Chapter-I

Introduction

Organic molecules having thioamide group (H-N-C=S) gives rise to four thioamide bands in their infrared spectra.\textsuperscript{(1-10)} These bands are effected differently by different modes of coordination. Coordination occurs through nitrogen and sulphur donor atom in case of bidentate or polydentate nitrogen and sulphur ligand\textsuperscript{(11-12)} or co-ordination occurs only through sulphur or nitrogen as donor atom as monodentate ligand. This aspect of coordination is very important and hence this work is concerned with investigation of this aspect of study. Moreover, the ligand chosen in the present work is 2-mercapto-3-phenyl-quinazole-4-one (MPQH) which contain thioamide moiety (Fig. I.1).

\begin{center}
\begin{tikzpicture}
\node at (0,0) {\includegraphics[width=0.5\textwidth]{thioamide.png}};
\node at (0.5,0) {Thioamide group.};
\end{tikzpicture}
\end{center}

\textsuperscript{[Fig I.1]}

2-Mercapto-3-phenyl-quinazole-4-one (MPQH)
These ligand mainly exist in the thione form (fig 1.2) in the solid state as indicated by their infrared spectra although in solution it may also occur in thiol form fig. I.3.

(Fig. I.2)

Thione form

(Fig. I.3)

Thiol form
2- Mercapto-3-phenyl quinazole-4-one has three potential donor sites such as carbonyl oxygen, thio carbonyl sulphur and imino nitrogen atom. They may act as monodentate ligand forming metal nitrogen band [Fig I.4] or metal sulphur band [Fig. I.5].

(Fig. I.4)
Metal nitrogen bond (Salt type)

(Fig. I.5)
Metal sulphur bond (Salt type)
They may also act as monodentate ligand as forming metal nitrogen (Fig I.6), metal-oxygen [Fig I.7] and metal sulphur [Fig I.8] as shown:

(Fig. I.6)

(Fig. I.7)
They may also act as bidentate ligand forming inner type of complex chelates by coordination through thio carbonyl sulphur and imino nitrogen as shown in Fig I.9.
These ligand may also form dimer [Fig I.10] or polymer [Fig I.11] as shown below:

(Fig I.10)

Dimer
Thus, it will be quite interesting to prepare and study the complexes of these ligands having different modes of linking with the central metal ions.

Moreover, these ligands are physiologically active compounds. Substituted thio quinazoles are also biologically active compounds and they are reported to be antimalarials,\(^{(13)}\) active as attractive agents\(^{(14)}\), potential hypnotics and analgesies.\(^{(13)}\) Metal ions [Zn (II), Cd (II), Pd (II) and Ru (II)] used in this work are also formed to be biologically active and have playsdrokin many biological activity reactions\(^{(15-19)}\). The ligand chosen in this study are such that the charge delocalised between among oxygen, nitrogen and sulphur atoms. This may lead in a semiquantitative way to show a better understanding of :-

![Polymer Diagram]
(i) The donor properties of nitrogen, sulphur and oxygen in general.

(ii) Nature of metal nitrogen, metal oxygen, metal sulphur and metal phosphorous linkage.

(iii) Position of ligand in spectrochemical series.

(iv) Stereochemistry and coordination no. of Zn (II), Cd (II), Pd (II) and Ru (II) metal ions.

(v) Stability of tetrahedral, square planer and octahedral complexes.

(vi) Investigation of $\nu$ Zn-N, $\nu$ Zn-S, $\nu$ Zn-O, $\nu$ Cd-N, $\nu$ Cd-O, $\nu$ Cd-S, $\nu$ Pd-S, $\nu$ Pd-N, $\nu$ Pd-O, $\nu$ Pd-Cl, $\nu$ Ru-S, $\nu$ Ru-N, $\nu$ Ru-P, frequencies in far infrared spectra.

(vii) Antifungal activity of Zn (II) complexes against a flavs and

(viii) Classification of new fungicides.

The metal ions used in this work for complexation with 2 mercapto-3-phenylquinazol-4-one are Zn (II), Cd (II), Pd (II) and Ru (II), carbondisulphide, triphenyl phosphine, phenyl thiourea and diphenyl thiourea are also taken as secondary ligand in this work.

**PREVIOUS WORK IN THIS FIELD**

A short survey of the complexes of nitrogen and sulphur containing ligands having thioamide moiety and their antimicrobial activities are given in the following paragraphs in order to throw light on the type of work already done in this field.
Thiourea is a simple ligand which contains thioamide moiety and a large number of complexes have been investigated\(^{20-23}\) in which it acts as a monodentate ligand coordinating through sulphur\(^{24-26}\) and through nitrogen\(^{27}\). In case of thiourea octahedral, triangular bipyramidal, square planar and tetrahedral complexes are formed and their relative stabilities are determined by electronic rather than steric factors\(^{28-29}\).

The nature of bonding in thiourea complexes can be either ionic or covalent depending on the metal ion used for complexation\(^{30}\). The stereochemistry of a number of covalent bonded thiourea complexes have been determined and their stereochemistry is either square planar or octahedral. Crystal structures of a large number of thiourea and substituted thiourea complexes have also been investigated by a number of workers\(^{31-33}\).

N, N'-substituted thiourea have been extensively studied and Cu (I), Ag (I) gives 1:1, 1:2, 1:3, 1:4 complexes. Ni (II) forms tetrahedral, octahedral and tetragonal complexes\(^{34}\) but Co (II) is reported to exhibit generally tetrahedral coordination but with strong tendency to form a penta coordination adduct\(^ {35}\).

Complexes of N, N'-dicyclohexyl and N,N'-diphenyl thiourea\(^{36-38}\), N, N'-diethyl thiourea\(^{39}\), N, N'-diaryl-N-hydroxythiourea\(^{40}\), 1-allyl-3-(2-pyridyl)-2-thiourea\(^{41}\) and N, N'-bis-(2-pyridyl)-thiourea\(^{42}\) have also been reported in literature.
Normal coordinate analysis of ethylene thiourea has been reported by Agarwala et al.\textsuperscript{43} Thioamide Bands I, II, III and IV are mixed bands having contribution from 60\% $\delta$NH + 20\% vC-N, 30\% vC-N + 36\% vC=S + 24\% $\delta$N-H, 34\% vCH$_2$N + 34\% vC-C + 26\% vC=S and 46\% vC-N + 30\% vC-S + 11\% sym. ring deformation respectively. Ethylene thiourea has been used as a ligand by a large number of workers.

