CHAPTER - I

GENERAL INTRODUCTION AND LITERATURE SURVEY
INTRODUCTION

Coordination chemistry is the meeting place of all chemistry, and it needs the methods of physical, theoretical and organic chemistry for the complete understanding of the structure of the compounds and their applications to the various branches of science\textsuperscript{1-5}.

For long time the coordination compounds were considered as a rare and special class, but now they have been recognised as most restored type of compounds, on which the very existence of life is depended. For instance carbon dioxide and water are converted into sugar by coordination compound called chlorophyll which is magnesium complex. A similar iron complex called haemoglobin operates in the red blood cells as a carrier of oxygen.

Nature of the coordination compounds varies with the change in the metal ion, the donor atom, structure of the ligand, and the metal ligand interaction\textsuperscript{6}. The most significant problem in the characterisation of coordination compound has been the nature and the strength of the metal ligand bond\textsuperscript{7-10}. It is noticed that usually a metal ion cannot form bonds of equal strengths, with two different donor atoms, and a particular donor atom cannot form the bonds of same strength with different metal ions\textsuperscript{11-14}. 
In the recent years there has resurgence of interest in the general field of metal complex chemistry, thanks to its presence in basic as well as applied chemistry\textsuperscript{15,16}. In this regard there are many points of interest such as:

1. Designing and synthesising various types of ligands.
2. Using these ligands, synthesising metal complexes.
4. Providing evidence for metal co-ordination centres and metal interactions and finally.
5. Exploring their biological activity and/or catalytic properties.

These points are considered fully in many reviews\textsuperscript{17-21}.

The metal chelates involved in a variety of biological processes, where coordination occurs, between various ligands and metal ions is explained in the literature\textsuperscript{22,23}. The polydentate ligand which can take more than one metal ion in the organic sphere has gained importance in recent years for their biochemical processes, especially oxygen transport\textsuperscript{24} and oxygen activation by oxidase\textsuperscript{25,26} and monoxygenase enzymes\textsuperscript{27-32}. Surprisingly the chemistry of metal is a fast growing branch of coordination chemistry. The multidentate complexes also hold considerable significance in case of bioinorganic and catalysis chemistry, and various type of enzymes and proteins which require more than one metal ion for the other activity\textsuperscript{33,34} have also been studied recently.
Various spectrochemical, X-ray, and magnetic susceptibility-methods have been widely used in elucidating the structure of the complexes and sometimes the coordination centres, and preference of one coordination centre over the other, have been established with the help of molecular orbital calculations.

The literature is replete with many examples of coordination compounds whose structures have been established utilising a variety of tools and many having relevance to the biological systems and catalytic activity. The material, before us, is very enormous and a review in their entirety will be voluminous. It is therefore our intention at this point is to slice and pick only that part of the literature relevant to the work incorporated in this thesis.

**The Schiff base complexes**

The condensation of primary amine with carboxyl compounds was first reported by Schiff, and the condensation products are often referred to as Schiff base, these bases have general structure $\text{RC} = \text{NR'}$ where $R$ and $R'$ are alkyl, cyclohexyl, aryl or heterocyclic radicals, which may be variously substituted.

Various studies have shown that $\text{C}=\text{N}$- group has considerable biological importance. In this respect we must remember the possibility of having a lone pair of electrons i.e. either a $\overline{\Pi}$ or
an SP\(^2\) hybridized orbital, on trigonally hybridized nitrogen in the C=N- group, this is the fundamental chemical and biological importance, and together with the variability of angles of hybridization, it makes possible, the formation of nitrogen containing molecules with all the delicate differences in physicochemical properties necessary to produce the various phenomena of life.

Schiff bases can be considered as useful chelating agents, when a suitable functional group e.g. -OH, -SH etc. is present sufficiently close to azomethine group (C=N-) so to form a five or six membered chelate ring upon reaction with metal ion (I, II).

\[
\begin{align*}
\text{I} & \quad \text{II} \\
\text{OH} & \quad \text{OH} \\
\text{N=CH-R} & \quad \text{CH=N-R}
\end{align*}
\]

The prominent place held in co-ordination chemistry by the metal complexes of Schiff base ligands, has been attested over many years, by the large number of publications and by comprehensive reviews\(^{35-36}\). The reasons for this substantiated interests in these
compounds are undoubtedly many; but important among them, must be their general ease of preparation, diverse properties and their use as biological models\textsuperscript{39}. Schiff bases are known to possess tuberculostic\textsuperscript{40}, fungicidal\textsuperscript{41} and bacterostatic activities\textsuperscript{42}. The phenolic compound in which azomethine group is situated on the orthoposition to the hydroxy group are known to give chelates which possess antibacterial and antifungal properties.

