Chapter I

General Introduction
1.1 Introduction

The coordination chemistry involving Schiff base ligands has occupied an important position in modern inorganic chemistry. The importance of Schiff base and their complexes has been well emphasized by many researchers.\textsuperscript{1,2} They are known to possess various biological activities. The Schiff bases are those organic ligands which contain azomethine (-C=N-) group and possess suitable bonding characteristics when react with metal ion giving metal complexes. Metal complexes with Schiff bases have been studied extensively due to flexible nature of structure of Schiff bases which ultimately depends upon the nature of reacting groups. The metal ligand formation is due to donation of electrons from nitrogen, oxygen or sulphur homo or heteroatoms present in the ligand. Recently there has been attraction in the field of metal complexes with tridentate and tetradentate Schiff bases. These ligands have a tendency to form dimeric or polymeric complexes with divalent metal ions resulting in the formation of compounds having distinguishable magnetic and spectral properties. A number of reviews have been published in coordination chemistry of Schiff's base metal complexes.\textsuperscript{3-18}

The complexing properties of Schiff bases with metal has led to the formation of various complexes. Scientists have ventured into the detailed study of these complexes with the help of various physico-chemical methods. Many investigators have characterized the Schiff base complexes by employing diverse techniques like electronic transitions. Infra-red spectral studies, magnetic susceptibility, ESR, X-ray diffraction in recent years.
A brief review of the literature on Schiff bases and substituted Schiff base complexes of transition elements are reported. The review consists of synthesis of various Schiff bases and their metal complexes along with few characterising techniques. The necessity of such review is also felt since most of the discussion and experimental findings can be supported with authenticity. Hence brief review of work published in the past related to the present work on complexes of transition metals with Schiff base, is therefore discussed here.

### 1.2 Historical account of Schiff’s Bases

Metal Schiff’s base complexes are known since the midnineteenth century\(^\text{19}\) and even before the general preparation of Schiff’s base ligands themselves.\(^\text{20}\) In 1840, dark green crystalline copper complex bis (salicyladimine) Cu(II) by the reaction of cupric acetate, salicylaldehyde with aqueous ammonia was synthesized by Ettling et.al.\(^\text{20}\)

![Schiff base structure](image)

Further, Schiff\(^\text{21}\) defined the composition of metal complex with this ligand by establishing the 1:2 metal ligand ratio in copper complex derived from N-aryl-salicylaldimine and prepared the complex from Schiff’s base derived from urea and salicylaldehyde.\(^\text{22}\) Delepine\(^\text{23}\) in 1899 synthesized complex [I] with R = methyl group or benzoyl group by reacting the metal acetate, salicylaldehyde and primary amine in alcohol and suggested 1:2 stoichiometry. Zelzsche et.al.\(^\text{24}\) reported the
coloured complexes of transition metals with Schiff's bases of substituted salicylaldehyde. In 1931, Dubsky and Sokol\textsuperscript{25} synthesized N-N'-bis salicylidene-ethylenediamino Cu(II) and Ni(II) complexes. However, there was no comprehensive, systematic study until the preparative work of Pfeiffer and associates\textsuperscript{26-34} in the years 1931 to 1942. During this period a systematic study was done on complexes of Schiff base derived from salicylaldehyde, o-aminobenzaldehyde and pyrrole-2-aldehyde.

![Schiff base structure](image)

\[ M = \text{Cu(II)}, \text{ Ni(II)} \]

### 1.3 General characteristics of Schiff base

The Schiff bases are those organic ligands which contain azomethine group (R-C=N-). These Schiff bases are generally prepared by condensation of primary amines (-NH\textsubscript{2}) with active carbonyl compounds. They are also known as anils, iminse, with general structure R.CH:N.R' where R and R' are alkyl, aryl, cyclohexyl or heterocyclic radical which may be differently substituted. The general reaction for formation of Schiff base can be represented as:

\[
R - \text{CHO} + R' - \text{NH}_2 \rightarrow \text{RHC = N R'} + \text{H}_2\text{O}
\]

R, R' = alkyl, aryl, cyclohexyl or heterocyclic group.
The Schiff bases are weak bases and are readily hydrolysed by mineral acids but not by aqueous alkali. They form salts by co-ordination of the electrons on nitrogen atom of azomethine group. The Schiff bases derived from lower aliphatic aldehydes are less stable than those derived from aromatic aldehydes. Aliphatic Schiff bases are difficult to isolate due to their tendency to polymerise. Schiff base derived from formaldehyde exhibit tendency to undergo polymerisation.

Schiff bases which are effective as coordinating ligands bear a functional group usually OH, sufficiently near the site of condensation that a five or six membered chelate ring can be formed upon reaction with a metal ion. Because of great synthetic flexibility of Schiff base formation, many ligands of diverse structural type can be synthesized. The size of the chelate ring formed can be controlled by changing the location of the donor atoms and groups to exploit the effect of substitution and steric factors. These products have received considerable attention as model compounds for theoretical studies and as the following reactions, precursors to heterocyclic compounds.

1.4 Synthesis of Complexes

Metal complexes of Schiff bases have been synthesized by one of

1) Reaction of metal salt, salicylaldehyde and amine in solution.
2) The direct reaction of primary amine with a preformed salicylaldehyde-metal complex.
3) The reaction of metal salt, usually in acetate, with a preformed Schiff base in aqueous ethanol or similar solvent.
4) The reaction of primary amine complex of a metal with aldehyde. The corresponding metal complexes of β-ketoamines are prepared in similar way.
The addition of alkali is necessary for some reactions. A base is often added to aid in the removal of an acidic proton from the ligand if required. Potassium, sodium or lithium alcoholate is used for removal of water in reaction. The preparative procedure including the reaction period, temperature and the amount and kind of solvent, vary both with ligands and the central metal ion. The preparation of β-Ketoaminato complexes is more difficult than the corresponding salicylideneiminato complexes\(^{35}\) and it is often necessary to carry out all procedure in an inert atmosphere.

1.5 Complexes with bidentate ligands

The bidentate Schiff base metal complexes have the general formula of the following type

![Complex Structure](image)

The structural variation of these complexes depends on the metal ion involved and also depends on the steric requirements of R group. For example, bis (N-methyl salicyledene iminato) Ni(II) (R = CH\(_3\)) has distorted planar structure\(^{36}\) while Ni(II) complexes with R = isopropyl group has quasitetrahedral structure.\(^{37}\) The Co(II) complexes with R = H or OH possess square planer structure but complexes with R = alkyl or aryl group have tetrahedral structure.\(^{38}\)

Most of the metal complexes have been prepared from bidentate Schiff bases containing O, N donor atoms; they are derived from condensation of salicylaldehyde or substituted salicylaldehyde,
2-hydroxy-1-naphthaldehyde with aromatic amines. The structural formula for ligands depicted in their Schiff base form are.

\[
\text{R} = \text{H, COOH, 4-CH}_3, 3-\text{CH}_3, 2-\text{CH}_3, 4-\text{Cl, 2-Cl}
\]

The ligands are monobasic, bidentate, and coordinate with metal ion through hydroxyl oxygen and imine nitrogen.

Costamagna reported that the Fe(II) complexes with salicylaldehyde and monosubstituted aniline shows anomalously high magnetic moment at room temperature while an antiferromagnetic behaviour at low temperature. A doublet Mossbauer spectrum with a normal isomer shift values for low spin iron (II) at room temperature and presence of hyperfine pattern Mossbaur spectra at 4K with at least a sextuplet and a doublet suggest the existence of at least two sites for the iron atom and having square planar geometry. Mehta et al. studied the complexing behaviour of Vanadyl(II), Cobalt (II) and Ni(II) complexes of salicylaldehyde and substituted aniline. The complexes were synthesized by refluxing, precipitation method at optimum pH. Magnetic and electronic absorption studies provide an information about the bonding of metal ion with ligand. The ESR spectra of Cu(II) complexes gives the value of \( g_{\|} (1.94 - 1.96) \) and \( g_\perp (2.01 - 2.02) \) and follow the trend \( g_{\|} < g_\perp \) indicating presence of unpaired electron in d\(_{xy}\) or b\(_{2g}\) orbital.
The synthesis of Schiff base ligand derived from 2-hydroxy-1-naphthaldehyde and \( p \)-anisidine and its 1:2 derivatives of \( \text{Cu}^{2+}, \text{Ni}^{2+}, \text{Co}^{2+} \) and \( \text{Mn}^{2+} \) complexes were discussed by Chaturvedi et al.\textsuperscript{49}. The structure of the complexes were proposed on the basis of analytical, magnetic and spectral studies. The mononuclear \( \text{Fe(II)} \) complexes\textsuperscript{50} were obtained by bonding the ligand through imine nitrogen and hydroxyl oxygen. The magnetic studies indicate paramagnetic behaviour of all complexes.

