SURVEY OF LITERATURE

The inorganic coordination complexes obtained from transition metals with ligands having nitrogen donor atoms present a wide scope for structural and pharmacological investigations. A large number of cobalt(II), nickel(II) and copper(II) complexes with various nitrogen donors, have been reported from time to time. In the following pages a brief review of such complexes which are relevant to the present investigation is presented under the following headings:

(1) 3-methyl-4-nitro-4'-(para-nitrophenyl)-pyrazole-5-one complexes.
(2) Ethylenediamine, propylenediamine, diethylenetriamine, triethylenetetramine and tetraethylenepentamine complexes.
(3) 2,2'-dipyridyl and 1,10-phenanthroline complexes.
(4) 2-methylimidazole and benzimidazole complexes.
(5) Urea, thiourea and substituted thioureas complexes.

(1) 3-methyl-4-nitro-1-(para-nitrophenyl)pyrazole-5-one Complexes:

Therapeutical importance of pyrazolone and its derivatives has long been recognised by several investigators and many 1,3-disubstituted pyrazole-5-ones and their derivatives were known to possess significant fungicidal and antibacterial activities\textsuperscript{38-45}. Some 4,4'-bis-5'-pyrazolones, their 4'-4'-unsaturated products and
Ni-substituted-3-methyl-5-pyrazolones as well as related compounds are known to act as potential fungicides\textsuperscript{46,47}. It thus appears that though a little work has been done in this field by different group of workers, no systematic approach has been made so far to study the structures and the fungicidal activities of those substituted pyrazolones which have been complexed with common divalent transition metals. Some such compounds reported are as follows:

Complexes of iridium(II) with derivatives of pyrazolones i.e. antipyrine, diantipyrylnyl-methane, diantipyrylnyl-propyl-methane and diantipyrylnyl-phenylmethane have been prepared\textsuperscript{48}. Cadmium(II) complexes of 4-amino-1-phenyl-2,3-dimethyl-5-pyrazolone and 4-methylamino-1-phenyl-2,3-dimethyl-5-pyrazolone have also been reported\textsuperscript{49}. Zinc(II) and beryllium(II) complexes with various electron donors containing 4-amino-antipyrine groups have been reported and studied\textsuperscript{50}. Halogen complex compounds of gold(II) with pyrazolone derivatives are used for separation of gold from tellurium while the similar antimony(III) complexes with diantipyrylmethyl, diantipyrylpropyl and diantipyrylphenylmethane are used simply as analytical reagents\textsuperscript{51,52}.

Certain halogen complexes of bismuth(III), mercury(II), nickel(II) and cobalt(II) with pyramidone, antipyrine, methylaminoantipyrine and amino-antipyrine have also been reported\textsuperscript{53,54}. Several rare earth complexes with 1-aryl-3-methyl-pyrazole-5-one,
4-sulphophenyl-3-methyl-5-pyrazolone and some mixed complexes with the noltrifluoro-acetone and 1-phenyl-3-methyl-5-pyrazolone derivatives have been prepared and studied\textsuperscript{55-57}.

Relative stability constants of metal derivatives of 1-phenyl-3-methyl-4-(R)-5-pyrazolone, where, \(R=3\)-methyl-phenylazo, 4-iodophenylazo, 3-bromophenylazo, 4-bromophenylazo, 3-chlorophenylazo and 3-nitrophenylazo were measured potentiometrically in 5\% dioxan. The stability decreased in the order Cu<Ni<Co<Zn, while for 1-phenyl-3-methyl-4-phenylazo-5-thiopyrazolones stability follows the order Cu > Ni > Cd > Co > Zn\textsuperscript{58,59}. Some chelate type complexes of cobalt(II) and nickel(II) with aminoantipyrine, methylaminoantipyrine and pyramidone were also reported\textsuperscript{60}. Chelates of silver(I), nickel(II) and manganese(II) with substituted 4-isonitroso-5-pyrazolones were prepared and their structure were investigated using thermogravimetric analysis\textsuperscript{61,62}. 1:1 complexes of thallium(I), 1:2 complexes of cobalt(II) or nickel(II) and 1:4 complexes of cesium(I) or thorium(IV) with 3-methyl-4-nitro-1-(para-nitrophenyl) pyrazole-5-one (enol form) have been studied conductometrically\textsuperscript{63}.

Complexes of 4-phenyl-3-methyl-4-benzoyl-5-pyrazolone with many transition and inner transition metals have been isolated by solvent extraction methods while some similar three component mixed complexes of neodymium(III) and erbium(III) containing the same ligand have also been separated using tributylphosphate as solvents\textsuperscript{64-67}.
The complexes of the metal acetates (M = Co, Ni, Mn, Zn and Fe) with 1-phenyl-3-methyl-4-isonitroso-5-pyrazolone(HL) have been prepared and studied spectroscopically and thermogravimetrically. In these complexes L group was found to be bidentate coordinating with the metals through the O atom of the ketone group and the N atom of the isonitroso group. In order to determine the influence of the ligand 1-phenyl-2,3-dimethyl-5-pyrazolone(A) on the spectral behaviour of copper(II) monohaloacetate complexes, a series of binuclear complexes of the type Cu(XCH₂COO)₂ A, where (X = F, Cl, Br or I and A = above ligand) have been synthesised and studied. Similar copper(II) propionates complexes with 1-phenyl-2,3-dimethyl-5-pyrazolone have also been prepared and characterised by thermal analysis, electronic, infrared and electron spin resonance spectra.