**The coordination behaviour of the ligands**

The azomethines and their complexing capabilities have been highlighted in considerable body of review articles\textsuperscript{35-38}. The literature pertaining to the bidentate ligands is not reviewed, systematically and the information available on the tridentate has been discussed. Impelling stress on mono-functional tridentates and considerable amount of space is utilised for the discussion of branched tetradeptates, pentadentates and hexadentates. Here author has made an effort to discuss the behaviour of tridentate and tetradeptate ligands, as the work in the thesis contains mainly ligands of these two types.

The tridentate Schiff bases containing two active centres form complexes with transition metals which are generally dimeric in nature. This extensive prevalancy of dimeric nature in Cu(II) and V(IV) complexes, has given scope for the detailed
magneto chemical studies. The structure of such complexes are principally, based on spectrochemical, and magnetochemical studies. The octahedral complexes with such type of tridentates are also on record in the literature\textsuperscript{38}.

The neutral tridentates are shown to form octahedral complexes, with the transition metals, where, the two ligands encompass, the metal ion in an octahedral array\textsuperscript{43}.

The monovalent tridentate containing -ONN- (in which -O- is an active centre) and -ONO- (in which one of the -O- is co-ordinating centre) have been synthesised in the recent years and their metal complexes have been studied. The simple example of base, containing -NNO-sequence is the result of condensation of aminophenol with pyridine-2-aldehyde\textsuperscript{46}.

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

A similar type of base can also result by condensing acetylacetone with quinoline-8-amine\textsuperscript{47}.
On similar lines Biradar et al. have synthesised a base containing -ONN- sequence having the following structure.

In this ligand the -NH- group situated on the para position of the aniline residue possess considerable steric hinderance and inhibits the formation of monofunctional tridentate behaviour. However the complexes of Sn(IV) where in -NH has taken part in the co-ordination, are also known. Here the ligand shows pseudo-tridentate behaviour attaching itself to two of metal moieties.

The Schiff bases resulted from N,N-dialkylo-phenylenediamine and salicylaldehyde behave as monofunctional tridentates. Banfield synthesised cobalt (III) complexes of such ligands and has suggested penta coordination for these complexes on the bases of IR results.
The ligand containing \(-S-N-O-\) sequences where \(-S-\) is a donor site have been reported, by Dunsky and Crawford, Ni(II) forms octahedral complexes with such ligands. They have also synthesised polymeric Schiff base containing \(-SNO-\) tridentate units.

There is acute paucity of the literature concerning ligands containing \(-ONO-\) sequence in which one of the \(-O-\) atoms (preferably oxygen on the aniline residue) is a donor centre and other one is active centre. Recently Paul et al. have reported the Cu(II) complexes with ligands containing \(-O-N-O-\) sequences. Kulkarni et al. have synthesised monofunctional tridentates by condensing methyl anthranilate with various substituted o-hydroxy aromatic aldehydes and have suggested a tetragonally distorted octahedral structure for their Cu(II) complexes, on the basis of the structural and magnetic data.
Rastogi and Panchauri\textsuperscript{53} have reported the complexes of Cu(II), Pd(II) and Pt(II) with Schiff bases derived from 2-\((2'\text{-aminoethvl})\text{)pyridine. They have observed that, the ligand displays monovalent tridentate behaviour.

\[
\begin{align*}
\text{N} & \equiv \text{C} \\
\text{HO} & \\
\text{Pyridine} & \\
\text{Schiff base}
\end{align*}
\]

There are considerable number of class of ligands possessing two coordination sites and the active centre in the form of-SNN-sequences, which have employed for complexation by various workers\textsuperscript{54-56,57} Voronkov et al.\textsuperscript{57} have reported a Ni(II) complex with a Schiff base containing coordinated amine. This Ni(II) complex of o-aminobenzenethiol, has been shown to react with pyridine-2-aldehyde to form a Schiff base complex with the following structure.

On the similar lines Biradar et al. have synthesised the
complexes of Sn(IV)$^{58}$ Ti(IV)$^{59}$, and Nb(V)$^{60}$ with ligands containing -ONN- sequences.

