CHAPTER - III

A BRIEF REVIEW ON METAL COMPLEXES
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The present chapter deals with various oxygen, nitrogen and sulphur donor multidentate ligands and their mono- and polymetallic complexes, reported by various workers from time to time.

The chlorophyll, a macrocyclic complex of magnesium (Fig -22) plays a vital role in the photosynthesis of plants. In the animal kingdom, blood is the indispensable constituent of life consisting of haemoglobin, an iron complex (Fig -23). The macrocyclic complex of cobalt (Fig -24), vitamin $\text{B}_{12}$ is also well known.

The schiff bases contain azomethine (-C = N -) linkage and they form stable complexes with a variety of transitional and non-transitional metal ions. The schiff bases are widely used as ligands which can be prepared by the condensation of carbonyl compounds, usually an aldehyde or ketone with primary amines.

Azodye and bisazodye ligands are normally synthesized by coupling diazonium salts of arylamines, substituted arylamines with N, O, S containing multibonded compounds and heterocyclic bases. Apart from its large applicational properties they provide novel coordination sites for complexation and chelation to form monomeric and polymeric complexes.

A brief outline on the metal complexes formed with the schiff bases and azodyes are described here. Bis (salicylaldimine) Cu(II) was prepared by the condensation of cupric acetate and salicylaldehyde in aqueous ammonia (Fig -25). In the year 1869 Schiff isolated,
Fig. 22

Fig. 23
schiff condensation of cupric acetate and salicylaldehyde in aqueous ammonia (Fig -25). In the same year he isolated schiff base complex (Fig -26) by refluxing cupric acetate salicylaldehyde and aniline. After this discovery a number of schiff bases were prepared by taking different carbonyl compounds with different primary amines and these were complexed with various metal ions\(^{3-9}\) (Fig -27). Holmes and his coworkers made an exhaustive study of the schiff base metal complexes.\(^{8}\)

A few interesting ligands and their metal complexes are discussed here.

**METAL COMPLEXES WITH BIDENTATE LIGANDS:**

The ligand field absorption spectra are in accordance with the trans-structure (Fig -23). The bidentate schiff bases, \(N\) - alkyl and \(N\) - aryl salicylaldiminates form dimeric copper(II) complexes.\(^{9}\) In copper complexes with bidentate salicylaldiminates, the ligand field absorption bands in the region 18,000 - 8,00 Cm\(^{-1}\) move to lower energies as the environment around the copper atom tends to form planar to tetrahedral.\(^{10}\) Because of trans structure, two copper atoms in the dimer adopt a configuration near to planar with a small degree of steric distortion towards tetrahedral as the \(R\) - group on the salicylaldimine nitrogen becomes more bulky which has been confirmed by Robinson etal. The geometry of \(\text{Cu} \quad \text{Cu}\) ring is less sensitive to charges in the phemylring. The 1 : 1 salicylaldiminates, \([\text{Cu} (R\text{-Sal}) \text{Cl}_2]\) are less antiferromagnetic than the aminoalcohol complexes. In both the complexes copper oxygen bridge is exactly planar, but the stereochemistry at copper derivatives form planarity more severely in the methyl complex than the ethyl complex.
Fig. 24

Fig. 25
The schiff base derived from 2-hydroxy - 5 - methyl acetophenone with arylamines form bidentate copper complex.\textsuperscript{12} The $g_{\text{eff.}}$ value found to be between 1.3 - 1.9 B.M. at room temperature. The electronic spectra are characterised by a single broad band with maxima at 15,000 Cm\textsuperscript{-1} and another band at 22,000 Cm\textsuperscript{-1} indicating square planar configuration of the Cu(II) ion. A series of square planar complexes of the type (Cu X). $\text{HL} = \text{Salicylidene amino - guanidine}, \ O - \text{hydroxy acetophenoneaminoguanidine}, \ X = \text{cl, Br, F, NO}_3$ have been synthesized\textsuperscript{13}.

The nickel (II) complexes of the type $[\text{Ni}(\text{R-sal})_2]$ (R = \text{C}_2\text{H}_5, \text{Cis and trans isomeric complexes are shown in (Fig - 29) for unsymmetrical tridentate chelates. The schiff bases of 2-hydroxy - 1 - napthaldehyde with N - methyl - 5 - alkyl dithio carbazate have formed square planar complexes with nickel(II)}\textsuperscript{14}. Mixed ketoimine schiff base complexes having the formula $[\text{MLL'}]$ (where M = Cu(II) and Ni(II), L = N - 1 -(2 hydroxy phenyl) ethylene diamine or N - 1 -(2-p-toly) ethylene diamine and L' = N-1-(2-hydroxy-m-toly) ethylene diamine or N-1-(6-hydroxy-m-toly) ethylene diamine, when subjected to amine exchange reaction with ethylene diamine and propylene diamine result in converting the bidentate ligand complexes to tetradentate complexes\textsuperscript{15} (Fig - 30)

The N - alkylsalicylaldimine complexes of nickel(II) show peculiar magnetic behaviour both in polar and non-polar solvents. $[\text{Ni (HO-sal)}_2]$ and $[\text{Ni(Me-sal)}_2]$ are both diamagnetic solids and become partially paramagnetic in chloroform ($g_{\text{eff.}} = 1.1 - 2.2$ B.M.) but completely paramagnetic in pyridine solution ($g_{\text{eff.}} = 3.1$ B.M.)\textsuperscript{16}. The conversion of diamagnetic to paramagnetic species has
been possible in solid phase. The diamagnetic green solid\(^{17}\) transfers to a light green at 180° with \(\mu_{\text{eff.}} = 3.45\) B.M. Heating of the green compound in biphenyl solution at 150-200°C forms an insoluble buff coloured product having the same composition as the green form and obeying Curie-Weiss law with \(\mu_{\text{eff.}} = 3.1\) B.M.

The Schiff base prepared through the reaction of salicylaldehyde with methyl substituted aminopyridine form square planar Cd(II) complex whereas the Zn(II) complex is found to be tetrahedral\(^ {18} \). The Sn(II) complex with the Schiff bases derived from salicylaldehyde and anisaldehyde with the substituted aniline reported by Srivastav and Co-workers\(^ {19} \). Electronic spectra and pKa values of Schiff bases derived from 2-amino-5-phenyl-1,3,4-thiadiazole and various aromatic aldehydes have been reported by Goel et al\(^ {20} \).

(Fig -31.).

Sahoo and Co-workers reported the rearrangement of Schiff bases on complex.\(^ {21} \) The trans form of 1, 2-diphenyl ethanedione - dihydrazine ligand undergoes a transformation to a cis-configuration in the metal complexes (Fig -32 ). The trans structure is believed to be stabilised by greater delocalisation of the \(\pi\)-electron, whereas in the cis form resulting in an increase in the charge density along C ....N bond vectors and increase in the \(\nu\) (C ....N) frequency.

The complexes of Ni(II) and Cu(II) with N, N-disalicylidene ethylene diamine (MaES) have been used as a bidentate ligand in the synthesis of novel binuclear alkali metal complexes of the general formula (MaES \(\text{MbL}\))\(^ {22} \). The ligand MaES coordinated through two phenolic oxygen to alkali metal salts \(\text{MbL} \); where \(\text{MbL} = \text{Li}, \text{Na}, \text{K}\) salts
Fig-30

\[ \text{M} = \text{Cu}^{(II)}, \text{Ni}^{(II)} \]
\[ \text{R} = \text{H, 3-CH}_3, \text{4-CH}_3 \]
\[ \text{R'} = \text{3-CH}_3, \text{4-CH}_3, \text{5-CH}_3 \]

Fig-31

\[ \text{R} = \text{P-N(CH}_3)_2, \text{P-OH, O-OH, P-0CH}_3 \]

Fig-32

\[ \text{X} = \text{Cl}^-, \text{Br}^-, I^-, \text{NO}_3^-, \text{SCN}^- \]

Fig-33

\[ \text{M} = \text{Cu}^{(II)}, \text{Ni}^{(II)} \]
of 1-nitroso-2-naphthol, 8-hydroxy quinoline, anthranilic acid as well as KSCN, LiCl, NaBr and NaI Salts (Fig -33).

The Schiff base have also been prepared from amino acids like DL-2-aminobutyric acid, glycine, alanine, L-valine and L-methionine which are in turn utilized for the synthesis of metal complexes. The schiff bases derived from salicylaldehyde and the amino acids form octahedral complexes with Co(II)$^{23}$. Pharmacological activities of the organic compounds increases on complexation with metal ions. Sulfa drugs and substituted O-hydroxy acetophenone have been used for the preparation of metal complexes$^{24}$.

The schiff bases derived from glyoxal and acid monohydrazides and dihydrazides form complexes with Ni(II), Cu(II) and Zn(II). The stereochemistry around Ni(II), Cu(II) and Zn(II) are octahedral, square planar and tetrahedral respectively, whereas in the (Fig-34) when $R = -OH$, the ligand acts as a tetradentate ligand. The schiff bases derived from 2-hydrazine benzoxazole and salicylaldehyde have been reported to be fungicidal and insecticidal.$^{26}$ Schiff bases have profound biological activities$^{27-30}$ Schiff bases derived from 4-substituted and 4,5-disubstituted-2-amino thiazoles and vanilline was synthesized.$^{31}$ Cycloaddition of these schiff bases (Fig -35) with chloroacetyl chloride and subsequent reaction with piperidine and morpholine yield corresponding acetoxy derivatives. The fungicidal tests of these compounds show that the presence of halogen, naphthyl and methoxy group in the compound enhances the fungicidal activity. It is also observed that the schiff bases are more active than the corresponding thiazolidones and acetoxy derivatives.
Fig. 34

R = -H, -OH

Fig. 35
The bivalent metal [Mn(II), Co(II), Ni(II), Cu(II)] form complexes with bidentate ligand, vanillin, anthranillic acid. The sub-normal magnetic moments obtained at room temperature in case of cobalt, nickel and manganese complexes are due to a O-bridged dimeric structure. Coto et al. have reported bivalent copper complexes with a bidentate ligand derived from 2-aminobenzimidazole and 4-methyl benzaldehyde. The i.r. spectra show that the ligand is bidentate through the tertiary 'N'. Mukkanti et al. derived bidentate ligand from 2-furfuraldehyde and thiophene - 2 - carboxaldehyde thiosemicarbazones and form complexes with Pd(II), which are 1 : 2 electrolyte and their room temperature magnetic moments indicate the absence of unpaired electron. The complexes possess square planar geometry around the metal ion. The bidentate ligand 2-hydroxy -5-sulphamido phenyl azoacetyl acetamide and its metal complexes with divalent Cu(II) and Zn(II) ion. Joginadhar and his coworkers have reported the Pd(II) and Cu(II) complexes with ON donor bidentate Schiff bases obtained from 2-thenylamine and different aldehydes. Salicylaldehyde benzoxylhydrazone forms metal complexes with divalent metals like Cu(II), Ni(II), Mn(II) and Zn(II).