Number of complexes of cobalt(II) and (III), nickel(II), copper(II), iron(II) and chromium(III) with 1-thiocarbamido-3-methyl-5-pyrazolone have been reported in which ligand acts as a bidentate chelating agent. Chelates of these metals with 3,5-dimethyl-pyrazolone-acetic acid have also been reported. Some complexes of different cobalt(II) salts as (halide, nitrate, sulphate and thiocyanate) with 3,5-dimethyl-1-pyrazolylacetohydrazide have been prepared and on the basis of electronic spectral data and corresponding ligand field parameters, a distorted octahedral configuration has been reported for all the complexes.
Some complexes of lanthanides with 1-phenyl-3-methyl-4-(0-carboxy-phenylazo)pyrazole-5-one have been prepared and studied. Two categories of complexes such as $M(L_2)$ or $L_2^2 X_2$ and $ML_2 Y_2$ (where $X = Cl^-$, $Br^-$, $NO_3^-$ and $Y = ClO_4^-$, $M =$ cobalt(II), nickel(II), copper(II) and zinc(II), $L = 1$-phenyl-3-methyl-4-nitroso-2-pyrazolin-5-one and $L' = 3$-methyl-4-nitroso-2-pyrazolin-5-one) have been synthesised and studied, on the basis of spectral and magnetic measurements an octahedral or distorted octahedral and tetrahedral or planar configurations have been suggested for the first and second categories of complexes respectively. Many tetrahedral cobalt(II) complexes with $4,4'$-arylidene-bis-(2-pyrazolin-5-one) have been synthesised and their fungitoxicities were also observed. Europium(III) and rhenium(IV) pyrazole and phenylazo-5-pyrazolone complexes have been prepared.

Solvent extraction of europium(III) and neodymium(III) with 4(P)-nitrobenzoyl-2,4-dihydro-5-methyl-2-phenyl-3H-pyrazone-3-one have been studied. Some new bis and tris complexes of iron(II) with 3,5-dimethyl-1-(2'-pyridyl)pyrazole have been prepared and studied by magnetic and spectroscopically.

Equilibrium studies of interaction of lanthanum(III) with substituted pyrazoles have been done. Complexes of copper(II), nickel(II) and cobalt(II) with 3-methyl-4-(p-ethoxyphenylazo)-2-pyrazolin-5-one have been studied. Complexes of niobium(V) with
1-phenyl-3-methyl-4-(2-methoxy benzeneazo)-5-pyrazolone have been studied. Many complexes of copper(II), nickel(II), cobalt(II), manganese(II), iron(II), zinc(II), cromium(III) and oxovanadium(II) with 4-benzoyl-semicarbazone-1-phenyl-3-methyl-2-pyrazolin-5-one have been prepared and characterised. Some complexes with 3-methyl-4-oximino-2-pyrazolin-5-one of niobium(V) and tantalum(V) have been prepared and studied. Solvent extraction of cobalt(II) chelate of 4-formyl-1-phenyl-3-methyl-2-pyrazolin-5-one has been studied.

M(HmMPzH)₂.2B·nH₂O and M(HmMPzH)₂·B·B·nH₂O (M=Co/Ni(II); B = H₂O, NH₃; B·B = 1.10-phenanthroline/2,2-dipyridyl; n = 0,2) (HmMPzH) = 1-hydroxymethyl-5(3)-methyl-pyrazole-3(5)-carboxylic acid have been isolated and characterised. These have pseudo-octahedral structure. Mixed ligand complexes of cobalt(II), nickel(II) and copper(II) with 1-guanyl-5-methyl-pyrazole-3-carboxylic acid as primary ligand and heterocyclic amines as co-ligand have been prepared and characterised. Complexes of cobalt(II) and nickel(II) with acetophenone-5(3)-methyl pyrazole-3(5)-carboxydrazone (AMPCH) have been synthesised and characterised. These complexes have the general formula; M (AMPCH)₂X₂nH₂O, (M = Co/Ni(II); X=Cl, Br, ClO₄, BF₄, NO₃, 0.5 SO₄; n = 0/1/2/4), magnetic moment and electronic spectral data indicate that the most of the complex species
are grossly octahedral\textsuperscript{89}. A new pyrazole-bridged binuclear copper(II) complex of the type $[L\text{Cu}_2(Prz)]$; where, Prz = Pyrazole and $L =$ Schiff base ligand, has been synthesised and characterised on the basis of x-ray diffraction and magnetic properties\textsuperscript{89A}.

(2) Ethylenediamine, propylenediamine, diethylentriamine, triethylentetramine, tetraethylenepentamine complexes:

These ligands possess maximum tendency for complex formation, because of five and six membered ring in their coordination geometries.