The ligands which behave as O, N donor and are derived from 4-Benzoyl, 3-methyl-1-phenyl-2-pyroazolin-5-one and various aromatic amines are reported by Shah et al.\textsuperscript{51}. The complexes of \( \text{Cu(II)}, \text{Ni(II)}, \text{Co(II)}, \text{Fe(III)} \) and \( \text{Cr(III)} \)

\[
\begin{array}{c}
\text{H}_3\text{C} \quad \text{C} \quad \text{N} \quad \text{R} \\
\text{C} \quad \text{C} \quad \text{C} \quad \text{N} \quad \text{R} \\
\text{C} \quad \text{C} \quad \text{C} \quad \text{N} \quad \text{R} \\
\text{C} \quad \text{C} \quad \text{C} \quad \text{N} \quad \text{R} \\
\text{C} \quad \text{C} \quad \text{C} \quad \text{N} \quad \text{R}
\end{array}
\]

\[
R = \text{C}_6\text{H}_5, \\
\quad \text{C}_6\text{H}_5\text{CH}_3 (o), \\
\quad \text{C}_6\text{H}_4\text{CH}_3(m), \\
\quad \text{C}_6\text{H}_4\text{CH}_3(P)
\]

formed are nonelectrolytes. The \( \text{Cu(II)} \) complexes are found to be square planer while all other complexes are octahedral.

The complexes of \( \text{Co(II)}, \text{Ni(II)}, \text{Cu(II)} \) have been reported with heterocyclic Schiff bases derived from aldehyde and \( 2 \)-amino \( 4 \)-phenyl thiazole.\textsuperscript{52} The Schiff bases used were salicylidene-2-amino, 4-phenyl
thiazole (L₁), p-hydroxy benzylidene-2-amino, 4-phenyl thiazole (L₂) and p- hydroxy 4-methyl benzylidene-2-amino, 4-phenyl thiazole (L₃). The Schiff bases L₂ and L₃ are found to be weaker ligands compared to the corresponding derivatives of arylidene-2-aminopyridine. This is ascribed to the low basicity of the nitrogen in the thiazole ring relative to the nitrogen in the pyridine ring. The Cu(II), Ni(II), Co(II), Mn(II), Zn(II), Cd(II) and Hg(II) complexes of 2-salicylideneimino-5-mercapto-1,3,4-thiadizole (H₂SB) were studied by Satpathy et.al.⁵³ Electronic and IR spectral data together with thermal analysis suggest octahedral and tetrahedral configuration for complexes of the type [M(SB)(H₂O)₂] and [M'(SB)], M = Cu(II), Ni(II), Co(II), Mn(II), M' = Zn(II), Cd(II), Hg(II) and Pb(II) complexes. A polymeric structure is suggested for the Mn(II), Co(II), Ni(II), and Cu(II) complexes.

\[
M = \text{Mn(II), Co(II) Ni(II),Cu(II)}
\]

Casellato et.al.⁵⁴ synthesized and characterized a catalytic property of mononuclear and dinuclear complexes of Uranyl(VI), Copper (II), Nickel (II) and were studied by magnetic, IR electronic and X-ray powder diffraction techniques. Copper(II) complex is distorted octahedral and others are intermediate between distorted tetrahedral and
square planar which coordinate via phenolate O and imino N group of the ligand. Some bidentate bifunctional Schiff base complexes of Co(II), Ni(II) and Cu(II) were studied. The complexes such as ML(H₂O)₂ (M=Co, H₂L=O(XC₆H₄(H:N)₂C₆H₄, X = O-OH), CuL (X=O-OH), CuL(H₂O)₂(OAC)₂ (X = H, p-Nme₂, p-OH, p-NO₂), NiL(H₂O)₂Cl₂ (X=p-Nme₂, p-OH, p-NO₂) and CoL(H₂O)(NO₃)₂ (X=p-Nme₂, p-OH, p-NO₂) were prepared. Formation, stoichiometry and stability of the complexes were studied in solution using electronic spectral measurements. CuL(H₂O)₂ (X=O-OH) has tetrahedral geometry whereas the other complexes exhibit a distorted octahedral geometry.

Sharma and his coworkers have prepared Pd(II), Rh(III), Ru(III) and Fe(III) complexes of 2-amino-4-phenyl-5-arylazothiazole and salicylaldehyde. The complexes are of the type Pd(SchB)₂ and M(Sch·B)₂, M = Rh(III), Ru(III) and Fe(III). The Schiff bases coordinate through the azomethine group and deprotonated phenolic group to the metal ion and have been assigned following general structure

Square planar geometry for Pd(II) complex whereas octahedral geometry for all other complexes were suggested.
The Schiff base ligands 2-pyrrole-[N-O-hydroxyphenyl] aldimine derived by condensation of 2-pyrrolecarboxyaldehyde and ortho-aminophenol were studied.\textsuperscript{57,58} They behave either as bidentate monoanionic ligand with the pyrrole nitrogen intact and uninvolved in bonding to the metal ion or as a tridentate dianion using the pyrrolate deprotonated nitrogen, the azomethine nitrogen and the phenolate oxygen in bonding.

Thus complexes of Cu\textsuperscript{2+}, Fe\textsuperscript{3+} and Co\textsuperscript{3+} were obtained with the ligand behave as bidentate monoanion and complexes of Zn\textsuperscript{2+}, Pb\textsuperscript{2+} and Pt\textsuperscript{2+} were synthesized with a ligand as a tridentate dianion. X-ray data indicate that the Zn\textsuperscript{2+} complexes have distorted bipyramidal coordination polyhedron that does not include the pyridine nitrogen atom.

The complexes of the type M\textsubscript{L}Cl\textsubscript{2} (M = Co(II), Ni(II), Cu(II), Cd(II) and M\textsubscript{L}Cl\textsubscript{2} (M = Zn(II), Hg(II), dioxouranium(VI) and Th(IV) with 4-hydrazinobenzofuro [3,2-d] pyrimidine and 4-hydroxy-3-aldehydo di-phenyl have been reported.\textsuperscript{59} The ligand field parameters and $\mu_{\text{eff}}$ value for Co(4.47 B.M.), Ni(2.87 B.M.) and Cu(1.81 B.M.) complexes suggested an octahedral geometry. The spectral and magnetic behaviour of the complexes suggest the halogen bridged octahedral
polymeric structure for Cd(II), Cu(II), Co(II), and Ni(II) complexes. While ligand bridged polymeric octahedral structure for Zn(II), and Hg(II) complexes.

The carbonyl bridged polymeric metal chelates of some quinolinol containing 2-iminoketones with Cu(II), Ni(II), Co(II), and Cd(II) ions were synthesized by Ibrahim et al. The metal chelates are four coordinate [ML₂Cl]Cl type, where L = 5-(2-imino cyclopentanone), 5-(2-imino cyclohexanone) and 5-(4-imino-1-phenyl-3-methylaxo pyrazoline)-8-hydroxyquinoline. Characterization of isolated complexes has been performed on the basis of elemental and thermal analysis, electronic and IR spectral data as well as conductance measurements. The complexes are polymeric with intermolecular carbonyl bridging. Tetrahedral or square planar stereochemical configuration was suggested for these complexes.

A series of ligands N-alkylmethyl-2-amino cyclopentene-dithiocarboxylate and their Zn(II), Ni(II), and Cu(II) complexes were prepared by Martin and Bereman. The complexes formed were characterized by NMR, ESR and electronic absorption studies.

The polystyrene supported O, N donor chelating ligand and its Ni(II), Co(II), Cu(II), Fe(II), Zn(II), Mo(VI) and U(VI) complexes were prepared by Syamal et al. The metal bound polymers of Co(II), and Cu(II) exhibit square planar structure. The Ni(II), Fe(II), Mo(VI) and U(VI) were octahedral while Zn(II) and Cd(II) were tetrahedral in shape. A thermally resistant coordinated polymer of poly (sulfonediphenyleneterephthalamide) and its Co(II), Ni(II) and Cu(II) complexes of salicylaldehyde, 2-hydroxy-1-naphthaldehyde showed enhancement in the thermal stability of polymers in comparison to the armid ligand.
The complexes of Cu(II), Ni(II), Co(II), and Zn(II), with 2-acetylenethiophene-anthranilic acid, 2-aminothiophenol are non-electrolytes, having 1:2 (M:L) stoichiometry.\(^6\) The ESR spectra of Cu(II) complexes show a sharp band corresponding to the value of \(g = 2.06\) which is in agreement with the magnetic susceptibility value for Cu(II) ion required for one unpaired electron. The Cu(II) and Ni(II) complexes are square planar while Co(II) and Zn(II) complexes are octahedral in nature. The antibacterial activity of ligand enhances several folds on complexation due to faster diffusion of metal complexes as a whole through the cell membrane.

Binucleating macrocyclic ligand comprised of two molecules of 2,5 diformylfuran and two molecules of 1, 3-diaminopropane have been synthesized as Co(II), Ni(II), and Cu(II) complexes by template reactions.\(^6\) On the basis of various spectral studies the 20 membered macrocyclic complexes can be described as having six coordinate octahedral structures where ligand is bonding through the nitrogen of 1, 3-diaminopropane and the oxygen of the furanyl moiety. The elemental analysis and molecular ion peak from the mass spectra confirm the proposed 2:1 metal ligand stoichiometry.

Goudar and his coworkers\(^6\) have synthesized few metal complexes of VO(IV), Mn(II), Fe(III), Ni(II), Co(II), Cu(II), and Zn(II) with 3,4-methylene dioxybenzalidene-2-amino 4,5,6,7-tetrahydrobenzothiazole and characterized by magnetic susceptibility, IR, electronic, NMR, ESR, Mossbaur, Thermal and X-ray powder diffraction studies. From electronic spectral data, various ligand field parameters have been calculated for Co(II) complex indicate tetrahedral geometry of the complex. The X-ray diffraction study of Cu(II) complex shows body centered cubic structure with lattice constant \(a = 10.43\text{Å}\).
The antibacterial activity of all complexes indicate they have antitumour activity greater than the Schiff base ligand.