Mahapatra and coworkers have reported a number of metal complexes containing bidentate Schiff bases. The complex of Cu(II) ion with 1,5-diphenyl formazan-3-carboxylic acid is monoclinic with a = 6.25, b = 6.21, c = 10.61 Å, \( \alpha = 97^\circ \) and \( z = 1 \). The i.r. spectra show that the complexes exists as 2-linkage isomers in which copper has \( N_4 \) and \( N_2O_2 \) coordination modes. Moreover ligand, 2,3,4-trihydroxy azobenzene and its 4'-ido, 4'-sulfo, 4'-nitro and 4'-carboxy derivatives.
2 - (2' - hydroxy - 1' - naphthalidene) imino - 5 (p - anisyl)
1,3,4-oxadiazole acts as a bidentate ON donor Schiff base to form
complexes with Co(II), Ni(II), Cu(II), Mn(II), Zn(II), Cd(II) and
Hg(II) ions 41 (Fig -36 ). The bidentate Schiff bases of dihydroacetic
acid with aniline have been reported 42 to form complexes with
divalent metal ions like Cu(II), Ni(II) and Pd(II). The bidentate
ligands derived from 2-, 1- or 3-, 2-hydroxy naphthaldehyde and
R - NH2 (R = H, Me, Et, iso-pr, tent-Bu, Ph-, Benzyl-1-naphthyl) have
been reported 43. N, N'-ethylene bis (acetylacetamine) behaves as
bidentate ligand to form tetrahedral complexes with Co(II) 44. Panda
et.al have reported 45 divalent metal complexes with bidentate lig­
ands derived from furfural and various aryl amines. The i.r. spectra
show the coordination of the ligand through the ring 'O' and the
azomethine 'N'. Singh et.al. reported 46 the complexes of Fe(II),
Co(II), Ni(II), Cu(II) and Zn(II) with bidentate pyridine - 4 -
carbonyl/enolic oxygen and the azomethine nitrogen (Fig -37). F.A.
Adam and co-workers have reported 47 divalent metal complexes with
bidentate ligands derived from salicylaldehyde and 6-amino picoline,
2 -, 3, - 4-aminopyridine, 3 -amin-1', 2,4-triazine or 2-amino 3-
hydroxy pyridine. Agarwal et.al. have reported 48 octahedral complex
ex of Co(II), Cu(II), Ni(II) and Zn(II) with a bridging bidentate
ligand derived from phenylhydrazine and acetylacetone. The bridging
bidentate ligand, 4-amino-salicylic acid has been reported 49 to form
bivalent cobalt and copper complexes. 2,5-dihydroxy acetophenone
form octahedral complexes with some bivalent metal ions 50. Das and
Dani have prepared heteronuclear Schiff base complexes of Cu(II)
with Zinc(II) or Cd(II). The complexes reported 51 are of the type
where \( \text{LH} = \text{schiff base derived from salicylaldehyde and ammonia} \) (Fig -38) \((M = \text{Zn}(II) \text{ or Cd}(II), X = \text{Cl}^-, \text{NO}_3^- \text{ or ClO}_4^-). \)

The complexes of 2-thio-3-benzoyl-hydantoin with \( \text{Cr}(II), \text{Mn}(II), \text{Fe}(II), \text{Co}(II), \text{Ni}(II) \text{ and Cu}(II) \) have been synthesised. The i.r. spectra of the complexes reveal the bidentate nature of the ligand. Krishnan Kutty et.al. reported the complexes of Cu(II), Ni(II) and Co(II) with 2-(Phenylazo)-2-cyano ethyl ethanoate. The i.r. and \(^1\text{H} \text{nmr spectra support the monobasic bidentate nature of the ligand, 5-phenyl-2-mercapto-1,3,4-thiadiazole with some divalent metal ions. Vindira and his co-workers have reported} \text{55 the Co}(II), \text{Ni}(II), \text{Cu}(II), \text{Pt}(II), \text{Pd}(II), \text{Th}(II), \text{and UO}_2(IV) \text{ complexes with bidentate O}N \text{ donor schiff base 2-hydroxynaphthaldehyde-2-amino fluorone (Fig -39). Planar geometry suggested for Co(II), Cu(II), Pt(II), Pd(II) complexes while the Ni(II) complexes to be a mixture of planar and tetrahedral forms. Th(IV) and dioxouranium complexes appear to be octahedral. Kandil et.al. have reported} \text{56 polynmetallic complexes with bidentate ligand-5-Vinyl salicylaldehyde and aniline. The schiff base derived from sulphanilamide and salicylaldehyde form complexes of the type} \text{57. The Schiff base acts as a mono-basic bidentate ligand and the complexes appear to be eight coordinated (Fig -40). Bhabe and co-workers have reported} \text{58 the azodye complexes of dioxouranium(VI) and thorium(IV).}

Patel and co-worker have prepared octahedral metal complexes of composition \([\text{ML}_2\text{X}_2\text{H}_2\text{O}] \text{ (M = Cu, Co, Ni; X = Cl, Br} ; L = \text{N-benzoyl-N-naphthyl-B-thiocarbamide). The ligand is bidentate coordi-
nating to the metal ions through the 'S' and 'O' atoms. Preparation and proposition of structure of Co(II), Ni(II), Cu(II) and Zn(II) complexes with bidentate ligands 3-amino-5-(4/5) pyridal-1, 2, 4-tri-azoles have been carried out by Mishra and co-workers. Some O - N donor bidentate ligands have been prepared by the condensation of aroyl hydrazine (benzoyl and salicyloyl) with benzophenone, acetophenone and benzaldehyde and from aniline with salicylaldehyde and 5-bromosalicylaldehyde. Divalent copper forms complex of composition [CuL₂] which has been suggested to be square planar. Thio-cyanato complexes of Ni(II), Co(II) and Zn(II) ions containing some bidentate neutral auxiliary ligands have been reported by Tarafdar et al. Magnetic and electronic spectral data support octahedral geometries for Ni(II) and Co(II) whereas Zn(II) complexes are tetrahedral.

Abu EL - Reash and coworkers, Zaitsev and his coworkers have synthesized and characterised the Cr(III), Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Hg(II) complexes of a bidentate ligand formed by the condensation of 8-benzyldiithiocarbazate and 2-aminoacetophenone (HSBAC) and have reported and established the structure of Cu(II), Ni(II) and Cr(III) complexes with 1-phenyl-3-methyl-4-naphthylazo-5-pyrazolones (Fig -41). In [Ni(HL)₂ and Cu(HL)₂] when (R = OH), the ligand is bidentate coordinating to the metal ions through the azo 'N' and hydroxy 'O' atoms. For [Cr(OH)L] the ligand is assured to be tridentate coordinating through the azo, 'N' Keto 'O' and hydroxy 'O' atoms.

The complexes of Cr(III), Fe(III), Co(II), Ni(II) and Cu(II) with 2-methylpiperazinedithiocarbamate have synthesized and chara-
characterised by Gogol and his coworkers. The ligand exhibits bidentate nature and the complexes are soluble only in strongly coordinating and highly polar solvents like DMF and DMSO. From the ESR spectral data the Copper(II) derivative, the bonding parameters ($\alpha^2, \beta$ and $\gamma$) have been calculated which indicate strong metal-ligand covalency.

Rai et al. have synthesized a series of complexes having the formula $[\text{M}(\text{HL})_2(\text{H}_2\text{O})_2]X_2$ (Fig. 42) where $\text{M} = \text{Co(II)}, \text{Ni(II)}, \text{Cu(II)}$; $X = \text{Cl}^-$, $\text{Br}^-$ and $\text{HL} = 1$-hydroxyimino-1,2-diphenyl(2'-iminopyridyl)ethane by allowing the ligand and the metal salts to react in the 2:1 molar ratio in an ethanolic medium. Studies on the oxovanadium(IV), iron(III), Cobalt(II), nickel(II) and copper(II) complexes of bidentate ligands derived from the condensation of sulfadimethoximl and 5-$(\chi$-substituted salicylaldehyde) have been reported by Goel et al. CuL$_2$ are tetrahedral whereas FeL$_3$ and NiL$_2$ are square planar complexes.

Alzvet and his coworkers have synthesized and characterised the metal complexes of Co(II), Ni(II) and Cu(II) with 5-acetamido-1,3,4-thiadiazole-2-sulphonamide(H$_2$ACM) and amines. ACM acts as a bidentate ligand bonding to the metal ions through the N-sulphonamide atom and the N-thiadiazole atom except for K$_6[\text{Co(ACM)}_4\text{6H}_2\text{O}]$ in which ACM behaves as monodentate through the N-Sulfonamido atom. Synthesis and characterisation of Co(II), Ni(II), Cu(II), Zn(II), Cd(II), Hg(II), dioxouranium(VI) and thorium (IV) complexes with a schiff base derived from 4-hydroxy-3-aldehyde - 6 - biphenyl are reported and characterised on the basis of analytical, magnetic, conductance, electronic and i.r. spectral data. The ligand and field parameters are evaluated for Co, Ni and Cu.
Fig. 43(a)

Fig. 43(b)

R = Phenyl
R' = H, Br
complexes, which suggest an octahedral geometry for each of them. The IR spectral data reveal the bidentate nature of the ligand. Zhdonov et al. have prepared chiral Co(II), Ni(II) and Cu(II) complexes with N-glycosyl-aminocarboxylic ligands. CuL₂ is square-planar with being bidentate coordinating to the metal ions through carboxylic and amino groups.

The synthesis of bidentate 0 N donor schiff bases and their metal complexes with Cr(III), Co(II), Ni(II) and Cu(II) have been reported by Parameswaram and his coworkers. Octahedral structure for Cr(III), Co(II) and Ni(II) complexes and a square planar structure for the Cu(II) complexes have been suggested. T.N. Hazarika has prepared a few complexes of Pd(II) and Pt(II) by the reaction of Pd Cl₂ and K₂ [Pt Cl₄] with some heterocyclic N-donor bases producing compounds of the type MLCl₂ (L = 1, 10, Phenanthroline, 2, 2'-bipyridyl and 2, 2'-biquinoline). Square planar geometry has been suggested for all the complexes. The schiff bases obtained 2 - amino-5-methyl-4-phenyl thiazole condensed with O-hydroxy aldehydes, form complexes of type [ML₂·2H₂O] (N = Ni(II), Cu(II) or Co(II)). The elemental analysis, magnetic susceptibility, electrical conductance, electronic and i.r. data suggested distorted octahedral structures for all the complexes (Fig -43(a), 43(b).

The synthesis and characterisation of complexes of Ni(II) and Cu(II) with 5-Aryl-1-phenylpent-1-yne-3, 5-diones have been investigated by Aly H.A. Hassan and et al., basing on different physicochemical studies. The cobalt(II) complex found to be octahedral and distorted octahedral geometry suggested for copper(II)
Fig - 44

Fig - 45

Fig - 46

M = Ni, Pt
n = 1, 2
complex. David A. Biro and et. al. have been synthesised\textsuperscript{75} metal complexes of maleonitriledithilate and methylviologen with nickel and platinum. The complexes are square-planar compounds (Fig -44) which display interesting oxidation – reduction properties.

The complexes of Fe(III), Co(II), Ni(II), Cu(II), Ru(II), Ru(III), Rh(III) and Pd(II) with N- (2-carboxy phenyl) and 2-amino-N-(2-carboxyphenyl) benzamide have been prepared\textsuperscript{75} and characterized by physicochemical, thermal, spectral and magnetic methods. The coordination sites of ligands are confirmed by the absorptions in the IR and NMR spectra\textsuperscript{76} of diamagnetic complexes. N-(2-carboxy phenyl) - benzamide is found to be uninegative bidentate ligand coordinating through carboxylic oxygen and amidic nitrogen (Fig - 45) while 2-amino-N (carboxy phenyl-) - benzamide has been a tridentate ligand in all its complexes except in the case of Ru(II), in which it coordinates through amine and amide nitrogen atoms only.