Complexes of type $[\text{Cu}_3(\text{dien})_4]^{6+}$ and $[\text{Co(}\text{dien})_2\text{]}\text{Cl}_3$ have been prepared from copper(II) sulphate, cobalt(II) chloride and diethylenetriamine. Spectrophotometric studies show the equilibrium constant and coordination number as three in both the cases\textsuperscript{90}. Copper(II) complexes with diethylenetriamine have been prepared and the coordination number has been determined\textsuperscript{91}. Complexes of type $[\text{Ni(}\text{trien})_3]^{3+}$ have been prepared from triethylenetetramine and nickel(II) and the magnetic properties of complexes indicate the existence of two unpaired electrons\textsuperscript{92}. Nickel(II) and copper(II) halide complexes with diethylenetriamine have been prepared and the formula corresponds to $[\text{M(dien)}X_2]$ and $[\text{M(dien)}_2X_2]$, when excess of diethylenetriamine was added, the complexes have been proved to be six coordinated\textsuperscript{93}. 
Cobalt(II) and nickel(II) complexes with diamines have been prepared and it has been shown that N-alkyl complexes are much more easily decomposed by refluxing with concentrated acid and all the nickel(II) complexes are less stable than the cobalt(II) complexes. The complexing tendencies of tetraethylenepentamine with cobalt(II) have been measured. The reaction of [Cu(en)₂][ClO₄]₂ with N₃⁻ and halide ion in aqueous solution cause a continuous shift in the absorption spectra toward red. This corresponds to the formation of [Cu(en)₂X⁺, (where X = N₃⁻, Cl⁻, Br⁻ or I⁻). Nonelectrolytic and mixed ligand complexes of type [Ni(phth)₂L₂], (where L = en, pn or dipy), have been prepared and their conductance and molecular weights have been determined. Complexes such as [CuL₂(SeCN)]NO₃, [CuQ₂X₂] and [CuQ₂(SeCN)]NO₃, (where L = pn, Q = diethylenetriamine and X = NCS⁻ or NCO⁻), have also been prepared and their structures were elucidated by infrared and elemental analysis. Complexes of type [CuL₂]₃[PO₄]₂ and [CuL₂]₃[AsO₄]₂ have been prepared, (where L = en or pn), and characterised by analytical, conductance, infrared and visible data. Complexes of type [Cu(C₂O₄)L] have been prepared and shown to be square planer in nature. Paramagnetic chelates of nickel(II) hemioxalate perchlorate with 1,2-diaminomethane, diethylenetriamine and triethylenetetramine have been prepared and their structures elucidated. Cobalt(II) and nickel(II) complexes of triethylenetetramine have been prepared and magnetic moments and
electronic spectra were obtained. Complexes of type MM'(SCSe)₄XL, 
(where M = Cu⁺⁺ or Ni⁺⁺, M' = Zn⁺⁺, Cd⁺⁺, Hg⁺⁺ and X = 2,3; 
L = 1,2-diamineethane and triethylenetetramine) have been prepared, 
the electronic and infrared spectra, magnetic moments, molar 
conductance studies indicate square planar structure for copper(II) 
and octahedral for nickel(II).

Complexes of type Cu₂X₂, (where X = Br⁻ or I⁻; L = 2,2'-
triaminotriethylamine, triethylenetetramine or 3,3'-diamino-dipropyl-
amine), have been prepared and electronic, infrared spectra, 
magnetic moments and conductivity determined to confirm the 
structures.

The formation constant of the complexes formed between 
nickel(II) and copper(II) diethylenetriamine and triethylenetetramine 
has been detected between 0°C. to 30°C.

Some nickel(II) and copper(II) phthalate complexes with 
ethylenediamine and diethylenetriamine have been investigated and 
structures assigned on the basis of magnetic susceptibility, 
electronic and infrared spectra.

The complexes of nickel(II) and copper(II) with triethylen-
etetramine have been reported, the nickel(II) complexes are orange in 
colour and diamagnetic. The absorption spectra have been 
reported.
Some nickel(II) complexes of ethylenediamine and propylenediamine of the type Ni(Me$_2$SO$_4$).en(NCS)$_2$, Ni(en)SO$_4$.6H$_2$O, Ni(en)(NO$_2$)$_2$.2H$_2$O have been prepared and structures elucidated by infrared spectra$^{112-114}$.

Complexes of nickel(II) acetate with ethylenediamine and propylenediamine have been reported. The conductance and molecular weights have indicated the complexes to be nonelectrolyte, suggesting the coordination of acetate ion. Visible spectral data have also been presented and used to discuss the structure of the complex$^{115}$.

Blue to purple copper(II) pyrophosphate with ethylenediamine and violet-red prismatic crystals of trisethylenediamine nickel(II) bisulphate complexes have also been reported$^{116,117}$.

Complexes of copper(II) and nickel(II) with triethylene-tetramine and ethylenediamine of the type [Ni(trien)(en)]X$_2$ (where X = Cl, Br, SCN, NO$_3$, ACO, ClO$_4$, BPh$_4$) have been prepared. The infrared and electronic spectra have indicated the complexes to be octahedral in solid state$^{118}$.

The complexes Ni(en)$_3$MoO$_4$.2H$_2$O, Ni(pn)$_3$WO$_4$.4H$_2$O and Ni(dien)$_2$MoO$_4$.H$_2$O have been isolated and characterised on the basis of elemental analysis, molar conductance, magnetic, infrared, electronic spectra and x-ray powder diffraction data$^{119}$. 
Differential thermal studies were made of the compounds of type $M(\text{en})_2L\text{SO}_4$, $M \text{en}_2L \cdot X_2 \cdot 2\text{H}_2\text{O}$ ($M = \text{Co, Ni, Fe}; L = \text{benzoylhydrazine, salicylhydrazine, histidine}$). It has been found that the thermal stability increases in the series $\text{Fe} < \text{Co} < \text{Ni}$\textsuperscript{120}. The compound $\text{Ni(dien)(DAO)}\text{Cl}$; ($\text{HDAO} = \text{H}_3\text{C(CO)C(CH}_3)_2\text{NOH}$) has been prepared and characterised\textsuperscript{121}. Homogeneous and heterogeneous salts of $M(\text{II})$ (where $M = \text{Cu(II)}, \text{and Ni(II)}$ with $\text{en}$ have been prepared\textsuperscript{122}.

Inhibitory activity of bivalent transition metal complexes with diamines towards a diamine oxidase has been studied by some workers\textsuperscript{123}.

Molar conductance, magnetic susceptibility, electronic, infrared spectra, thermogravimetric analysis, nuclear magnetic resonance and electron spin resonance studies on a large number of amine complexes of cobalt(II), nickel(II) and copper(II) have been made to elucidate their structure\textsuperscript{124-154}.