These Schiff bases contain, one active centre (-OH) and two coordinating centres (HC=N- and -NH). Depending on the mode of the reaction with the metal ion, they can be called monodentates, bidentates, and tridentates. Curiously enough, it is seen that, no coordination through the -NH was observed, in titanium and niobium complexes, while there are distinct proofs to show certain coordination through the -NH of the p-aminodiphenylamine in Ti(IV) complexes alone. There are recent reports to confirm
the coordination through the secondary amine in case of Cu(II) complexes and U(VI) complexes. The copper complex has the following structure.

![Copper complex structure]

Tabibian investigated the tridentate Schiff bases having -SNS- and -SNO- and used them in quantitative estimation of metals and they have following structures.

![Schiff base structures]

Tabibian investigated the tridentate Schiff bases having -SNS- and -SNO- and used them in quantitative estimation of metals and they have following structures.
In the recent years not much work is done in monovalent tridentate Schiff bases containing -NNO- and -SNO- sequences. It was matter of curiosity for the author to synthesise the complexes containing this class of ligands and investigate probable coordination or non-coordination in U(VI) Th(IV) and Zn(II), Cd(II), Hg(II) complexes.

Considerable amount of space is utilized for the discussion on various types of tetradentate Schiff bases with different sequences and a special asset on branched tetradentates.

The following are the possible arrangement of donor atoms in quadridentate ligands.63

![Diagram of possible arrangements of donor atoms in quadridentate ligands.](image)
Pattern (1) is an established linear tetradentate. The pattern (2, 4) represent branched tetradentates. The arrangements (5-11) are the pattern for cyclic tetradentates. Except pattern (10), the other (5-9) and (11) are the special cases of linear pattern. The pattern (6) is an example of branched tetradentates (2). The patterns (7, 9, 10 and 11) are also the examples of branched pattern (3).

The majority of tetradentates Schiff base have the linear arrangement of the type (1). However Goodwin has subdivided these ligands into the following three stereochemical types.

A. Planar quadridentates:
These ligands co-ordinate through all the donor atoms, to a single metal ion, in such a way that all the donor atoms lie in a plane.

B. Tetrahedral tetradentate:
In these ligands the donor atoms cannot lie in a plane, but may be arranged tetrahedrally above a metal ion.

C. Facultative tetradentates:
These ligands are flexible and can be oriented, so that four donor atoms can coordinate either from a planar or from a non-planar arrangements.
The tetradental Schiff bases are the condensation products of diamines with pyridine-2-aldehyde, \( o \)-aminobenzaldehyde, \( o \)-hydroxybenzaldehyde or \( o \)-mercaptobenzaldehyde. Lions et al.\(^6^5\), Bailar and Bush\(^6^6\) have reported the bases containing four coordination sites. These are the condensed products of ethylenediamine with either pyridine-2-aldehyde or quinoline-8-aldehyde.

\[ \text{R} = \text{NH}_2, \text{OH} \]

These are reported to form cationic complexes of the following types, all the chelate rings are five membered.
Bis(8-quinalidene) — ethylenediamine complexes have terminal six membered rings and middle five membered rings.

The bis(pyridylhydrozone) of diacetyl is similarly constituted and functions as quadridentate. Branca et al. have synthesised Fe(III) complexes of N,N-bis(2-pyridyldimethyl)-ethylenediamine and have studied the stereochemistry and spin configuration in solid state as well as in solution state.
The findings have lead them to propose the following structures depending on the disposition of 'X' in the configuration.

**Cis α**

**Cis β**

**Trans**

Blum et al. have designed a new type of quadridentate containing -SNNS- donor sequences by condensing sulfosalicyl-aldehyde with ethylenediamine. This is a planar ligand and
hence can easily form square planar complex. Thus a spectrochemical, and magnetochemical studies envisage that the complex formed of such ligands have square planar configurations.

