CHAPTER II

SURVEY OF LITERATURE
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The inorganic coordination complexes obtained from transition metals with ligand having nitrogen donor atoms present a wide scope for structural investigations. Copper is an important trace element for plant and animals\textsuperscript{27, 28} and is involved in mixed ligand complexes\textsuperscript{29, 30} in a number of biological processes\textsuperscript{31}. There has been considerable interest in recent years in the study of complexes with heterocyclic ligands due to its importance in biological, pharmacological, antileukemic areas\textsuperscript{32-38}, and antifungal, antibacterial activities\textsuperscript{39}. Imidazole and its derivatives are known to play an extremely crucial part in the functioning of number of biologically important molecules by virtue of their being coordinated to metal ions\textsuperscript{40}. A perusal of literature shows that no work has been done on transition metal complexes of barbitone, phthalimide, phthalate, succinate and benzoate with imidazole, 2-methylimidazole and benzimidazole. In the following pages a brief review of such complexes which are relevant to the present investigation is presented under the following headings.

1. Barbitone, phthalimide, phthalate, succinate and benzoate complexes.

2. Imidazole, 2-methylimidazole and benzimidazole complexes.
(1) Barbitone, phthalamide, phthalate, succinate and benzoate complexes

Stability constants of ternary complexes of copper(II) with 2,2'-bipyridyl as primary ligand and barbituric acid or its 5,5 substituted derivatives as secondary ligand in 50% (v/v) aq. ethanol have been determined pH meterically at $\mu = 0.1M$ (NaNO$_3$) and temperature $30^\circ \pm 1^\circ C$.$^{41}$

Copper(II), nickel(II) and cobalt(II) complexes with substituted Benzoic acid have been prepared and characterised on the basis of analytical, conductivity, magnetic susceptibility, thermal, infrared, ESR and NMR spectral studies.$^{42}$

Some mixed ligand complexes of nickel(II) and cobalt(II) with heterocyclic bases and homophthalic acid and tetra-chlorophthalic acid were prepared and characterised on the basis of elemental analysis, conductance, magnetic moment, infrared and electronic spectral studies.$^{43}$ Some mixed ligand pentacoordinated complexes of nickel(II) and cobalt(II) with phthalamide and succinimide as monodentate and dien as tridentate have been prepared and characterised on the basis of elemental analysis, infrared, electronic spectra, conductance and magnetic measurements.$^{44}$ Non electrolytic mixed ligand complexes of type [Ni(phth)$_2$L$_2$] (where L= en, pn, dipy.) have been prepared and their conductance and molecular weight have been determined.$^{45}$
Cobalt(II) phthalimide complexes with ligands such as en, pn, 2,2'-dipyridyl have been prepared and visible absorption measurements confirm their octahedral structure. Complexes of type CoL₂X₂ (where L=phth, X=en, pn, NH₃, dipy or phen) have been prepared and characterised.

Some copper(II) and nickel(II) complexes with ethylenediamine and diethylenetriamine have been investigated and structures assigned on the basis of magnetic susceptibility, electronic and infrared spectra. The formation constants of the ternary complexes of copper(II) with malonic acid as a primary ligand and oxalic, formic, succinic, phthalic, salicylic acids as secondary ligands have been evaluated pH meterically at 25°C and μ=0.1 M (KNO₃).

Some complexes of copper(II), nickel(II) and cobalt(II) with 0-(N-α-pyrrolidimino)benzoic acid have been synthesised and characterised on the basis of elemental analysis, magnetic, UV and infrared spectral, molar conductance and thermal studies.

Monosubstituted copper(II) benzoates have been studied on the basis of infrared. Copper(II) chelates of substituted succinic and malonic acid have been studied. Six new, four coordinate macrocyclic complexes of copper(II) and nickel(II) possessing the general formula [M(LL)]X, where M = Cu(II) or Ni(II), L=tetrazeno [b, i, j, n] [1, 5, 9, 13]
tetrazacyclohexadecine, X = succinate, phthalate; have been prepared and studied\textsuperscript{57}. Nickel(II) succinate complexes with various amines have been prepared and characterised\textsuperscript{58}.