Complexes of copper(II) and nickel(II) with ethylenediamine and propylenediamine have been studied\textsuperscript{155}. Pentacoordinated mixed ligand complexes of cobalt(II) and nickel(II) derived from diethylenetriamine, phthalimide and succinimide as a anion have been prepared and characterised\textsuperscript{156}.

Cobalt(II), nickel(II) and copper(II) selenate and tungstate
complexes with amines and diamines have been prepared and characterised by esr and nmr\textsuperscript{157}. Metal complexes as ligand binuclear alkali metal complexes with ethylenediamine oxalate and cobalt ethylenediamine oxalate have been prepared\textsuperscript{158}.

Complexes of cobalt(II), nickel(II) and copper(II) with \(N\)-(8-Aceto-7-hydroxy-4-methyl coumarin)ethylenediamine and propylenediamine have been synthesised and characterised\textsuperscript{159}. Copper(II) and nickel(II) complexes with \(N^1, N^3\)-bis (2,4-dinitrophenyl)diethylenetriamine, \(N^1, N^4\)-bis (2,4-dinitropheynyl)triethylenetetramine have been prepared\textsuperscript{160}. Nickel(II) complexes with ethylenediamine have been prepared and studied\textsuperscript{161}. Some mixed ligand complexes of copper(II) and nickel(II) with various amines, (ethylenediamine, propylenediamine, diethylenetriamine and triethylenetetramine) have been prepared and characterised by elemental analysis, magnetic susceptibility, infrared spectra, and electronic spectra\textsuperscript{162}.

A square-planer complex of copper(II) with diethylenetriamine has been isolated and characterised on the basis of elemental analysis, magnetic susceptibility, electronic and Infrared spectra\textsuperscript{162A}.

(3) \textit{\textbf{2,2'-dipyridyl and 1,10-phenanthroline complexes}}:

Magnetic moments and type of bond formation in cobalt(II) and copper(II) with 2,2'-dipyridyl have been studied\textsuperscript{163}. Complexes
of cobalt(II) and nickel(II) with 2,2'-dipyridyl have been prepared and their physical constants and X-ray data obtained\textsuperscript{164}. Complexes of type Ni(chel)\textsubscript{2}X\textsubscript{2}.XH\textsubscript{2}O, (where chel = dipy on phenan for X = a univalent anion), have been prepared with 2,2'-dipyridyl and 1,10-phenanthroline in nonaqueous media. The magnetic study and conductance measurements have confirmed octahedral structure\textsuperscript{165}.

Bis(Phthalimide)cobalt(II) complexes with ligands such as ethylenediamine, propylenediamine, 2,2'-dipyridyl and 1,10-phenanthroline have been prepared and visible absorption measurement confirm their octahedral structure\textsuperscript{166}. Absorption data have been compiled for a series of copper(II) complexes with 2,2'-dipyridyl and 1,10-phenanthroline. The effect of pH in nonaqueous solvents and reactant have also been discussed\textsuperscript{167}. Cobalt(II) and nickel(II) complexes with 2,2'-dipyridyl and 1,10-phenanthroline have been prepared and absorption spectra recorded\textsuperscript{168}. Fulminato complexes of cobalt(II) and nickel(II) have been prepared with 2,2'-dipyridyl and 1,10-phenanthroline\textsuperscript{169}. Complexes of type CoL\textsubscript{2}X\textsubscript{2} (where L = phth., X = en, Pn, NH\textsubscript{3}, dipy or phenan.) have been prepared and characterised\textsuperscript{170}.

Ultraviolet spectra of complexes of cobalt(II) with 2,2'-dipyridyl and 1,10-phenanthroline have been obtained and discussed\textsuperscript{171}. Complexes of type [M(phen)(NCS)\textsubscript{2}], (where $M = \text{Co}^{2+}$, $\text{Ni}^{2+}$ or Cu\textsuperscript{2+}), have been isolated and their behaviour on combination
with acid have been established. Dimeric structure with bridging NO$_3^-$ group in complexes of cobalt(II) nitrate with 1,10-phenanthroline have been confirmed by infrared and differential thermal analysis studies. Complex [Co$_5$(phen)$_4$(OH)$_2$(NO$_3$)$_8$] has also been prepared and infrared spectrum recorded.

The studies of infrared and magnetic data on [CoL$_3$(NCS)$_2$], [CoL$_2$(ClO$_4$)$_2$] and [CoL$_3$I$_3$], where (L = dipy), have confirmed the octahedral and for [CoLX$_2$], where (X = Br$^-$, I$^-$), tetrahedral geometries.