Furlani\textsuperscript{44} et.al. studied Co (II) complexes of ethylene thiourea and suggested higher position of ethylene thiourea in spectrochemical series, than that of R$_2$S. They found B' value to be 66\% of free ion value. However, non of these workers could concentrate on the study of the nature of shift in all four thioamide bands as a result of metal-sulphur bonding, metal-nitrogen bonding and simultaneous metal-nitrogen and metal-sulphur bonding.\textsuperscript{45-50} Singh et al.\textsuperscript{51} have reported complexes of Pt (O), Rh (I) with ethylene thiourea. Starting from Pt (P$_3$)$_4$, three complexes of Pt (O) having formula [Pt (P$_3$) (ETU) (H$_2$O)$_4$], [Pt (PO$_3$) (ETU)$_3$] and [Pt (PO$_3$) (ETU)$_5$] have been prepared and investigated by these workers. Rh (I) complex is square planar. As (III), Sb (III) and Bi (III) form penta coordinated triangular bipyramidal structure with this ligand.\textsuperscript{52} 

Thiosemicarbazide is also an important chelating agent having thioamide group and it behaves both as monodentate and bidentate ligand. The inner complexes of Ni (II), Pd (II) and Pt (II) were prepared by Jensen et al.\textsuperscript{53-54} and they have been found in the cis and trans forms. In the trans square planar [Ni (tscaz)$_2$] complexes, there is complete
localization of the double bond between carbon and nitrogen indicating thiol form of structure and coordination occurs through enolic sulphur and hydrazinic nitrogen. The green compound [Ni (Htscaz) a] SO₄·3H₂O is found to have a square planar trans configuration with coordination occurring between thio-keto sulphur and terminal nitrogen atom. The other isomer of [Ni (tscaz)₂] is diamagnetic, but structure determination is not possible. The series of Cu (II) complexes, Cu (thiosemicarbazide)₂X₂ (X=Cl, Br, NO₃, ClO₄, ½SO₄) have also been prepared and investigated. 1-Phenyl thiosemicarbazide forms tetrahedral complexes with Pt (IV). The complexes are mostly of 'b' class ions with a few derivatives of thiosemicarbazide e.g. schiff bases derivatives. Octahedral metal complexes of salicylaldehyde thiosemicarbazide have also been reported and a series of new ligand have been prepared by reacting aliphatic and aromatic aldehyde with ethylene dithiosemicarbazide. These compounds form 1:1 complexes with Cu (II) and bonding occurs through thiocarbonyl sulphur of the ligands.

Thiosemicarbazide complexes of Zn (II), Co (III), Cu(II), Pd (II) and Pt (II) involve structure similar to that of [Ni (Htscaz)₂ SO₄] 3H₂O. The crystallographic measurements of Ag (Htscaz) Cl have shown that the ligand is monodentate, coordinating only through the sulphur atom.

Thioacetamide and the N-substituted thioacetamide are iso-electronic with thioured ligand which contain thioamide moiety. Thioacetamide forms complexes [ML₄]⁺ (M=Cu, Ag), [ML₄Cl₂]⁺ (M=Ni & Cd), [Au (L)₂] Br, [ML₂ Cl₂] (M=Fe, Co, Zn & Cd) and [ML₂
Various complexes of Co (II) with, N, N'-dimethyl thioacetamide (L'), [Co (L')$_2$ X$_2$] (X = Cl, Br, I, NO$_3$) and [Co (L')$_4$] (ClO$_4$)$_2$ have been prepared and investigated by Mueller et al. Goodgame et al. have prepared compounds [ML$_2$X$_2$] (M=Fe, Co, Zn, Cd; X = Cl or Br; M=Co, Zn or Cd; X=I; and M=Co or Ni; X = NCS) and [ML$_4$ X$_2$] (M=Ni, X = Cl, Br, NO$_3$, ClO$_4$ or ½ SO$_4$; M=Pd, Pt; X=Cl, and M=Cd; X=NO$_3$). These workers have suggested that these complexes have the tendency to decompose forming metal sulphides but the decomposition can be slowed down at 0°C. Coordination in these complexes occur though sulphur atom [M (L$_2$) X$_2$], (M=Co$^{2+}$, X = Cl, Br, I, NCS; M=Fe, X=Cl, Br; M=Zn or Cd) form tetrahedral complexes. In these complexes thioacetamide occupies the same position in spectrochemical and nephelauxetic series as thiourea. [ML$_4$ X$_2$] (M=Ni, X=Br, Cl O$_4$, NO$_3$, ½ SO$_4$; M=Pd, Pt; X = Cl) form planar complexes. [Ni (L$_4$) Cl$_2$] and [NiL$_2$ (NCS)$_2$] from octahedral complexes. The value of 10Dq and β (=0.65) places N, N'-dimethyl thioacetamide in spectrochemical and nephelauxetic series in between ethylenethiourea and thione ligands.

Ackerman et al. have reported five coordinate Cu (II) complex with new thioacetamide ligands. Amma and coworkers have determined the crystal and molecular structure of tetrakis (thioacetamide) Ni (II) bromide. Spectral and magnetic properties of same thioacetamide complexes of Ni (II) and Co (II) have also been reported. While the Co (II) forms the tetrahedral complexes, the Ni (II) forms both octahedral
and square planar complexes. R.R. Iyengar et al.\textsuperscript{76} have also reported two new thioacetamide complexes of Ni (II) and Cu (I) chlorides, viz., [NiCl\textsubscript{2}ITAM] and [CuCl.ITAM] (where TAM = thioacetamide). Infrared and electronic spectral evidences suggests that the Ni (II) complex has chloride bridge and ligand is coordinated to the nickel atom through sulphur at axial positions giving rise to octahedral polymeric structure. The bridging chlorides may account for the superexchange phenomenon giving rise to low magnetic moment of the complex. The insolubility of the complex in the most of the organic solvents is consistent with the polymeric structure.