The several mononuclear and dinuclear Cu(II), Ni(II), and Co(II) complexes of 3-formylsalicylic acid and carbohydrazide were prepared by Satpathy et al. The magnetic and ESR spectral study indicate the antiferromagnetic character of dinuclear Cu(II) complex. The mono and dinuclear Cu(II) complexes exhibit maximum fungitoxicity in comparison to corresponding Co(II) and Ni(II) complexes. The complexes of Ni(II), Co(II) and Cu(II) of 3,5-diacytelyl, 1,2,4-triazole and corresponding aniline were prepared by template condensation. The dinuclear nature of the complexes have been demonstrated by FAB mass spectrometry and magnetic character, which indicate the presence of antiferromagnetic interaction.

Nazimuddin et al. have synthesized Ni(II), Cu(II), Zn(II) and Cd(II) complexes of pyrrole-2-carboxyaldehyde Schiff base of 5-alkyl esters of dithiocarbazic acid having general formula [Ni(HL)₂], [Cu(HL)x] and [ML]*H₂O (H₂L = pyrrole-2-aldehyde-5-methyl and 5-benzylthiocarbazates) X = Cl or Br, M = Ni(II), Cu(II), Zn(II) or Cd(II). The ligand coordinates as NS bidentate chelating agent in [Ni(HL)₂] and [Cu(HL)x] and as tridentate NNS chelates in [ML] (M= Ni(II), Cu(II), Zn(II) or Cd(II)). Both the [Ni(HL)₂] and [NiL] complexes are diamagnetic and square planar. Based on magnetic and spectroscopic evidence thiolate sulphur bridged dimeric square planer structure for [Cu(HL)x] and [ML] (M = Ni(II) or Cu(II)) where as the complexes of the type ML((M = Zn(II) or Cd(II)) are polymeric and have octahedral structure.

The X-ray powder crystallographic studies of mononuclear and binuclear Cu(II) complexes with Schiff base was studied by
The complexes were of type (CuL) and [(CuL₂)Cl₂]
[HL-2-hydroxy-1-naphthylmethyl-(x-substituted)aniline] where x = H, Me, Ome, Ph and Cl. The lattice constants were determined with accuracy of 0.01Å. All the mononuclear complexes are tetragonal while binuclear complexes have orthorhombic symmetry.

The chelation behaviour of the Schiff base derived from sulfadiazine viz. 4-[(2'-pyridyl-methyl)imino]-N-(2'-pyrimidyl) benzene sulphonamide with Cu(II) ion was studied. The complex is MCl₂·2H₂O type. The ligand is bonded to the metal ion via azomethine and pyridyl nitrogen leading to octahedral configuration.

The Co(II), Ni(II) and Cu(II) complexes of thiophene-2-aldehyde-4-chloro / bromoaniline indicate 1:2 metal ligand stoichiometry. The molar conductance of thiophene-2-aldehyde-4-chloroaniline complexes confirm the bi-bivalent electrolytic nature while that of thiophene-2-aldehyde-4-bromoaniline complexes of cobalt and nickel suggest non electrolytic nature. The magnetic moment of all complexes indicate high spin octahedral geometry. Anomalous complexes of transition metal ion obtained, when 2-furfurylidene-p-nitroaniline (HL₁) and 2-furfurylidene-m-nitroaniline were used. The magnetic moment of all complexes of HL₁ type indicate high spin octahedral geometry while for HL₂, tetrahedral structure of Co(II) and square planar structure for Ni(II) and Cu(II) complexes was suggested. The fungistatic activity of the metal chelates was found to be in order of Cu > Ni > Co.

The Co(II), Ni(II) and Cu(II) complexes with 4-hydroxy-3-aldehydodiphenyl and substituted aniline has been reported. The magnetic moment of Cu(II) complexes (1.1 – 1.4 B.M.) and Ni(II)
complexes (diamagnetic) indicate square planer geometry. The magnetic moment of Co(II) complexes (4.2 – 4.5 B.M.) suggesting tetrahedral geometry around metal ion.

When quinolin-2-carboxyaldehyde condensed with 2-aminophenol behave as bidentate ligand and form complexes with Co(II), Ni(II), Cu(II), Fe(III) metal ions. It gives tetrahedral geometry for Co(II), Ni(II) and Cu(II) complexes while Fe(III) complexes shows octahedral dimeric structure. The physicochemical characterization of Cu(II), Ni(II) and Co(II) complexes of ethyl-methyl ketone-2-aminophenol have been described and formulated as $[MLCl_2(H_2O)_2] \cdot 2H_2O$ and $[ML(H_2O)_2]Cl_2 \cdot 2H_2O$. The magnetic moment value for Cobalt (5.02 B.M.), Nickel (2.97 B.M.) and Copper (1.87 B.M.) complexes indicate that cobalt and nickel complexes are octahedral while copper complexes are square planar. The biological activity of all complexes shows that copper complexes are more active than cobalt and nickel complexes (Cu > Co = Ni) and also the metal complexes exhibited more activity than the Schiff base alone.

Dubey and his coworkers have synthesized two types of complexes of Co(II), Ni(II) and Cu(II) with Schiff base derived from furfuraldehyde and 4-amino-5-mercapto-S-triazole (AMT), 4-amino-5-mercapto-3-methyl-S-triazole (AMMT), 4-amino-3-ethyl-5-mercapto-S-triazole (AEMT) and 4-amino-5-mercapto-3-n-propyl-S-triazole (AMPT). All the complexes were characterized by physicochemical methods. Octahedral geometry for Co(II), and Ni(II) complexes where as square planar geometry for Cu(II) complexes was suggested.

Few complexes of Ni(II) and Cu(II) with bidentate ligand furfurylidene-2-aminopyridine have also been reported by non-
involvement of pyridine nitrogen in coordination. The magnetic moment of Nickel (diamagnetic) and Copper (1.84 B.M.) shows square planar geometry around metal ion. Both the complexes are found to be biologically more active than ligand.

Reiss et.al\textsuperscript{80} have synthesized metal complexes with 3-Aminobenzofuran and salicylaldehyde. The complexes are [ML(OAC) \cdot 2H\textsubscript{2}O] type where M = Co\textsuperscript{II}, Ni\textsuperscript{II}, Cu\textsuperscript{II}, Zn\textsuperscript{II} and Cd\textsuperscript{II}. The magnetic moment of Co\textsuperscript{II} (4.54 B.M.), Cu\textsuperscript{II} (1.86 B.M.) indicate tetrahedral and square planar geometry respectively. The Ni\textsuperscript{II}, Zn\textsuperscript{II} and Cd\textsuperscript{II} complexes are diamagnetic and found to have four coordination numbers. The EPS spectra of Cu\textsuperscript{II} complex gives anisotropic parameter $g_{\parallel}$ (2.24) and $g_{\perp}$ (2.07) suggest a tetragonal geometry specific for Cu\textsuperscript{II} in square planar coordination.

1.6 Complexes with tridentate ligands

Most of the metal complexes prepared from tridentate Schiff bases containing ONO, ONN or ONS donor atoms. They have the general formula

\begin{center}
\includegraphics{complex.png}
\end{center}

The magnetic behaviour of the metal complexes of tridentate Schiff base are depend upon the structural nature of substituted group and the presence or absence of ligand occupying the fourth coordination sphere. The transition metal ions viz. Cu(II), Ni(II), Co(II), Fe(II),
Mn(II), Zn(II), VO(II), UO₂(II), form complexes with tridentate Schiff bases. The vacant coordination positions are occupied by the solvent molecules or by bridging donor atoms in the binuclear complexes.

The complexes obtained from tridentate ONO donor Schiff bases show low magnetic moment for number of copper complexes than its spin only value (S=½). This has been attributed to dimerisation in the solid state leading to copper-copper interaction. Three isomers are suggested for these complexes.

Isomer I

Isomer II

Isomer III

A cursory examination revealed that transition metal ions formed coloured complexes with variety of substituted salicylaldehyde Schiff
bases. Pujar et al. have synthesized transition metal ion complexes with ONN donor Schiff base derived from 5-phenylazo salicylaldehyde aniline. These complexes are found to be di or polymeric in nature with tetrahedral geometry around metal ion. The physico-chemical data also suggest the coordination of azo and azomethine nitrogen with involvement of phenolic OH group of the ligand in coordination.

Most of the binuclear complexes have been prepared from tridentate Schiff bases derived from the condensation of salicylaldehyde with o-aminophenol, o-aminobenzoic acids, o-amino benzoyl alcohol, o-amino thiophenols. The structural formula depicted in their Schiff base form are:

\[
\begin{align*}
\text{SAP-H}_2 & \quad \text{SABA-H}_2 \\
\text{SABA'-H}_2 & \quad \text{SASP-H}_2
\end{align*}
\]

Shukla et al. have reported Cu(II), Ni(II), and Co(II), complexes with SAP-H\(_2\) and SABA-H\(_2\) ligands. The magnetic moment of nickel
complexes (1.95-2.36 B.M.) indicate square planar geometry whereas Copper complexes show very low value of magnetic moment (0.94-1.24 B.M.) than its spin only value, planar structure is proposed for these complexes. Cobalt complexes are hexacoordinated and show magnetic moment (5.46-5.97 B.M.) and two absorption bands around 500 nm and 1300 nm. The complexes undergo ligand replacement reaction with pyridine, ammonia, ethylene or propylenediamine. The Cu(II), Ni(II), Co(II), Zn(II), and Fe(III), complexes with SABA-H₂ shows dimeric or polymeric structure.⁸⁷ The Co(II) complex have dimeric structure with two alkoxy bridges. The magnetic moment of Cu(II) complex (1.85 B.M.) at 298 K indicate some extent of antiferromagnetic interaction between two copper centers. All the complexes show an octahedral geometry.

