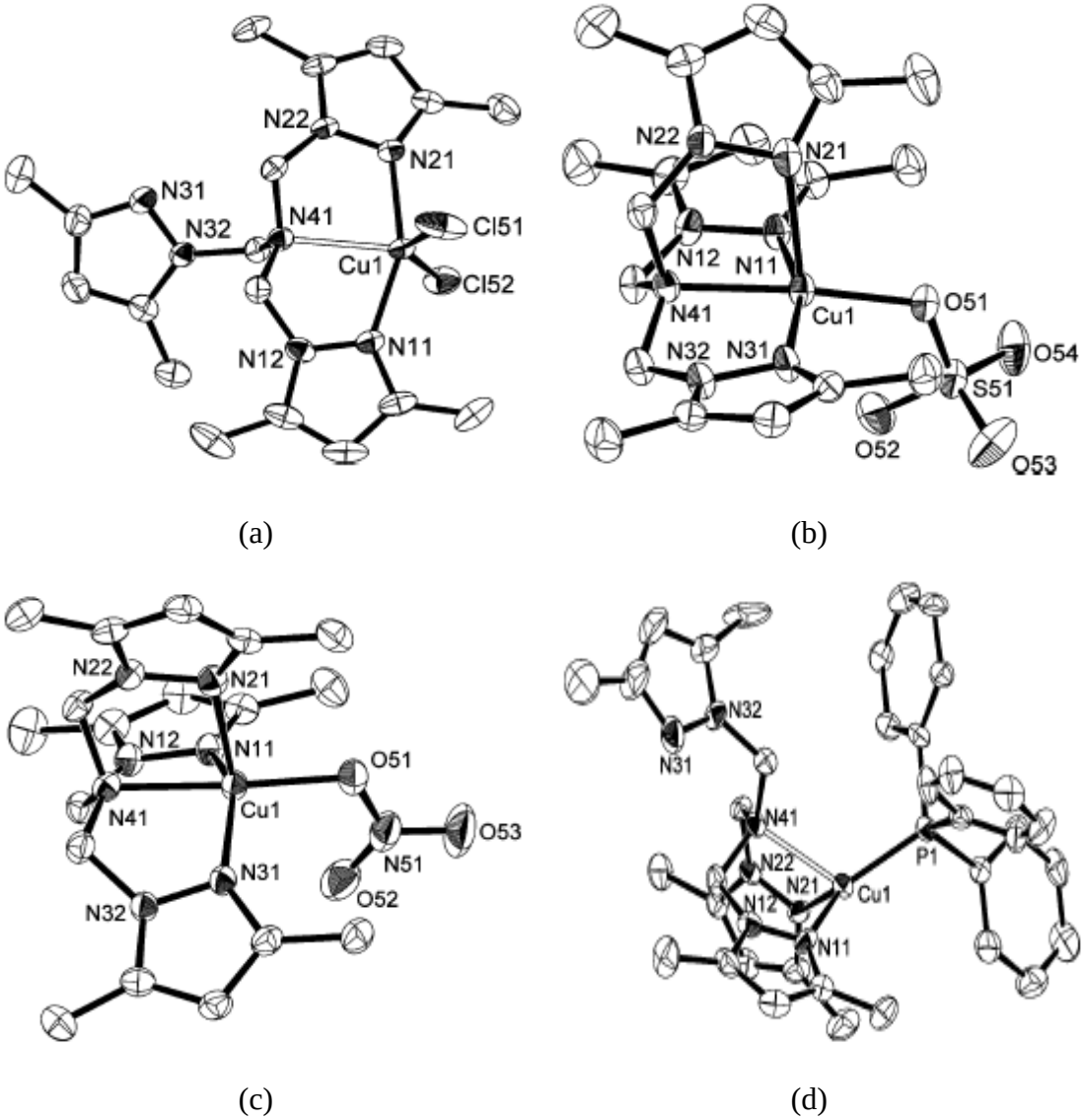
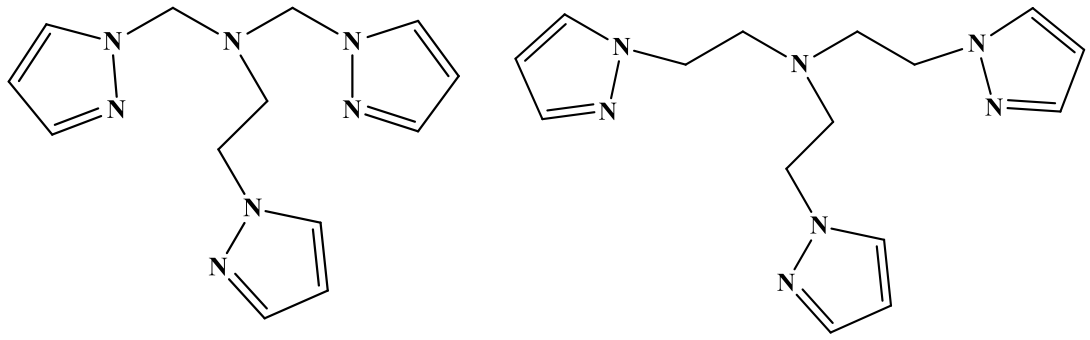


Fig.1.10. Crystal structures of (a) $[Cu(MeTPyA)Cl_2]$, (b) $[Cu(MeTPyA)(SO_4)]$, (c) $[Cu(MeTPyA)(NO_3)](NO_3)$ and (d) $[Cu(MeTPyA)(PPh_3)](ClO_4)$. (adapted from Ref. 112).

Two low symmetry tetradentate pyrazole based 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) and metal

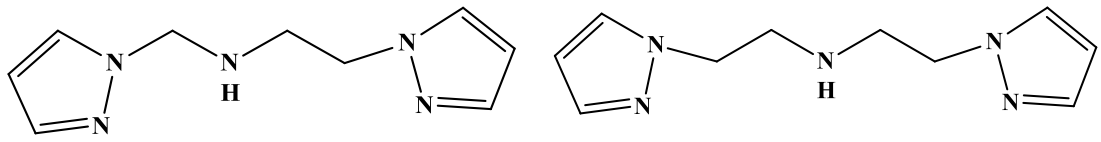
complexes containing these ligands were synthesized and characterized by Cubanski et al [113].