Dubsky and Sokol have reported the bases by reacting salicylaldehyde with diamines. These display tetradentate behaviour by forming square planar complexes with Ni(II) and Cu(II).
The complexes of transition and nontransition metals, with Schiff bases, derived from aliphatic diamines have received considerable attention in these years. Sn(IV) and organotin(IV) complexes of bis(salicylidene)ethylene diamine have been investigated spectrochemically. Mössbauer spectra of Sn(IV) have been used to focus upon the stereochemical disposition of donor atoms around Sn(IV). On the basis of this information bis (salicylidene) ethylene diamine Sn(IV) complex has been assigned all cis-configuration, whereas organotin(IV) complex has trans-configuration.
Pfeiffer\textsuperscript{79} has extended the field to various aromatic diamines; like the derivatives of bis(salicylidene)ethylenediamine, \(o\)-phenylenediamine derivatives, yield useful complexes containing two six membered and one five membered ring.

\[
\begin{array}{c}
\begin{array}{c}
\text{C} = \text{N} \quad 5 \quad \text{N} = \text{C} \\
\text{6} \quad \text{M} \quad \text{6}
\end{array}
\end{array}
\]

Pfeiffer has shown that \(m\)-phenylenediamine, \(\pi\)-phenylenediamine and \(4,4'\)-benzidine Schiff bases, form only the dimeric complexes with the metal ions, because of the steric demands.
The complexes of the IV group elements with such type of binuclear tetravalent Schiff bases have been reported.

A very interesting observations relating the colour of the Cu(II) complexes with the lengthening of the bridge between the two azomethine groups observed by Tanka and Kono. They have observed that the copper complexes change the colours from yellowish green to pale blue with the change in number (n) from 2 to 6.

Similar synthesis have been tried in case of Co(II) and Ni(II). It is found that lengthening hydrocarbon bridge has profound effect on the geometry of Co(II) complexes. These complexes change their geometry from square planar to tetrahedron.
whereas Ni(II) complexes retain their square planar configuration, however long the chain may be.

Mention may also be made the work of Warren et al. They have also isolated a diameric Cu(II) complexes with diketone bis(thiosemicarbazone) and have suggested the following structure.

Elder has synthesised tridentate and unsymmetrical, tetradeptates containing \( \text{ONN} \) and \( \text{ONNO} \) sequence from ethylenediamine and aromatic aldehydes. The Ni(II) complexes with these ligands
have been prepared and studied spectrochemically and magneto-chemically.

Biradar et al. and Vidali et al. have reported some substituted aldoxines and arylhydrazones (containing -ONO- sequences) and concluded that they possess an octahedral structure based on evidence from ir spectra.
Survey of literature

Literature survey of previous years has shown that ligands were obtained from the pyridine and substituted amino pyridines with condensation of aromatic aldehydes, ketones and (furfuraldehyde) and other organic substances. These ligands are used to prepare complexes with different metals, and they are found to be either biologically active or a very good reagents for estimation of metal ions in inorganic and analytical chemistry.

Malkion et al.\textsuperscript{91} prepared aryl(2,6-diaminopyridine) dichloro palladium complex, and this complex was used to study synthesis of DNA in tissue of human beings.

Balch et al.\textsuperscript{92} synthesised Pt(II) and Pd(II) complexes formed by the chelative addition of amines to isocyanides. The addition of amines to co-ordinated isocyanides were explored as a method of preparation of new chelating ligands. The addition of 2,6-diaminopyridine to M(CN-Me)\textsubscript{2}\textsuperscript{+} produced a tridentate ligand with one pyridine N donor and two trigonal CN donors. The properties of these complexes and related cations obtained by the addition of \(N_2H_4\) to M(CN-Me)\textsuperscript{+2} are compared.

Dombrowski\textsuperscript{93} et al. used 2,6-diaminopyridine as a fluorometric determination of primary aromatic amines. Sensitive fluorometric
A method for determination of primary amine was developed. The diazotisation of the amino group followed by coupling with 2, 6-diaminopyridine and the reaction of resulting azodyes with ammonical CuSO$_4$ produced an intensively fluorescent derivatives.

Packam et al.\textsuperscript{94} prepared polymers from aromatic nitriles and diaminopyridines. Macrocyclic and linear polymers were prepared by condensing 2, 6-diaminopyridine with (i) phthalonitrile (ii) pyromellitonitrile in alcohol with sodium alkoxide catalysis. Ni(II) and Cu(II) derivatives of polymers were also prepared.

Brodaki et al.\textsuperscript{95} synthesised the Rhodium(IV) complexes with amino pyridine and aminomethyl pyridine as ligands and studied two possibilities of co-ordination to the metal viz. heterocyclic N atom, and amino group or both.