Parashar et.al⁸⁸ studied the mode of bonding between Cu(II), Ni(II) and Co(II) complexes of SAP-H₂, SABA-H₂ by using IR spectrophotometry. The shift in the band position of the groups of ligand involved in coordination has been utilized to estimate metal-nitrogen bond length. The antibacterial activities of ligands and their metal complexes indicate that the activities of ligand on gram positive and gram negative bacteria increases on chelation. The Co(II) complexes also exhibit anti-inflammatory activity.

The Schiff base ligand SABA-H₂ also form complexes with lanthanide and vanadyl metal ions. Lanthanide complexes⁸⁹ are six coordinated. The NMR study indicates that the signals for both COOH and OH group of the ligand vanishes, confirming the complexation of ligand with the lanthanide ion after deprotonation. Molar conductance value indicate that the complexes are 1:1 electrolyte in DMF. The
vanadyl complexes\textsuperscript{90} are dimeric and their oxidative instability depends on the substitutent on the salicylaldehyde ring. The $E_{\text{v}}$ values are $\approx$660 mV indicating that the carboxylate group favour vandyl (IV) binding.

The complexes of Cu(II), Ni(II), Co(II), and Fe(III) with SABA'-H\textsubscript{2} were synthesized by Nath et.al\textsuperscript{91} The synthesized complexes were characterized by elemental analysis, IR, UV and magnetic susceptibility studies. Tetrahedral geometry for Ni(II), square pyramidal geometry for Cu(II) and Fe(III) while octahedral geometry for Co(II) complexes are suggested.

The literature survey reveals that extensive work has done by Syamal and his coworkers\textsuperscript{92-100} on Schiff bases having ONO donor groups and their complexing behaviour. They have reported that the VTMS study of several complexes with ONO donor Schiff bases indicate that their effective magnetic moment decreases significantly as the temperature is lowered. This is due to antiferromagnetic exchange interaction in these complexes.

The Cu(II) complexes\textsuperscript{95} of SABA'-H\textsubscript{2} exhibit subnormal magnetic moment (0.98-1.48 B.M.) at room temperature indicating presence of antiferromagnetic exchange. The exchange interaction constant (-J) of the complexes is to be observed in the range of 189-382 cm\textsuperscript{-1}.The complex exhibit d-d band around 1600 cm\textsuperscript{-1}, these facts suggest dimeric structure with animobenzoyl alcoholic oxygen atom as the bridging atom. The Fe(III) complexes\textsuperscript{96} are also dimeric in nature and show magnetic moment values in the range of 4.37– 4.56 B.M. The Mn(II) complexes of SABA'-H\textsubscript{2} with substituted salcylaldehyde are dimeric in nature.\textsuperscript{97} The complexes show octahedral geometry around metal ion by occupying two water molecules at trans position. The complexes show magnetic moment value in the range of
5.88-5.92 B.M. which is close to the spin-only value of 5.92 expected for \( S = \frac{5}{2} \) system which indicates magnetically dilute nature of the complexes.

The complexes of Ni(II), Co(II), Mn(II), Cu(II), Zn(II) dioxouranium (VI) and dioxomolybdenum derived from 2-benzothiazole carbohydrazide and salicylaldehyde or 2-hydroxy-1-naphthaaldehyde have been synthesized and characterized. Cu(II) complexes indicate subnormal magnetic moment where as Ni(II) and Mn(II) complexes behave normally at room temperature. Zn(II), UO\(_2^{2+}\) and MoO\(_2^{2+}\) complexes are diamagnetic. The Zn(II) complexes are octahedral, Cu(II) are square planar and all other complexes are octahedral.

The polymer supported transition metal ion complexes of Schiff base show general formulation as PS-L·Cu·DMF, PS-L·Ni·3DMF, PS-L·FeCl·2DMF, PS-L·Zn·DMF, PS-L·Cd·DMF, PS-L·MoOCl·DMF, PS-L·UO\(_2\)·DMF, PS-L·Zr(OH)\(_2\)·DMF, where PS is deprotonated styrene bound Schiff base derived from o-hydroxy benzyl amine, o-aminophenol and 3-formyl-salicylic acid having the general structure as

![Structure I](image1)

![Structure II](image2)

The polymer supported Cu(II) complex formed is square planar, Zn(II), Cd(II) are tetrahedral, Ni(II), Fe(III), U(VI) and Mo (V and VI) are octahedral while Zr(IV) complex is pentagonal bipyramidal. The
polymer anchored Ni(II), Cu(II), Fe(II) and Mo(IV) complexes are paramagnetic while Zn(II), Cd(II), Mo(IV) Zr(IV) and U(VI) complexes are diamagnetic in nature.

Rema et.al.\textsuperscript{101} have studied physico-chemical characterization of Fe(II), Co(II), Ni(II), Mn(II), Cu(II) and Cd(II) complexes of n-(5-bromosalicylaldehyde)-5-bromoantranilic acid. The complexes are [ML(H\textsubscript{2}O)\textsubscript{3}] type except Cu(II) complexes. Thermal decomposition data of Co(II), Ni(II) and Cu(II) complexes obtained by thermal analysis were used to determine the energy and entropy of activation based on Coats-Redferm and Horowitz-Metzger equation. The relative thermal stabilities observed for the complexes are in the order of Co < Ni < Cu.

The Schiff base ligand SAP-H\textsubscript{2} with some neutral nitrogen donor ligands form complexes with Co(II), Ni(II), Cu(II) metal ion.\textsuperscript{102} The complexes are [MLL\textsubscript{3}'] type where L\textsubscript{3}' - are neutral nitrogen donor ligands such as \(\chi\) -picoline, quinoline pyridine. The Cu(II) complexes show magnetic moment value in the range 1.81-1.89 B.M., Ni(II) shows 3.08-3.21 B.M. While Co(II) complexes shows magnetic moment in the range 3.9 - 4.28 B.M. The magnetic and electronic spectral studies provide the evidence for the existence of octahedral geometry for all complexes.

The Ni(II), Cu(II), Cd(II), Fe(III), and La(III) complexes of isatin-o-aminophenol have been studied.\textsuperscript{103} The complexes were isolated in two types. The [M(ITAP)\textsubscript{2}]Cl\textsubscript{m} xH\textsubscript{2}O complexes are octahedral, where as dimeric [M(IAP)Cl H\textsubscript{2}O]\textsubscript{2} attain the octahedral structure with bridging nature of ligands. The Cu(II) complexes with diketone and 2-aminothiophenol\textsuperscript{104} indicate subnormal magnetic moment and hyperfine splitting ascribed to an antiferromagnetic exchange interaction.
arising from dimerisation. The cyclic voltammogram shows that the electron transfer occurs in two steps corresponding to Cu II – Cu II and Cu I – Cu I redox state.

Havinale and Pujar\textsuperscript{105} have synthesized Cu(II) complexes with salicylaldehyde, 2-hydroxy-1-naphthaldehyde, orthohydroxy actophenone and 1-aminoethyl-2-naphthol. The complex shows antiferromagnetic exchange (\(\mu_{\text{eff}} = 1.39 - 1.46\) B.M.) and exhibit one broad and two sharp intense electronic spectral bands in the range 600 – 630, 390 – 410 and at 320 nm (\(2E_g \rightarrow ^2T_{2g}\)) respectively. The ESR spectra at room temperature resembles those of standard dimer giving \(g_{||} = 2.3\) and \(g_{\perp} = 2.07\). A dimeric structure with 1-aminomethyl, 2-naphthalic oxygen atom as the bridging atom is suggested. The Mn(II) and Mn(III) complexes with 2-hydroxy naphthyl-methylamine and salicylaldehyde are also dimeric.\textsuperscript{106} Octahedral and square planar structure was suggested for Mn(II) and Mn(III) complexes respectively.

Reddy and Lingappa\textsuperscript{107} have synthesized Cu(II) complexes with ONS donor Schiff base derived from 2,4-dihydroxy acetophenone, 2,4-dihydroxybenzophenone with 2-iminoethanethiol and 2-imino-benzenethiole. The structure of the complex was assigned as

\[ R = \text{CH}_3, \text{C}_6\text{H}_5 \]
The complexes are nonelectrolytes. Low intensity band in electronic spectra observed at 16000, 15625, 17860 and 15870 cm\(^{-1}\)\((^{2}B_{15} \rightarrow ^{2}B_{2g})\) indicate square planar geometry for all complexes. The ESR spectra of the complexes in polycrystalline state shows one broad signal which is attributed to dipolar broadening and enhanced spin lattice relaxation which further support the square planar geometry of the complexes.

Ali et al.\(^{108}\) have synthesized Cu(II), Ni(II), Zn(II) and Cd(II) complexes with Schiff bases of pyrrole-2-carboxaldehyde and 5-methyl and 5-benzyladithiocarbazate. The ligand has tendency to coordinate as bidentate chelating agent in [Ni(HL)]\(_{2}\) and [Cu(HL)]\(_{x}\) and as tridentate NNS chelate in [ML], M = Ni(II), Cu(II), Zn(II) and Cd(II). Both the [Ni(HL)]\(_{2}\) and [NiL] complexes are diamagnetic and square planar. Based on magnetic and spectroscopic evidence, thiolate sulphur bridged dimeric square planar structure was assigned to the [Cu(HL)]\(_{x}\) and [ML] (M = Ni(II), Cu(II)). The complexes [ML] (M = Zn(II), and Cd(II)) are polymeric and octahedral.