(a) (b)

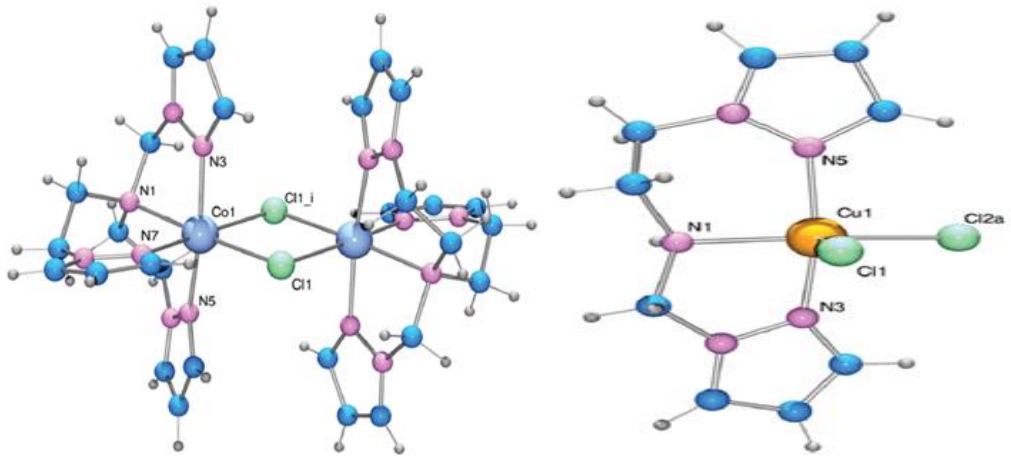
Fig.1.11. Structures of ligands (a) bmpz and (b) bepz. (adapted from Ref. 113).

Single crystal X-ray study of mononuclear metal complexes $[Co(bmpz)Cl]_2[CoCl_4]\cdot H_2O$, $[Co(bmpz)MeCN](ClO_4)_2\cdot 0.13H_2O$, $[Zn(bmpz)MeCN](ClO_4)_2\cdot 0.15H_2O$, $[Zn(bepz)OH_2](ClO_4)_2\cdot 0.5H_2O$ and binuclear complex $[(Co(bepz)Cl)_2]Cl_2\cdot 6H_2O$ confirmed that all four N atoms of synthesized tripodal ligands were utilized for the coordination to the metal ions. However, X-ray study of mononuclear complexes $[Cu(L)Cl_2]\cdot 0.2H_2O$ and $[Cu(L')Cl_2]$ showed that one pedant arm of ligands is removed and tetradentate ligands (bmpz/bepz) was transformed into tridentate ligand (L/L'), respectively. It has shown that protic solvents is responsible for transformation reaction even in the absence of metal ions and it is due to amine functionality in the tripodal ligands.



(a) (b)

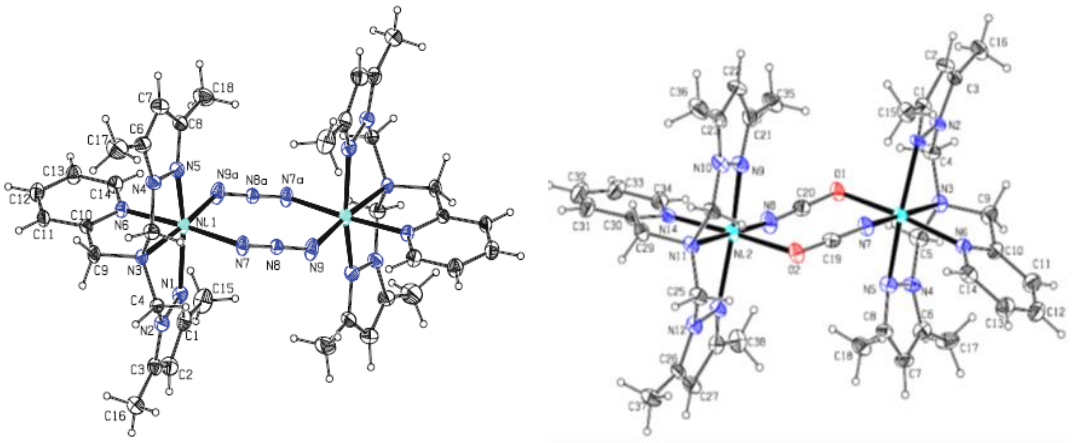
Fig.1.12. Structures of ligands (a)L and (b) L′. (adapted from Ref. 113).



(a) (b)

Fig.1.13. Crystal structures of (a) $[(Co(bepz)Cl)_2]^+$ and (b) $[Cu(b)Cl_2]$. (adapted from Ref. 113).

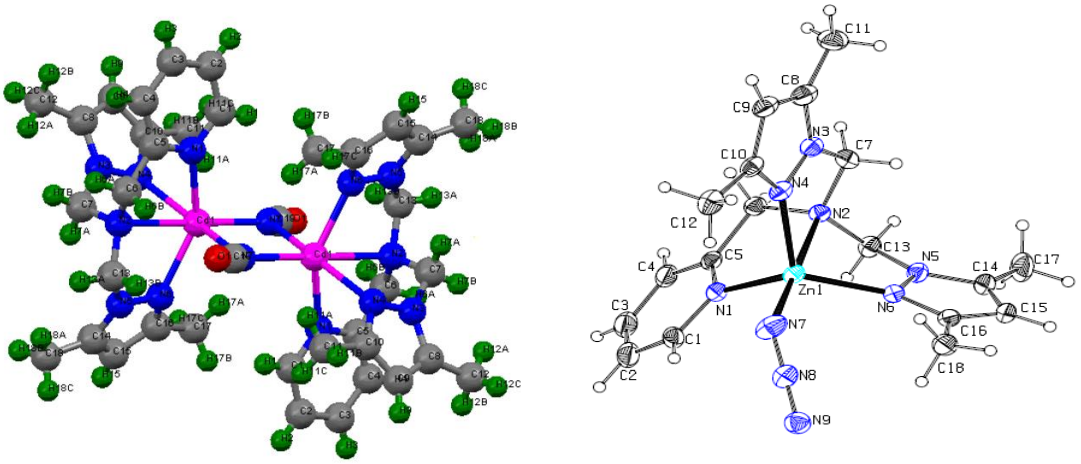
Pyridylpyrazole based N_4-coordinated tripodal ligand *N,N*-bis(3,5-dimethylpyrazol-1-ylmethyl)aminomethylpyridine (L_3) and a series of binuclear transition metal complexes with double pseudohalide (NCO/N_3) bridged were reported by Zala et al [114-115]. Structural data of complexes shows that binuclear Ni(II) complexes $[Ni_2(L_3)_2(N_3)_2](ClO_4)_2.2EtOH$ and $[Ni(L_3)(NCO)]_2(PF_6)_2$ are six coordinated with distorted octahedral geometry and two nickel(II) centres are bridged by a pair of (μ-1,3) N_3/NCO ions whereas binuclear copper(II) complexes $[Cu_2(L_3)_2(N_3)_2](ClO_4)_2$ and $[Cu_2(L_3)_2(NCO)_2](ClO_4)_2$ are six coordinated with distorted octahedral geometry and azide / isocyanate ligands bridged two copper(II) centres via end-to-end (μ -1,3) and end-on (μ-1,1) coordination modes, respectively. The variable temperature magnetic susceptibility data of binuclear Ni(II) complexes show weak antiferromagnetic behaviour whereas $[Cu(L_3)(NCO)]_2(PF_6)_2$ complex shows very weak ferromagnetic interaction.



(a) (b)

Fig.1.14. Crystal structures of (a) $[Ni_2(L_3)_2(N_3)_2]^{2+}$ and (b) $[[Ni(L_3)(NCO)]_2^{2+}$. (adapted from Ref. 114, 115).