Thiobenzamide behaves similar to the thioacetamide and forms complexes with class 'b' metal ions.\textsuperscript{77}

The ligand thiocarbohydrazide forms a series of 1:2 complexes\textsuperscript{78} with Zn (II), Cu (II) and Pt (II) with the exception of Co (II), Fe (II) and Pd (II) which form 1:3 complexes. In these complexes bonding occurs through thioketo sulphur atoms. They all form distorted octahedral complexes as shown by the reflectance spectra, the magnetic moment data and the mossbauer spectra.

Diphenylthiocarbazone (H\textsubscript{2}dz) is a nitrogen and sulphur containing ligand having thioamide group and forms highly coloured complexes with the elements which tend to form M-S bonds in preference to M-O bonds.\textsuperscript{79-80} Considerable amount of work has been done on the structure of diphenyl thiocarbazone complexes. Several workers\textsuperscript{81-84} have
concluded that nickel, palladium and platinum complexes of this ligand are unusual and are characterised by multiple instead of single bands in the visible spectrum, a very high formation constant and a strong IR absorption band at 1220 cm$^{-1}$. From these results it was suggested by Math et al. that the dithizone (diphenylthiocarbazone) moiety was bonded through two nitrogen atoms in the nickel complex.

Ahmed and his coworkers have studied a series of ligands of the general structure:

$$\text{H} \quad \text{S} \quad \text{H} \quad \text{H} \quad \text{O} \quad \text{H}$$

$$\text{R} - \text{N} - \text{C} - \text{N} - \text{N} - \text{C} - \text{N} - \text{R}$$

The Ni (II), Cu (II), Zn (II), Cd (II) and Pd (II) complexes of the following four derivatives of hydrazine have been prepared and investigated.
They all form square planar complexes. Earlier, N-thio-carbomoyl-
N'-thiocarbamoyl and N-phenylguanyl-N'-thiocarbamoyl hydrazine\textsuperscript{89-91} have also been used as complexing ligands. Co (II), Ni (II), Cu (II), Zn (II), Cd (II) and Pd (II) complexes of N-phenylthiocarbamoyl-N'-
guanylhydrazine have been reported by Ahmed et al.\textsuperscript{92} The ligand is monobasic in all these complexes. Both nickel and palladium complexes are diamagnetic. IR and UV spectra of the ligand and the complexes support the view that Cu, Ni and Pd are linked to the sulphur of enolized thiocarbamoyl group through valency link whereas in zinc and cadmium complexes the enolization of sulphur is not observed. It appears that the guanyl nitrogen is attached to zinc and cadmium either through coordination or through valency link. Planar complexes of Zn (II), Cd (II), Cu (II), Ni (II) and Pd (II) have also been prepared and investigated by the same authors.\textsuperscript{93}

Thioamidopyridine is a simple ligand which also contains thioamide group. It forms high spin complexes of the formula (ML\textsubscript{3})
(CLO₄)₂ where M = Co (II), Fe (II) and Ni (II). The complexes of Co (III), Cu (I), Zn (II), Hg (II) are also reported in literature. The complexes of Rh (III), Au (I), Au (III) and Cu (II) have also been studied. Copper forms complexes with this ligand of general formula [CuL₂X].4H₂O (X = CuCl₂, CuBr₂, CuI₂, Cu (SCN)₂, I and PF₆), and [CuL₂Y] Z (Y = ClO₄, OH and HNO₃; Z = ClO₄.H₂O, NO₃.H₂O and PF₆.H₂O).

Dithiooxamide (NH₂CSCSNH₂) is a simple ligand which also contains thioamide moiety and complexes of Ni (II), Cu (II), Cd (II) and Pd (II) have been reported in literature by several workers. Complexes of Cu (II), Zn (II), Cd (II) and Hg (II) chlorides with 1,5-disubstituted 2,4-dithiobiurets have also been reported in literature. Complexes of 4-amino-3, 5-dimercapto-1,2,4-triazole (H₂AMT) have been reported by Mishra et al. The analytical results of complexes show that the ligand forms complexes with tautomeric form B & C with Ru (II), Rh (III), Pd (II), and Pt (II) ions.
Pd (II) and Pt (II) are diamagnetic having square planar structure and octahedral structure of Rh (III) and Ru (II) have been suggested on the basis of various physico-chemical measurements. Thioamide bands (I to IV) of the ligand are affected appreciably in all complexes. Complexes of Co (II), Ni (II), Cu (II), Pd (II), Pt (II), Zn (II), Hg (II), Rh (III) and Ru (III) with this ligand contain usual stereo-chemistry and nitrogen as well as sulphur coordination. Far infrared spectra have been used to locate M-N, M-S and M-Cl modes of vibration in the complexes.\textsuperscript{106-108}

Complexes of some bivalent metal ions with furan-2-thiohydrazide (fthH) of the general formula \([M (fth)_2]_{n}H_2O\) (M=Ni (II), Cu (II), Zn (II), Cd (II), Pb (II) or Hg (II) and \(n = 0\) or 1) have been reported very recently by Mishra et al.\textsuperscript{109} They have observed that in neutral or alkaline solution (pH>6), the ligand forms neutral bis-chelates with bivalent ions and in acedic medium (pH~3) the ligand coordinates in thione form and forms bischelated complex salts \([Ni (fthH)_2] X_2\) (\(X = \text{Cl}^-\) or \(\frac{1}{2} \text{SO}_4^{2-}\)); \([\text{Cd} (fthH_2\text{Br}_2]\) as well as dihalo complexes \([M (fthH)_2 \text{Cl}_2]\) (M = Cd\(^{2+}\) or Hg\(^{2+}\)). In neutral bischelates, the thioamide band IV is shifted to lower frequencies and thioamide band I to II are shifted to higher frequencies by 20-40 cm\(^{-1}\) and observed with reduced intensity in almost all complexes.