Cis octahedral arrangement has been confirmed by infrared and visible spectra for the complexes [Co(phen)$_2$X$_2$], where (X = anionic ligand). The infrared spectra of twentytwo transition metal 1,10-phenanthroline perchlorate complexes and of free ligands and perchlorate salts have been obtained in the region 2000 cm$^{-1}$ and 600 cm$^{-1}$. Complexes of cobalt(II) with 2,2'-dipryridyl and 1,10-phenanthroline have been prepared and their structural aspects discussed. Octahedral complexes of nickel(II) with 1,10-phenanthroline have been isolated and ligand field parameters calculated. Complexes of type [ML$_3$(ClO$_4$)$_2$], (where L = dipy or phen and, M = Co$^{2+}$, Ni$^{2+}$ or Cu$^{2+}$) have been prepared and their infrared and visible spectra have been studied. Mixed ligand complexes of nickel(II) having general formula [M(A)(L)(H$_2$O)$_2$] SO$_4$ have been prepared and characterised.
Distorted octahedral structure for the complexes [Cu(AA)X₂],
(where, AA = dipy or phen, and X = NO₂⁻, NCS⁻ or N₃⁻), has been
confirmed by magnetic measurement, infrared, diffuse reflectance and
solution spectra. Complexes of type [M(dipy)H₂OAB₄], (where
M = Ni²⁺ or Cu²⁺ and AB₄ = sulphate or tetrafluoro beryllate), have
been isolated in aqueous medium and their T.G.A. and crystallo-
graphic data studied. Mixed ligand complexes of copper(II),
cadmium(II), zinc(II) and manganese(II) cyanide with 2,2′-dipyridyl
and 1,10-phenanthroline have been isolated and subjected to chemical
analysis, infrared and magnetic measurements. The formation of
mixed chelated [CuAB]₄⁺ in aqueous media containing [Cu A₂]₂⁺,
(where A = 2,2′-dipyridyl or 1,10-phenanthroline) and [CuB₂]₄⁺⁺,
(where B = 1,3-propanediamine), β-alaninate, malinate or
pyrocatechol 1,3-,5-sulphonate ion), has been studied spectro-
photometrically.

Crystalline complexes of type [Co(phen)₂X₂].nH₂O (where
X = Cl⁻, Br⁻, NO₂⁻, 0.5 SO₄²⁻, 0.5 CO₃²⁻, NCS⁻, or NO₂⁻; phenan =
phenanthroline) have been prepared in presence of KI. Mono
complexes of 2,2′-dipyridyl and 1,10-phenanthroline with
manganese(II), iron(II), cobalt(II), nickel(II) and copper(II) have
been prepared from the diamine and analogous metal(II) halides and
the far infrared spectra indicate that except Co(phen)Cl₂ which is
tetrahedral, all the other are octahedral. 1,10-phenanthroline-N-
oxide reacts with different 3d metal(II) chloride and the complexes
of different types are obtained which have been characterised by electronic spectra, magnetic susceptibility, x-ray powder diffraction pattern and molar conductance\(^1\). 

Cobalt(II) complexes of 2,2'-dipyridyl and 1,10-phenanthroline with dimethylglyoxime have also been prepared and studied\(^2\). 

X-ray study of complexes of type (2,2'-dipyridyl) bis(\(o, o'\)-dimethylldithiophosphato) nickel(II) has confirmed monocyclic space group and the right angle orientation of chelate group\(^3\). Complexes of type [Co(\(OH\))(\(H_2O\))\(_{2}\)]\(_{2}\)O\(_{6}\) \(\cdot\) \(X\) \(H_2O\), (where \(X = 2\); \(L = \) phen, and \(X = 10\), \(L = \) dipy) and [Co(\(OH\))(\(H_2O\))(dipy)\(_2\)]\(_{2}\)O\(_{6}\) have been studied\(^4\). NMR study of \([M(\text{dipy})_3]\text{Br}_2\cdot6\text{H}_2\text{O}\), (where \(M = \text{Co}^{2+}\) or \(\text{Ni}^{2+}\)) complexes has shown satisfactory evidence for the independent ratio and magnetic anisotropy methods for estimating dipolar moments\(^5\). Mixed ligand complexes of nickel(II) cyanide and 1,10-phenanthroline have been prepared and studied\(^6\). Complexes of copper(II) acetate have been prepared with 2,2'-dipyridyl and their stability in different solvents determined\(^7\). Copper(II) complexes with 1,10-phenanthroline, biquanide and glycinate have been prepared and studied\(^8,\)\(^9\). 

Electronic properties and stereochemistry of copper(II) with mono(1,2-diamineethane) and mono(2,2'-dipyridyl) have been studied
and the series of type CuLX₂.nH₂O, (where L = en or 2,2'-dipyridyl, X = various ions), complexes have been studied by esr, electronic and infrared spectra. Complexes of cobalt(II), nickel(II), copper(II) and iron(II) with 1,10-phenanthroline derivatives have been reported. Mixed ligand complexes of Cobalt(II) imidoacetate, 2,2'-dipyridyl and 1,10-phenanthroline have been prepared and studied. Complexes of type [Cu(Phen) (acac)]Cl and [Cu(Phen)L].nH₂O, (where phen = 1,10-phenanthroline, acac = acetylated acetic, L = a bidentate o donor ligand, n = 0, 1, 2 or 3), have been prepared and characterised by infrared and electronic spectra.

Mixed ligand ternary complexes of the type [MII.B.m ba]; [M = Co(II), Ni(II); B = neutral amines eg. 2,2'-dipyridyl (dipy), 1,10-phenanthroline(phen) have been prepared and characterised physicochemically. Mixed ligand ternary complexes of the type Cu(II)B-H₂A. (B = 1,10-phenanthroline (phen) and 2,2'-dipyridyl (dipy); H₂A = Pyridine-2-6-dicarboxylic acid, phthalic acid, oxalic acid etc.), have been synthesised and characterised.