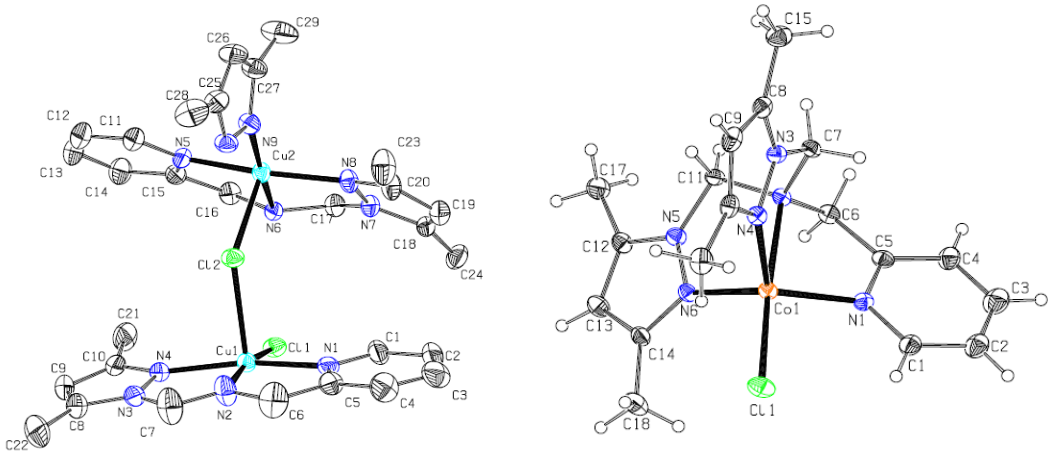
Zala et al also reported synthesis of Cd(II) and Zn(II)complexes with same ligand L_3 in presence of coligands N_3, NCO and NCS of the type $[M(L_3)(NCS)_2]$, $[M(L_3)(N_3)]PF_6$, $[M_2(L_3)_2(NCO)_2](PF_6)_2$ [where, M = Cd(II), Zn(II)] [116] and characterized. Single crystal X-ray diffraction studies confirmed that $[Cd(L_3)(NCO)]_2(PF_6)_2$ complex is binuclear where both cadmium centres are six coordinated with distorted octahedral geometry and two bridged NCO^- ions are in end-on coordination mode whereas $[Zn(L_3)(N_3)]PF_6$ complex is five coordinated with distorted square pyramidal geometry.



(a) (b)

Fig.1.15. Crystal structures of (a) $[Cd_2(L_3)_2(NCO)_2]^{2+}$ and (b) $[Zn(L_3)(N_3)]^+$. (adapted from Ref. 116).

The synthesis, characterization and cytotoxic activity of 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 $[Co(Cl)L_3]PF_6$ by the ligand L_3 is reported [117]. X-ray crystallography analysis revealed that the chloride ligand bridges the two centers in $[L_3'(Cl)Cu\text{-}(\mu\text{-}Cl)\text{-}Cu(pz)L_3'](PF_6)_2$ and geometry of both copper centers are square pyramidal but environment around the copper atoms are different. Cobalt(II) complex $[Co(Cl)L_3]BF_4.½CH_3OH$ is five coordinated with distorted trigonal bipyramidal geometry. The interesting thing of the reaction is that the ligand L_3 transformed into ligand L_3' during in situ complexation reaction. The cytotoxic activity of the ligand (L_3) and the complexes were measured in vitro against the human lymphocyte HL-60 cell line and result shows that the metal complexes have different cytotoxic activities to the organic ligand.

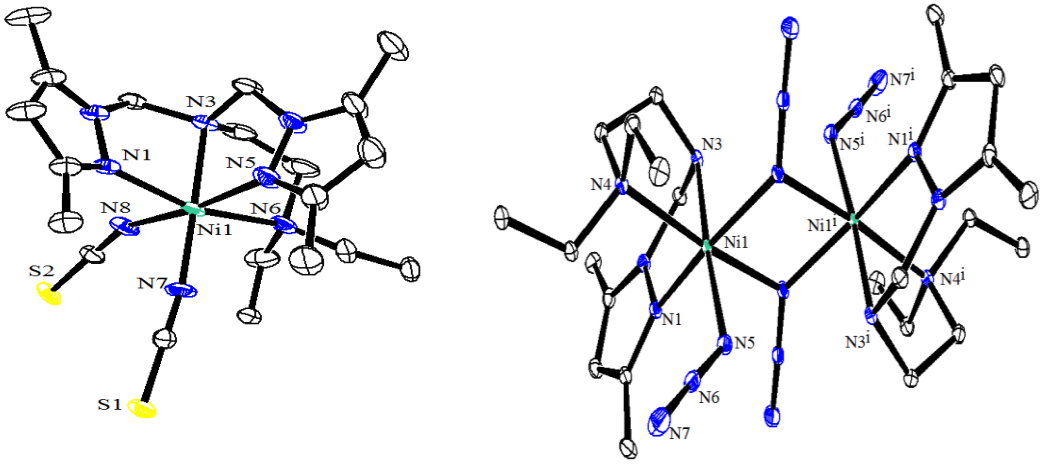


(a) (b)

Fig.1.16. Crystal structures of (a) $[L_3'(Cl)Cu\text{-}(\mu\text{-}Cl)\text{-}Cu(pz)L_3']^{2+}$ and (b) $[Co(Cl)L_3]^+$. (adapted from Ref. 117).

Two tetradentate tripodal 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) and their mononuclear and binuclear complexes of the type $[Ni(dbdmp\textbf{(1)}/dbp\textbf{(2)})(NCS)_2]$ and $[Ni_2(L'_1\textbf{(3)}/L'_2\textbf{(4)})_2(N_3)_2(\mu\text{-}N_3)_2]$, respectively have been reported by Ankita et.al [118]. Single crystal X-ray diffraction analyses showed that geometry of Ni(II) centre in all complexes were distorted octahedral but the interesting thing was that tetra dentate ligands dbdmp and dbp form mononuclear complexes when NCS^- used as co-ligand but when azide ion

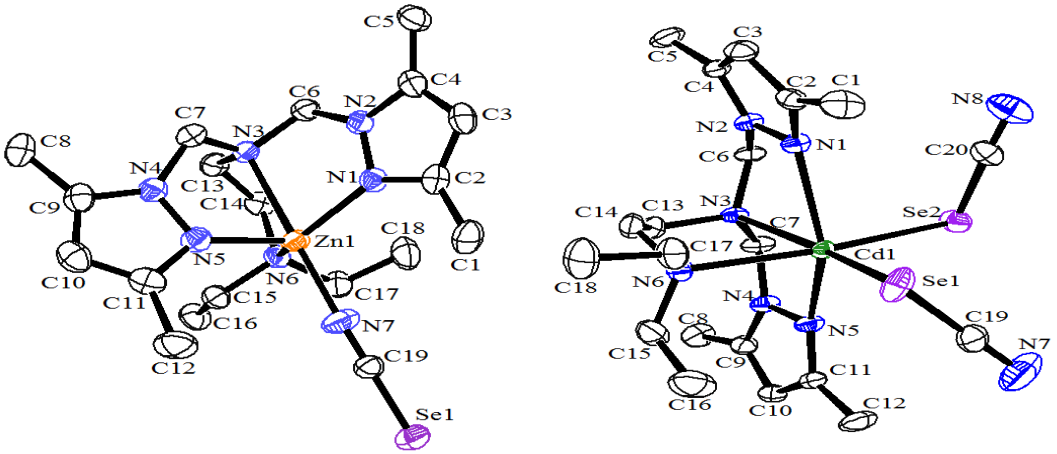
was used as co-ligand, the complexes were binuclear with end-on (μ-1,1) coordination mode of azido ion and one pedant arm of the tripodal ligand was removed and tetradentate ligand *N*,*N*-diethyl-*N'*-((3,5-dimethyl-*1H*-pyrazol-1-yl)methyl)ethane-1,2-diamine (L'_1) was transformed into tri dentate ligand *N*-((*1H*-pyrazol-1-yl)methyl)-*N'*,*N'*-diethylethane-1,2-diamine (L'_2). Variable temperature magnetic studies of binuclear azide bridged Ni(II) complexes shows it has ferromagnetic interaction.