Rastogi et al.\textsuperscript{96} synthesised the Pt(II) and Pd(II) complexes with 2-(2'-aminoethyl)pyridine. They have shown that ligands are tetradentate, and complexes of Pt(II) and Pd(II) or square planar. IR study shown that the metals are coordinated through the N of the amino group and the pyridine N atom.

Ranavidya B. Singh et al.\textsuperscript{97} prepared trivalent Cr(III) Mn(III), Fe(III) and Co(III) of tetradentate N$_6$ macrocyclic ligand. Trivalent Cr, Mn, Fe, Co salts react in situ with 2,6-diaminopyridine
and acetyleacetone to form complex of 16 membered $N_6$ tetradsentate macrocyclic ligand. The chelates are characterised as distorted square pyramidal of $[MLX]$ type where $M = \text{Cr, Mn, Fe, Co}$, $H_2L = \text{Macrocyclic ligand}$ $X = \text{Cl, Br, NO}_3\text{NCS, OAc}$. The ligand co-ordinated through all $N$ atoms through deprotonation of two of them. However pyridine nitrogen did not take part in the coordination. The chelate incorporates one anion, or hydroxyl group in the coordination sphere. The magnetic, electronic and IR spectral studies indicated lower symmetries for these chelates. X-ray measurements on powder form of the complexes has shown their isomorphous nature.

Paolucci et al. synthesized and characterised a polynuclear uranyl complexes. The new compartmental ligand 2,6-diaminocarboxylic acid-bis(salicylidenehydrazide) $H_4L$ reacted with variable amount of uranyl salt to give $UO_2(OAc)_2L$. The ligation around the uranyllon with the help of $H^1$ NMR and IR spectra are discussed.

Natan Lawrence C. et al. synthesized first row transition metal complexes of pyridine-2,6-dicarboxylated $N$-oxide and crystal structure of diaqua(Pyridine 2,6-dicarboxylate $N$-oxide) $\text{Mn(III), Mn(II), Co(II), Ni(II) and Zn(II) complexes}$ with above ligand were prepared and characterised by elemental analysis IR, ESR magnetic susceptibility measurements. They have shown that the
complex is orthorhombic with Mn six co-ordinated to two bridging N-oxide groups (trans) 2, terminal carboxyl group (cis) and two water molecules at cis position. X-ray powder diffraction pattern indicated that all 5 complexes are not isomorphous.

Decola, L. et al.\textsuperscript{100} prepared hexaaza macrocyclic complexes of lanthanides. The metal templated cyclic condensation of 1,2-diaminoethylene and 2,6-diacetylpyridine was achieved for all members of lanthanide series. Except radio active Pm, visible, UV, IR, 13C, and H'NMR magnetic and thermogravimetric properties showed the macrocyclic moiety to be thermally very stable, as well as inert in solution with respect to metal release or exchange.
Shrivastav V.S. et al.\textsuperscript{101} synthesised octahedral complexes of Mn(II), Co(II), Ni(II) and Cu(II) with ligand derived from 2-furylglyoxal and 2-aminopyridine. These complexes were screened for antibacterial activities against number of microorganisms and exhibited potential activity. The geometries of the complexes proposed on the basis of magnetic and electronic spectral datas.

Nishida et al.\textsuperscript{102} prepared and studied ESR and optical spectra of low spin square planar cobalt(II) complex with some quadridentate Schiff bases of \(N_2S_2\) type.

Analysis of ESR parameters shown that unpaired electron is in the \(dyz\) orbital of the cobalt atom. On this bases the absorption at 10x10\(^{-3}\) cm was attributed to the \(dx^2-y^2\) \(dyz\) transition.

Tandon J.P. et al.\textsuperscript{103} have reported Schiff base complexes of dioxouranium(II), U(IV) chloride complexes with mono basic, bidentate Schiff bases. \(UO_2Cl_2L_2\) (\(L =\) Schiff base) type complexes with yellow and orange colours were reported. Complexes are characterised by IR and conductance data. In these complexes ligand co-ordinated as neutral bidentate, using its N and O atoms.

Biradar et al.\textsuperscript{104} reported addition compounds of Sn(IV) chloride with tetradeionate Schiff bases. The 1:1 addition compound
of SnCl\textsubscript{4} with Schiff base containing 2-coordinating centres (-C=N) and 2-active centres (-OH) were prepared in benzene and characterised by elemental analysis. Compounds are non-electrolytes. According to IR spectra these are cis addition compounds with co-ordination number 6. The ligands exist in the phenolimine form and also contain intramolecular hydrogen bonding.