Structural study on the complexes of nickel(II), and cobalt(II) with 2,2'-dipyridyl formed in presence of MoO₄²⁻ o xoanion have been made. Mixed ligand octahedral complexes of copper(II) anthranilates with 1-10-phenanthroline and 2,2'-bipyridyl have been prepared and characterised. Some ternary complexes
of cobalt(II), nickel(II) and copper(II) with 2,2'-dipyridyl/1,10-phenanthroline have been studied\textsuperscript{210}. Tris 2,2'-bipyridyl nickel(II) tungstate hexahydrate and Tungstamonoaquobis-2,2'-bipyridyl cobalt(II) monohydrate have been prepared and characterised\textsuperscript{211}. The mixed ligand complexes of cobalt(II) and nickel(II) with 1,10-phenanthroline(phen) and 2,2'-dipyridyl(dipy) have been prepared and characterised\textsuperscript{212}. Some mixed xanthate complexes of nickel(II) with 1,10-phenanthroline and 2,2'-dipyridyl have been synthesised and characterised on the basis of elemental analysis, magnetic susceptibility, infrared and electronic spectral data. These measurements suggest octahedral structure of these complexes\textsuperscript{213}. Base adducts of cobalt(II) and nickel(II) chelates with some Schiff's bases have been prepared and characterised\textsuperscript{214}. Complexes of cobalt(II)/nickel(II) with 1,10-phenanthroline/2,2'-dipyridyl have been prepared and characterised. They suggested pseudo-octahedral structure of these complexes\textsuperscript{215}. Mixed ligand complexes of metal cyanides with 1,10-phenanthroline and 2,2'-dipyridyl, \((M = \text{Cu(II)})\), have been prepared and characterised\textsuperscript{216}. Ternary complexes of some metal ions with 2,2'-dipyridyl and 1,10-phenanthroline as primary ligand and naptalam as a secondary ligand with general formula \(\text{MAL}^+\), \((\text{where, } M = \text{Co(II)}, \text{Ni(II)}, \text{Cu(II)} \text{and } \Lambda = 2,2'-\text{dipyridyl}, \text{and } 1,10-\text{phenanthroline have been studied potentiometrically in solution}\textsuperscript{217}.\)
New copper(II) squarate complexes of formula. 

\[ \text{[Cu(bpy)(H}_2\text{O})(\text{C}_4\text{O}_4)] \cdot \text{H}_2\text{O; [Cu}_2\text{(bpy)}_2\text{(H}_2\text{O})_2\text{(C}_4\text{O}_4)](\text{NO}_3)_2; \]
\[ \text{[Cu(phen)(H}_2\text{O})_2\text{(C}_4\text{O}_4)] \cdot 2\text{H}_2\text{O.} \]

(where, bpy = 2,2'-bipyridyl; phen = 1,10-phenanthroline and dianion \( \text{C}_4\text{O}_4^{2-} \) = 3,4-dihydroxy-cyclobutenedione) have been synthesised and characterised by x-ray diffraction infrared spectra, electronic spectrums, magnetic and esr spectra.\(^{217}\text{A}\).

(4) 2-methylimidazole and benzimidazole complexes:

Some cobalt(II), nickel(II) and copper(II) chelate complexes with areneazo-2-imidazoles were prepared and their dipole moment have been measured. In the solid state, either a tetrahedral configuration may be proposed in which half of the molecule rotated at right angles along the horizontal axis, or a polymeric octahedral structure resulting from further coordination of the metal with \( N^3 \) atom of imidazole may be possible.\(^{218}\) Large number of complexes of cobalt(II), nickel(II), copper(II), iron(II), manganese(II) and cadmium(II) have been prepared with N-butylimidazole as ligand and structural analysis has been done through X-Ray power diagrams, ligand field spectra, vibrational spectra and magnetic measurements.\(^{219}\) Some complexes of copper(II) thiocyanate have been prepared with imidazole and benzimidazole, in which thiocyanate was terminal N-bonded, while the manganese(II) complexes with 2-benzyl-benzimidazole have also been prepared and studied.\(^{220-222}\).
The nickel(II) and copper(II) sulphate and fluoroberyllate complexes with imidazole and pyrazole were prepared and characterised by electronic spectroscopy, thermogravimetric analysis and X-ray crystallographic studies\textsuperscript{223}. Some complexes of cobalt(II), nickel(II) and copper(II) have been prepared with organic ligands viz. substituted 2-(2-hydroxyphenyl) - benzotriazoles and 2-(2-hydroxyphenyl) - benzimidazoles and studied spectrophotometrically\textsuperscript{224}. The copper(II) complexes with 4-methyl-imidazole have also been prepared. TGA and DTA studies have been made for some of the complexes which were shown to decompose with the loss of imidazole ligand\textsuperscript{225}. The copper(II) halide complexes with azoles have been prepared and infrared and electron spin resonance spectral studies showed coordination of the ligand through pyridine type nitrogen\textsuperscript{226}. Several copper(II) and copper(I) chloride complexes with substituted imidazoles have been prepared and studied through spectral and magnetic data. The copper(II) complexes are very stable while others are oxidised in moist air. It has been observed that the presence of bulky substituents in the ligand further stabilises the compounds\textsuperscript{227}. Some complexes of 2-guanidinobenzimidazole with copper(II) have been prepared and studied\textsuperscript{228}, while the mixed ligand complexes of chromium(III) with 2-(2'-pyridyl) - benzimidazole were reported in which the ligand functions as a neutral bidentate nitrogen donor\textsuperscript{229}. 
Manganese(II) and cobalt(II) ions react with imidazole to give complexes for which a correlation between the bonding of a series of metal(II) with ammonia and with imidazole was deduced\textsuperscript{230,231}. Some cobalt(II) and nickel(II) nitrate and perchlorate complexes with substituted imidazole have been prepared and magnetic moments, molar conductance, infrared and electronic spectra have been studied\textsuperscript{232}, while the corresponding 4-methyl-imidazole complexes of cobalt(II) and nickel(II) have been prepared and their stereochemistry and stoichiometry have been deduced from analytical data, electronic and infrared spectral data, molar conductance and room temperature magnetic moments\textsuperscript{233}. N-vinylimidazoles complexes with cobalt(II) chloride have been prepared and their thermal decomposition has also been studied, which revealed that the ion catalysed the oxidation of the alkyl group in the second position of the imidazole ring of the ligand\textsuperscript{234}. Luminiscence of benzimidazole and its complexes with cobalt(II) have been studied and a new absorption band in the region 300-400 nm has been found in concentrated solutions of benzimidazole in dimethylsulphoxide\textsuperscript{235}.