(a) (b)

Fig.1.17. Crystal structures of (a) $[Ni(dbdmp)(NCS)_2]$ and (b) $[Ni_2(L'_1)_2(N_3)_2(\mu\text{-}N_3)_2]$. (adapted from Ref. 118).

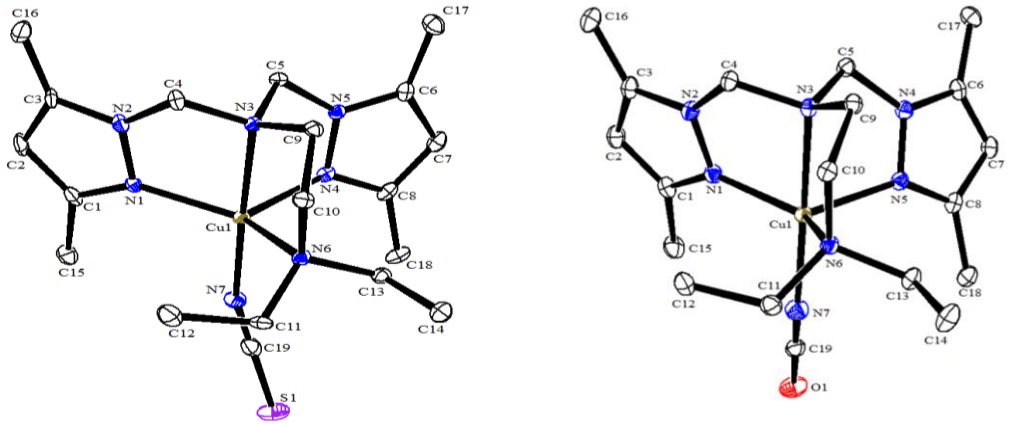
A series of selenocyanate containing mononuclear complexes of the types $[M(NCSe)(dbdmp)]ClO_4$ [M = Co(II)**(1)**, Zn(II)**(3)**], $[Ni(dbdmp)(NCSe)_2]$ **(2)** and $[Cd(dbdmp)(SeCN)_2]$ **(4)** were synthesized with ligand bdpab and characterized with structures [119]. Crystal structures data of four complexes showed that SeCN ion coordinated to metal centres in all complexes through nitrogen atom except cadmium complex and in cadmium complexes, both SeCN ions are coordinated via selenium atoms. Cobalt(II) and zinc(II) complexes are five coordinated with distorted trigonal bipyramidal geometry whereas nickel(II) and cadmium(II) complexes are six coordinated with distorted octahedral geometry.



(a) (b)

Fig.1.18. Crystal structures of (a) $[Zn(NCSe)(dbdmp)]ClO_4$ and (b) $[Cd(dbdmp)(SeCN)_2]$. (adapted from Ref. 119).

Ankita et al reported series of pseudohalides containig mononuclear copper(II) complexes [Cu(X)(dbdmp)]Y, where X = N_3^-, NCS^-, NCO^-, Y = ClO_4^-, PF_6^- and BF_4^- with same tripodal tetradentate ligand (dbdmp) and studied their CT-DNA binding study by absorption and fluorescence spectroscopy methods [120]. Crystal structure analysis showed that complexes $[Cu(N_3)(dbdmp)]ClO_4$ (**1**), $[Cu(NCS)(dbdmp)]ClO_4$ (**4**), $[Cu(NCS)(dbdmp)]PF_6$ (**5**) and $[Cu(NCO)(dbdmp)]ClO_4$ (**7**) are five coordinated with distorted trigonal bipyramidal geometry. They also reported antimicrobial activity of azide and thiocyanate complexes were studied against *Gram positive* (*Bacillus subtilis)* and *Gram negative* (*Escherichia coli*) bacteria strain by dilution method, result shows the complete inhibition of the tested strains by the complexes.



(a) (b)

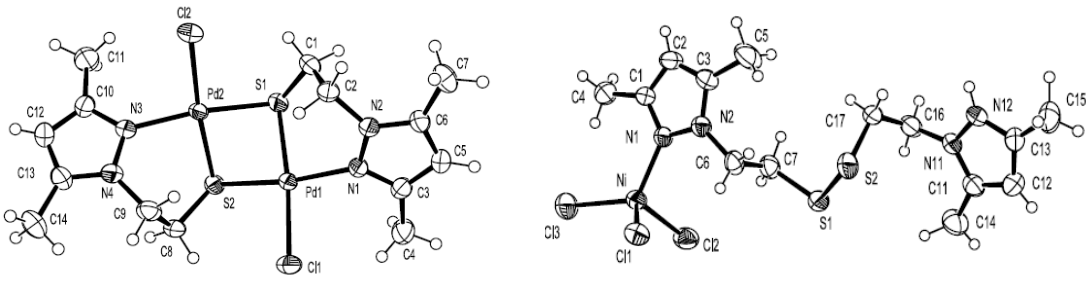
Fig.1.19. Crystal structures of (a) $[Cu(NCS)(dbdmp)]PF_6$ and (b)$[Cu(NCO)(dbdmp)]PF_6$. (adapted from Ref. 120).

1.4. Review of the chemistry of pyrazole nitrogen and thioether containing ligands and their compounds

Recently both sulphur and nitrogen donor atoms containing various chelating ligands have been designed and synthesized [121-123]. There are few pyrazole based chelating ligands with thioether are reported in literature.

1.4.1. Pyrazole and thioether containing bidantate ligands and their compounds

Leon et al were synthesized thiolate bridged binuclear complexes $[MCl(med)]_2$ [where, M= Ni(II), Pd(II)), Pt(II)] using bidentate *N*-(2-mercaptoethyl)-3,5-dimethylpyrazole (Hmed) ligand and characterized. Structural data of $[PdCl(med)]_2$ complex shows that two Pd atoms bridged through two S atom from Med ligand and remaining positions are occupied by a pyrazole nitrogen and one chlorine atom. When the complexation reaction of complex $[NiCl(med)]_2$ was carried out in acetonitrile and a new complex $[NiCl_3(Hdeds)]$ was formed with an unique $NiCl_3N$ core. Structural data of $[NiCl_3(Hdeds)]$ complex showed that each nickel(II) ions coordinated to three chloride ions and one pyrazol nitrogen atom. Ligand Hmed oxidized in to ligand deds = 1,1'-(dithiodiethylene)bis(3,5-dimethylpyrazole)) during the in situ reaction [124].