The synthesis and characterisation of Co(II), Ni(II) and Cu(II) complexes of some alkylimino derivatives of isonitroso propiophenone (NIPP) are reported\textsuperscript{77}. The Co(II) complexes indicate their octahedral geometry while Ni(II) complexes are square-planar. The square-planar of elongated octahedral environment is suggested for Cu(II) complexes. I.R. reports show a Co-N\textsubscript{3}O chromophore for the Co(III) complexes and M – N\textsubscript{2}O chromophore for Ni(II) and Cu(II) (Fig - 46).

Mahapatra and his co-worker have prepared\textsuperscript{78} two azodye ligands, bis [4,4-(8-hydroxy quinolyl-5')-azo-Phenyl] methane and bis [4, 4-(8-hydroxy quinolyl-5)azo-phenyl] sulphone and their dinuclear
**Fig-47**

\[ M = \text{Co(II), Cu(II), } X = \text{H}_2\text{O} \]

\[ M = \text{Ni(II), Zn(II), Cd(II), Hg(II), } X = \text{NII} \]

**Fig-48**

**Fig-49**

\[ R = \text{C}_6\text{H}_5, 4 - (\text{OME})_2\text{C}_6\text{H}_3 \]

\[ \text{OR} 3, 4 - (\text{OME})_2\text{C}_6\text{H}_3 \]

\[ B = \text{Pyridine, Piperidine, Morpholine} \]
complexes (Fig -47) with divalent metal ions. The Co(II) and Cu(II) complexes are either octahedral or distorted octahedral, both the Ni(II) complexes are square planar and the Zn(II), Cd(II) and Hg(II) complexes are tetrahedral in configuration basing upon analysis, conductance, magnetic moments, IR, electronic, ESR and NMR spectral studies.

Angadi et.al. have reported\textsuperscript{79} the synthesis of seven coordinated ZrO(II) complexes with bidentate aryl hydrazones (Fig - 48). The broad weak band in the region 2750 - 2700 Cm\(^{-1}\) attributable to the intramolecular hydrogen bonded - OH is retained in the complexes suggesting that the O-hydroxy group has not taken part in the bond formulation. The hexa coordinated ruthenium(II) complexes of the type \([\text{RuCl(CO)}(\text{LL})(\text{pph}_3)_2]\) and \([(\text{RuCl})\text{(Co)}(\text{LL})'(\text{B})\text{pph}_3]\) (Fig - 49) where \(\text{HLL}' = 2\)-hydroxychalcone, \(2'-\)hydroxy-4-methoxychalcone, \(2'-\)hydroxy-3, 4-dimethoxychaleone and \(\text{B} = \text{pyridine, piperidine and morpholine}\) have been reported by Natarajan et.al. In all these complexes 2-hydroxychalcone behave as a uninegative bidentate (O O\(^{-}\)) chelating ligand.

Joshua et.al. have reported\textsuperscript{81} that the antimicrobial activity of Co(II) and Ni(II) complexes of bidentate acetyl derivatives of Urea and thiourea. More significantly the N-acylurea and N-acylthiourea complexes have greater inhibitory activity on the organisms-\textit{candida albicans}, \textit{pincillium SP} and \textit{Tritophora species}. Singh et.al. have studied\textsuperscript{82} the complexes of La(III), Pr(III), Nd(III), Sm(III), Eu(III), Cd(III), Tb(III) and Dy(III) with bidentate ligand of 2-acetylaminothiazole (Fig - 50) The IR spectra reveal the interaction of ring nitrogen and carbonyl oxygen with lanthanide ions. Mahapatra
Fig. 50

**pSH Complex®**

M = Ni(II)

**febh Complexes**
Mn(II), Co(II), Ni(II), Cu(II).

(A)

**MbcbH Complexes**
M = Mn(II), Co(II)
Ni(II), Cu(II), Zn(II).

(B)

**FSH Complexes**
M = Ni(II)

(C)
and his coworkers have reported the complexes of Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Hg(II) with bis-bidentate chelating donor azo dye ligands. The complexes of Co(II), Ni(II), and Cu(II) are suggested to be octahedral geometry whereas Zn(II), Cd(II) and Hg(II) complexes are assigned to be tetrahedral basing upon analytical and i.r. spectral data.

The metal complexes of Fe(III), Co(II), Cu(II) and Zn(II) with 4-dimethylaminomethylamtipyrine have been synthesized by Boopathy et al. The octahedral geometry is proposed for the Fe(III) complex whereas the rest of the complexes of Co(II), Cu(II) and Zn(II) are suggested to possess a tetrahedral geometry. Agarwal and coworkers have prepared fifteen complexes of the type $[M\text{L}_2(H_2O)_2]$ and three of the type $[ML_2]$ from four aroylhydrazone Schiff bases viz. 2-furaldehyde-p-chlorobenzoylhydrazone (fcbh), p-methoxy benzaldehyde-p-chlorobenzoylhydrazone (mbcbh), p-methoxy-benzaldehyde salicyloylhydrazone (mbsH) and 2-furaldehydesalicyloylhydrazone (fsH). The mode of chelation of the ligand and geometry of the complex molecules have been assigned and accordingly Co(II)-mbsH and the diamagnetic Ni(II)-mbsH, Ni-fsH complexes are formulated as square pyramidal whereas an octahedral environment around each metal is proposed in rest of the bipositive aroylhydrazone complexes (Fig. 51).

The complexes of 2-(3-coumarinylthioacetyl) benzimidazole (CTBZ) and 2-(3-coumarinyl) imidazo [1,2-a] pyridine (CIP) with U(IV), UO₂(IV) and Th(IV) have been synthesized and characterised on the basis of their elemental analysis, conductivity, magnetic
Fig. 51
Mbsh Complexes
$M = \text{Co}(II), \text{Ni}(II)$

Fig. 52
moment, thermal studies, infrared, PMR and reflectance spectral data. The ligand behave in a neutral bidentate fashion.

The potentially bidentate ligand, \(N,N'-\text{bis(2-phenylbenzimidazolyl)}\) methane (BFBM) has been used to synthesize iron(III) complexes. \(^1\text{H NMR}\) spectra showed both off field and downfield shifted peaks for ligand protons. The Mossbauer spectral data reveal the presence of high spin ferric ion and lower value of isomer shift indicates substantial covalency in Fe(III) ligand bond.

Few complexes of Mn(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Hg(II) with 4-oxo-4H-1-benzopyran-3-(carboxaldehyde-4-chlorobenzylhydrazone) (BCBH) and 4-oxo-4H-1-benzopyran-3-(carboxaldehyde-4-methylbenzylhydrazone) (BMBH) have been synthesised and characterized by N.Nawar and co-workers (Fig -52).

Athappan et.al. have been reported a few complexes of the type \(ML_2 \cdot nB\) [where \(M = \text{Cu(II), Ni(II), Co(II), Zn(II), Cd(II)}\); \(L = 5,6\)-diphenyl-3-(2-hydroxyphenyl)-1,2,4-triazine(DFPTH); \(B = \text{H}_2\text{O}; n = 0,2\)] The Fe(II), Fe(III), Co(II), Co(III) and Ni(II) dipyridyl complexes have been synthesized by Awadallah.

Metal complexes of the type \(ML_2 \cdot nB\) [\(M = \text{Co(II), Ni(II)}\) and Cu(II); \(HL = 3-(2-hydroxy-1-naphthyl)-5-(4-X-phenyl)-2-1\text{soxazoline} (X=\text{H,C1, CH3})\); \(n = 0,2; B = \text{H}_2\text{O, Py}\)] have been synthesized and characterized by Athappan and Co-workers.

Khan et.al. have prepared and characterized the metal complexes of Cr(III), Mn(II), Fe(III), Co(II), Ni(II) and Cu(II) with 5-(2-hydroxy benzylidene) aminobenzopyrazole (HBAB). The IR spectral
Fig. 53
studies indicate that the ligand acts as a bidentate donor and co-ordinates through the nitrogen of the azomethine group and deprotonated OH group. The complexes \([\text{M(HEAB)}_3]\) (M=Cr,Fe) and \([\text{M(HEAB)}_2\cdot2\text{H}_2\text{O}}]\) (M=Mn, Co and Ni) have been assigned an octahedral geometry whereas \(\text{Cu(HEAB)}_2\) is proposed to be square-planar.

The complexes of bis(vanillin) benzidine(Vn2bZ) of the type \([\text{M(Vn}_2\text{bZ})(\text{H}_2\text{O})_2\text{Cl}_2]\)_2 Cl_2 \(\text{[where M = Ti(III), V(III) and Fe(III)\]}\) and \([\text{M(Vn}_2\text{bZ})(\text{H}_2\text{O})\text{Cl}]_2\) Cl_2 \(\text{[where M = Mn(II), Co(II) and Ni(II)\]}\) have been synthesized and characterized by Arvind and co-workers.

The transition metal(II) ions form complexes with Quinoline-8-sulphinic acid (QNSOOH). Copper(II) forms a dimer, \(\text{Cu}_2(\text{QNS0O})_2\) Cl_2. 4H_2O with sulphinato-N,S at pH=1 and a monomer, \(\text{Cu(QNS0O)}_2\). 2H_2O with sulphinato-N,0 at pH=3 Nickel(II) forms a high spin octahedral sulphinato-N, S complex, while cobalt forms a low spin octahedral sulphinato-N, S complex, Zinc(II) forms sulphinato-N, O complex and cadmium forms only sulphinato-0,0 complex.

Srivastava et.al. have reported the synthesis of some Hg(II) complexes with bidentate aromatic Schiff base ligands derived from ethylenediamine/phenylenediamine and 2-acetylpyrrole; 2-pyrrole carboxylaldehyde; 2-pyridylcarboxyaldehyde and 2-naphthylaldehyde.

Sudershan et.al. have been synthesised and characterised the complex of Cu(II) with ligands derived from some 2-amino-5-substituted-1,3,4-oxadiazole and benzoyl isothiocyanates.
METAL COMPLEXES WITH TRIDENTATE LIGANDS

The transitional metal ions with Schiff bases obtained from 3,5-substituted salicylaldehyde and aminophenols (Fig-53) form metal complexes. The Cu(II) complexes give subnormal moments the values indicate dimerisation of the ions in the solid state. Three possible isomeric forms of the complex are given (Fig-54). In the first isomer both the bridging oxygens coming from aminophenol moieties. In the isomer II, one oxygen from the aminophenol and the other from the salicylaldehyde moiety. The isomer-III have both the oxygens from salicylaldehyde, when \( R_{II} = NO_2 \), due to the steric hindrance, the isomer-I is predominant over II and III isomers.

The binuclear complexes are convertible to the mononuclear species by refluxing the complex with pyridine. The exchange integral \( (J) \) value increases if electron withdrawing groups present in the salicylaldehyde moiety but if it is in the amino-phenol moiety the value of 'J' decreases. The different order for \( J(R,R') \) has been established, \( J(H,Cl) > J(H,Br) > J(NO_2,NO_2) > J(H,H) > J(H,CH_3) > J(NO_2,H) > J(Cl,H) > J(Cl,Cl) \).