Some nickel(II) complexes with benzimidazole and 2-(hydroxy methyl)benzimidazole have been prepared and studied, while the corresponding 2-aminobenzimidazole complexes with cobalt(II) and nickel(II) have also been prepared. Spectral studies showed that all the cobalt(II) complexes had pseudotetrahedral
configuration while the nickel(II) complexes were either pseudo-tetrahedral, square planar or distorted octahedral\textsuperscript{236-238}. Some nickel(II) complexes with 2-isopropylimidazole with formulae such as $\text{NiL}_4X_2$ (X = Cl\textsuperscript{-}, Br\textsuperscript{-}, I\textsuperscript{-}, SCN\textsuperscript{-}, SeCN\textsuperscript{-}, NO\textsubscript{3}\textsuperscript{-}, ClO\textsubscript{4}\textsuperscript{-}, PF\textsubscript{6}\textsuperscript{-}) have been prepared. All the complexes have been assigned tetragonally distorted octahedral structure and the extent of tetragonal distortion has been found to vary with the nature of the axial ligands. Thermal decomposition of $\text{NiL}_4X_2$ (X = Cl\textsuperscript{-}, Br\textsuperscript{-}, NO\textsubscript{3}\textsuperscript{-}) gave strongly tetragonal diamagnetic $\text{NiL}_2\text{Cl}_2$ and weakly tetragonal paramagnetic $\text{NiL}_2X_2$ (X = Br\textsuperscript{-}, NO\textsubscript{3}\textsuperscript{-})\textsuperscript{239}.

Thermal decomposition of some complexes of cobalt(II) and nickel(II) with 4-methylimidazole and N-methylimidazole has been studied. In the N-methylimidazole complexes, metal-ligand bonding has been found to be stronger than in the imidazole complexes\textsuperscript{240,241}. The complexes of 2,2'-bimidazole with cobalt(II), nickel(II), copper(II) and iron(II) have also been reported which are high spin and remarkably less stable than corresponding complexes of 2,2'-bipyridine or 2-(2-pyridyl) imidazole\textsuperscript{242}. Some complexes of cobalt(II) and nickel(II) with 5-nitrobenzimidazole have been studied with a view to find out the effect of nitro substitution on the donor ability of the ligand\textsuperscript{243}.

Thermal behaviour of imidazole and benzimidazole complexes with copper(II), cobalt(II), nickel(II) have been studied. In all
complexes no transition change occur. All broad exothermic peaks above 300°C corresponds to the rapid mass-loss\textsuperscript{244}. Few complexes of nickel(II) with \(B = \text{imidazole}, \ 2\text{-methyl-imidazole and 1,2-dimethyl imidazole of the type NiL}_2\text{Bn.XH}_2\text{O (where n = 2, and X = 0-6, L = different anion)} have been prepared and characterised with the help of various physical and spectroscopic techniques\textsuperscript{245}.

Six mixed ligand complexes of copper(II) with imidazole have been prepared and studied\textsuperscript{246}. Nickel(II) complexes with 2-substituted benzimidazoles have been prepared and studied by infrared, electronic spectral, magnetic susceptibility measurements\textsuperscript{247}.

Cobalt(II), nickel(II) and copper(II) complexes of 2-(1'-benzenesulphonylamino-3'-methyl-mercaptop)- propyl-benzimidazole have been studied\textsuperscript{248}. The complexes of the type MX\sub{2}L\sub{2} (where, \(M = \text{Co(II), Ni(II), Cu(II)}; X = \text{Cl, Br, I, NO}_3, \text{ClO}_4 \text{ or NCS and L = 2-coumarinylbenzimidazole)} have been synthesised\textsuperscript{249}. Some sulphonamidobenzimidazoles complexes with cobalt(II), nickel(II) and copper(II) have been studied\textsuperscript{250}.

Mixed ligand complexes of copper(II) with imidazole and N-protected aminoacids have been synthesised and characterised spectroscopically and magnetic moments. Crystal and molecular structures of bis(lippurate)bisimidazole copper(II) have been studied\textsuperscript{251}. 
Coordination compounds of copper(II) with 2-methylimidazole and 1-2-methyl-benzimidazole have been prepared and characterised²⁵².

(5) **Urea, thiourea, phenylthiourea, diphenylthiourea and benzoylthiourea complexes:**

Complex compounds of thiourea and other sulphur containing ligand with copper(II) salts have been studied from very early times notably by Maly, Claus, Rothke, Rosenhelum, Kohlchutter and many others²⁵³,²⁵⁴.

In copper(II) thiourea complexes, the particular ion shows a great diversity in the coordination number in many cases fractional molecule of thiourea, permetal is present. Copper(II) thiourea ratio varying from 1:4 to 1:1 has been reported²⁵⁵. Several complexes with thiourea and substituted thiourea have been reported in which copper ion appears to be bivalent²⁵⁶.

Thiourea complexes with nitrosopentacyanoferate(II) have been prepared at different pH values and their structure determined by using infrared spectral and X-ray diffraction methods²⁵⁷.

Complexes such as CuSO₄.2Acth (Acth = N-acetylthiourea) and CuCl.3Phth.3H₂O (phth = N-phenylthiourea) have been isolated in which copper ion appears to monovalent²⁵⁸,²⁵⁹.
Many tris(thiourea)copper(II) halide have been isolated and characterised. Several complexes with substituted thiourea such as N-phenylthiourea, and N-acetyli thiourea have been isolated. All the complexes have been shown to have copper in +2 oxidation state\(^{260}\).