A series of Mononuclear Ni(II) complexes of tridentate ligand have also been reported.\(^{109}\) Ni(II) forms mononuclear complexes with two tridentate ligands 5-methyl and 5-benzyl beta-N-(pyridine-N-oxide-2yl methylidene) dithiocarbozate. On the basis of magnetic and spectral studies both square planar and octahedral configurations were obtained for these complexes. The X-ray diffraction study indicates that nickel atom lies in a square planar coordination environment.

Singh et al.\(^{110}\) have synthesized Co(II), Ni(II), Cu(II), Mn(II), Zn(II), Hg(II), Vo(IV) complexes of 2-acetylthiophene-2-thenylhydrazone. The complexes were characterized by elemental analysis, IR, UV and magnetic susceptibility studies. The X-ray

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diffraction study of Cu(II) complexes has been used to determine the shape and the dimensions of unit lattice. The ESR spectra follow the trend of $g_{ll} > g_{l} > g_{e} (2.0023)$ indicate that the presence of unpaired electron in $dx^2 - y^2$ orbital. Based on magnetic and spectroscopic studies octahedral geometry is suggested for these complexes.

The complexes of Ni(II), Cu(II), and Zn(II), with N-(2-pyrrolylmethylene)-pyrimidiamine were synthesized by Cohan et.al.\textsuperscript{111} These complexes were characterized by elemental analysis, magnetic susceptibility, IR, electronic and HNMR studies. The ligand and its complexes were screened for antibacterial activity and indicate that the activity of ligand substantially increases on co-ordination.

The structural and spectroscopic studies of Cu(II) complex was done by Larramendi e.al.\textsuperscript{112} The complex is of $[\text{CuL(NCS)}_2]$ type. Where L=[N - (2'- 6 methyl pyridylethene-2-(2'-pyridyl) ethylene] is five coordinated. The coordinates behavior of some tridentate Schiff base and its normal and hemiacetal form towards 3d metal ion have been studied.\textsuperscript{113} The complexes of Mn(II), Co(II), Ni(II), Zn(II), with pyridoxal N-benzoglycylhadrazone are ML\textsubscript{2} type. IR and NMR spectral data indicate that ligand is uninegative and tridentate and coordinates through hydrazide carbonyl/imidolic oxygen, azomethine nitrogen and phenolate oxygen with its pyridoxal moiety in hemiacetal as well as normal forms. Magnetic and electronic spectral data suggest distorted octahedral geometry for all complexes.

The Schiff base derived from quinoxaline-2-carboxaldehyde and 2-aminophenol (HQAP) when condensed with transition metal ion form complexes\textsuperscript{114} giving general formulation $[\text{M(QAP)}_2]$ M = Co(II), Ni(II), Mn(II), Cu(II), and $[\text{M(QAP)}_2]\text{Cl}$ M = Fe(III). The tetrahedral structure was assigned for Mn(II), Co(II), Ni(II) and Cu(II) complexes whereas
octahedral dimeric structure for Fe(III) complex. The Schiff base derived from 6-methyl, 3-formyl,4-hydroxy-2-(1H)-quinolone and ethanolamine also form complexes with transition metal ion.\textsuperscript{115} The monomeric and dimeric complexes were obtained that depend upon metal: ligand ratio. The dimeric products were bridged through Cl, acetate or sulfate group or phenolic or alcoholic oxygen of the ligand. Both nickel and copper chlorides yield similar type of complexes.

The Schiff base derived from salicylaldehyde, 2-hydroxy-1-naphthaldehyde and 2-aminopyridine form complexes with transition and inner transition metal ions. The ligand behaves as ONN donor by involvement of ring nitrogen in coordination. Its complexes with Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) metal ions are of [ML$_2$(H$_2$O)$_2$] type.\textsuperscript{116} All the complexes show octahedral geometry around metal ions. Thermal, magnetic and ESR spectral studies of Co(II), Ni(II) and Cu(II) complexes suggest octahedral geometry for Co(II) and Ni(II) complexes where as square planar geometry for Cu(II) complex.\textsuperscript{117} The antibacterial activities of all these complexes indicate they are more active than their parent Schiff base.

The divalent nickel, cobalt and trivalent chromium metal ion form complexes with ligand derived from 2-(2'-amino ethyl)pyridine and substituted salicylaldehyde.\textsuperscript{118} The complexes are [ML$_2$] type except Cr(III), where M = Ni(II) and Co(II) the magnetic moment of Ni(II) (2.96-3.42 B.M.) and Co(II) (4.85 – 5.12 B.M. and Cr(III) complexes (3.70 – 3.82 B.M.) are consistent with octahedral geometry.

The structural features of Cu(II), Co(II), Zn(II) and Mn(II) complexes of 2-hydroxy-1-naphthaldehyde and tris (hydroxymethyl) methylamine have been studied by Sreenivasulu and his coworkers.\textsuperscript{119}
The complexes are 1:1 (metal:ligand) type. On the basis of magnetic and spectral studies, square planar geometry for Cu(II), tetrahedral geometry for Zn(II) while octahedral geometry for Co(II) and Mn(II) complexes was suggested.

A perusal of literature reveals that the bivalent metal ions can form complexes with tridentate amino acid Schiff bases. The salicylaldehyde amino acid Schiff base complexes have been used to model N-pyridoxylidene amino acids which are considered to be an important intermediate in biological amination process. The ESR spectra of Cu(II) complexes with salicylaldimines derived from amino acids (glycine, α- alanine, β- alanine, serine, tyrosine, tryptophane, histidine etc.) indicates the formation of two types of adducts. The divalent Co, Cu and Zn complexes of N-salicylidenamino acids indicate octahedral geometry for Co(II) and Zn(II) complexes and square planar geometry for Cu(II) complex. The magnetic moment of Cu(II) complex (1.70 – 2.20 B.M.) and broad absorption band around 16000 cm⁻¹ (²E_g → ²T_2g) confirm its square planar geometry.

Few transition metal complexes such as Co(II), Ni(II), Zn(II) and Cd(II) have been synthesized by template condensation of aminoacids (L-phenylalanine, L-leucine, L-histidine, L-tryptophan) and aldehyde or Ketone. The thermal degradation of complexes were studied in air by DTA and dynamic thermogravimetric analysis from ambient temperature to 900°C. These studies indicate the basic steps are similar in the thermal degradation of these complexes.

1.7 Complexes with tetradeutate ligands

Tetradeutate Schiff bases result by condensation of aliphatic or aromatic diamines and salicylaldehyde or acetylacetone or their
derivatives. In case of metal complexes of Schiff base derived from aliphatic diamines and salicylaldehyde or its derivatives, the stereochemistry of the complex depends upon the number of carbon atoms in the methylene bridge viz. value of ‘n’. For e.g. Co(II) and Cu(II) complexes with \( n = 2 \) have square planar geometry while the complexes with \( n = 3 \) or 4 possess tetrahedral geometry.\(^{126,127}\)

The \( \text{N} \text{N'} - \text{ethylene bis (salicylaldimine)} \) copper(II) complexes is dimeric in the solid state.\(^{128}\) Increasing the methylene chain length for complexes may cause a change in stereochemistry from cis planar to tetrahedral and less likely to trans planar.

Literature survey reveals that, extensive work has been done on tetradeutate Schiff base and their metal complexes. Harris and Mckenzie reported\(^{129}\) five coordinate Cu(II) complexes of \( \text{N, N'}-\text{Bis- (2-pyridyl-methylene ethane 1,2-diamine)} \) and other related ligands. A series of binuclear metal (II) complexes of tetradeutate Schiff base macrocycles formed by condensation product of propane 1,3-diamine and 2-hydroxy-5-methyl isophthaldehyde have been reported.\(^{130}\) The Cu(II) complexe with Schiff base obtained by condensation of ethylenediamine and 2,5-dihydroxyacetophenone have been synthesized.\(^{131}\) The ESR spectra indicate the square planar geometry around metal ion.

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Torihara et al. studied the antiferromagnetic spin exchange interaction in Cu(II)-Co(II) heterometal complexes of Schiff base derived from 3-formylcyclic acid and propylenediamines, 2,3-butane diamine or o-phenylenediamine. The magnetism of CuNi (F Saph) 5H2O and CuCo(F Saph) obeyed the Curie law and the Curie-Weiss law respectively. The dimeric Ni(II) complexes of asymmetric tetridentate Schiff base ligand from salicylaldehyde and diamines were studied by Elder. The dimeric structure for Ni(II) complexes was assigned as

Patel and Bhattacharya studied the binuclear Cu(II) complexes of the type [Cu(TSB)Cu(AA)](ClO4)2 with symmetrical and unsymmetrical tetridentate Schiff base derived from salicylaldehyde or 2-hydroxyacetophenone and o-phenylenediamine or 2,2'-bipyridy 1,10 phenathroline or 2-(2'-pyridyl) benzimidazole. The low magnetic moment (0.99 to 1.16 B.M.) of the complexes at room temperature is suggested due to antiferromagnetic superexchange interaction between the two non-equivalent Cu(II) ions through phenolate bridge.