Polymeric complexes of nickel(II) have been obtained using \(\alpha\)-dipyridyl disulphide\textsuperscript{[L]}\textsuperscript{[L]}. The complexes cation possess the general formula \([-\text{NiL}_2]^{2n^+}\) the anion used is \(\text{C}_2\text{H}_4\text{O}_7\text{H}_3\). The complexes are assigned planar structure on the basis of analytical, magnetic and spectral studies\textsuperscript{59}. Correlation of electrode behaviour and spectral properties of some mixed ligand complexes of copper(II) with succinic, benzoic and phthalic acids containing 2,2'‐dipyridyl and 1,10‐phenanthroline as a secondary ligand have been prepared and characterised\textsuperscript{60}. Studies on complexes of copper(II), nickel(II) and cobalt(II) with thiodisuccinic acid have been done\textsuperscript{61}. Mixed ligand complexes of nickel(II) and cobalt(II) with 2-marcapto benzoic acid and some biologically active neutral bases have been studied\textsuperscript{62}.

Characterisation of some dimeric complexes of nickel(II) benzoate derived from schiff's bases have been done\textsuperscript{63}.

Preparation and characterisation of some complexes of nickel(II) succinate with aromatic, heterocyclic and diamines have been done\textsuperscript{64}. Nickel(II) phthalate mixed ligand complexes containing nitrogen donor atoms have been prepared and characterised\textsuperscript{65}. Dimeric complexes of copper(II) anthranilate,
benzoate, acetate and oxalate derived from schiff's bases, have been characterised on the basis of elemental analysis, conductance, TGA, infrared, magnetic and electronic spectral data. The simple and mixed ligand complexes of phthalimide with cobalt(II) using ammonia, dipyridyl and o-phenanthroline as secondary ligands have been studied in relation to their preparation, magnetic and infrared studies. Some complexes of cobalt(II) phthalimide with different ligand have been prepared and studied.

A number of metal complexes of the type \( \text{K} \left[ \text{Ni}_{x} \text{a}(\text{H}_{2}\text{O})\text{b(OH)} \right] \) where l-isoquinoline or pyridine and \( \text{a} \)-deprotonated succinic acid have been prepared and characterised on the basis of chemical analysis, conductance, magnetic measurements, infrared and electronic spectral studies, these were found to have an octahedral structure.

Some nickel(II) complexes of benzoate and substituted benzoates with heterocyclic amines have been prepared and studied. A number of copper(II), nickel(II), cobalt(II) and manganese(II) complexes of phthalimide, succinimide, oxalate, formate, benzoate and succinate ions have been prepared and characterised.

Some complexes have been prepared and characterised with o-aminobenzoic acid. Mixed ligand complexes of
copper(II) succinate or phthalate with 2,2'-bipyridyl have been prepared and studied\(^8\).

**Phenobarbiturato complexes of copper(II) in methanolic media** have been prepared and characterised\(^9\). The schiff base have been synthesised by condensing o-aminobenzoic acid and terephthaldehyde in ethanolic medium forms complexes \([ML_2H_2O_n\]) with copper(II), nickel(II) and cobalt(II). The polymeric octahedral structures of the insoluble complexes have been arrived on the basis of elemental, ir and rs studies, magnetic measurements and thermal analysis\(^10\).

(2) **Imidazole, 2-methylimidazole and Benzimidazole complexes**

Some copper(II) and cobalt(II) chelate complexes with areneasos-2-imidazole were prepared and their dipole moments have been measured. In the solid state, a tetrahedral configuration has been proposed in which half of the molecule is 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 is also possible\(^11\). Some complexes of transition metals with imidazole and substituted imidazole have been prepared and studied\(^12\).

A large number of complexes of copper(II) nickel(II) and cobalt(II) has been prepared with \(N\)-butyl-imidazole as ligand and structural analysis has been done through X-ray
powder diagrams, ligand field spectra, vibrational spectra and magnetic measurements. Some complexes of copper(II)thiocyanato have been prepared with imidazole and benzimidazole, in which thiocyanato is terminal N-bonded.