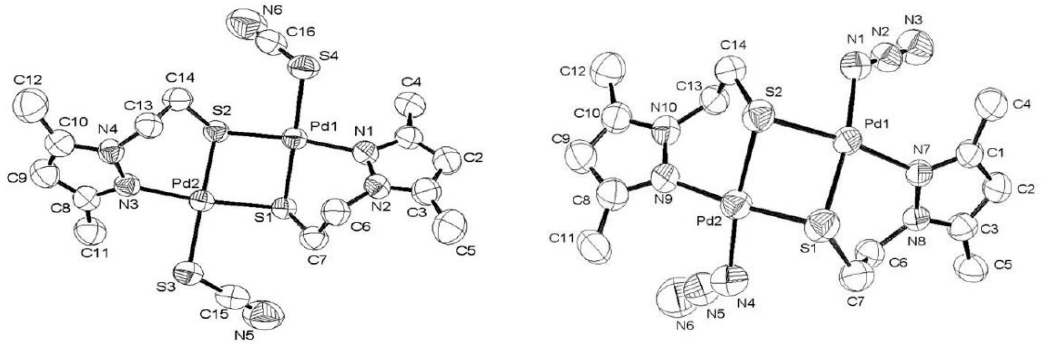


(a) (b)

Fig.1.20. Crystal structures of (a) $[NiCl(med)]_2$(a) and (b) $[NiCl_3(Hdeds)]$. (adapted from Ref. 124).

Synthesis and characterization of NS-bidentate ligand Hmed = N-(2-mercaptoethyl)-3,5-dimethylpyrazole) containing complexes with general formula $[Pd(X)(\mu\text{-med})]_2$ [X = CN^-, SCN^-, N_3^-] were reported by same group [125]. X-ray crystal structures of $[Pd(SCN)(\mu\text{-med})]_2.0.5CH_3CN$ and $[Pd(N_3)(\mu\text{-med})]_2$ show both

complexes are binuclear in nature and each Pd(II) centers are coordinate to pyrazole nitrogen, two bridging sulfur atoms and one SCN^- or N_3^- anion.



(a) (b)

Fig.1.21. Crystal structures of (a) $[Pd(NCS)(\mu\text{-med})]_2$ and (b) $[Pd(N_3)(\mu\text{-med})]_2$. (adapted from Ref. 125).

1.4.2. Pyrazole and thioether containing tridentate ligands and their compounds

Irene Bassanetti et al prepared a series of ligands based on a bis(pyrazolyl)methane moiety attached to functionalized with a rigid (-Ph-S-Ph) or flexible ($-CH_2$-S-Ph) thioether function: L^RPhS (R = H, Me) and L^RCH_2S (R = H, Me, ^{i}Pr) [126]. They synthesized Ag(I) and Cu(I) binary complexes with L^RPhS or L^RCH_2S using different types of counter ions such as BF_4^-, PF_6^- and $CF_3SO_3^-$ and obtained their single crystal X-ray structure. Structural study showed metal centers of all complexes are N_2S-coordinated with two nitrogens from pyrazole moieties and one from bridged thioether group of respective ligands. The flexible ligand L^RCH_2S provide N_2S-coordination sites for chelation whereas the rigid ligand L^RPhS ligand class is capable of chelating only two N atoms from pyrazole. In presence of triphenylphosphine (PPh_3) as an ancillary ligand, mononuclear ternary complexes $[M(L)PPh_3]^+$ (M = Cu(I) or Ag(I); L = L^RCH_2S or L^RPhS) are formed and binuclear structures are not obtained. Density functional theory (DFT) performed by (B3LYP/6-31+G) apply on the ligands L^HPhS and L^HCH_2S to calculate rigid potential-energy.

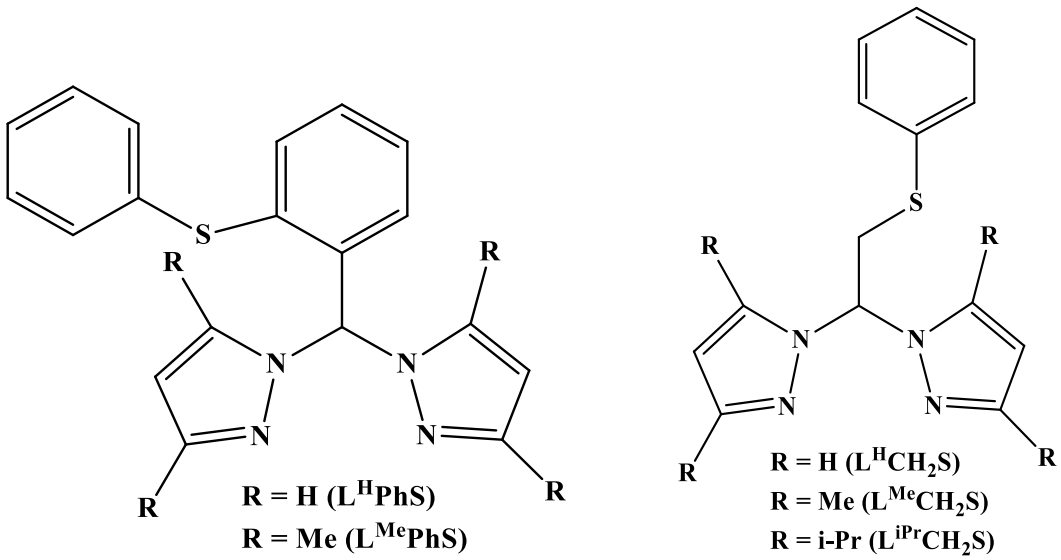
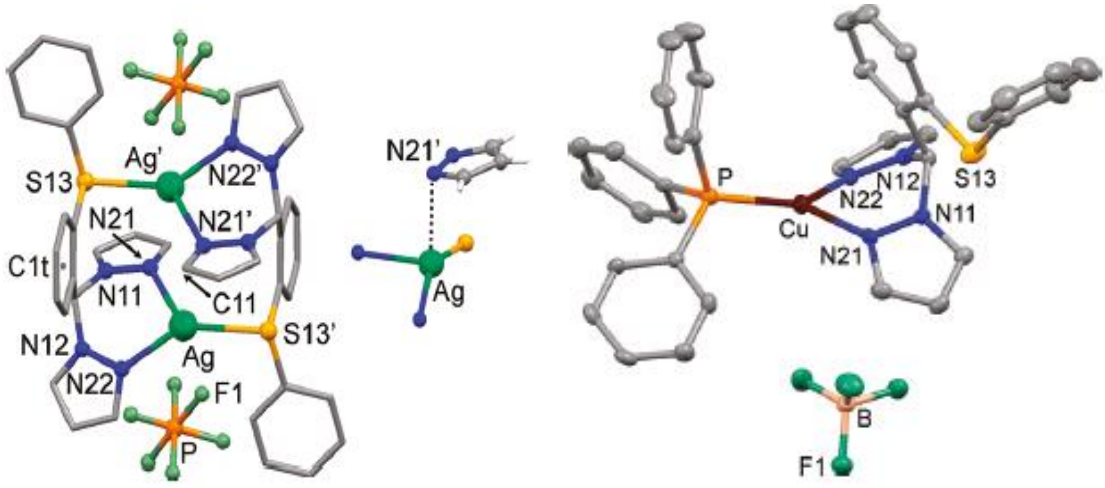


Fig.1.22. Structure of ligands $L^{R}PhS$ (R = H, Me) and $L^{R}CH_2S$ (R = H, Me, ^{i}Pr).