Quinazoline (1H, 3H)-2, 4-dithione has also been used as chelating agent for several metal ions.\textsuperscript{110-112} The structure of its metal chelates and position of \(\nu\text{M-N}\) and \(\nu\text{M-S}\) modes have been investigated in these cases.
Cobalt (II) forms tetrahedral complexes, Ni (II) forms square planar complexes, Cu (II) forms polymeric complexes, Zn (II), Cd (II) and Hg (II) form 1:2 tetrahedral complexes. Pt (II) and Pd (II) form square planar bis-chelates with these ligands. In all these complexes, coordination occurs through one of the four nitrogen atoms and thione sulphur of the ligands. Magnetic moment measurements, electronic spectroscopy and in some cases H'n.m.r. spectra together with other physical measurements have been used to arrive at their molecular structure. Far infrared spectra of the ligands and the complexes have been recorded to investigate the metal-sulphur and metal-nitrogen stretching frequencies. M-N modes have been found in the range of 340-510 cm\(^{-1}\) depending on the nature of metal ions and the ligand used. M-S modes are found in the range of 260-410 cm\(^{-1}\).

Some Rh (I) and Pt (O) complexes of l-phenyl-tetrazoline-5-thione have also been prepared and investigated by Singh et al.\textsuperscript{113} and they have found that when a benzene solution of Pt (P\(\phi_3\))\(_4\) is treated with benzene solution of l-substituted tetrazoline-5-thione, replacement reaction occurs and two of the P\(\phi_3\) groups are replaced by two molecules of l-phenyl tetrazoline-5-thione bonded through sulphur and tetrahedral complexes such as [Pt (P\(\phi_3\))\(_2\) (lPT5TH\(_2\))] are formed. Pt (O)-tetrahedral complexes of other monodentate ligands have also been reported by several workers.\textsuperscript{114-117}

Dithioxamide (NH\(_2\)CSCSNH\(_2\)) is a simple ligand, which also contains thioamide moiety and complexes of Ni (II), Cu (II) Cd (II) and
Pd (II) have been reported in literature by several workers complexes of this ligand with group IV halides have been reported by Rivest et al.\textsuperscript{118}

Sreenivasulu et al.\textsuperscript{119} have studies the complexe of zinc-, candimium-, and mereury (II) with some diamine (N\textsubscript{2}O\textsubscript{2}) schiff-Base ligands containing non-coordinations azomethine nitrogen atom. The complexes of Zn, Cd and Hg with salophen, nalophen, solmphen and nalmphen are not soluble in methanol or ethanol but readily soluble in chloroform, toluene, dimethyl formamide, dichlоро methane and dimethyl-sulphoxide and slightly in ethanol. The low molar conductivities of solution ($\sim 10^{-3}$M) of the complexes prepared using dimethyl formamide in the range 5-20 $\Omega^{-1}$ cm\textsuperscript{2} mol\textsuperscript{-1} indicate their non-electrolytic nature. Free shiff base ligands show weak intramolecular-hydrogen bonding (O------H-N) which give rise to a broad adsorption bond at 3450 (solophen), 3435 (salmphen), 3474 (nolophen) and 3454 cm\textsuperscript{-1} (nalmphen in their respective infrared spectra).

Adsorption of Pb\textsuperscript{+2}, Cd\textsuperscript{2+} and Cu\textsuperscript{2+} on different agricultural biproducts has been measured at different temperatures Adsorption of metal ions follows the order : Polymerized orange skin < banana husk for Cd (II) and Pd (II) and oronge skin > banana husk for Cu (II). It could also be seen that Cu (II) is a good adsorbing agent as compared to Cd (II) and Pb (II). Thermodynamic parameters have also been evaluated.\textsuperscript{120}

Upadhya and Coworkers\textsuperscript{121} have studied the formation of binary, binucleating and mixed metal complexes of catechol violet. pH metric
studies on interaction of Ni", Cu", Zn", Pd", Ag' and Cd" with 3, 4-, 4-
trihydroxyl 4 (some-2"-sulphonic acid (catechoviolet, CAV) have been
carried out in aqueous solution at 25⁰ and an ionic strength of 0.1
MKNO₃. Studies reveal the formation of the species MH₂A, MHA, MA
(M=Ni", Cu", Zn", Pd", Ag' and Cd"); Pd-A (OH)³⁻; M (H₂A)₂, (HA),
M (HA)₂ (M = Ni", Cu", Zn", Cd"); m (HA) (A) (M = Zn", Cd"), M₂ A
(M = Ni", Cu", Zn", Pd", Cd"); M₂ A (OH) M= Cu", Zn", Pd", Cd"); M₂A
(OH)₂ (m=Zn", Cd"); Cu NiA, CuZnA; Pd NiA, PdC₄A, PdZnA; (C₄ NiA
(OH), Cu Zn A (OH), Pd Zn A (OH), Cu NiA (OH)₂, Cu ZnA (OH)₂ in
the corresponding metal-ligand mixtures for which equilibrium constants
have been evaluated.

Kriza, et al¹²² have worked on, Template Synthesis of chromium
(III), cobalt (II), nickel (II), copper (II) and Cadmium (II) complexes with
a tetradeutate schiff base, glyoxilidene-bis-2-aminoethylpyridine. Some
new complexes of Cr³⁺, Co²⁺, Ni²⁺, Cu²⁺ and Cd²⁺ have been synthesized
with a tetradeutate schiff base, glyoxilidene-bis-2 aminoethylpyridine.
An octahedral geometry have been proposed for the Cr³⁺ and Ni²⁺
complexes and tetrahedral geometry for the rest of the compounds. In the
group IV metal halide complexes, bonding occurs through nitrogen and
not through thio carbonyl sulphur. Complex Compound of dithiobiuret
with Cu (II) Ni (II) have been prepared and investigated by Melson.¹²³ An
I.R. assignment has been proposed for the silver dithiobiuret
complexes.¹²⁴ The effect of various solvents on the spectra of 1,5-
disubstituted 2,4-dithiobiurets have reported by Agrawal and
Coworkers. Complexes of Cu (II), Zn (II), Cd (II) and Hg (II) chlorides with 1,5-disubstituted 2, 4-dithiolebiurets have also been reported in literature. Through sulphur on the basis of magnetic, conductometer, electronic adsorption and infrared spectral data.

Dithiocarbazic acid and its derivatives form stable complexes with various metal ions. In all these complexes co-ordination of the ligand occurs through nitrogen.