The copper(II) and nickel(II) sulphate and fluoroberyllate complexes with imidazole and pyrazole have been prepared and characterised by electronic spectroscopy, thermogravimetric and X-ray crystallographic studies. Some complexes of copper(II), nickel(II) and cobalt(II) have been prepared with 2-(2-hydroxyphenyl) benzimidazole and studied spectrophotometrically. The copper(II) complexes with 4-methylimidazole have also been prepared. TGA and DTA studies have been made for some of the complexes which were shown to decompose with loss of imidazole ligand. The copper(II) halide complexes with azoles have been prepared and infrared and electronic spin resonance spectral studies have shown coordination of the ligand though pyridine type nitrogen.

Several copper(II) 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.

Some complexes of 2-guanidino-benzimidazole with copper(II) have been prepared and studied. Cobalt(II) ions react with imidazole to give complexes for which a correlation
between the bonding of a series of metal(II) ions with imidazole has been deduced\(^{98,99}\). Some nickel(II) and cobalt(II) nitrate and perchlorate complexes with substituted imidazoles have been prepared and magnetic moments, molar conductance, infrared and electronic spectra have been studied\(^{100}\). While the corresponding 4-methylimidazole complexes of nickel(II) and cobalt(II) were prepared and their stereochemistry has been decided from analytical electronic and infrared spectral data, molar conductance and room temperature magnetic moments\(^{101}\). N-Vinylimidazoles complexes with cobalt(II) chloride have been prepared and their decomposition studied, which revealed that the ion catalysed the oxidation of the alkyl group in the second position of the imidazole ring of ligand\(^{102}\). 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 solution of benzimidazole in dimethylsulphoxide\(^{103}\).

Some nickel(II) complexes with benzimidazole and 2-(hydroxymethyl) benzimidazole have been prepared and studied, while the corresponding 2-aminobenzimidazole complexes with nickel(II) and cobalt(II) have also been prepared. Spectral studies showed that the nickel(II) complexes were either pseudotetrahedral, square planar or distorted octahedral while cobalt(II) complexes had pseudotetrahedral configuration\(^{104-106}\).
Some nickel(II) complexes with 2-isopropylimidazole with formula such as NiL₄X₂ [X=Cl⁻, Br⁻, I⁻, SCN⁻, NO₃⁻, ClO₄⁻, PF₆⁻] have been prepared. All the complexes were assigned tetragonally distorted octahedral structure. Tetragonal distortion has been found to vary with the nature of the axial ligands. Thermal decomposition of NiL₄X₂ (X=Cl⁻, Br⁻, NO₃⁻) gave strongly tetragonal diamagnetic NiL₂Cl₂ and weakly tetragonal paramagnetic NiL₂X₂ (X=Br⁻, NO₃⁻)

Thermal decomposition of some complexes of nickel(II) and cobalt(II) with 4-methylimidazole and N-methylimidazole has also been studied. In the N-methylimidazole complexes, metal-ligand bonding has been found to be stronger than in the imidazole complexes.

The complexes of 2,2'-bimidazole with copper(II), nickel(II) and cobalt(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.

Some complexes of nickel(II) and cobalt(II) with 5-nitrobenzimidazole have been studied with a view to find out the effect of nitro substitution on the donor ability of ligand.

Thermal behaviour of imidazole and benzimidazole complexes with copper(II), nickel(II) and cobalt(II) has been studied. The exothermic peaks above 300°C corresponds to the rapid mass loss. Few complexes of nickel(II) with
[B=imidazole, 2-methylimidazole and 1,2-dimethylimidazole of type NiL₂X₄O (where n=2 and X=0-6, L=different anion)] have been prepared and characterised with the help of various physical and spectroscopic techniques.

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

Copper(II), nickel(II) and cobalt(II) complexes of 2-(3'-benzenesulphonylamino-3'-methylmercapto) propylbenzimidazole have been studied. The complexes of the type MX₂L₂ (where M=Cu(II), Ni(II) or Co(II), X=Cl⁻, Br⁻, I⁻, NO₃⁻, ClO₄⁻ or NCS⁻ and L=2-coumarinylbenzimidazole) have been synthesised.