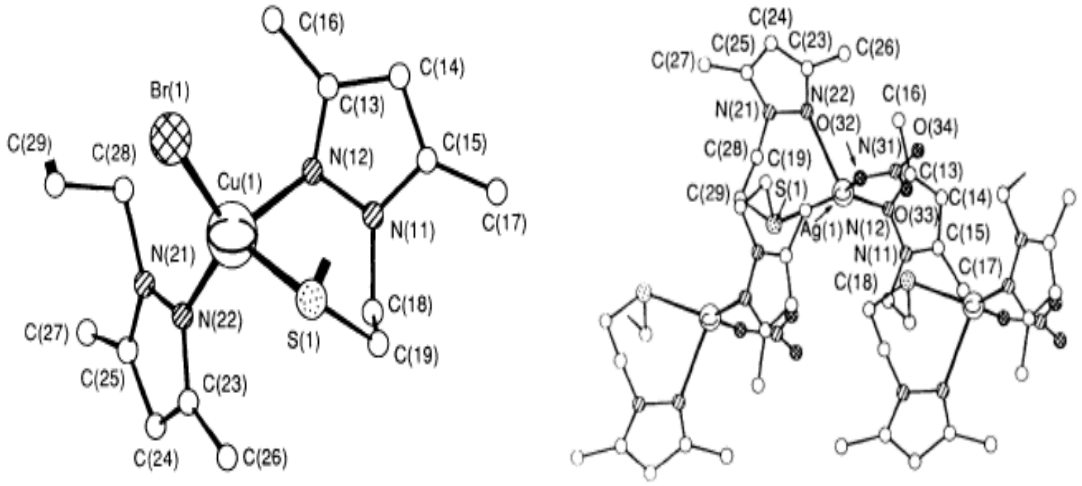


(a) (b)

Fig.1.23. Crystal structures of (a) $[Ag(L^{H}PhS)]2(PF_6)_2$ and (b) $Cu(L^{H}PhS)PPh_3]BF_4$. (adapted from Ref. 126).

Haanstra et al reported synthesis and characterization of N_2S-tridentate ligand1,5-bis(3,5-dimethylpyrazol-l-yl)-3-thiapentane (bdtp) and its transition metal complexes of the type $[M(bdtp)(NCS)_2]$ (M = Co or Zn), $[Ni(bdtp)(NCS)_2(H_2O)]_2$, $Cu(bdtp)(F)(BF_4)_2$, $M(bdtp)Cl_2$ (M = Co or Cu), $Zn(bdtp)Cl_2.0.5EtOH$, $M(bdtp)(NO_3)_2$ (M = Co or Cu), Cu(bdtp)X (X = Br or CI), $[Cu(bdtp)]BF_4$-H_2O and $Ag(bdtp)(NO_3)$ [127]. X-ray single-crystal structures of $[Co(bdtp)(NO_3)_2]$, Cu(bdtp)Br and $Ag(bdtp)(NO_3)$ were solved. The complex $[Co(bdtp)(NO_3)_2]$ is mononuclear and geometry of cobalt(II) atom is pseudo-octahedral and compound $[Cu_4(bdtp)_2Br_4]$ is polynuclear in nature and geometry of copper(I) atom is pseudo-tetrahedral whereas

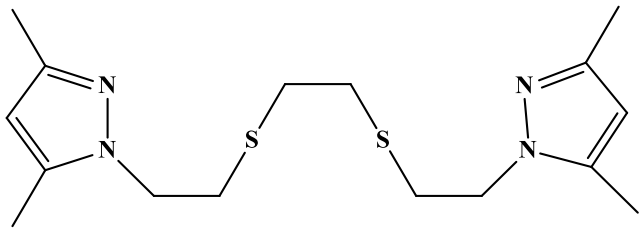
compound [Ag(bdtp)(NO_3)] is polynuclear in nature and geometry of silver atom is distorted-tetrahedral. Both polynuclear complexes have structures with bridging ligands.



(a) (b)

Fig.1.24. Crystal structures of (a) Cu(bdtp)Br and (b) Ag(bdtp)(NO_3). (adapted from Ref. 127).

1.4.3. Pyrazole and thioether containing tetradantate ligands and their compounds



bddo

Fig.1.25. Structure of ligand bddo.

Haanstra et al [128] synthesizd and characterized of the ligand 1,8- bis(3,5-dimethyl-l-pyrazolyl)-3,6-dithiaoctane (bddo) and its metal complexes [M(bddo)(NCS)] [where M = Ni, Co, or Zn] and Cd_2(bddo)$(NCS)_4$ with isocyanate as co-ligand. Crystal structures of the compounds Zn(bddo)$(NCS)_2$, Ni(bddo)$(NCS)_2$ and Cd_2(bddo)$(NCS)_2$ were solved and X-Ray structural data shows that zinc(II) complex is polynuclear and two zinc atoms are coordinated by two pyrazole nitrogen atom of one ligand molecule and geometry of the complex is distorted tetrahedral surrounded by two pyrazole nitrogen atoms and two thiocyanate nitrogen atoms. Mononuclear [Ni(bddo)$(NCS)_2$] complexes are six coordinated surrounded by two pyrazole N atoms

in a *trans* position, two S atoms in a *cis* position and two thiocyanate anions bonded through their N atoms in a *cis* position. $Cd_2(bddo)(NCS)_2$ form 2D-polynuclear complex bridged by double thiocyanate ligands as well as one ligand molecule.