The complexes form by Cu(II) ion is of the type \([Cu(H \text{ Sal } R)(Cl)(H_2O)](R=CH_3, C_6H_5 \text{ and } p-CH_3O C_6H_4)\). Hydrated complexes suggest distortion square pyramidal structure whereas the anhydrous chelates possess a square planar arrangement with chloride ion occupying the fourth position. In the i.r. spectra of these complexes a strong band appears at 1630 cm\(^{-1}\) while the band due to N-H stretching and \( \nu(C=O) \) are absent. This band is due to stretching vibration of conjugated (=N=N=C) system and is diagnostic of enolisation of hydrazone moiety. The electronic spectra of these complexes in nujol
show a multicomponent band system over the range 600-730 nm along with a CT band at 480 nm consistent with a square planar geometry. These complexes form mono pyridine derivative indicating the presence of bridging oxygen from hydrazine. Tridentate ONO donor Schiff base is prepared by refluxing salicylaldehyde with α-amino acids. Binuclear octahedral complexes (Fig-55) suggest for Ni(II) complexes whereas Cu(II) complexes are classified in two groups (i) those having subnormal magnetic moments and (ii) those with normal magnetic moments. For Cu(II) complexes, $\gamma(C=O)$ vibration is observed with about 25 cm$^{-1}$ higher than those of the corresponding Ni(II) complexes.

The complex of binuclear Cu(II) have been reported derived from salicylaldehyde and amino alcohols. For these compounds two structures are possible viz (i) coordination of phenolic oxygen or (ii) coordination of alcoholic oxygen atom. If the phenolic oxygen coordinate to the metal then C-O stretching frequency shift from 1540 cm$^{-1}$. If the bridging through alcoholic oxygen atoms then the phenolic 'C-O' stretching frequency remain same. The higher magnetic moments are observed for complexes with phenolic bridging atom then that of alcoholic oxygen atom which indicate the bridging occurring alcoholic oxygen atoms which indicate the bridging occurring preferentially through alcoholic oxygen atoms. If the Schiff bases when 1-propanal is replaced by ethanol or substituted ethanol the magnetic moments range lie between 1.77-2.09B.M. at room temperature. The complex $[\text{Cu Sal N(CH}_2)_2\text{OH}]$ tetrameric in nature where four copper ions are bridged tetrahedrally. The normal magnetic moments have been attributed to a negligible type super-exchange interaction
Fig - 56

Fig - 57
among the four Cu(II) ions via the bridging oxygen atoms. The composition $[\text{Cu}_2\text{R Sal N}(R)\text{OH}]_x$ (R = -(CH$_2$)$_5$-CH$_2$-CH(CH$_3$)$_2$-CH$_2$-; x = Cl$^-$, NO$_3^-$, ClO$_4^-$) of copper complexes have been reported, their magnetic moment values depend upon the anion. The complexes are found to be dimeric with phenolic oxygen atoms bridging the two Cu(II) ions. The low magnetic moment (1.01 BM at 300 K) values rules out the metal-metal interaction. The complex is planar but unsymmetrical, the long and short Cu-0 distance are 1.78 Å and 1.72 Å respectively. The geometry around copper ion is trigonal bipyramidal with the nitrogen and oxygen in the axial position. The complex $[\text{Cu Sal N}(\text{CH}_2)_3\text{OH}]_2$ transferred to $[\text{Cu Sal N}(\text{CH}_2)_3\text{OHX}]_2$ when it treated with HCl in methanol but the reverse reaction takes place when pyridine is used in place of HCl. In the nitrato complexes, the i.r. bands appearing at 790-830, 1005-1022, 1280-1286 and 1488-1495 Cm$^{-1}$ suggest that the nitrato is bonded to the metal atom. The electronic spectra of nitrato complexes are characteristics of four co-ordination with slight distortion from planar configuration indicating monodentate coordination of nitro group (-O, NO$_2$). The perchlorate group in the perchlorate complex remains unaffected conforming a binuclear structure (Fig -56). Analytical data suggest the square pyramidal configuration.

The mono, bi-and tri-nuclear nickel(II) complexes can be obtained from the Schiff bases, N-hydroxy-ethyl salicylaldehyde and N-hydroxy propylsalicylaldehyde, the structure of which is given in (Fig-57). Dimeric five coordinated structure of Copper(II) complex obtained from the Schiff base derived from Salicylaldehyde and 3-amino-1-propanol, the fifth position is occupied by a chloride
The bridging Cu-O-Cu angle is 110.3° and $|\mu_{\text{eff.}}|$ is 1.1 B.M. at room temperature.

The Schiff bases formed by the condensation of salicylaldehyde, 5-chloro, 5-bromo, 3-methoxy and 5,6-benzosalicylaldehyde with o-amino benzyl alcohol behaves as dibasic tridentate ligand. The subnormal magnetic moment values (0.98 - 1.45 B.M.) at room temperature explained on the basis of super-exchange through bridging oxygen atoms in a dimeric structure. Absence of a band above 1540 Cm$^{-1}$ suggests that the alcoholic oxygen acts as the bridge between the copper atoms. Coordination of the nitrogen atoms of the azomethine group is proved by the appearance of a band at 1600-1615 Cm$^{-1}$ due to $\gamma$(C=N) stretch. Usually the free $\gamma$(C = N) vibration appears at 1640 Cm$^{-1}$ in aromatic Schiff bases. The complexes show a d-d transition band at 15,400 - 17,000 Cm$^{-1}$ along with a symmetry forbidden ligand - metal CT band $\sim$ 27,000 Cm$^{-1}$.

The Copper(II) complexes have been prepared and characterised with the Schiff bases derived from salicylaldehyde and salicylhydrazide or benzoyl hydrazide. The low $|\mu_{\text{eff.}}|$ values at room temperature is due to antiferromagnetic spin-spin exchange ($J = 297-347$ Cm$^{-1}$). The complexes are dimeric with hydrazine (enolic) oxygen bridge. Schiff bases obtained from salicylaldehyde and its 5-chloro, 5-bromo, 5-nitro, 5-ethoxy and 3,5-dichloro derivatives and o-hydroxy benzylamine have been studied.

Ablov and his coworkers have synthesized Co(II), Ni(II), Cu(II) and Zn(II) complexes with Schiff bases obtained from the condensation of this semicarbazide with a number of aldehydes and ketones. This suggests an octahedral structure of Co(II) and
Fig - 58

Fig - 59

Fig - 60

Fig - 61

Fig - 62
Ni(II) complexes but X-ray study showed that the Ni(II) complex has a trigonal bipyramidal geometry\(^{123}\). The Schiff base obtained from pyridine-2-aldehyde and thiosemicarbazide (Fig -58) behaves as a neutral tridentate ligand. The iron complex \([\text{Fe (NHSH)}_2]_2\) \(X_2\) (\(X = \text{Cl, Br}\)) are spin-paired but nickel complexes \([\text{Ni (NHSH)}_2]_2\) \(X_2\) (\(X = \text{Cl and NO}_3\)) are spin-free\(^{124}\), whereas the Schiff base derived\(^{125}\) from 0 - methylthiobenzaldehyde and N,N-diethylethylene-diamine (Fig -59) forms high spin complexes \([\text{M(N-N-Sme)X}_2]_2\) with cobalt and nickel, here \(X = \text{Cl, Br, I, SCN}\). The nickel complexes are five coordinated in the solid state but in liquid state they give temperature dependant equilibrium between tetrahedral and five coordinate species. The cobalt complexes are pseudotetrahedral both in solid as well as in solution, the cobalt atom being coordinated to two nitrogen atoms of the ligand.

The Schiff base N-(2-methyl-thio-phenyl)-2-methyl thiophenyl - methyleneimine (Fig-60) forms complexes of the type \([\text{M(SNG)}]_2\) with cobalt and nickel, \(X = \text{Cl, Br, I, SCN}\) show by the Livingston and his coworkers. The electronic spectral data indicate that the Cobalt(II) halide complexes are five coordinated whereas when \(X = \text{SCN}\) and all the nickel complexes are six coordinated polymer. The copper(II) complex \(\text{Cu(SNS)}\) \(X_2\) (\(X = \text{Cl, Br}\)) are possibly five coordinated\(^{126}\). The Schiff base dithiocarbazic acid derivatives, \(-\text{N-methyl-S-methyl-B-N-(6-methyl pyridyl-zye) methylenedithiocarbazate (Fig- 61) and -N-methyl-S-methyl-B-N-(6-methyl pyridyl-zye) methylenedithiocarbazate (Fig -62) act as an neutral tridentate ligand and stable complexes with some transition elements. The second moiety have a great tendency to form five coordinate metal complexes with a distorted trigonal bipyramidal geometry}\(^{127}\). The ligand \(2-[2-(2,3 \text{ diaza-4-methyl}}\)
5-thiohexa-1, 3-dienyl) pyridine (Fig-63) act as a NNS tridentate in the complexes \[ \text{Ni(N-N-SMe)}_2 \text{(ClO}_4\text{)}_2 \text{ and Ni(N-N-SMe)}_2 \text{X} \](\(X = \text{Cl, Br, I, NCS}\)) the later complexes are six coordinated and anion bridged. The cobalt(II) complexes are tetrahedral with the ligand acting as a N-bidentate.

The complexes of Ni(II) and Cu(II) with the ligand pyridine-2-carbaldelhyde-3-methyl thiosemicarbazone acts as tridentate. The complexes Ni(L)\(X_2\)\((X = \text{Cl, Br})\) are halogen bridged\(^{129}\). The bis-ligand complexes \[ \text{Ni(L)}_2 \text{X}_2 \text{(X = ClO}_4\text{, BF}_4\text{ and NO}_3\text{)} \text{are ionic. Thiocyanate radical is coordinated in the complexes in which the ligand is bidentate. The schiff base quinolialdehyde (dithio carbomethoxy) hydrazone (Fig-64) behaves as a tridentate ligand and forms complexes with Ni(II) and Cu(II) ions}\(^{130}\). The schiff base salicylaldehydethiosemicarbazone acts as a single charged tridentate chelating agent losing phenolic proton. The ligand is coordinated to the metal through the phenolic oxygen, the imino nitrogen and this one sulphur atoms. It can also act as a doubly negatively charged tridentate ligand by losing an additional proton from the mercapto group of the tautomeric form\(^{131-132}\).

The schiff base salicylaldehydethiosemicarbazone (H\(_2\)L) form\(^{133}\) a nickel complex of composition \[ \text{NiL(NH}_3\text{)} \text{spectral data indicate that the enol form of the ligand (thiol form) coordinates to the metal atom (Fig-65). Mossbauer spectral data have been recorded for the Fe(II) and Fe(III) complexes of salicylaldehydethiosemicarbazone and butyl monoximethiosemicarbazone at 80°K and 300°K. The Fe(II) complexes are in low spin state even at 323°K. The Fe(II) complex of salicylaldehydethiosemicarbazone and biacetyl monoxime-
**Fig-66**

![Chemical structure](#)

\[ R = 5-\text{Cl}, 5-\text{Br}, 3-\text{OCH}_3 \]

3, 5-dichloro

**Fig-67**

![Chemical structure](#)

**Fig-68**

![Chemical structure](#)
thiosemicarbazone are respectively of high spin and low spin type \(^{134,135}\).