The binuclear Cu(II) complexes involving mixed tetridentate Schiff base derived from reaction of copper (II) chloride and copper (II) percholrate with some mixed aromatic diamines (bis-Phenylenediamine) and substituted salicylaldehyde. The sub-normal magnetic moment of complexes (μeff = 1.00 - 1.08 B.M.) at room temperature indicating a strong magnetic interaction between two
copper centers in the binuclear complex.

The polymeric complexes of Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) with ortho aminobenzoic acid and terephthaldehyde have the general formula \([\text{ML}.2\text{H}_2\text{O}]_n\). The octahedral structure of the complexes have been arrived on the basis of magnetic, spectral and thermal studies. The IR spectra indicate the strong band at 1680 cm\(^{-1}\) and 1350 cm\(^{-1}\) due to \(\nu\text{C}=\text{O}\) and \(\nu\text{C}–\text{OH}\) stretching in the ligand, disappears on complexation and are replaced by two equivalent C–O bands intermediate in force constant between \(\text{C}=\text{O}\) and \(\text{C}–\text{OH}\). The ligand to metal ratio is 1:1 in DMF, which is approached as

\[
\text{M} = \text{Co(II)}, \text{Ni(II)}, \text{Cu(II)}, \text{Zn(II)}, \text{Cd(II)}
\]

polymerization of complexes, supported by extreme insolubility and high thermal stability of the complexes.

Deshpande and Shah\(^{137-139}\) have synthesized coordination polymers of Cu(II), Ni(II), Co(II), Zn(II) and Cr(III) with the Schiff base of 4,4'(4,4'-biphenylenesazo) di(salicylaldehyde) with \(\text{o-toluidene}, \text{m-toluidene}\) or \(\text{aniline}\). The electronic spectra of ligand indicate the band appearing at 24390cm\(^{-1}\) and 20833cm\(^{-1}\) corresponds to \(n\rightarrow\pi^*\) and \(\pi\rightarrow\pi^*\) tansitions respectively.
The metal chelate formed shows 1:1 (metal:ligand) ratio with nonelectrolytic nature and high thermal stability. The magnetic moment of Co(II) (4.4 B.M.), Ni(II) (3.6 B.M.), Cu(II) (2.3 B.M.) and Cr(III) (4.3 B.M.) chelate suggest square planar geometry for Co(II) and Cu(II) chelate while octahedral geometry for Ni(II) and Cr(III) complexes. The ligational behaviour of 4, 4' (4,4' - biphenylenebisazo) di(salicylaldehyde thiosemicarbazone) have been determined by studying Vo(IV) Cr(III), Mn(II), Co(II), and Zn(II) polychelates. The magnetic moment of Cr(III) (3.88 B.M.), Mn(II) (5.93 B.M.), Ni(II) (2.92 B.M.) chelates are as required for on octahedral structure. The tetrahedral structure for Co(II) ($\mu_{\text{eff}} = 4.78$ B.M.) is suggested. The Vo(II) shows $\mu_{\text{eff}} = 1.84$ B.M. corresponding to the unpaired electron.

Few complexes of Cu$^{2+}$, Co$^{2+}$, Ni$^{2+}$, Mn$^{2+}$, Pd$^{2+}$, Fe$^{3+}$, have been synthesized by condensation of equimolar quantities of salicylaldehyde and 2-amino, 5-(phenylazo) pyridine or its derivatives in anhydrous benzene.\[^{140}\] The complexes are ML$_2$ type except Fe$^{3+}$ (ML$_3$). The Cu(II) Ni(II), Pt(II) and Pt(IV) complexes with azolo–2,4 petanedione were synthesized by L.Mishra.\[^{141}\]. The biological relevant azolo (triazolo and thiazolo) diazonium salt were coupled with 2,4-pentanedione and condensed with 1,6-diaminohexane in the presence of chloride salts of
respective metal ion. The resulting binuclear or polynuclear complexes were characterized on the basis of magnetic and spectral studies.

The polychiff bases derived from 5,5'-methylene - bis (salicylaldehyde) or 5,5'-sulphone-bis (salicylaldehyde) and various diamines have general structure.

\[
\begin{align*}
\text{X} &= \text{CH}_2 \text{ or SO}_2 \\
\text{Y} &= \text{CH}_2, \text{SO}_2, \text{O} \text{ or I}
\end{align*}
\]

The Schiff bases can coordinate through ONON as bivalent tetradenate ligands. The magnetic moment of Co(II) complexes (3.50 - 4.51 B.M.) with these ligands indicate presence of a mixture of high spin tetrahedral and low spin square planar forms. On the basis of magnetic and spectral studies, tetrahedral structure is assigned for these complexes. The Ni(II), Cu(II) and Zn(II) complexes are thermally stable. The specific conductivity of these solid complexes are 1.74, 10-12-1.1 10-10 \text{ W}^{-1} \text{ cm}^{-1} \text{ with activation energy of 10.49- 20.01 Kcal mol}^{-1}. The chelate polymers of Cu(II), Ni(II), Co(II), Mn(II) and Zn(II) with 5,5'-methylene-bis(3,3"dinitrosalicylaldehyde and 1,6-hexane- diamine prepared by polycondensation reaction are dark coloured and insoluble in common organic solvents. Thermal studies indicate, all polychelates are thermally stable at varying temperatures.

Thermal stability of Mn, Fe, Co, Cu and Ni complexes with polyschiff base derived from 4,4'- dihydroxy -3,3'-diacety biphenyl and
1,3-propanediamine studied by Aswar et.al. The decomposition of all polychelates decreases in order of Ni>Co>Fe>Mn>Cu. The complexes are \([M(L)_n\cdot n\text{H}_2\text{O}]_n\) type. Octahedral geometry for Mn(II) and Fe(II), squareplanar for Ni(II) and Cu(II) while tetrahedral geometry for Co(II) chelates is suggested.

The Co(II), Ni(II), Zn(II), Cd(II) and Hg(II) complexes with benzoinhydrazone with salicyaldehyde or \(\alpha\)-hydroxyacetophenone obtained in solid form shows high melting point. The subnormal magnetic moment of Co(II) (~ 2.8 B.M.), Ni(II) (~ 2.3 B.M.) and Cu(II) (~ 1.2 B.M.) indicate metal-metal interaction in polymeric structure. Octahedral geometry for Co(II), Ni(II), Cu(II) and Zn(II) complexes and tetrahedral geometry for Cd(II) and Hg(II) complexes are suggested.

The ON-X-NO donor doubly bidentate ligand derived from 4,4'-diaminodiphenylsulphone with salicyaldehyde or 2-hydroxy-1-naphthaldehyde form binuclear complexes with \(\text{Co}^{2+}, \text{Ni}^{2+}, \text{Cu}^{2+}, \text{Zn}^{2+}, \text{Cd}^{2+}\), and \(\text{Hg}^{2+}\) ions. An octahedral geometry for Co(II), Ni(II) and
Cu(II) complexes and tetrahedral geometry for Zn(II), Cd(II) and Hg(II) complexes has been assigned.

The Schiff base ligand derived from N,N'-bis(salicylidene), N,N'-bis (methoxysalicylidene), N,N'-bis (4-hydroxysalicylidene) and 1,5-diaminonaphthalene can form binuclear complexes with Cu(II), Co(II), and Ni(II) metal ions. The complexes are nonelectrolytes. The pseudo tetrahedral geometry for binuclear Cu(II) complexes whereas pseudo octahedral geometry for binuclear Co(II) and Ni(II) complexes have been suggested.

The complexes of Fe(II), Co(II) and Ni(II) with ethylenediamine and salicylaldehyde [Sal(en)₂] are known to have aromatic diamine dependent structural features. The complexes are monomeric and low spin. The binuclear structure for complexes are possible due to longer chain length and less steric strain present in the ligand. Low conductance value (5–20 Ω⁻¹cm²mol⁻¹) indicate nonelectrolytic nature of the complexes. The Zn(II), Cd(II), and Hg(II) complexes with [Sal(en)₂] are 1:1 type having N₂O₂ donating sites with noncoordinating azomethine group. Tetracoordinated structure for Zn(II), Hg(II) and hexacoordinated structure for Cd(II) is suggested. A number of Fe(II), Fe(III), Co(II), Co(III), Ni(II), and Cu(II) complexes with [Sal(en)₂] are ML and MLCΙ type and characterized by various physicochemical techniques. The magnetic and spectral measurements helped to propose the structural behaviors of complexes. The electrochemical and EPR studies of Ni(II), complexe for oxidized solution in DMF or DMSO revealed that in these strong-coordination solvents almost all Ni(II) complexes were oxidized to low spin six coordinate Ni(II) complexes.

Parashar and Sharma have synthesized Cu(II), Ni(II), Co(II), Zn(II) and Mn(II) complexes with N, N'-O-phenylenebis (salicylald-
imine) and its meta and para analogous. The metal complexes are 1:1 (metal:ligand) type and are non-electrolytes. The complexes are tested for antibacterial and antifungal activities at 37°C indicate a considerable increase in the biological activities in these ligands on being coordinated with metal ion in terms of their minimum inhibitory concentration values of these compounds.

The SNNS donor tetradentate Schiff base derived from 2,5-hexanedione-S-alkyl dithiocarbazic acid have been synthesized\textsuperscript{154} and formulated as [M(SNNS)] with Zn, Cd and Ni. Based on magnetic and spectroscopic studies the square planar structure is suggested for Ni(II) complex. The Zn(II) complexes are assigned with polymeric structure with mercapto sulphur bridging, whereas Cd(II) complexes presumably have the polymeric structure.