Complexes of Zn (II), Cu (II), Ni (II) and Co (II) with 3-eryloxymethyl 4-aryl-5-mercapto-1, 2, 4-triazale have been prepared by Bahel et al. These complexes have been characterized on the basis of elemental analysis, infrared spectra, thermogravimetry, managetic susceptibility and power X-ray differaction patterns, Fungitoxicity of the complexes and free ligand have been evaluated against H. Oryzae-X-ray studies showed that all the complexes possess cubic structure.

Complexes of 4-amino-3, 5-di-mercapto1,2,4-triazole (H AMT) have been reported recently by Mishra et al. However bonding of this ligands occurs through imino nitrogen in TI (I) and Au (III)
complexes$^{133}$ of Co (II), Ni (II), Cu (II), Pt (II) Zn (II), Hg (II) Rh (III) and Ru (III) with this ligand contain usual stereo chemistry and nitrogen as well as sulphur coordination. For infrared spectra have been used to locate M-N, M-S and M-Cl modes of vibration in the complexes.$^{134-135}$

Complexes of some bivalent metal ions with furan 2-thiohydrazide (fth H) of the general formula [M (fthH)$_2$].nH$_2$C (M=Ni) (II), Cu (II), Zn (II), Cd (II), Pd (II), or Hg (II) and n= O or l) have been reported very by Mishra et al.$^{136}$ They have observed that in neutral or alkaline salution (pH>6), The ligand from neutral chelets with bivalent ions and in acidic medium (pH~3) the ligand co-ordinates in thione form and forms metal ions and metal-ligand $\pi$-bonding-complex formation equilibria have been elucidated with the aid of specification curves.$^{137}$

Prasad and Mathur$^{138}$ have worked on the template synthesis of Cr (II), Fe (II), Co (II), Ni (II), Cu (II) and Zn (II) complexes of 14 and 16-membered tetraazamacrocycles. Complexes of the types [ML (NO$_3$)$_2$] NO$_3$ [(M=Cr (II), F (II), (ML (NO$_3$)$_2$) M = Co$^{II}$, Ni (II), [Cu IV] Cl$_2$ and [ZnI$_2$ Cl$_2$] (where L= tetraazamacrocycle having 14 or 16 membered ring) have been synthesized by the condensation of 2, 3-hexanedion with 1, 3-diaminopropane or 1, 4-diaminobutane in the presence of metal ions as templates.

Joshua, et al$^{139}$ have worked on synthetic, spectral and antibacterial studies of some noval first transition metal complexes of 4, 6-diamino-1, 3, 5-triazine-2-thiol. A series of complexes of Cu$^{II}$, Ni$^{II}$, Co$^{II}$, Fe$^{II}$, Vo$^{II}$
and Zn\textsuperscript{II} with the s-triazine, 4-6-diamino-1, 3, 5-triazine-2-thiol known as thioammeline (HTA) and its sodium salt (NaTA) have been prepared and characterized through elemental analysis, magnetic moment measurements, electronic, IR, and ESR spectroscopic techniques. The complexes were found to be neutral and both HTA and NaTA coordinate to the metal ion as anion TA in the thiol form to give identical complexes for each metal ion. The electrochemical behaviour of the complexes was explored using cyclic voltammetry and it is seen that the metal ligand linkage has high covalent nature. The Cu\textsuperscript{II} and Ni\textsuperscript{II} complexes are square-planer, Co\textsuperscript{II}, Mn and Zn\textsuperscript{II} complexes are tetrahedral, V\textsuperscript{II} complex is square pyramidal and Fe\textsuperscript{II} complex is octahedral. The copper complex has a tetragonal unit cell with $a=b=12.6 \text{ Å}$ and $C=10.1\text{ Å}$. HTA, NaTA and the complexes were screened for their antibacterial activity against S. aureus.

Viswanathan and Krishnan\textsuperscript{140} have studied the synthesis and characterization of manganese (II), cobalt (II), nickel (II), copper (II), zinc (II) and cadmium (II) complexes of N, N'-Triethylene diamine-bis-(3-carboxypropenamide). A series of complexes of transition metal ions with a new hex dentate ligand, N, N'-triethylene diamine-bis-(3-carboxypropenamide) (TEBCP) have been synthesized and characterized by chemical analysis, conductance, magnetic, x-ray Powder diffraction and infrared, electronic and ESR spectral studies. The complexes except that of copper (II) have been assigned the formula $[M (TEBCP)]$ where $M=\text{Mn, Co, Ni, Zn or Cd}$. These have octahedral geometry. The
proposed formula of the complex of copper is \([\text{Cu}_2 (\text{TEBCP}) (\text{OH})_2]\) and has square-planer structure.

Rani et al\textsuperscript{141} have studies the synthesis of the complexes of \(\text{S}_3\text{N}_3\text{Cl}_3\) with cadmium (II) and mercury (II). The complexes of \(\text{S}_3\text{N}_3\text{Cl}_3\) with \(\text{Cd}\) (II) and \(\text{Hg}\) (II), were synthesized and analyzed and assigned as \((\text{S}_3\text{N}_3\text{Cl}_3)_4 \text{Cd (CH}_3\text{COO)}_2\) and \(\text{S}_3\text{N}_3\text{Cl}_3\). Hg Cl\(_2\), possessing paramagnetic nature due to \(\text{sp}^3\text{d}\) and \(\text{sp}^3\) hybridization in subsequent metals and forming quadridentated and bidentated complexes coordinated through chlorine atom of \(\text{S}_3\text{N}_3\text{Cl}_3\) ring to metal ions.

Yadav et al\textsuperscript{142} studied the synthesis and characterization of Cd (II) complex the mixture of \(\text{S}_4\text{N}_3\text{Cl}\), cadmium (II) complex of \(\text{S}_4\text{N}_3\text{Cl}\) was prepared by refluxing the mixture of \(\text{S}_4\text{N}_3\text{Cl}\) and cadmium acetate in \(\text{DMF}\). The chemical data assigned the complex as \((\text{S}_4\text{N}_3\text{Cl})_2 \text{Cd (OOCCH}_3)_2\). The spectrosic data infer that the complex is quadridentate coordinated complex having triclinic geometrical structure.