The Schiff bases derived from salicylaldehyde or substituted salicylaldehyde with aminophenols, aminothiophenols, aminoalcohols and aminothioalcohols have been investigated \(^{136-138}\) (Fig -66,67). The metal(II) complexes obtained from these Schiff bases are found to exhibit subnormal magnetic moments at room temperature due to antiferromagnetic exchange. The Co(II) and Ni(II) complexes are reported to be monomers with octahedral geometry around the metal ions. But the Cu(II) complexes are binuclear square planar where phenolic or the alcoholic oxygen act as a bridge between the two copper centers. Tridentate dibasic ONO donor Schiff bases derived from 0-hydroxy acetophenone, 3-methyl-2-hydroxy-acetophenone, 5-methoxy-2-hydroxy acetophenone and 0-aminophenol form dimeric Cu(II) complexes\(^{139}\). But the Schiff base obtained from 0-hydroxy acetophenone and hydroxylamines having ONO donor atoms are found to be monomeric in nature\(^{140}\) (Fig -68).

The tridentate dibasic Schiff bases form a complex with oxovanadium(IV) show unusual magnetic properties, due to the dimeric or polymeric structure of the complexes\(^{141-143}\). The magnetic moment values decreases as the temperature lowered indicating the antiferromagnetic exchange with \( S = 0 \) as the ground state. The exchange integral (\( J \)) of the complexes is in the range 121-245 Cm\(^{-1}\). The complexes exhibit the \( \nu (V = 0) \) frequency in the region 910-985 cm\(^{-1}\) and the electronic spectral bands observed around 13000, 18000 and 22000 cm\(^{-1}\) due to transition \( d_{xz}, d_{yz}, d_{xy}, d_{x^2-y^2} \) and \( d_{xy} \) \( d_{z^2} \) respectively. Copper(II) complexes of tridentate dibasic ONO
Fig - 69

Fig - 70

Fig - 71

Fig - 72

Fig - 73

Fig - 74

Fig - 75
Donor Schiff bases derived from O-aminophenol and 3-chloro, 4-chloro, 4-methyl and 5-methyl-2-hydroxyacetophenone are found to be dimeric square planar. Gopinath et al. reported organotin and organo-oxytitanium compounds with Schiff bases derived from salicylaldehyde and 5-benzylidithiocarbazate (Fig -69).

The ONO donor Schiff bases obtained from furan 2-carbaldehyde or salicylaldehyde with some aminophenols or aminocarboxylic acids (Fig-70,71) form complexes with Co(II), Ni(II) and Cu(II). Syamal et al. reported complexes of Co(II), Ni(II) and Zn(II) using dibasic tridentate Schiff bases, obtained from the condensation of salicylaldehyde with aminobenzyl alcohol (Fig-72) or with O-hydroxy benzylamine (Fig -73). The preparation of metal chelates of Mn(II), Fe(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II), Pd(II), UO$_2^+$ and VO$_2^{+2}$ (L - benzoyl methyl benzyldieneimino) benzenesulphonic acid (Fig-74) and 2-(L-benzoyl methyl benzyldieneimino) ethane sulphonic acid (Fig -75) are reported.

Mohapatra et al. have reported a number of metal complexes containing tridentate Schiff bases. The tridentate ligands, 2-hydroxyacetophenone and 2-hydroxy naphthaldehyde have been reported to form square planar complexes while tridentate ligand N-(2-hydroxy-1-naphthalidene) anthranilic acid which coordinated through the azomethine 'N' carboxylic 'O' and hydroxy 'O' atoms. The Schiff bases (Fig-76) derived from 2-benzoylpyridine benzoyl hydrazone form complexes with a number of divalent metal ions.

West and his coworker have reported the complexes of bicyclic compounds with a tridentate ligand, 3-azabicycle [3,2,2] nonane-3-thiocarboxylic acid 2-[1-(6-methyl-2-pyridyl) - ethyldene].
Fig - 76

\[
\text{X = H, 5-Chloro, 5-Brorno, 5-Nitro, 3-Ethoxy, 5-Benz} \\
\]

Fig - 77

\[
X = H, 5 - Chloro, 5 - Bromo, 5 - Nitro, 3 - Ethoxy, 5 - Benzo
\]

Fig - 78
hydrazide. The ligand coordinates through the thione 'S' the imine 'N' and the pyridyl 'N'. Mahapatra et al. have reported Co(II), Cu(II) and Zn(II) complexes with a ONN donor tridentate Schiff base derived from salicylaldehyde with 2-amino-5-phenyl-1,3,4-oxadiazole. They have also synthesized metal complexes with tridentate Schiff bases, derived from the condensation of salicylaldehyde with 3-amino-1-phenyl-pyrazole-5-one.

Syamal and coworkers have reported metal complexes with tridentate Schiff base ligand derived from ethanolamine and salicylaldehyde, 5-nitrosalicylaldehyde, 3-ethoxysalicylaldehyde, 2-hydroxy-1-naphthaldehyde. The same workers also have reported the preparation and characterisation of Cu(II) complexes with dibasic tridentate ONS donor Schiff bases (Fig-77) obtained by the condensation of 4-amino-5-mercapto 3-3 methyl-1,2,4-triazole and salicylaldehyde, substituted salicylaldehyde or 2-hydroxy-1-naphthaldehyde. The complexes exhibit subnormal magnetic moments in the range 1.15 - 1.34 B.M. due to the presence of antiferromagnetic exchange. The exchange coupling constant values are in the range of 269 to 389 cm\(^{-1}\) and are indicative of \(S = 0\) ground state with antiferromagnetic spin-spin coupling. An oxygen bridged dimetallic square planar structure has been deduced (Fig - 78).

The complexes of Zr(IV) with tridentate ONO donor Schiff bases have been reported by Syamal and Kumar. Gromor and his coworkers reported the complexes of Co(II) and Ni(II) with phenylazo-\(\text{p}\)-napthols. Some mixed ligand complexes with ligand pyrrole-2-carboxaldehyde and acetyl acetone have been reported.
by Mehta et al. The binegative tridentate ligand, acetone (N - benzoyl) - glycylhydrazone forms metal complexes with the composition \( [ML \, 3H_2O] \) (\( M = \text{Mn(II)}, \text{Co(II)}, \text{Ni(II)} \) and \( \text{Zn(II)} \)). The same author also have synthesized and characterised the structural features of some bivalent tridentate O - hydroxyacetophenone (N - benzoyl) glycylhydrazone. The dinegative tridentate behaviour of the ligand is suggested for i.r. spectral study. An octahedral structure is suggested for Co(II) and Ni(II) as evident from magnetic and electronic spectral study.

Subramanian and his coworkers have prepared Ni(II), Co(II), Mn(II), Cu(II) and Zn(II) complexes with salicylaldimino biacetyl monohydrazone (Fig - 79) and suggested distorted octahedral geometry for these complexes. The Schiff base 2-hydroxy-1-naphthalidene - 3- 5 - dinitrobenzoyl hydrazone acts as a tridentate ligand and forms oxobridged binuclear complexes with Mn(II), Co(II), Ni(II) or Cu(II) ions.

Choudhury and coworkers have reported two mono-basic tridentate O - (N - furfuraldimino) phenol(HFP) and O - (N - thiophene-2-aldimino) phenol(HTP) and their bivalent metal chelates with Cr(II), Mn(II), Co(II), Ni(II) and Cu(II) and they have studied their physico-chemical measurements. The bivalent metal ions exhibit octahedral geometry. Nickel(II) complexes of some ONO donor tridentate schiff bases derived from aroylhjrdrazines and salicylaldehydes have been prepared and characterised by analytical, IR, electronic spectral, conductivity and magnetic measurements. Mahajan and coworkers have prepared complexes of Co(II), Ni(II) and Cu(II) with 2, 6-bis (N, N - diethylamino methyl) pyridine (damp) and character-
ised then by physicochemical technique. IR studies of all these complexes indicate that the ligand coordinating to the metal through its N N N donor sequence. Magnetic moment and electronic spectral data support a 5'-coordinated structure for all these complexes except Ni(damp) (NCS)$_2$ which is assigned a binuclear (dimeric) bridged structure contains both bridging and terminal NCS groups. A number of polymetallic complexes of iron(II), Cobalt(II), nickel(II), Copper(II), Zinc(II) and mercury(II) with O N O donor tridentate Schiff bases have been prepared by Mahapatra et al.\textsuperscript{175}.

Swamy and coworkers\textsuperscript{176} have been carried out the preparation and characterisation of some transition metal complexes of type $[\text{ML(H}_2\text{O})\text{Cl}_2] M = \text{Co, Ni, Cu, Zn; } L = \text{R-CO-NH-N = CHR}_1 (R = \text{Ph, P-tolyl, p = cl (}6\text{H}_4; R_1 = 2 - \text{aminopyridyl}). A distorted octahedral stereochemistry has been suggested for the complexes with the tridentate Schiff base ligands. Jahagirdar et al. have prepared and characterised\textsuperscript{177} some bimetallic complexes of Co(II), Ni(II) and Cu(II) with long chain fatty acid hydrazones. Various physicochemical studies reveal that the ligands behave in a monobasic tridentate manner in all the complexes except in Cu(II) complexes where they act as dibasic tridentate ligands with O : N : O donor sequence. Co(II) complexes have square planar structures. The complexes are relatively more active as bactericides than H$_2$L.

Satapathy and coworkers\textsuperscript{178} have prepared some binuclear metal complexes of Cu(II), Co(II) and Ni(II) with 1-hydroxy 2,3-dimethyl-6-amino-6-mercapto-1,4,5-triazal-1,3-hexadiene. IR spectra of the complexes suggest that the ligand coordinates to the metal ion through its azomethine 'N', oxime 'O' and 'S' atoms.
Fig-80 (a)

Fig-80 (b)

$X = \text{ClO}_4^-, \text{BF}_4^-, \text{NO}_3^-$

Fig-81 (a)

$M = \text{Mn(II), Co(II) OR Ni(II)}$
$M = \text{Cu(II), H}_2\text{O = Ni(II)}$

Fig-81 (b)
Reflectance spectra of the complexes indicate octahedral geometry round the metal ions. Chu et al. have studied the preparation, properties, structure and bactericidal activity of Zn(II), Cu(II), Ni(II) and Fe(II) complexes with nitrogen and sulphur containing schiff bases. The tridentate schiff bases were obtained by reaction of 2,4-dihydroxybenzaldehyde and thiosemicarbazide with the appropriate metal(II) chlorides. Copper(II) and Zn(II) complexes of schiff bases derived from the condensation of 2,4-dihydroxy-L-Leucine and L-phenylalanine have been investigated. These complexes are nonelectrolytes and they are coordinated through the ONO donor atoms of the ligands.

Shukla and her coworkers have reported the synthesis and spectroscopic studies of several new complexes of organotin(IV) with macrocyclic ligands derived from acetylacetone and ethylene diamine or O-phenyl enediamine. The IR and NMR spectra show that only three out of the four nitrogens of ligand and two phenyl groups are coordinated to tin atom leading to trigonal bipyramidal structure of the complexes. Complexes of Mn(II), Co(II), Ni(N), Cu(II) and Zn(II) with dibasic tridentate ligands, benzyl, ortho-substituted anilides have been prepared and characterised by elemental and thermogravimetric analysis. IR and $^1$H nmr spectral data indicate that bonding occurs through deprotonated COOH, SH or OH; enolate oxygen; and anilide nitrogen. Electronic and EPR spectra reveal that Mn(II), Co(II) complexes are squareplanar and Zn(II) complexes are tetrahedral.