The Schiff base derived from carbohydrazide H$_2$N-NH-Co-NH-NH$_2$ with aldehydes were investigated and their properties as tetradentate ligand with Co(II), Ni(II), Cu(II), Vo(IV), salts were studied.\textsuperscript{155} The magnetic properties of Co(II) (2.04 - 2.29 B.M.) Cu\textsuperscript{II} (1.73 - 1.93 B.M.) and Ni\textsuperscript{II} (diamagnetic) indicate square planar geometry around metal ion. The metal complexes are found to be biologically active against E.Coli, S.aureus, A.niger and C.albicans.

The sulphur-nitrogen chelating agent derived from salicylaldehyde, 2-hydroxy-1-naphthaldehyde with S-methyl-β-N-(2-aminophenyl) methylenedithiocarbazate form stable complexes of Cu, Ni, Zn, Cd, Hg and Pt giving general formula M(ONNS).XH$_2$O (X=0, 1 or 2).\textsuperscript{156} The Ni(II) complexes are diamagnetic while Cu(II) complexes are paramagnetic. Both the complexes show square planar geometry. The Cu(II), Ni(II), and Zn(II), complexes with thiocarbohydrazide and salicylaldehyde, O-vanillin, 2-hydroxy-
acetophenone or 2-hydroxy-1-naphthaldehyde have been reported and formulated as \([\text{M}_2\text{L}_2\text{H}_2\text{O}]\).\textsuperscript{157} The electronic spectra of \(\text{Ni(II)}\) complexes shows d-d bands around 10900, 16000 and 27700 cm\(^{-1}\) indicate binuclear octahedral structure. The broad band around 15625 cm\(^{-1}\) suggests distorted octahedral configuration for \(\text{Cu(II)}\) complex. The abnormality of magnetic moment of \(\text{Ni(II)}\) (3.28 – 3.40 B.M.) and \(\text{Cu(II)}\) (1.2 – 1.68 B.M.) complexes is due to binuclear structure, which may be due to either the overlap of Cu-Cu orbital, or through the ligand participation. The X-ray diffraction studies indicate the ligand and its \(\text{Cu(II)}\) complex fit well with tetragonal system.

Kumar and Sinha\textsuperscript{158} have synthesized the monomeric and dimeric complexes of Mn(II), Fe(II), Co(II), and Ni(II) with pyridine-3-carboxaldehyde and o-phenylenediamine. The square planar and octahedral geometry was suggested for monomeric and dimeric complexes on the basis of elemental analysis, molar conductance, IR, UV and magnetic susceptibility studies. The \(\text{Cu(II)}\), and \(\text{Ni(II)}\) complexes with thiophene-2-aldehyde and ortho or meta phenylenediamine are paramagnetic.\textsuperscript{159} The magnetic moment of \(\text{Cu(II)}\) (1.89 – 1.95 B.M.) and a broad band around 16600 cm\(^{-1}\) as expected for tetrahedral structure. The magnetic moment of nickel(II) complexes (3.1 – 3.4 B.M.) are consistent with octahedral geometry.

Few complexes of \(\text{Cu(II)}, \text{Co(II)}, \text{Ni(II)}, \text{Fe(II)}\) and oxovanadium(IV) ions of a pair of Schiff base ligand BAMC-Sal and BAMC-pyrogal. derived from 1,3-bis(aminomethyl) cyclohexane and either salicyaldehyde or pyrogallaldehyde have been reported.\textsuperscript{160} The \(\text{Cu(II)}\) complexes stack as dimers in solid state with square pyramidal geometry around the metal centers which on dissolution monomerised to give pseudo tetrahedral geometry. The \(\text{Co(II)}\) salts besides \(\text{Ni(II)}, \text{Fe(II)}\)
and Vo(IV) ions gives monomeric ML type complexes. An octahedral geometry for Co(II), tetrahedral for Ni(II) and Fe(II) while square pyramidal geometry was assigned for Vo(IV) complexes.

The nickel, cobalt and copper complexes with N₆ macrocyclic ligand were synthesized by template reaction involving 2,6-diaminopyridine, 2,3 butanedione and metal salts in EtOH. The IR spectra suggest the pyridine nitrogen is not involved in coordination with metal ion. The distorted octahedral configuration is suggested for these complexes. The metal mediate condensation of o-phenylenediamine yields 14 membered tetraza macrocyclic coordinate complexes of the type [M(Mac)Cl₂], [M(Mac)SO₄·H₂O] with Fe²⁺, Co²⁺, and Cu²⁺ metal ions.

The metal ions are coordinated by four azomethine nitrogen’s, bridged by acetylacetone moieties. The low magneton values of FeⅡ sulphato and chloro complexes (4.89- 3.61 B.M.) which may be attributed to the quenching of orbital contribution arising from lower symmetry.

The X-ray diffraction study of macrocyclic ligand 4-amino-3-hydrozino-5-mercapto-1,2,4-triazole (22-membered) and its Cu(II), Ni(II) and Zn(II) complexes indicate, the number of molecules per unit
cell \( n = 6 \) for both ligand and their complexes.\(^{162}\) This indicates the metal atom is inside the macrocyclic structure and coordinated by \( N_2N_2 \) sites. Magnetic and spectral studies indicate tetrahedral structure for these complexes. The electrochemical and magnetochemical studies of \( \text{Cu(II)} \) complexes\(^ {163}\) with macrocyclic ligand derived from 1,2-phenylenediamine and 5-tert-butyl-2-hydroxy 1,3-benzene-dicarbaldehyde indicates \( \text{Cu(II)} \) have distorted square pyramidal coordination by four donor atoms. The two \( \text{Cu(II)} \) ions show only a small antiferromagnetic exchange interaction.

The Schiff base derived from isatin and \( o \)-phenylenediamine, forming non electrolytic metal chelates with \( \text{Co(II)}, \text{Ni(II)}, \text{Cu(II)}, \text{Mn(II)}, \text{Zn(II)}, \text{Pb(II)}, \text{Cd(II)} \) and \( \text{Cr(III)} \) metal ions.\(^ {164}\) The ligands behave as dibasic and form 1:1 metal ligand stoichiometry.

When \( o \)-phenylenediamine condensed with 2-formylocyclohexanone behave at dibasic, ONNO donor Schiff base forms complexes with \( \text{Ni(II)}, \text{Cu(II)}, \text{Co(II)} \) \( \text{Zn(II)}, \text{Pb(II)}, \text{Cd(II)} \) and \( \text{Cr(III)} \) metal ions.\(^ {165}\) The mode of bonding and geometrical features of metal complexes suggested by magnetic and spectral studies.

Gutierrez et.al.\(^ {166}\) synthesized \( \text{Cu(II)}, \text{Ni(II)}, \text{Pd(II)}, \text{Hg(II)} \) complexes with benzoylacetylacetone and N-benzylethlenediamines having two adjacent coordination sites \( \text{NNO(x)} \) (\( x=\text{Cl}, \text{NO}_3 \)) and \( \text{00(xy)} \) where \( x \) and \( y \) are exogenic donor units. Mononuclear and binuclear \( \text{Ni(II)}, \text{Cu(II)}, \text{Uranyl(VI)}, \text{Vanadyl(IV)} \) and \( \text{Fe(III)} \) complexes of 4-hydroxy 2-(1H) quinolone and ethenenediamine or \( 1,2 \)-propylenediamine have been studied.\(^ {167}\) The ESR spectra of \( \text{Cu(II)} \) complex gives only single g value \( \text{g}_{\text{eff}} = 2.097 \) indicating \( \text{Cu(II)} \) cation is in a square planar symmetry slightly distorted towards tetrahedral geometry.
The Schiff base derived from isonitroacetophenone and benzidine and their binuclear complexes of the type \( M_2L_2\cdot 4H_2O \) \( \{L=bis[2-hydroxyimino-1-(4-x-phenyl)-1-ethylidene} \) Benzidine \( x = H, \text{Cl, Br, CH}_3, \text{M} = \text{Fe(II), Co(II), Ni(II)} \) have been synthesized.\(^{168}\) Substitution in the phenyl ring of the complexes produces shifts in the azomethine stretching vibration \( \nu C= N \) which are related to the Hammett's substituent parameters. The magnetic moment of Co\(^{II}\) and Ni\(^{II}\) complexes are in the range 4.44 - 5.04 B.M. and 2.88 - 2.98 B.M. respectively and are suggestive of an octahedral geometry. The Ni\(^{II}\) and Co\(^{II}\) polymeric complexes\(^{169}\) are formed by reaction with isonitroacetophenone and diamines (1,4-phenylenediamine, 4,4'-diaminobiphenyl, 4,4'-diaminophenyl methane or 4,4'-diaminodiphenyl ether). The complexes show composition \( ML \quad [M=\text{Ni(II), Cu(II)}] \) and \( \text{CoL(H}_2\text{O})_2 \). The Ni\(^{II}\) and Cu\(^{II}\) complexes are square planar while Co\(^{II}\) complexes are octahedral with water molecules at the axial position.