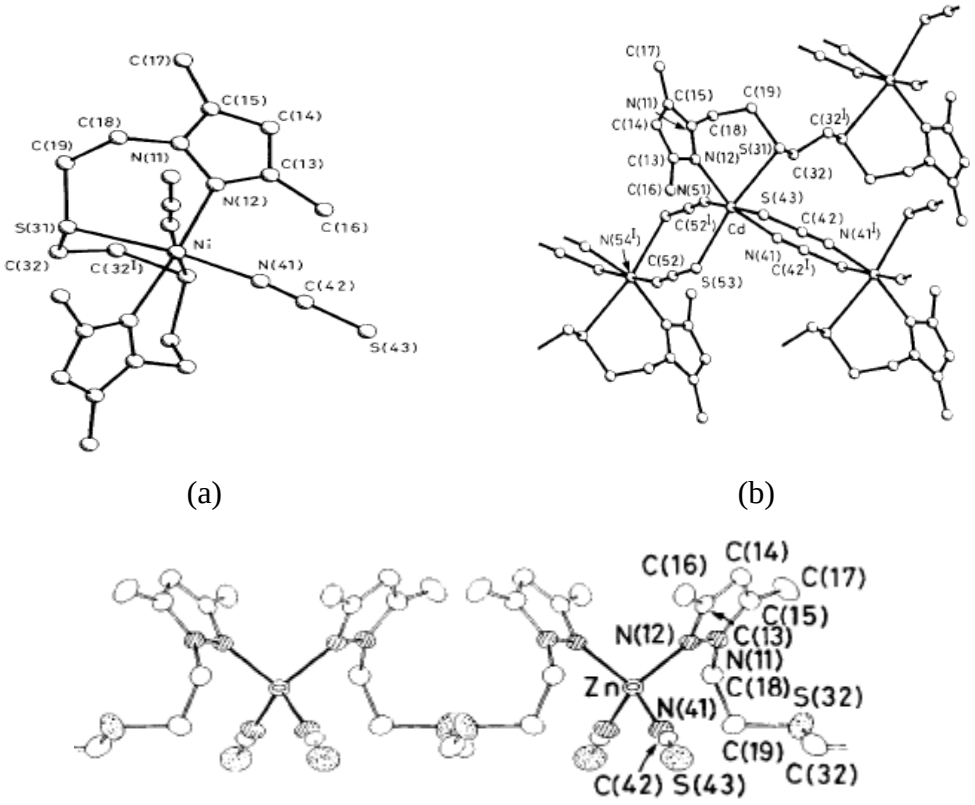
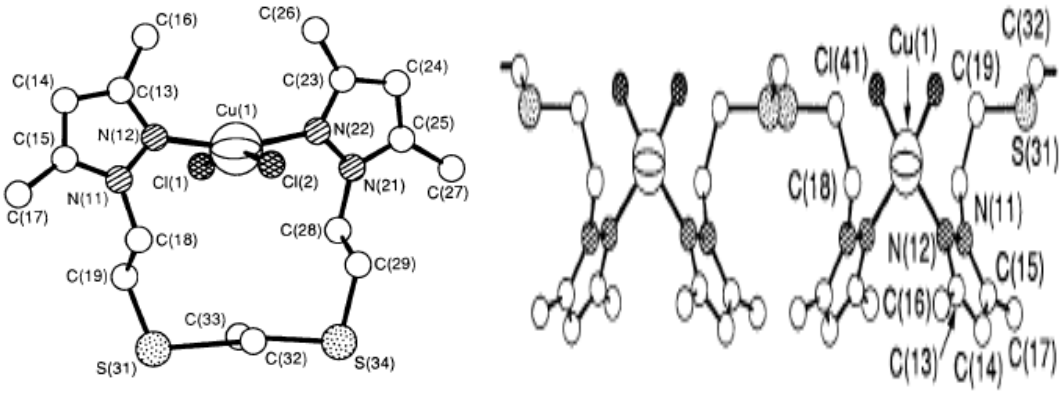


Fig.1.26. Crystal structures of (a) $[Ni(bddo)(NCS)_2]$, (b) $Cd_2(bddo)(NCS)_4$ and (c) $Zn(bddo)(NCS)_2]$. (adapted from Ref. 128).

The co-ordination behavior of N_2S_2-tetradentate ligand (bddo) towards the various metal salts MX_2 (M = Fe, Mn, Ni, Co, Zn, Cu, or Cd), X = C1; M = Mn, Co, Ni, or Zn, X = Br), $Cu(BF_4)_2$ and CuX (X = BF_4, NCS, Cl, Br, or I) were also reported [129]. The interesting thing was that ligand bddo on reaction with $CuCl_2$ produced two different color crystals- the green color crystal form mononuclear complex crystallizes with $P2_1/n$ space group and geometry around metal center is distorted square-planar, co-ordinated by two pyrazole nitrogen atoms and two chloride atoms whereas the red color crystal contains $CuCl_2$ units linked together by ligand molecules form polynuclear complex, crystallizes in *Pbcn* space group with distorted-tetrahedral geometry of each copper atoms, co-ordinated by two nitrogens from pyrazole of ligand and two chloride

atoms are in *cis* positions. For both the cases sulphuratoms do not participate in the co-ordination.



(a) (b)

Fig.1.27. Crystal structures of (a) [Cu(bddo)Cl_2] and (b) [Cu(bddo)Cl_2]. (adapted from Ref. 129).

1.5. Project outline of this work

From the above discussion it has been observed that the coordination chemistry of pyrazolyl containing tripodal ligands are very interesting and form mono-, di- and multinuclear complexes with different metal ions in presence of halides or pseudohalides such as N_3^-, NCS^-, NCO^-, $NCSe^-$ ions as co-ligands with different geometries such as tetrahedral to square planer for four coordination, square pyramidal to trigonal bipyramidal for five coordination and octahedral for six coordination transition metal complexes. Transition metal complexes with pyrazolyl based ligand have biological activities and have applications in the field of catalysis and magnetism. Pyrazolyl based tetradentate ligand shows flexidentate coordination behaviour in many metal complexes. The variety of structures and application of transition metal complexes with pyrazolyl containing ligand inspired us to synthesis two new series of pyrazolyl based ligands with N_4 and N_3S coordination sites and compare their coordination behaviours and bioactivities towards copper(II), nickel(II), cobalt(II), zinc(II) and cadmium(II) complexes in presence of pseudohalides (N_3, SCN, NCO, SeCN) or halides (Cl/Br) or carboxylate as co-ligands. A number of N_4-containingtetradentate ligands and their transition metal complexes are reported in the literature but sulfur containing tripodal ligands and their transition metal complexes are limited.

Objectives of present work

- To synthesis and characterization new pyrazole containing tetradentate N_4- and N_3S-coordinated tripodal ligands.
- To study the coordination behavior of synthesized ligands with different 3d-metal ions such as Cu(II), Ni(II), Co(II), Zn(II) and Cd(II) in presence of halides (Cl/Br) or pseudohalides (N_3/NCS/NCO/SeCN) / alkyl acetates / nitrite.
- To characterize the synthesized complexes by spectroscopic methods such as IR, NMR, microanalysis, UV-Vis etc., magnetic and EPR spectroscopy.
- To determine the structure of some synthesized complexes by single crystal X-ray diffraction studies.
- To study the variable temperature magnetic properties of binuclear pseudohalide bridge complexes.
- To study the biological activities such as antimicrobial activity, DNA cleavage and cytotoxic activity of synthesized ligands and complexes.

In the following chapters we discuss our attempts to synthesis of new ligands, their coordination behavior and their various applications.

The work has been carried out in to five chapters to complete the objectives.

In the **chapter 1**, brief introduction about the coordination chemistry of tetradentate ligand is presented.