The metal complexes of composition $\text{M}L(H_2O)\text{Cl}_2$, $\text{M} = \text{Co(II)}$,
Fig-82

Fig-83

M = Mn(II), Fe(II), Co(II), Ni(II) and Cu(II)
Ni(II), Cu(II), Zn(II), Cd(II) and Pd(II); L = 2 - aminonicotinaldehyde acetyl hydrazone or phenylacetyl hydrazone have synthesized and reported by Swamy and his coworkers\textsuperscript{183}. The 'Pd' complexes are square planar whereas all other complexes show octahedral geometry. The ligands are bidentate with Pd and tridentate in other complexes. Some Ni(II) and Cu(II) complexes of the type ML with ONS donor tridentate schiff base ligands derived from the condensation of benzoylaceton or 2-hydroxy-naphthaldehyde with S-alkyleesters of dithiocarbazic acid have been prepared and characterised\textsuperscript{184} by Nazimuddin et al. Rema et al. have studied\textsuperscript{185} the preparation and characterisation of Mn(II), Fe(II), Co(II), Ni(II), Cu(II) and Cd(II) complexes of N-(5-bromosalicylidene)-5-bromoanthranilic acid which acts as a tridentate ligand. Thermal decomposition of Co(II), Ni(II) and Cu(II) chelates have been analysed to obtain the energy and entropy of activation based on Coats-Redfern and Horowite-Metzger equation. The monobasic tridentate ligand DHAS derived\textsuperscript{186} from 3-acetyl-6-methyl-2H-pyrren, 2,4(3H) dione (dehydro acetic acid) and hydrazine carbamid (semicarbazide) coordinated to the metal ions through ONO potential donor atoms of the ligands. The chelating ligand possesses fungicidal activities. The general formula for the metal complexes like Mn(II), Fe(II), Co(II), Ni(II) and Cu(II) is $[M(DHAS)_2]$ (Fig -82) and that of VO is $[M(DHAS)_2 SO_4]$ (Fig -83).

Schiff bases derived from benzaldehyde/Salicylaldehyde and Salicylaldehyde hydrazone have been synthesized\textsuperscript{187}. The metal complexes of Ni(II), Co(II), Mn(II), Cu(II), Zn(II) and UO$_2$ (VI) have been prepared and characterised by i.r., electronic spectra and magnetic studies. It has been shown that the benzylidene -
Fig. 84

Fig. 85

Fig. 86

Where $n = 3$

$M = \text{Co(II)}, \text{Ni(II)}, \text{Cu(II)}$

$n = 2$ $M = \text{VO}^{2+}$

$n = 1$ $M = \text{VO}^{2+}$
Salicylaldehyde hydrazone schiff base acts as dibasic tridentate while other monobasic bidentate.

The complexes of Ni(II), Cu(II), Zn(II), Pd(II) and Cd(II) with 1-salicylidene-4-pyrrolidinothiosemicarbazone has been synthesized by Saxena et al. The absorption band at 70 ± 10 cm⁻¹ indicates the tridentate nature of the ligand coordinating Cu(II), Ni(II) ions through (C = S) sulphur atom by deprotonation in the thiol form whereas the same ligand forms complexes with Zn(II) Cd(II) and Pd(II) of the type [M(H-Sp+SC)₂] indicating the non-coordination of thione sulphur atom and bidentate nature of the ligand. The complexes of Co(II), Ni(II), Cu(II) and Zn(II) with tridentate ligand (Fig -85) derived from hydrazone and isonicotinoyl hydrazone of acetoaceticanilide have been reported by Aravindakshan and his coworkers, Co(II) complex is assigned to be distorted octahedral whereas complexes of Ni(II) and Cu(II) are suggested to be tetrahedral and square planar respectively.

Gupta et al. have investigated the art of synthesis and stability constants of the complexes of Co(II), Ni(II), Cu(II), Zn(II), Cd(II), UO₂⁺ and VO²⁺ with bidentate tridentate ligands, [(pyrrole-2-acetylideneamino)propionic acid (H₂pp) and 1-(2- mercapto-phenylamino)-1,3-diphenyl-propan-3-one (H₂BT)] (Fig-86). Some Ni(II) and Cu(II) complexes of the type ML with ONS donor tridentate Schiff base ligands derived from the condensation of benzoyl-acetone or 2-hydroxynaphthaldehyde with S-alkylesters of dithio-carbazic acid have been prepared and characterised by Nazimuddin and coworkers. Magnetic and spectral evidence suggest a dimeric structure for these complexes.
**Fig-87**

**Fig-88**

**Fig-89**

(a) + (b) 2+ (X = Cl, Me)
Tris (3-mitroformazanato) rhodium(III) chelates have been synthesised and characterised\textsuperscript{192} by elemental analysis, IR and PMR studies. The present study reveals that the co-ordination of these ligands to rhodium(III) occurs through nitrogen atom 1 and 5 of the formazan ring and the $\text{NO}_2$ group does not take part in coordination. These trischelates contain three symmetric six-membered $\text{CN}_4\text{Rh}$ rings. (Fig - 87).

Kamalendu Dey\textsuperscript{193} and co-worker have been isolated Fe(III) complexes of salicylaldehyde-4-methoxybenzoylhydrazone. (Fig - 88). Bis(3-aminopropyl)telluride (L) and its complexes with platinum(II) and palladium(II) of the types $\text{PtCl}_2(\text{Ph CN})_1.25(1), [\text{Pd ClL}] \text{Cl}(2)$ and $[\text{Pd MeL}] \text{Cl}(3)$ have been prepared and characterized\textsuperscript{194} by elemental analysis and molar conductance measurements, IR and multinuclear NMR data. The complexes have square planar geometry around the metal with the ligand coordinated in a tridentate mode (Fig - 89).

A series of thorium(IV) and dioxouranium(VI) complexes have been synthesised\textsuperscript{195} with tridentate Schiff base ligands obtained by in situ condensation of $\text{N-N}$-dimethylethylenediamine with $\text{O}$-hydroxy aromatic aldehydes such as salicylaldehyde (HL) or $\text{O}$-hydroxy naphthaldehyde, while with dioxouranium(VI) the ligands are co-ordinated in a neutral manner and act as tridentate donors forming complexes of the type $\text{UO}_2(\text{HL})X_2$ or $\text{UO}_2(\text{HL}')X_2$ ($X = \text{Cl, I, NCS, NO}_3, \text{CH}_3\text{COO}$). With thorium(IV) they are coordinated as deprotonated tridentate ligands yielding complexes of the type $\text{Th(L')}_2X_2$ ($X = \text{I, NCS, NO}_3$).
Fig. 90
Transition metal complexes of the general formula \([\text{M(DHAS)}_2]_3\)
where \(\text{M} = \text{Mn(II), Fe(II), Co(II), Ni(II)}\) and \(\text{Cu(II)}\); \([\text{M(DHAS)}_2 \text{SO}_4]\)
where \(\text{M} = \text{V, VO}_2^{2+}\) and \(\text{3-acetyl-6-methyl-2H-pyran-2, 4(3H) dione semicarbazone (DHAS) (Dehydroacetic acid semicarbazone) have been prepared and characterised}^{196}.\) The ligand coordinate through \(\text{ONO}\) donor atoms, behaving as a monobasic tridentate ligand.

The complexes of \(\text{Cr(III), Co(II), Mn(II), Cu(II)}\) and \(\text{Ni(II)}\) with 
5-cyano-1,6-di-hydro-4-methyl-1-phenyl-6-oxopyridazine-3-carboxylic acid hydride(II) have been isolated and characterised by Shoukry\(^{197}\) and his co-worker. The ligand forms complexes of the type \([\text{MLCl}]\)
with \(\text{Cu(II)}\) and \(\text{Mn(II)}\) and of the type \([\text{ML}_2]\) \(\text{NH}_2\text{O}\) (where \(n = 1,2\) and 4) with \(\text{Co(II)}, \text{Ni(II)}\) and respectively.

Thakkar\(^{198}\) et.al. have been synthesised the complexes of \(\text{Co(II)}, \text{Ni(II)}\) and \(\text{Cu(II)}\) with 2-hydroxyimino-1-[\(\text{1-aminobiphenylimino}\)]
-1-(4'-X-phenyl) glyoxal \((X = \text{H, Cl, Br, CH}_3)\) - condensation of 2-aminothiazole and its derivatives with vic-hydroxyaldehydes gives schiff bases which form complexes of the type \([\text{ML}_2]\) with bivalent transition metals has been reported by Bhaskare et.al\(^{199}\).

Oxovanadium(IV), chromium(III), manganese(II), iron(II), cobalt(II), nickel(II) and Copper(II) complex of the schiff base derived from salicylhydrazide and 6-methyl-4-hydroxy-3-acetylcoumarin (Mc-HACSH ) have been synthesized by Mrs. Sharada and Co-workers\(^{200}\).

Sharma et.al.\(^{201}\) have synthesized complexes of \(\text{Ca}^{II}\) with \(\text{N-salicylidene and N-(2-hydroxy-1-naphthylidene) amino acid. (Fig-90)}\) The ligand are co-ordinated to the metal ions in a tridentate manner with \(\text{O,N,O}\) donor site.
METAL COMPLEXES WITH TETRADENTATE LIGANDS

The tetradentate schiff base is derived by the condensation of salicylaldehyde with ethylene diamine in 2:1 proportion. The copper(II) complexes \( \left[ \text{Cu}(\text{Salen})_2 \right] \) have been found to be a five-coordinated dimer containing noncoplanar Cu-O bonds. It has been possible to prepare a large number of binuclear complexes containing both similar and dissimilar metal atoms from these mononuclear complex ligands. The general method involves the mixing of the chloroform solution of the complex ligand with an alcoholic solution of metal halides. All the mononuclear complexes of Copper(II) are antiferromagnetic and fit into the Bleamy-Bowers model. But the heteronuclear complexes of Cu(II) with other paramagnetic or diamagnetic metals and nickel(II) with other paramagnetic metals have normal magnetic properties obeying Curie-Weiss law over the temperature range 80-400 K.