N-phenylthiourea complexes of copper(II) using different anions such as hydroxide, chloride, sulphate, nitrate and acetate have been isolated\(^{261,262}\).

Several complexes of substituted thiourea with copper(II) have also been reported by various workers. Infrared spectral studies have shown that the ligands are bonded by sulphur atom in all the complexes\(^{263-269}\).

Some copper(I) and copper(II) complexes with substituted thiourea viz. mono and di-N-acetyli thiourea have been prepared\(^{270}\).

Some bivalent metals where \(M = Mn, Fe, Co, Ni,\) or Cd form complexes with thiourea in which \(M\) appear to be tetracoordinated on the basis of crystallographic data\(^{271}\). Conductivity, infrared spectra and magnetic moments of some complexes of cobalt(II), nickel(II) and cadmium(II) thiocyanates with thiourea have been studied\(^{272}\). Complex compounds of substituted thioureas(I) copper derivatives of N-acetyli thiourea, S-acetyli thiourea and N-phenylthiourea have been prepared and characterised\(^{273}\).
The compounds \( \text{Co(py)}(\text{tu})_2\text{Cl}_2 \), \( \text{Co(py)}(\text{tu})_2\text{Br}_2 \) have been prepared and studied\(^{274}\). Molecular and electronic structure of some thiourea complexes of cobalt(II) have also been studied\(^{275}\).

The non-electrolytic, monomeric, thiourea(tu) complexes of the type \([\text{Co(tu)}_3\text{Cl}_2]\) (Blue), \([\text{Co(tu)}_3\text{Br}_2]\) and \([\text{Co(tu)}_2\text{I}_2]\) (green) have been prepared and characterised on the basis of magnetic moment\(^{276}\).

Polymeric complexes of cobalt(II) thiocyanates with thiourea, N-methylthiourea and N,N'-ethylenethiourea have been prepared and studied\(^{277}\). Some complexes of urea and thiourea with cobalt sulphate have been studied spectrophotometrically\(^{278}\). Many complexes of cobalt(II) and copper(II) with substituted thioureas have been prepared and characterised\(^{279}\). Some nickel(II) coordination compounds with phenylthiourea have been investigated\(^{280}\).

Complexes of cobalt(II), nickel(II) and copper(II) with some N'-2-(substituted pyridyl)-N-substituted thioureas have been prepared and characterised by infrared, electronic spectra and molar conductance\(^{281}\).

Some complexes of cobalt(II) and copper(II) with N-(1-Benzoyl-substituted-phenyl - thiosemicarbazide) N'-substituted phenylthiourea have been synthesised and characterised\(^{282}\).
Complexes of cobalt(II), copper(II) with disubstituted thioureas have been synthesised and characterised by elemental analysis. Molar conductance, infrared, ultra-violet and magnetic measurements have been made. Metal complexes of the type \([M(BBTuB)X_2]\), (where, \(M = \text{Cu(II)}, \text{Ni(II)}, \text{Co(II)}; \text{BBTuB} = p-p'\text{-bis(benzoylthiourea)}\) and \(X = \text{Cl}^-, \text{Br}^-, \text{NO}_3^-, \text{ClO}_4^-\)), have been prepared and characterised on the basis of infrared spectra, electronic spectra and magnetic susceptibility measurements.

Mixed ligand complexes of nickel(II) with alkyl-1-amidino-2-thioureas have also been isolated.

Some complexes of \(M(\text{NCS})_2(\text{NCSTi})_2\), \(M = \text{Co(II)}, \text{Ni(II)}\) or \(\text{Cu(II)}\), with urea have been prepared and characterised by elemental analysis, molar conductance, magnetic measurements, infrared and electron spectral studies were made, indicating that all complexes are non-conducting. Binuclear complexes of the type \([\text{NiL}_3(L')\text{NCS X}]\), \(L = \text{thiourea (tu)}, \text{o-tolythiourea (ototu)}, L' = \text{o-chlorophenylthiourea (o-clptu)}, X = \text{Cl}, \text{or NO}_3^-\) have been synthesised and characterised by physical and analytical methods.

Complexes of cobalt(II) and nickel(II) with urea and thiourea have been characterised.

Several mixed ligand complexes of cobalt(II) with thiourea, allylthiourea, diphenylthiourea, \(N\)-methylthiourea, \(N,N'\)-dimethyl-
thiourea etc. have been reported and cobalt(II) perchlorate with N-allylthiourea and 1,10-phenanthroline has been prepared and characterised\textsuperscript{289}. The mixed ligand complexes of the bis (ethyl-acetoacetate) copper(II) with thiourea and substituted thiourea have been prepared and characterised. The infrared spectra indicate thioureas are coordinated to the metal ion through sulphur atom. Magnetic data indicate that all complexes are paramagnetic\textsuperscript{290}.

Some complexes of copper(II), nickel(II) and cobalt(II) with N-(2-thiazolyl)-thiourea have been prepared and characterised. The elemental analysis suggest the formula a MLX\textsubscript{2}: where, M = Cu(II), Ni(II) and Co(II), L - ligand (TTU) and X = Cl\textsuperscript{-}, Br\textsuperscript{-}, NO\textsubscript{3}\textsuperscript{-} and ClO\textsubscript{4}\textsuperscript{-}\textsuperscript{291}.

Complexes of cobalt(II), nickel(II) and copper(II) with N-benzoyl-N'-(2-thiazolyl)thiourea have been prepared and characterised on the basis of elemental analysis, I.R., electronic spectra, magnetic measurement and molar conductance\textsuperscript{291A}. 