Biradar et al.\textsuperscript{105,106} reported thorium(IV) Schiff base complexes, and dioxouranium complexes with aromatic Schiff bases, and have explained nature of bonding of ligand with uranyl atom and thorium atoms.

Poddar S.N. et al.\textsuperscript{107} reported synthesis of Sn(IV) complexes with tetradeutate Schiff bases derived from salicylaldehyde
and diamines, and reported co-ordination of azomethine N with the metal on the bases of IR and other spectral studies.

Biradar N.S. et al.\textsuperscript{108} reported Cd(II) complexes with aroyl hydrazones. Cd(II) complexes of type CdL\textsubscript{2} of tridentate benzoyl and salicyloylhydrazones (HL) of 2-hydroxy-1-nephaldehyde and of salicylaldehyde and its 5-chloro and 5-methyl derivatives were synthesised and characterised by spectral and conductance, and elemental analysis data.

Csaszar, J. et al.\textsuperscript{109} have reported Ni(II) complexes Schiff bases formed from aminopyridines and salicylaldehyde. Schiff bases of salicylaldehyde with 2- and 3-aminopyridine and with the 3-, 4-, 5-, and 6-Me derivatives of 2-aminopyridine and their Ni(II) complexes were prepared and characterised by IR, NMR spectra and magnetic moments. The Schiff base acts as a bidentate ligand to give the octahedral complex NiL\textsubscript{2}(H\textsubscript{2}O)\textsubscript{2}. Except in the case of ligand derived from 6-methyl-2-aminopyridine which is tridentate and give octahedral NiL\textsubscript{2}.

Ni(II), Co(II) complexes of the type (ML\textsubscript{2}) where HL= tridentate Schiff base derived from 2-(2'-aminoethyl)pyridine and salal substituted salal are reported by Rastogi et al.\textsuperscript{110} Conductance, magnetic, and electronic and IR spectral data have shown that all the complexes have octahedral geometry.
Th(IV) complexes with tetradentate Schiff base ligands have been reported by Dash et al.\textsuperscript{111} Th(IV) complexes of the tetradentate Schiff base ligands ($N_2O_2$ donor set) obtained by the condensation of ethylenediamine with salicylaldehyde or acetylacetone have shown that in all cases the neutral Schiff bases and not the anions are co-ordinated to the central Th(IV) atom. The stoichiometries and co-ordination numbers of the complexes is either 12 or 8 for the bis or monocomplexes respectively.

Dioxouranium(II) with tridentate dibasic Schiff bases containing ONO donor sets were reported by Symal et al.\textsuperscript{112} Dioxouranium(II) complexes with Schiff bases derived from condensation of Salal, 5-chloro, 5-bromo, 5-nitro, 3,5-dichloro 4-methoxy, 5-methoxy and 3-ethoxysalicylaldehyde, and 2-hydroxy-1-naphthaldehyde with o-aminobenzylate were prepared from uranylacetate dihydrate, and the Schiff base in MeOH. In the complexes (U:O) stretching frequency occurs at $\sim 900 \text{ cm}^{-1}$ and the U-O distance is 1.74Å. The complexes are monomers dimagnetic, and octahedral.

Complexes of Pd(II) and Zn(II) with Schiff bases derived from methyl substituted aminopyridines, and salicylaldehyde were reported by Ranganathan et al.\textsuperscript{113,114} spectral reports have shown that Pd(II) complexes are square planar and Zn(II) complexes are tetrahedral.
Saxena Anil et al.\textsuperscript{115} synthesised Sn(IV) complexes of tridentate Schiff bases having ONS donor system. The complexes were characterised by UV, IR, $^1$H NMR and Moessbauer spectroscopies and powder diffraction method. They observed that Sn(OAc)$_2$L is 5-coordinated with distorted trigonal bipyramidal geometry. But SnL$_2$ shown hexa coordination about tin atom which is arranged in distorted octahedral geometry with orthorhombic lattice.