A number of complexes of the type \( \left[ \text{Cu(TBS) Cu X}_2 \right] \) (TBS = tetradentate schiff base, \( X = \) halogen have been reported by Sinn et.al.\textsuperscript{203-205}. A series of tetradentate schiff base copper(II) complexes have been reported\textsuperscript{206-208} Bhattacharya et.al. The complexes have \( \left[ \text{Cu(TBS) Cu X}_2 \right] \) and \( \left[ \text{Cu(TBS) Cu(A-A)} \right] \) (ClO\textsubscript{4})\textsubscript{2} types, (A-A = tertiary diamine like 2,2'-bipyridyl, 1,10-phenothroline and 2,2'-pyridyl benzimidazole, TSB = symmetrical or unsymmetrical tetradentate schiff base and \( X = \) Cl. The TSB (symmetrical) prepared by the condensation of salicylaldehyde or 2-hydroxyacetophenone, ethylene diamine, 1,3-propylene-diamine while the unsymmetrical TSB ligands are derived from the condensation of salicylaldehyde, 0-phenylenediamine and 2-hydroxy acetophenone, ethylenediamine, 1,3-propylene diamine with salicylaldehyde at one end and 2-
hydroxy acetophenone at other end. Mixed diaurine-diamine ligands obtained from 2-hydroxy-1-naphthaldehyde and benzoyleacetone and their diamagnetic complexes with Ni(II) and Pd(II) have been synthesized. But the Copper(II) complexes are paramagnetic in nature and the magnetic moment value very close to the spin only value, expected for one unpaired electron. The ONNO donor schiff bases derived from 2,5-dihydroxy acetophenone/benzophenone with NN' - hexa methylenediamine form square planar complexes of Cu(II), Co(II) and Ni(II) ions (Fig -91).

Biacetyl (bis-benzoylhydrazone), schiff base coordinated to the trivalent rare earth metals through (Fig -92) the inolic oxygen and azomethine nitrogen atoms. The i.r. and ¹H nmr study have shown that the schiff base bis (blacetyl acetone) benzidine in its enol form acts as a tetradentate ligand (Fig -93). Distorted tetrahedral Cu(II) complexes derived from some diamines with salicylaldehyde and pentane 2,4-dione, where as Co(II) complexes are found to be pseudo tetrahedral.

The metal complexes with a tetradentate ligand as shown in (Fig-94) have reported by Abu-EL-wafa et.al. where M = Mn(II) and Cu(II) and Z = (CH₂)₂-O-C₆H₄ with composition [MnL(H₂O)₂] and [CuL.H₂O] respectively. An isomonomeric structure is suggested for [MnL(H₂O)₂] while polymeric structure is suggested for copper complex. Severo et.al. have reported Cu(II) complexes with tetradeante ligands, 1-5-diphenyl-3-ethoxy carbonyl formazan and 1,5-diphenyl-formazan 3-carboxylic acid. Woon et.al. have reported mononuclear and polynuclear complexes with potentially
tetradentate hydrazone ligands \((R'R'C:NN:CRR', R = CH_3, R' = 2 - pyridyl, 6 - methyl-2-pyridyl, 1-methyl-2-imidazolyl)\). The tetradentate Schiff bases derived from reaction of diamines with dihydroxybenzophenone form copper complexes.

Mahapatra et al. have reported Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Hg(II) with various tetradentate Schiff bases. The Schiff base \(^{225}\) 2-salicylidene acts as a tetradentate ligand with binuclear metal complexes (Fig. 95, 96). The Cu(II) complex has tetrahedrally distorted square planar. Das and Dani have reported\(^{226}\) hetero binuclear Schiff base complexes of Ni(II) with Zn(II) or Cd(II). The composition has \([\text{Nil. MX}_2]\) (Fig. 97) where \(LH_2 =\) tetradentate Schiff base derived from salicylaldehyde with O-phenyl diamine and \(X = \text{Cl, NO}_3, \text{ClO}_4\).

The Schiff bases obtained from 2-acetyl-1-naphthol, salicylaldehyde, 2-hydroxyacetophenone, 2-hydroxy propiophenone or 2-hydroxy-1-naphthaldehyde with suitable diamines form\(^{227-228}\) tetradentate ONNO donor ligands of Cu(II) and Ni(II) complexes (Fig. 98, 99). The abnormal magnetic moment in some complexes indicate antiferromagnetic exchange. Absence of any significant interaction between the \(^\pi\)-orbital of the ligand through the metal ion \(^d\) orbital has been proposed from a study\(^{229}\) of binuclear Cu(II) complexes involving unsymmetrical tetradentate Schiff bases. Binuclear Cu(II) complexes of the type \([\text{Cu(TSB) Cu X}_2]\) and \([\text{Cu(TSB) Cu(A-A)}](\text{ClO}_4)_2\) (Fig. 100, 101) have been prepared (\(X = \text{Cl, ClO}_4; \text{TSB} = \) various unsymmetrical Schiff bases obtained from the condensation of ethylene diamine or 1,3-propylene diamine, with salicylaldehyde at one end \(A - A = 2,2'\)-bipyridyl, 1,10-phenanthroline or 2-(2'-pyridyl)
Fig - 102

Fig - 103

\[ M = \text{Cu}(II), \text{Ni}(II) \]
The magnetic moments of the complexes at room temperature are found to be much lower than expected for two Cu(II) ions. Values of Cu(II) complexes of bis(Salicylidene) - O-alkyl-1-amidinourea (Fig-102) much less than corresponding parent O-alkyl-1-amidino urea moiety.

Eirader et al. using Ni(II) and Cu(II) complexes with the schiff base derived from 3-formyl salicylic acid and ethylenediamine as the starting parent complex have prepared a few bimetallic complexes of Cu(II) and Ni(II) (Fig-103) with tetravalent metal ions as Si(II), Sn(IV), Te(IV) and Ti(IV). Jalger et al. have studied some metal complexes with tetradentate ligands. Chose et al. prepared schiff base 3-hydroxyl amino-2-butane-1-benzoyl hydrazone and their metal complexes. The schiff base ligand derived from acid hydrazides and acetylacetone form tetrahedral complexes with oxouranium(VI) and hydroxy Zirconium(IV). Morozon et al. have studied metal complexes with a tetradentate ligand. The ligands act as N₂O₂ donor. The structure of the complex is explained by the conformational mobility of the coordination sphere. Chose has reported metal complexes with a dibasic tetradeutate ligand, O-OH₂₆₄CR: NR': CR C₆H₄OH - O, (R = CH₃, C₆H₅, R' = (CH₂)n, (n = 2-4), P-C₆H₄. The metal complexes with schiff base ligands, N,N'-disalicylidene ethylene diamine or N,N'-disalicylidene, 2-propane diamine; N,N-bis (3-aminopropyl)amine, prepared by Handa and his coworkers.

Balasubramanium and his coworkers form Co(II) macrocyclic complexes with highly unsaturated ligands derived from 5-methyl-1,2,9,10-tetraphenyl-3,4,7,8-tetrazadeca 2,4,6,8-tetraen-1,10-dione.
with some diamines (Fig-104). The Schiff bases derived by the condensation of 1,8-diamino naphthalene with salicylaldehyde or vanillin (Fig-105) form dioxouranium(II) thorium(IV) metal complexes, the same authors also prepared another Schiff base from 2,6-diminepyridine and their metal complexes. Verma and his coworkers have synthesized ONNO donor tetradentate Schiff base complexes with dioxouranium(IV). The Schiff base is prepared by the condensation of diacetyl with 4-methoxy benzoyl hydrazine (Fig-106). Ghose and coworkers have reported zirconium metal complexes with tetradentate ligands (Fig-107). Zaitsev et al. have reported Cu(II) complexes with a tetradentate ligand, 2-hydroxy-5-sulphamidophenyl azo acetylacetamides.

Jahagirdar et al. have studied Co(II), Ni(II) and Cu(II) complexes of malonoanilic acid hydrazones. IR data show that the ligands behave in a dibasic tetradentate manner in all the complexes except in the case of Cu(II) complexes where they act as dibasic tridentate ligands with O:N:O donor sequence. Co(II) and Ni(II) complexes have octahedral geometry while Cu(II) complexes have square planar structures. Kwiatkowski et al. have studied the reaction of 4-chloro or 4-methyl-2, 6-diformyl phenol with 7-amino-4-methyl-5-azahept-3-en-2-one which leads to the formation of either quadridentate mononucleating or heptadentate binucleating Schiff base ligands depending on the reaction condition. Nickel complexes with both type of ligands have been obtained and characterised by Physico-chemical measurements.

Mahapatra and coworker have synthesized ONNO donor
Fig-108

\[ R = \text{Et, Ph} \]
\[ n = 3, 4, 6, 8, 12 \]

Fig-109
tetradentate schiff base complexes of Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Hg(II) and characterised them by physico-chemical techniques. Mrs. Shukla and her coworker have reported the synthesis and characterisation of tetradentate ligand di (O-aminophenyl) disulphide (Fig-108) containing two sulphur and two amino groups and its complexes with Ni(II), Co(II), Mn(II) and Cr(II).

The twelve tetra coordinated macrocyclic complexes of Cu(II), Ni(II) and Co(II) have been synthesized by Srivastav and his co-worker. Which possess the general formula \([MLX_2]\) and \([\text{Col}(\text{H}_2\text{O})_2]X_2\) where \(L\) = title macrocyclic ligands; \(M = \text{Co(II)}\) and \(\text{Ni(II)}\) and \(X = \text{Cl}^-, \text{SCN}^-, \text{BF}_4^-\) and \(\text{ClO}_4^-\). The ligand behaves as a tetradentate \(N_2O_2\) donor macrocyclic ligand (Libenzo -(dinitrobenzo), 5,8-diaza, 1,12-dioxocyclotetradeca 4,8-diene) and it forms complexes of Cu(II) and Ni(II) which are assigned to have square planar structures, whereas Co(II) complexes an octahedral by the axial coordination of two water molecules. Prasad and his coworkers have reported Zn(II) complexes of large ring tetrazamacrocycles of composition \([\text{ZnLCl}_2]\) (Fig 109) derived from the condensation of benzil or 3,4-hexanediene and diphenyl diamines such as 1,3-diaminopropane, 1,4-diaminobutane, 1,6-diaminohexane, 1,8-diamino-octane and 1,12-diaminododecane. Long range binuclear Copper(II) chelates with tetradequate schiff base derived from heterocyclic-diketones and aromatic diamines have been prepared. The ligands coordinate through all the azomethine 'N' atom and enolic 'O' atoms after deprotonation.

K. Sahu has synthesized the complexes of Ni(II), Co(II),
I. $R_1 = R_2 = R_3 = R_4 = \text{CH}_3$

2. $R_1 = R_2 = R_3 = R_4 = \text{H}$

3. $R = \text{CH}_3$, $R_2 = R_3 = R_4 = \text{H}$

4. $R_1 = R_2 = \text{CH}_3$, $R_3 = R_4 = \text{H}$
Mn(II) and Cu(II) of the type \( [M_2L_2 \times H_2O] \) with chelates of 1,2,5, 6-tetraphenyl-3, 4-diaza-1,6-dihydroxyimino-2, 4-hexadiene. IR spectra show coordination of the ligand with the metal ions through azomethine nitrogen atoms in a bi-dentate manner. Electronic spectra and magnetic moment suggest dinuclear square planar structure about the metal ion. The cadmium(II) complexes of the type \( [CdLNO_3]NO_3 \) and \( [CdLCl_2] \) (\( L = \) tetrazamacrocyclic having 12 to 32 membered ring) have been prepared\(^{252}\) by the 2:2 cyclocondensation of 2,3-pentanediene with 1, n-diaminoalkanes Viz. 1,2-diaminoethane, 1,3-diamino-propane, 1,4-diaminobutane, 1,6-diaminohexane, 1,8-diamino octane or 1,12-diaminododecane (Fig-110). These physico-chemical studies indicate that the ligands act as tetradentate and coordinate to metal ion through nitrogen atoms of the ligands.