Recently the polystyrene supported chelating resin containing the Schiff base derived from salicylaldehyde and triethylene tetramine and its Cu\(^{II}\), Co\(^{II}\), Ni\(^{II}\), Fe\(^{II}\), Zn\(^{II}\), Cd\(^{II}\), Mo\(^{VI}\) and Zr\(^{IV}\) complexes have been synthesized by Symal el.al.\(^{170}\) The complexes of PS-LCu, PSL-FeCl and PSL-Co have square planar structure PS-LFeCl.DMF, PS-LMoO\(_2\) and PS-L-UO\(_2\) have distorted octahedral where as PS-LZn, PS-LCd have tetrahedral geometry. The negative shift of \( \nu (C= N) \) azomethine and positive shift of \( \nu (C-O) \) phenolic stretch indicate ONNO donor behaviour of the polymer anchored Schiff base.

### 1.8 Complexes with polydentate ligands

The polydentate Schiff base complexes reported so far are very few. Sacconi and Bertin\(^{171}\) have reported that pentadentate Schiff bases
derived from substituted salicylaldehyde and dipropyleneetriamines (with N₃O₂ donor atoms) and their complexes of Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) ions. Nickel(II) complexes have been reported to form six coordinated adduct with molecules of pyridine, as shown

\[
\text{R} = \text{H, CH₃}
\]

The Schiff bases 1-8 bis(salicylidene-imino) 3-6 dithioacetone and 4-methyl-1-8 bis (salicylidene-mino) 3-6 dithioactane behave as hexadentate ligands.

These forms diamagnetic, octahedral Co(II) complexes. Sharma and Bailar have studied Co(III), Fe(III), Mn(III), Co(II), Ni(II) and Cu(II) complexes of hexadentate Schiff bases derived from salicylaldehyde and triethylene tetramine. The Schiff bases formed by condensation of pyridine-2-aldehyde and 1-8 diamino 3,6-dithiaoctane also form hexadentate complexes.

A pentadentate Schiff base ligand 2,6, 10-tetrazo-1-,11-bis(2'-aminophenyl) and eCa-1, 10-dine(L) and MLX₂ (M = Cu, Ni, X = Cl, Br, I, NO₃, ClO₄) were studied by Kwiatkowski et.al. The complexes were characterized by elemental analysis, IR, EPR, magnetic moment
and molar conductance. The IR data suggest an interaction between halide union of outer coordination sphere and the complexed amino group. The spectroscopic and EPR data of Cu(II) complexes are consistent with distorted octahedral geometry.

Two asymmetric pentadentate tribasic ligands with N_2O_3 donor sites have been reported. The ligand containing two adjacent coordinating compartments is capable of coordinating two similar or dissimilar metal cations. Mononuclear complexes were obtained when it react with metal cations to produce homo or hetero bi or trinuclear complexes. Both the Cu(II) and Ni(II) coordinate either to mixed nitrogen and oxygen or O_2 and N_2 donating atom.

When 1-(o-hydroxy phenyl) butane-1,3-dione and 1,2 diamino ethane which is condensed in second step with the bidentate aromatic aldehyde or ketone such as o-hydroxyacetophenone, salicylaldehyde or 2-hydroxyl-1-napthaldehyde to obtain the Schiff base of following type.

```
\begin{center}
\begin{tikzpicture}
\node (A) at (0,0) {\text{C}};
\node (B) at (0.5,0) {\text{N}};
\node (C) at (1,0) {\text{H}};
\node (D) at (1.5,0) {\text{CH}_2};
\node (E) at (0,-1) {\text{O}};
\node (F) at (0.5,-1) {\text{O}};
\node (G) at (1,-1) {\text{H}};
\node (H) at (1.5,-1) {\text{C}};
\node (I) at (2,-1) {\text{CH}_3};
\node (J) at (0.25,0.5) {\text{OH}};
\node (K) at (0.75,0.5) {\text{H}};
\node (L) at (1.75,0.5) {\text{N}};
\node (M) at (2.25,0.5) {\text{CH}_2};
\draw [dashed] (A) -- (B) -- (C) -- (H) -- (I);
\draw (E) -- (F) -- (G) -- (H) -- (I);
\draw (J) -- (A) -- (K) -- (L) -- (M);
\end{tikzpicture}
\end{center}
```

The ligand behave as pentadentate by coordinating as N_2O_3 sites to form mono-, bi- and trinuclear complexes with transition metal ions.
The ligand bis(isatin) carbohydrazone behave as bi, tri, tetra and pentadentate and form complexes with Mn(II), Co(II), Cu(II), Zn(II) and UO$_2$(II) metal ions. The Cu(II) complexes so obtained are square planar, Co(II) are tetrahedral whereas Mn(II) and Ni(II) are octahedral.

Mahapatra et.al have synthesized trinuclear metal complexes of Cobalt, Nickel and Copper with octadentate ligand N,N'-bis(3'-hydroxyphenylazo)-2-hydroxy-benzylidene]ethylenediamine. The ligand behave as ONNNNO donor sites. The characterization of metal complexes has been made on the basis of element analysis, conductance, magnetic measurements, IR and electronic spectral studies. The octahedral geometry for Co(II) and Ni(II) complexes while distorted octahedral geometry is suggested for Cu(II) complexes.

The dibasic hexadentate ligand derived from diamine and salicylaldehyde or 2-hydroxy-1-naphthaldehyde form complexes with Cu(II), Ni(II) and Co(II) metal salts. The ligand field strength of the complexes increases with increase in chelate loop size from six to seven. The EPR spectral study reveals that the Cu(II) complexes assume monomeric distorted octahedral or pseudo-octahedral geometry.

A macrocyclic hexadentate ligand was prepared by cyanuric chloride, hydrazine and terephthaldehyde and its Cu(II), Ni(II) and Zn(II) complexes were isolated. The X-ray diffraction studies shows the number of molecules per unit cell $n = 3$ is same for both macrocyclic ligand and their complexes indicating the metal atom is inside the cage structure and coordinated by six nitrogen atoms supported by IR spectra, Magnetic measurements indicate octahedral structure for the complexes.
1.9 Application of Schiff bases and their metal complexes

The Schiff base metal complexes have occupied an important position in the modern inorganic chemistry. The interest in these compounds arises from their various applications in the field of bioinorganic chemistry\textsuperscript{183-185}. The Schiff bases are known for their biological importance as fungicides. The fungicidal activities of Schiff bases such as anti-inflammatory activity\textsuperscript{186}, antibiotic activity\textsuperscript{187} and antimicrobial activity\textsuperscript{188} have been studied thoroughly. Among the Schiff bases those containing thiazole moiety are biologically more active and its activity increases on complexation. A number of Schiff base complexes are reported to be of great utility in pharmacological and biological aspects\textsuperscript{189,190}. Metal complexes with sulphur containing ligands show anticancer and antitumour activity\textsuperscript{181}.

Schiff base complexes possess an important property to take up molecular oxygen reversibly\textsuperscript{192-198}. The synthetic reversible oxygen carrying chelates\textsuperscript{192-199} are of interest as model compounds in the study of reversible oxygenation mechanism involved in very complex natural oxygen carriers. The Schiff base complexes carrying molecular oxygen are useful in biological and industrial process because of importance of molecular oxygen in these fields.

The Schiff base complexes have been found useful in organic synthesis and pigment industry, polymer industry, and textile industry. More recently azo dispersed dyes 2-(6'-hydroxy Schiff's base-5'-arylazo-1-yl)-5-nitrobenzothiazole were synthesized and their dyeing performance on polyester fibre were assessed\textsuperscript{200}. The usefulness of transition metal complexes in pigment and dyestuff industries\textsuperscript{201,202} is due to their coloured nature. A number of Schiff base pigments or dyes
are used in textile and rubber industries and also in the manufacture of varnishes and printing inks.

Dey\textsuperscript{203} has studied the use of cobalt and chromium mixed ligand complexes in dyeing wool, silk and nylon. The Co(II), Cu(II), Ni(II), Fe(III) and Cr(III) complexes of Schiff base triethylenetetramine 5-5' sulphonyl bis-salicylaldehyde and bis(2-pyridinal) biphenylene 4,4'-diamine are used as inorganic polymers in polymer industries\textsuperscript{204,205}.

Schiff bases can also be used as analytical reagent for the analysis of transition metals. Researchers\textsuperscript{206,207} have made an attempt to utilize Schiff bases as an important tool for separation and selection of trace amounts of metals like Cr\textsuperscript{3+}, Fe\textsuperscript{3+}, Mn\textsuperscript{2+}, Ni\textsuperscript{2+}, Cu\textsuperscript{2+}, Co\textsuperscript{2+}, V\textsuperscript{5+}, UO\textsubscript{2}\textsuperscript{2+} and Th\textsuperscript{4+}. The Schiff bases impart selectivity towards metal leading to complex formation. These metals were estimated using analytical techniques like HPLC or spectrophotometry. Literature\textsuperscript{208-210} also reveals that the transition metal complexes of Schiff bases have been found to be effective catalyst for epoxidation of various olefins.

Schiff base complexes possess an interesting properties of fluorescence\textsuperscript{211-213}. Aluminium, Zinc, Tin and yttrium complexes of Schiff base derived from salicylaldehyde and ortho-aminophenol have green, bluish green or blue fluorescence. The Fluorescence emission is utilized for the fluorometric determination of this metal ions\textsuperscript{211-214}. The Zn(II),Co(II) complexes of 2-2'-dimethylthio-N-salicylidene ethylamine have been studied which exhibit fluorescence.

The biological activity, catalytic activity and analytical applications can be correlated to the structure of Schiff base and substituent group on it and the redox potential of the metal ion.
References


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