In the **chapter 2**, synthesis and characterization of new N_3S-coordinated tripodal *N*,*N*-bis((3,5-dimethyl-*1H*-pyrazol-1-yl)methyl)-2-(phenylthio) ethan-1-amine (bdmpe) ligand, two binuclear double end-on azide bridged copper(II) complexes and two double end-on azide and carboxylate bridged binuclear triple bridged copper(II) complexes have been discussed. Variable temperature magnetic properties of all the complexes discussed in detail.

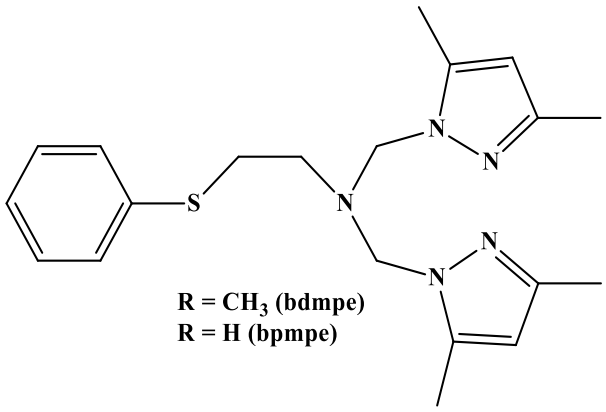


Fig.1.28. Structure of *N*,*N*-bis((3,5-dimethyl-*1H*-pyrazol-1-yl)methyl)-2-(phenylthio)ethan-1-amine **(bdmpe)** and *N*,*N*-bis((*1H*-pyrazol-1-yl)methyl)-2-(phenylthio)ethan-1-amine **(bpmpe)**.

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

Chapter 3(A) describes synthesis and characterization of a new N_3S-coordinatedtripodal *N*,*N*-bis((*1H*-pyrazol-1-yl)methyl)-2-(phenylthio)ethan-1-amine (bpmpe) ligand. A series of mononuclear copper(II) halides and binuclear nickel(II) chloride complexes in the presence of ligand bdmpe/bpmpe have been synthesized and characterized by IR, UV–Vis spectroscopy, elemental analysis, magnetic and EPR spectral data as well as single-crystal X-ray diffraction studies.The antimicrobial activity of ligands and all complexes were investigated against Gram positive (*Bacillus subtilus*, *Streptococcus aureus*) and Gram negative (*Escherichia coli*, *Pseudomonas aeruginosa*) bacterial strain by agar well dilution method. The studies on the interaction of complexes with DNA by agarose gel electrophoresis method investigated in detail.

Chapter 3(B) consists of the syntheses, characterization and structures of copper(II) and cobalt(II) complexes with ligand bdmpe and azide / thiocyanate/ nitrite as co-ligands. The synthesized complexes were characterized by microanalysis, IR, electronic spectra studies, magnetic studies and EPR spectral data including single crystal X-ray diffraction studies. Structural data confirmed that the copper(II) complexes are five coordinated with distorted square pyramidal geometry, $[Co(bdmpe)(NCS)_2]$ complex is five coordinated with distorted trigonal bipyramidal and binuclear cobalt(II) complex $[Co(bpmpe)(N_3)]_2(ClO_4)_2$ has distorted octahedral geometry and the two cobalt centres is bridged by two azide ions with end-on coordination mode.

Chapter 4 describe the synthesis and characterization of new N_4-coorinated tripodal ligand *N,N*-bis(3,5-dimethyl-1H-pyrazol-1-yl)methyl-N_2-phenylethane-1,2-diamine (bdpab) and their [Cu(II)/Co(II)] halides complexes.

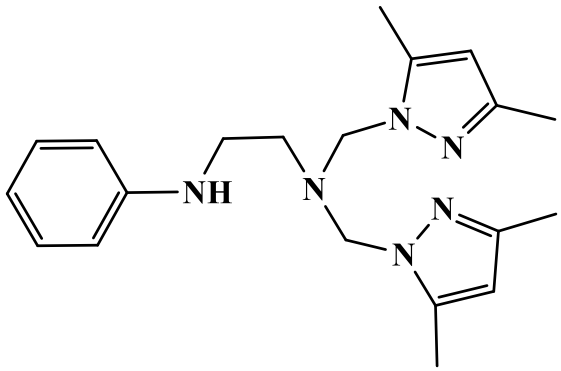


Fig.1.29. *N,N*-bis(3,5-dimethyl-*1H*-pyrazol-1-yl)methyl-N_2-phenylethane-1,2-diamine **(bdpab).**

The complexes were characterized by elemental analyses, IR spectral data, molar conductivity measurement, EPR and crystal structure determination. Antimicrobial activity of few complexes were investigated against *Gram positive* (*Bacillus subtilis, S. aureus)* and *Gram negative* (*Escherichia coli, P. aeruginosa*) bacterial strains and the result shows that complexes have very good antimicrobial activity. The interaction of complexes and DNA were investigated in detail by agarose gel electrophoresis method. The cytotoxic activity of ligand and metal halides complexes with this ligand were screened against A549 lung carcinoma cell line.

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

Chapter 5(A) describes the syntheses, characterization and structures of copper(II), cobalt(II), nickel(II), zinc(II) and cadmium(II) complexes of tetradentate ligand bdpab with coligands (isocyanate / thiocyanate). Structural data shows copper(II), zinc(II) and cobalt(II) complexes have five coordination with MN_5 [M = Cu(II) and Co(II)] coordination environment with distorted square pyramidal geometry, zinc(II) has distorted trigonal bipyramidal geometry and mononuclear $[M(bdpab)(NCS)_2]$ [M = Co(II), Ni(II)] complex has octahedral geometry and the geometry around each metal center in binuclear isocyanate bridged complex $[M'(bdpab)(NCO)]_2(Y)_2$ is distorted octahedral. In binuclear isocyanate bridged complexes, the bridging mode is end-on ($\mu_{1,1}$-NCO) in the Cd(II) complex whereas for Ni(II) complex, the bridging mode is end-to-end ($\mu_{1,3}$-NCO).

Chapter 5(B) consists of the selenocyanate containing mononuclear Ni(II), Co(II), Zn(II) complexes and selenocyanate or thiocyanate containing polynuclear Cd(II) complexes with tetradentate ligand bdpab have been synthesized and characterized by elemental analysis, infrared spectra, ^{1}H NMR and single-crystal X-ray diffraction studies. Structural data confirmed that zinc(II), Ni(II) and Co(II) complexes are mono nuclear whereas Cd(II) complexes are polynuclear. The bidentate N_2-coordinated ligand 3,5-dimethyl-1-((3-phenylimidazolidin-1-yl)-methyl)-*1H*-pyrazole (dpip) is formed from N_4-coordinated teradentate ligand *N*,*N*-bis(3,5-dimethyl-*1H*-pyrazol-1-yl)methyl-N_2-phenylethane-1,2-diamine (bdpab) by removing one pyrazole group and formation of saturated imidazole ring during in situ complexation reaction of ligand bdpab in presence of NCS/SeCN with cadmium(II) salt and their DFT calculations have been performed to corroborated the observed crystal structures and the structural parameter.

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