A reversed Phase paper chromatographic method is developed for separation of zinc, cadmium and mercury and studied by H.R. Aher et al.\textsuperscript{143} The separation have been performed on a whatman paper no. 1 Using liquid ion exchanger \(\text{n-octylaniline}\) and \(\text{N-n-octylaniline}\) as a stationary phase while various weak acids as the mobile Phase. Various experiments were carried out to study the effect of pH (4-9). Concentration of mobile phase (0.01-0.1 M) and concentration of stationary phase (0.1-1.5\% using chloroform as a diluent) on the R values
of individual cations. optimum concentration of n-octylaniline, N-n-octylaniline and mobile phases were determined. The proposed method is applied for separation and detection of zinc, cadmium and mercury in pharmaceutical samples.

Krishnan and Coworkers\textsuperscript{144} have studied the synthesis and characterization of manganese (II), cobalt (II), nickel (II), copper (II), zinc (II) and cadmium (II) complexes of a polydentate ligand and come to the conclusion that, A few complexes of Mn (II), Co (II), Ni (II), Cu (II), Zn (II) and Cd (II) with a polydentate ligand, N, N' - diethyleneamine - bis (3-cabxy propanamide) (DBCPH\textsubscript{2}) have been synthesized and characterized by elemental analysis, conductance, thermal, Magnetic, IR, electronic spectra and X-ray diffraction methods.

Sundaram et al\textsuperscript{145} have performed the synthesis and characterization of heterobinuclear cadmium-tungsten complexes of dithiocabamates and stated that, The heterobinuclear complexes [Cd WO\textsubscript{2}(1)\textsubscript{3} (H\textsubscript{2}O\textsubscript{2})] (L=diethyl-dithiocarbamatem 4-morpholinyldithiocarbamate, 1-Piperidinyl-dithiocarbamate) were prepared by the interaction of cadmium tungstate with the respective ligand in aqueous DMF. The magnetic moment (1.7 BM) and EPR studies suggested the presence of tungsten in the pentavalent state. The IR spectral bands suggested the presence of V(W=O) (900 cm\textsuperscript{-1}) and V(Cd-O-W) (790 cm\textsuperscript{-1}) and bidentate dithiocarbamate ligands (1500 and 960 cm\textsuperscript{-1}) in the molecule. The IR and thermal decomposition studies confirmed the presence of coordinated water molecules. The 'H NMR chemical shifts
indicated non-identical environment of protons coming closer due to rigidity in rotation around C-N bond of dithiocarbamate ligand and coordination to the heterometal atoms. The mass spectral data showed 16 lines at m/z 808-824 and subsequent peaks correspond to the fragmentation of water and dithiocarbamate ligands in steps from the complex. The proposed structure consists of a tetrahedral cadmium (II) and octahedral tungsten (V) bridged by an oxo group.

Taher and coworkers\textsuperscript{146} have studied the, preconcentration of cadmium on to amberlite XAD-4 resin loaded with 5-Br-PADAP and determination by anodic stripping differential pulse polarography and says from his work that, A procedure for seperation and preconcentration of trace amount of cadmium has been proposed. For the retention of cadmium a column of amberlite XAD-4 loaded with 2-(5-bromo 2-pyridylazo_5- diethylaminophenol (5-Br-PADAP) was used. cadmium is quantitatively retained on the column at pH 9.5. The cadmium was removed from the column with 10.0 ml of 1M nitric acid and determined by anodic stripping differential pulse polarography. A preconcentration factor of 100 was obtained. The detection limit value for the preconcentration of 1000 mL of aqueous solution of cadmium was 0.035 μg/mL. The precision of eight replicate determinations at the 1μg/mL cadmium levels of 0.36% relative standard deviation (RSD), calculated with the peak height obtained. The calibration group using the preconcentration system for cadmium was liner with a correlation coefficient of 0.9995 at levels near the detection limits upto atleast
150µg/mL. The method was successfully applied to the determination of cadmium in natural samples.

Bartaria, et al\textsuperscript{147} have studied the, formation and stability of heterobinuclear complexes containing Hg\textsuperscript{II} and divalent metal ions with EDTA and CDTA, The Stability constant for the heterobinuclear complexes of the type HgLM (L = EDTA or DCTA (trans-1, 2-diaminoclohexane tetraacetic acid) and M = Be, Mg, Ca, Pb, Cd, Mn, Co, Ni, Cu) have been determined by computer analysis of the pH titration data. The results are discussed to obtain the solution structures of the above mixed-metal complexes.

Gautam, et al\textsuperscript{148} and G.K. Chaturvedi have studies the synthesis, characterisation and biological studies of Cu\textsuperscript{II} and Zn\textsuperscript{II} metal complexes with drug lorazepam [7 - chloro-5 (O-Chlorophenyl)- 1,3 - dihydro- 3-hydroxy - 2H - 1, 4 - benzodiazepine - 2- one]. 1:1 complexes of Cu\textsuperscript{II} and Zn\textsuperscript{II} with drug lorazepam having general formula [ML (NO\textsubscript{3})\textsubscript{2}. 2H\textsubscript{2}O] have been synthesized and characterized on the basis of elemental analysis, IR and thermal studies. Analytical and IR suggest that both complexes are monomeric due to coordination by N (1) and N (4) atoms. The ligand and complexes have been screened for their antimicrobial activities. Antimicrobial studies suggests that the Cu\textsuperscript{II} complex is more toxic than Zn\textsuperscript{II} complex.

Gurubasavaraj et al\textsuperscript{149} have studies the synthesis and characterisation of Co (II), Ni (II), Cu (II), Zn (II) and Hg (II) complexes
of bidentate ligand of schiff base and he concluded that, A few metallic complexes of Co (II), Ni (II), Cu (II), Zn (II) and Hg (II) metals with bidentate schiff base have been prepared and characterized. The complexes were coloured, amorphous in nature and are soluble in DMSO and DMF. The conductance measurement shows the complexes are non electrolytes in DMF. Elemental analysis confirmed to the 1:2 stoichiometry. magnetic, electronic, IR and NMR spectral information suggest the squareplaner structure for Co (II), Ni (II) and Cu (II) complexes while tetrahedral geometry to Zn (II) and Hg (II) complexes.