Some sulphonamidobenzimidazoles complexes with copper(II), nickel(II) and cobalt(II) have been studied. Mixed ligand complexes of copper(II) with imidazole and protected amino acids have been synthesised and characterised spectroscopically and magnetic moments. Crystal and molecular structures of bis(lippurate) bisimidazole copper(II) have been studied. Coordination compounds of copper(II) with 2-methylimidazole and 2-methyl-benzimidazole have been prepared and characterised.
Studies on formation constants of copper(II) chelates of some substituted benzenesulphonamidoethyl-benzimidazole have been done\textsuperscript{121}. Structural studies of copper(II), nickel(II) and cobalt(II) complexes of substituted benzenesulphonamido-benzimidazoles have been reported. The geometries of the complexes have been proposed on the basis of magnetic and electronic spectra\textsuperscript{122}.

Metal complexes of 2,4(or 7)-Dimethyl-benzimidazole with different metal ions like copper(II), nickel(II) and cobalt(II) have been characterised\textsuperscript{123}.

Transition metal complexes of 6-methyl-2-amino-benzothiazole and 2-methylbenzimidazole have been prepared and characterised on the basis of analytical magnetic moment, molar conductance, electronic and infrared spectral data. The mixed ligand complexes have six coordinated octahedral configuration\textsuperscript{124}. Metal complexes of 4(or 7)-Nitrobenzimidazole with copper(II) and nickel(II) have been synthesised and characterised by elemental analysis, molar conductance, infrared, electronic, esr spectra and magnetic susceptibility\textsuperscript{125}.

Binary and ternary metal complexes of copper(II), nickel(II) and cobalt(II) with ethylenediamine, glycine catechol and 2-hydroxymethyl-benzimidazole have been studied\textsuperscript{126}. Complexes of copper(II)-azide and tetrafluoborates have been prepared with several substituted imidazoles\textsuperscript{127}. 
Mixed ligand complexes of copper(II), nickel(II) and cobalt(II) with pyridine-2,5 dicarboxylic acid and ethylenediamine or imidazole have been prepared and studied\(^{128}\). A number of spin free complexes of manganese(II) have been prepared with 1-propylimidazole and characterised by elemental analysis, conductance, magnetic susceptibility, infrared and UV spectral measurements\(^{129}\). Several mixed ligand of bis (benzoylacetonato)-nickel(II) with imidazole, morpholine and their derivatives were synthesised and characterised on the basis of magnetic, spectral and thermogravimetric analysis\(^{130}\). Several complexes of various transition metal ions with benzimidazole and substituted benzimidazoles have been prepared and characterised\(^{131-136}\). Series of metal chelates of copper(II), nickel(II) and cobalt(II) with 2,2'-bi-2-imidazoline were prepared and studied\(^{137}\). The preparation, spectral and magnetic properties of complexes of type Co(Im)\(_6\)X\(_2\) and Ni(Im)\(_6\)X\(_2\) (X=Cl,Br,I,NO\(_2\), Im=Imidazole) and Cu(Im)\(_4\)X\(_2\)(X=Cl,NO\(_3\)) and Co(Im)\(_2\)Cl\(_2\) have been done\(^{138}\).

Five ternary metal complexes containing imidazole and glycine or amino acid have been prepared and characterised by the proton magnetic and infrared spectra\(^{139}\). The complexes of nickel(II) and cobalt(II) halides with imidazole have been prepared. The complexes \((\text{Im}_4)\) NiX\(_2\), \((\text{Im}_4)\) NiX\(_2\) \((X=\text{Cl}^-,\text{Br}^-,\text{I}^-)\), \((\text{Im}_2)\) \(_2\) NiX\(_2\) \((X=\text{Cl}^-,\text{Br}^-)\); Im NiX\(_2\) \((X=\text{Cl}^-,\text{Br}^-)\) and Im CoI\(_2\) have essentially octahedral structure while \((\text{Im}_2)\) NiI\(_2\), \((\text{Im}_2)\) CoX\(_2\)
(X=Cl\(^-\), Br\(^-\), I\(^-\)) and (Im) CoX\(_2\) (X=Br, I) pseudotetrahedral\(^{140}\). A number of tetrahedral and octahedral complexes of cobalt(II) salts with imidazole have been prepared and their structures described\(^{141}\). The complexes of type NiL\(_2\)X\(_2\) (H\(_2\)O)\(_m\)
\(\text{(L=imidazole, m=0-4, X=Cl\(^-\), Br\(^-\), I\(^-\), NCS\(^-\)) were synthesised and ligand field parameters were calculated from spectral data. The Ni\(^{2+}\) ions were octahedrally coordinated in [NiL\(_6\)]X\(_2\) with tetragonal elongation in [NiL\(_4\)]X\(_2\), NiL\(_2\)X\(_2\) and NiLX\(_2\) have probably an anion bridged distorted octahedral coordination with L in axial position\(^{142}\). The complexes of type [Cu(CNS)\(_2\)L\(_2\)] (L=Quinoline, imidazole benzimidazole etc.) were synthesised and characterised\(^{143}\). Copper(II) complexes of glycolglycine with imidazole, 1-methylimidazole, 2-methylimidazole and benzimidazole have been synthesised\(^{144}\). Complexes of the type Cu(NCO)\(_2\)L\(_2\) (L=Imidazole, 1 or 2 methyl or 2-ethylimidazole 1,2-dimethylimidazole, 2-methyl and 2-ethylbenzimidazole were synthesised and characterised\(^{145}\) and also [CuL (Im)]X type of complexes (L=MeNCH\(_2\)NMe\(_2\)), 2,2,pipy, 1,10 phenan., X=ClO\(_4\), PF\(_6\), BF\(_4\), Im=Imidazole\(^{146}\).