Binuclear Cu(II) complexes of \( [M_2L_2X_4] \) type, where \( L = 4,4'\)-di(furan-2-formylimino) diphenyl sulphone (FD); \( X = Cl, NO_3 \) and \( CH_3COO \) having octahedral environment around metal ions, have been reported\(^{253}\). Characterisation of the complexes has been done on the basis of elemental analysis, conductivity, magnetic, i.r., U.V. and e.s.r. spectral measurements. The complexes of Ni(II), Co(II) and Cu(II) with 1,4,8,11-tetramethyl-1,4,8,11-azacyclotetradecane (Fig-111) has interesting and peculiar properties. The spectral data\(^{254}\) indicate that the Ni(II) and Cu(II) complexes are square-planar and pentacoordinated whereas Co(II) complex is penta-coordinated high-spin species.

The polydentate macromolecular ligands\(^{255}\) possessing carboxyamide, -NH-CO-A-COOH functional set where A is an ethylenic or ortho-phenylene linkage moiety not only have fungicidal character. But also they
Fig-112

Fig-113

Fig-114

Fig-115 (a)

Fig-115 (b)

M = Cu(II), Ni(II), Co(II).
form coordination complexes with Co(II), Ni(II), Zn(II), Cu(II) and Fe(II) ions. The reaction of $\left[\text{CuL}_2 \text{H}_2\right]$ (HL = B-alanine) with formaldehyde and ammonia at pH 6.8 - 8.8 gives the complex compound given in (Fig-112). The chelate molecules are linked in chains by a carbonyl oxygen-copper interaction which results in square pyramidal coordination of the copper ion.

Bivalent metal complexes of the type $\text{MLnB}$ (where $\text{M} = \text{Mn(II)}, \text{Fe(II)}, \text{Co(II)}, \text{Ni(II)}, \text{Cu(II)}, \text{Zn(II)}$ and $\text{Cd(II)}$, $\text{LH}_2 = 2,2'$-dihydrooxanilide; $\text{B} = \text{water or pyridine}, n = 0$ or $2$ have been synthesized by Athappan et. al. In all these complexes the ligand is found to be tetradentate coordinating through phenolic oxygen and amino nitrogens. Cu(II) complex is reported to be square planar and monomeric (Fig-113) while other anhydrous complexes are assigned to be polymeric with high spin octahedral configuration (Fig-114).

The Schiff base (Fig-115) derived from 3-formylsalicylic acid and carbohydrazide form mononuclear complexes (Fig-116) with Cu(II), Ni(II) and also form dinuclear complexes (Fig-117) with the same metal atoms. In the former case carboxylate groups do not take part in coordination but in the later case it coordinates and the phenolic oxygen atoms act as a bridge. A few homo/heteno trinuclear complexes of the type $[\text{M Ni M (BTDO)}_2 \text{X}_2 (\text{H}_2\text{O})_4 \text{nH}_2\text{O}]$ where $\text{M} = \text{Ni(II)}, \text{Co(II)}$ and $\text{Cu(II)}$, $\text{X} = \text{Cl}^-$ or $\text{NO}_3^-$, $n = 0$ or $0.5$ and $\text{BTDO} = 1,3,5,7$-octatetraene have been synthesized by Panda and coworkers.

The chelate compounds of $\text{La(III)}, \text{U(III)}, \text{Pr(III)}, \text{Nd(III)},$
\[ \text{Fig - 117} \]

\[ \text{Fig - 118(A)} \]

\[ \text{Fig - 118(B)} \]

\[ \text{Fig - 119} \]

\[ M = \text{Cu(II), Ni(II), Co(II)}. \]
Dy(III), Sm(III), Eu(III), Yb(III) and Lu(III) with tetradeinate N,N′-ethylene-bis-(2-aminobenzamide) has been reported by Swamy et al. Macroyclic complexes of Cu(II), Ni(II) and Zn(II) with 22-membered macrocyclic quadridentate schiff base ligands derived from the condensation of terphthaldehyde and 4-amino-3-hydrazino-5-mercapto-1,2,4-triazole have been investigated by Tejurkar and coworkers. The electronic spectra indicate the Cu(II), Ni(II) and Zn(II) complexes to be distorted octahedral.

Two series of uranyl-thioether complexes of the type UO₂LMe OH(III) and UO₂L (IV) with schiff base pentadentate and hexadentate ONS donor ligands (Fig-118a,b) derived from the condensation of salicylaldehyde and bis, (2-aminophenyl) disulphide or 1,2-di(2-aminophenylthiol) ethane have been synthesized by Chattopadhyay and coworkers. The complexes of Cr(II), Mn(II), Fe(II), Cu(II), Ni(II) and Zn(II) with macrocyclic tetradentate ligand 5, 12-dioxa-7, 14-dimethyl-1, 4,8,11-tetraazacyclotetradeca-1,8-diene(Fig-119) derived by the condensation of 1,2-diamino ethane and alkylacetoacetate in methanol have been studied by Shakir et al. The complexes of Cr(II), Mn(II), Fe(II), Cu(II) and Zn(II) an suggested to be octahedral whereas Ni(II) is assigned to be square planar.

The complexes of Cr(III) have been synthesized by Pal et al. using bidentate, tridentate and tetradeinate ligands of N,N′,bis-2-aminoethyl 1,3-propanediamine, diethylenetriamine and tri ethylene-tetramine. The chromium complex is suggested to be octahedral. Dutta and his coworkers have synthesized a novel tetranuclear macrocyclic nickel(II) complexes [Ni₄L (μ-OAC)₂(OAC)₄(H₂O)₄] with a
Fig-120 \quad M = \text{Ni(III)}, \quad X = \text{Cl, Br, I, NO}_3

Fig-121
polydentate ligand obtained from the condensation of 2,6-diformyl-4-methyl phenol and triethylenetetramine. The acetate bands in the complex observed at 1570 $\nu$ OCO (a sym) and 1400 and 1330 cm$^{-1}$ ($\nu$ OCO (SYM)). The magnitude of the differences between $\nu$ OCO(SYM) and OCO stretches ($\Delta\nu$) indicates the presence of bridging ($\Delta\nu = 170$ cm$^{-1}$) as well as monodentate ($\Delta\nu = 240$ cm$^{-1}$) acetates. De and his coworkers have investigated the complexes of Co(II) with bidentate and tetradentate Schiff base ligands derived from the condensation of salicylaldehyde, 3-carboxysalicylaldehyde with ethylenediamine, 0-aminophenol and 2,2-dipyridyl. Electronic spectra reveal the metal complexes to be octahedral.

Saha and Maji have studied Zn(II) complexes of the type ZnL$_2$ (H$_2$O)$_6$ with 3-co-carboxyphenyl)-1-phenyltriazene -1-oxide(LH$_2$). In all the complexes triazene 1-oxide behaves as a dibasic tetradentate ligand showing a marked tendency to form mixed ligand complexes. The ligands derived from crown ether, oximes and hydrazines encapsulate the central metal ion which exhibit some interest in properties. Trinuclear acetylacetone dioximate nickel(II) form complexes of the $[\text{Ni (aado)}_2 X_2 (\text{H}_2\text{O})_8]$ ($X = \text{Cl}^-$, Br$^-$, I$^-$ or NO$_3^-$ aado = acetylacetorodioximate ion) (Fig-120). The cadmium(II) complexes of the type $[\text{CdL NO}_3]$ and $[\text{CdLCl}_2]$ CL = tetraazamacrocyclic having 12 to 32 membered ring ) have been prepared by the 2:2 cyclocondensation of 2,3-pentanediene with 1,n-diaminoalkanes viz. 1,2-diaminoethane, 1,3-diaminopropane, 1,4-diaminobutane, 1,6-diaminohexane, 1,8-diaminooctane or 1,12-diaminododecane (Fig-121). The physicochemical studies indicate that the ligands act as tetradentate and coordinate to metal ion through nitrogen atoms of the ligands.
The complexes of oxomolybdenum(IV), (V) and (VI) with diamines of the type \([\text{Mo} \, 0 \,(\text{L})], \, \text{Mo}_2 \, 0_2 \,(\text{L})_2] \) and \([\text{Mo}_2 \, 0_2 \,(\text{L})] \) \( \text{L} = 1,2\text{-bis(2-aminobenzylideneam} \text{nins) propane} \) (Fig-122) have been synthesized and characterized by Perumal Subramani\(^{284}\) and co-worker.

Metal complexes of Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Hg(II) have been synthesized and characterized\(^ {285}\) with the ligand 1,8-dibenzoyl-2,7-diphenyl-3,6-diazaoctane and 1-9-dibenzoyl-2,8-diphenyl-3,7-diazanonane, Both ligand behave as \(\text{O} \, \text{N} \, \text{N} \, \text{O} \) tetradeutate donors.

Metal complexes of Cu(II), Ni(II), oxovanadium(IV), Mn(II), Zn(II), Cd(II), Cd(II), Hg(II), Zro(II) and dioxouranium(VI) ions with a new tetraduarte schiff base derived from 3-salicylideneacetone and anthranilic acid (Fig-123) have been synthesized and characterized\(^ {286}\). The IR, UV and magnetic data suggest a six-coordinate octahedral geometry for the complexes.

Mahapatra et al.\(^ {287}\) have been reported the bis-azodye ligands as bis \([4,4'-(8'-\text{hydroxyquinolyl}-5')-\text{azo-phenyl}]\) methane and bis \([4,4'-(8'-\text{hydroxy quinolyl-5'})-\text{azo-phenyl}]\) sulphone form dinuclear complexes with divalent metal ions. The Co(II) and Cu(II) complexes are either octahedral or distorted octahedral, both the Ni(II) complexes are square planar and the Zn(II), Cd(II) and Hg(II) are tetrahedral configuration. They have also reported\(^ {288}\) a polynuclear complexes with bis-bidentate ligands 1-(2-carboxyphenyl-azo)-2,4-dihydroxy-benzone and \(4,4'-\text{bis}(2,4\text{-dihydroxyphenyl}-1\text{-azo-3,3'}\text{dimethyl})\) - diphenyl having \(\text{O} \, \text{N} \, \text{N} \, \text{O} \) and \(\text{O} \, \text{N} \, \text{N} \, \text{O} \) potential donor atoms.
Schiff bases derived from 4,4'-diaminodiphenylsulphone with Salicylaldehyde and 2-hydroxy-1-naphthaldehyde behave as ON - X - NO donor doubly-bidentate ligands and form dinuclear complexes with divalent Co, Ni, Cu, Zn, Cd and Hg ions have been reported by Mahapatra & Co-worker\textsuperscript{289}. The Co', Ni', and Cu' complexes are found to be either octahedral or distorted- Octahedral, whereas a tetrahedral stereochemistry can be assigned to the Zn', Cd' and Hg' complexes. They have also reported\textsuperscript{290} complexes of Cobalt, Nickel, Copper, Zinc, Cadmium and Mercury(II) with chelating azo dye ligands, 1-(2'-hydroxyphenyl-1')-azo-1-cyanoethyl acetate and 1-(2'-carboxyphenyl-1')-azo-1-cyanoethyl acetate. Mahapatra and Co-worker\textsuperscript{291} have also synthesized complexes with bivalent Co, Ni, Cu, Zn, Cd and Hg with bis-bidentate azo dye ligand having ONNO donor atoms, 4,4'-Bis (ethylcyanoacetate - 2'-azo) diphenyl.
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