Meshram et al\textsuperscript{150}, have studied the adsorption on toxic metal Pb (II), Cd (II), Hg (II) and Cu (II) Ions on agricultural by products and came to the conclusion that, agricultural byproducts like orange, banana, pomegranate, apple, chickoo, sweetlime were used in their natural state on which the study of adsorption of toxic metal ions Pb (II), Cd (II), Hg (II) and Cu (II) at 27\textdegree C has been made. The values of freundlich constant (n and k) are estimated from the study. It can be seen that adsorption increases with the increase in concentration of metal ions.

Rekha and Nagasundara et al\textsuperscript{151} have studied the complexes of N-(4-methoxy-benzilidene)-2-(4-aminophenyl) benzimidazole with Zn (II), Cd (II) and Hg (II) halides and he concluded that the synthesis and characterisation by elemental analysis, conductivity measurements, IR and proton NMR spectroscopy of complexes of the schiff base derived from 2-(4-aminophenyl) benzimidazole and 4-methoxy benzaldehyde with Zn (II), Cd (II) and Hg (II) halides have been reported. Mercury
halide yield complexes with the general formula \([\text{Hg (POM4APB)}_2\text{X}_2]\); \(X=\text{Cl, Br, Zinc and cadmium halides yields binuclear complexes with the general formula } [(4\text{APB})\text{X}_2]; \ M = \text{Zn, X - Cl; M - Cd, X } = \text{Cl, Br. The complexes are all non-electrolytes and the ligand acts as a monodentate.}

Recently Banerjee and Coworkers\textsuperscript{152} studied cation exchange and adsorption behavior of a hatrolite-type natural zeolite collected as a geological specimen as a powdered sample. Cd III hatrolite was prepared with saturated aqueous cadmium (II) sulfate solution with continuous shaking at 60\(^\circ\) for maximum interaction. A portion of this exchanged derivative was then heated over a meker burner for several days in a nickel crucible. Both the original and the preheated Cd\textsuperscript{II}-zeolite samples were also interacted with gaseous H\textsubscript{2}S and liquor ammonia to study their adsorption capacity and preheating affects. All the derivatives and the original zeolite before and after heating were analyzed by XRD, FTIR and thermal methods.

Recently Sain et al\textsuperscript{153} have reported thereaction of equimolar proportion of septadentate tripodal schiff base ligand, tris [2-salicylidene (amino) ethyl] amine, H\textsubscript{3} [(I) and Ru Cl\textsubscript{3}H\textsubscript{2}O in refluxing methanol in presence of alkali has afforded a dark coloured compound of composition [Ru\textsuperscript{III} L].CH\textsubscript{2} Cl\textsubscript{2}H\textsubscript{2}O.X-ray analysis of the complex shows that the septadentate ligand is coordinated octahedrally to ruthenium and tripodal nitrogen is not in bonding distance (Ru........N (I) = 3.545 (12) \text{Å}) to ruthenium. The complex is redox-active and displays one one-electron
reduction and one one-electron oxidation with \( E_{1/2} \) values = 0.58 and 0.61 Vs SCE, respectively.

Recently Choudhary et al.\textsuperscript{154} and they have been found the complexes of Rh\textsuperscript{III} Pd\textsuperscript{II} and Pt\textsuperscript{II} with 2-(2\textsuperscript{1}-pyridyl) benzthiazole (PBT) of composition (PBTH)\(_2\) [RhCl\(_5\)H\(_2\)O], Rh (PBT)\(_2\) X\(_2\)/X, [Rh (PBT) X\(_2\)] Cl\(_4\) (X=Cl, Br, I, NCS or NO\(_2\)) and [M (PBT) X\(_2\)] M=Pd II or Pt (II) and X = Cl, Br, I, NCS or NO\(_2\) have been prepared.

Recently Sharma and Coworkers\textsuperscript{155} by The study of the kinetics of oxidation of phosphorous acid by peroxomonomosulfate in acetate buffers in the presence of ruthenium (III) chloride has been studied. The rate of disappearance of the peracid in the reaction has been observed to be zero order with respect to peroxomonomosulfate. The proposed mechanism conforms to the rate law,

\[
\frac{-d[\text{PMS}]}{dt} = k^1 = kKd[H_3PO_4][\text{Ru}^{III}][H^+]^{-1}
\]

Where \( k^1 \) is zero order rate constant. Thermo-dynamic parameters such as energy and entropy of activation have been calculated by conventional methods.

Recently Vyas et. al.\textsuperscript{156} have studies the complexes of ruthenium with bilogically important benzimidazole derivatives, viz.2-(2\textsuperscript{1}-hydroxyphenyl) benzimidazole (HOPBI), 2-(2\textsuperscript{1}-mercapto phenyl)
benzimidazole (HSPBI), 2-(2'-hydroxynapthyl) benzimidazole (HONBI) have been synthesized and characterized.

Roy and Coworkers\textsuperscript{157} have performed the nanoparticle. Recently Cd S, Zn S and mined crystals of ZnX\textsubscript{1-x} S can be generated in situ in AOT-heptane-water and CTAB-chloroform water micromulsions using an ultrasonic processor. The nanoparticles exhibit the "quantum size effect". The average diameter of nanoparticles, as manifested in the photoabsorption threshold of colloidal semiconductors, increases as the water content of reverse micelles and the concentration of quantum state particles increases. The composition of mixed sulfides and water content (poolsize) of inverted micelles can be varied systematically and the band gap energies of the semiconductor particles can be determined from photo absorption threshold (edges) A method is proposed for determine the bulk optical dielectric constant of solid solutions of two semiconductor employing the Brus equations.

Recently Bansal et. al.\textsuperscript{158} They have observed that the oxidation reaction of hexacyanoferrate (II) by peroxodisulphate (S\textsubscript{2}O\textsubscript{8}\textsuperscript{2-}) is accelerated by irradiation with visible light in aqueous acid solutions containing tris (2, 2'-bipyridine ruthenium (II) ion [Ru (bipy)\textsubscript{3}\textsuperscript{2+}], the latter acts as a photocatalysts The mechanism of the reaction consists of a chain reaction initiated by the quenching reaction of the photo excited ruthenium (II) complex ion [Ru (bipy)\textsubscript{3}\textsuperscript{2+}], with S\textsubscript{2}O\textsubscript{8}\textsuperscript{2-}. The rate law is expressed by the equation-
\[
- \frac{1}{2} \frac{d[S_2O8^{2-}]}{dt} = \frac{K_q la [S_2O8^{2-}]}{K_o+kq [S_2O8^{2-}]}
\]

Where \( ka \) is the bimolecular quenching rate constant and has been determined kinetically. Other terms have their usual meaning.