Complexes of type CuR\(_2\)L\(_2\).nH\(_2\)O and CuR\(_2\)L\(_4\) (HR=2-furonic acid; L=pyrazole, imidazole) have been synthesised and characterised by visible, ESR spectra and magnetic moment measurements\(^{147}\).

Isocyanoato complexes of nickel(II) with substituted imidazole of type Ni(NCO)\(_2\)L\(_4\) (L=imidazole, 2-methylimidazole) and Ni(NCO)\(_2\)2H\(_2\)O (Q=1,2 dimethylimidazole); and complexes
of type CuL_2X_2 \ (L=1-vinylimidazole, \ 1-vinyl-2-methylimidazole, 2-ethylimidazole, 2-isopropylimida, \ n=2, 4, 6; \ X=Cl, Br, NCS, NO_3, ClO_4, X=SO_4), also have been prepared and characterised on the basis of elemental analysis, conductance, magnetic susceptibility, electronic and infrared spectral data\textsuperscript{148,149}. 

On the basis of infrared, solid state electronic and ESR spectral data the structure of complexes of type Cu(NCS)_2L_2 \ (L=imidazole, benzimidazole) have been proposed\textsuperscript{150}. 

Some complexes of binuclear copper(II) bridged by imidazolato, 2-methylimidazolato, benzimidazolato, bi-imidazolato and bibenzimidazolato have been reported with one binuclear nickel(II) complex bridged by bi-imidazolato\textsuperscript{151}. 

On the basis of chemical analysis, infrared, far-infrared, Raman, ligand field and ESR spectral data a polymeric structure have been proposed for the complexes of type ML_2(OX)\_2 \ (OX=oxalate dianion; \ M=nickel(II) and cobalt(II); \ L=imidazole). Each metal ion is coordinated by four oxalate O atoms and two donor atoms (N or O) forming distorted octahedron, while other different transition metal complexes with imidazole and benzimidazole also have been prepared and characterised\textsuperscript{152-156}. 

N-donor ligands as imidazole, morpholine and their derivatives\textsubscript{\textit{L}} with bis(acetyl acetanato) nickel(II) form solid 1:2 adducts of type Ni(AA)_2L_2 in which nickel(II) is
hexacoordinate. These adducts have been characterised by elemental analysis, electronic, infrared spectra and magnetic susceptibility measurements\textsuperscript{157}.

The complexes of type Cu\{Salgly\}(L)(H\(_2\)O)\(_x\) \([H\textsubscript{2}Salgly = N\text{-Salicylidene}glycine, L=imidazole and its derivatives, }\ X=0,1,2\) have been proposed and their ESR spectra, antimicrobial activity studied\textsuperscript{158}.

Equilibrium study has been done on the complex formation of copper(II), nickel(II) and cobalt(II) with 2-chloroacetylaminomethyl benzimidazole\textsuperscript{159}. Some complexes of copper(II) with L-histidine, glutamic and aspartic acid as primary ligand and imidazole, 2-methylimidazole and 2-ethylimidazole as secondary ligands have been studied\textsuperscript{160}.