Recently Sheela and Patil et. al.\textsuperscript{159} The analytical results of complexes show that the ligand bis (hydroxyisonitroso benzoyl acetone) thiocarbohydra zone (H1NBA)\textsubscript{2} tez, has been synthesized by the interaction of thiocarbohydrazone with isonitrosobenzoyl acetone in 1:2 molar proportion in menthanol. Its complexes with Ru\textsuperscript{III}, Rh\textsuperscript{III}, Pd\textsuperscript{II} and Pt\textsuperscript{II} have been prepared and characterized by elemental analyses, magnetic susceptibility, IR, H NMR, Spectral data, thermal analysis and electrical conductance measurements.

Subhi and Coworkers\textsuperscript{160} have studied the several new palladium II and platinum (II) complexes containing two types of ligands: tertiary monophosphines (L) and 5-phenyl-1, 3, 4-oxadiazole-2-thione ion (A) or 4, 5-diphenyl-1, 2, 4-triazole-3-thione ion (B) have been prepared the so obtained complexes trans- [PdA\textsubscript{2}L\textsubscript{2}], trans-[PdB\textsubscript{2}L\textsubscript{2}] and cis-[PtA\textsubscript{2}L\textsubscript{2}] were characterized by elemental analysis, IR, UV-Vis, PNMR spectroscopy, molar conductance and magnetic susceptibility measurements.

Reddy and Coworkers\textsuperscript{161} has been prepare the neutral and cationic mono-nuclear palladium (II) substituted tertiary phosphine complexes
containing acetylacetone, carbonmonoxide and chloride as co-ligands have been synthesized in quantitative yield and characterized on the basis of elemental analysis, conductance measurements, IR, NMR (\(^1\text{H}, ^{13}\text{C}, \text{and}^{31}\text{P})\), mass and electronic spectral data. The catalytic hydrogenation activity of some of these complexes has been studies and found that they are efficient catalysts for reduction of organic nitro, olefinic, acetylenic and aldehyde groups under mild reaction conditions.

Recently Neelakantan and Coworkers\(^{162}\) are prepared in Cu"/, Ni", Zn", Co", Mn" and VO" schiff base complexes derived from indole-3-carboxaldehyde (Ind) and amino acid viz. L-alanine (ala), L-phenylalalanine (pola) and L-histidisne (his) have been prepared and characterized by elemental analysis, molar conductance, magnetic susceptibility IR, electronic absorption and EPR (at room temprature and at 77K) spectroscopic techniques. The electrochemical properties of Cu" complexes exhibit a well defined quasireversible redox wave attributed to one electron transfer process. The Cu\(^{II}\) and Zn\(^{II}\) schiff base complexes were screened for their biocidal activities in vitro on common bacteria.

Recently Mukherjee and Das et. al.\(^{163}\) The complexes of 6-guanidine 2, 4-dimethyl-3, 5-diazine and 6-phenyl guanidino-2, 4-dimethyl-3, 5-diazine with Pd\(^{II}\), Pt\(^{II}\) and Rh\(^{II}\) have been reported. Complexes have been characterised on the basis of analytical, magnetic and spectral characterisation and power diffraction studies. Crystal field parameters, have also been calculated. The Pd\(^{II}\) and Pt\(^{II}\) complexes are square planer as expected and Rh\(^{III}\) complexes are pseudo-octahedral. IR
data indicate that the imino nitrogen of the guanidine residue and one of the pyrimidyl nitrogen atom acts as bonding sites in the formation of these complexes.

Recently Patra and Cowarker\textsuperscript{164} are proposed the ionization constants of three ONO donor azo ligands (H\textsubscript{2}L\textsuperscript{1-3}) containing different functional groups, viz. 2-hydroxy-2\textsuperscript{1}-carboxy-5-methyl azo benzene (H\textsubscript{2}L\textsuperscript{1}), 2, 2\textsuperscript{1}-dihydroxyazo benzene (H\textsubscript{2}L\textsuperscript{2}), and 2-hydroxy-2\textsuperscript{1}-hydroxy methyl-5-methylazo benzene (H\textsubscript{2}L\textsuperscript{3}) and their formation constant with M\textsuperscript{2+} ions (M=Co, Ni, Cu and Zn) have been determined in dioxane-water (50\% v/v) medium at 25\textdegree{}C at a fixed ionic strength (I=0.1mol dm\textsuperscript{-3}-NaNO\textsubscript{3}) by pH-potentiometric method. The nature of the species present in solution have been elucidated on the basis of their electronic spectra. Job's method of continuous variation study indicated the formation of 1:1 complex with Cu\textsuperscript{2+} on an 1:2 complex with Co\textsuperscript{2+} and Ni\textsuperscript{2+} ions with all these three ligands. Formation constants of these metal ions with all these three ligands have been found to follow the order: Co\textsuperscript{2+} < Ni\textsuperscript{2+} < Cu\textsuperscript{2+} > Zn\textsuperscript{2+}, with respect to any particular metation, the formation constant values follow the order: (L\textsubscript{1})\textsuperscript{2-} < (L\textsubscript{2})\textsuperscript{2-} < (L\textsubscript{3})\textsuperscript{2-} which is explained on the basis of overall basicity of these ligands.

Recently Sharma et.al.\textsuperscript{165} have reported some 0 valent organo palladium complexes with 2-mercapta-3phenyl quinazole-4-one. The oxidation state of palladium metal after coordination of ligand to palladium metal is assigned through sulphur.
Very recently, Choudhary and coworkers\textsuperscript{166} have reported the complex of Co (II), Ni (II), Pd (II), Cu (II) 2-phenyl-benzimidazole. Their reported planer geometry of Pd (II) complex.

Very recently, Sinha and Coworkers\textsuperscript{167} have reported Cd (II) azido and thiocyanato complexes of N-[2-pyridyl methylideno]-\(\alpha\) (or \(\beta\)) amino naphthalene. Examination of luminescence activity of the complexes suggests that the complexes are highly emissive and have reasonably good life.
References


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