Uranyl complexes of Schiff bases derived from salicylaldehyde and substituted anilines, were reported by Dodwad et al.\textsuperscript{116} by spectral data of complexes have shown, that the bonding with the metal in the complex occurs from the hydroxy O and imine N of the ligand. The co-ordination number of these complexes is eight giving hexagonal bipyramidal structure. Complexes of Sn(IV) iodide, with multidentate dibasic Schiff bases were reported by Ghose\textsuperscript{117,118}. Tetridentate dibasic Schiff bases, having the -ONNO- donor system with SnI$_4$ gave complexes of type SnI$_2$L$_2$ which were characterised by IR, NMR, Mass spectral data. Tin complexes were evaluated for fungicidal and bactericidal activity. It was found that Sn(IV) complexes found to be very effective fungicides and antibacterial.

Panda C.R.\textsuperscript{119} reported furfurylidene arylamine complexes of dioxouranium(II) chloride and thiocyanate. In these complexes, co-ordination of the ligand through the furon ring O and the azomethine N
is observed. The thiocyanate groups are N-bonded and terminal.

Bhaskare C.K. et al. reported Ni(II), Cu(II) and Zn(V) complexes of tridentate Schiff bases derived from 4-aryl-2-aminothiozole and its substituted derivatives, condensed with substituted o-hydroxyalddehydes. These tridentate Schiff bases form $ML_2$ ($M = \text{Ni, Cu, Zn}$) type complexes. Magnetic, IR, and conductance data show that, complexes have octahedral structure.

**Hydrazones**

The hydrazones are condensed products of hydrazides and aldehydes or ketones belong to a huge class of azomethines.

![Hydrazone structure](image)

$X = \text{H, NH}_2, \text{NO}_3, \text{Cl, NH-R, COOH etc.} \quad Y = \text{OH, SH, H.}$
The hydrazone as a ligand have attracted much attention during the past few years. This is because of their importance as promising chelating agents for number of transition and non-transition metals, biological activities and wide applications in analytical chemistry as very good reagents for the extraction and spectro photometric determination of transition metal ions.

They are known for their varied stereochemical behaviours in the complexes, with the help of IR studies they are known to exist both in the enol and keto-forms. These ligands with the chromophore grouping -CO-NH-N- can enter the inner sphere of complexes either in the enol or keto form. This tendency of the grouping -CO-NH-N- to react with metal ions in the enol or keto form depends on the pH of the medium, and the nature of the substituents present on the carbonyl carbon atom and the -nitrogen atom. If the ligand exist in the keto form in the complexes, one would expect the -NH- and stretching vibrations. Whereas the absence of both of these frequencies is the characteristic of the enol form in the complexes.

The study of the complexes formed with hydrazones is much interesting because the tautomerism exhibited by them.
Thus the hydrazones are capable of reacting in both the keto and enol form depending on the reaction conditions.

Aroylhydrazones of salicylaldehyde or its derivatives which in many ways resemble the tridentate dibasic Schiff bases form metal chelates with novel structural and magnetic properties. In support of this quite a few hydrazone complexes with subnormal magnetic moments have already been reported in the literature.

The hydrazones resulted by condensing benzoylhydrazide with o-hydroxybenzaldehyde and o-hydroxy acetophenones have received special interest, because of their behaviour. These can at very outset, in view of the co-ordination sites and reactive groups, show monovalent and bivalent tridentate behaviours.
respectively, if OH, C=N, and C=O are involved in the bond formation. A number of Cu(II), Ni(II), Co(II) and Mn(II) complexes have been reported and they have been studied spectrochemically and magnetochemically. The Ni(II) and Cu(II) complexes are shown to be tetrahedral, Co(II) octahedral and Mn(II) square planar.

Aroyl hydrazones of salal in enolic form resembles the tridentate dibasic Schiff bases and therefore, are expected to give complexes with subnormal magnetic moment attributable to spin-spin, exchange in the dimer. Kubo et al. \cite{kubo1987} reported the magnetic moment of Cu(II) complex of salicyol hydrazone of salal as 1.2 BM. Narang and Aggarwala \cite{narang1989} reported the magnetic moment of the above complex as 1.6 BM attributing to the low magnetic moment to the antiferromagnetic exchange of super exchange type. Biradar et al. \cite{biradar1991} synthesised the Cu(II) complexes of benzoyl and salicyol hydrazones of salal or its derivatives and characterised them by magnetic IR and electronic spectral data. The low magnetic moment was attributed to the dimeric nature of the complexes involving phenolic oxygen bridge. In the view of the conflicting magnetic moments reported for Cu(II) Salicyol hydrazone complex, Syamal and Kale \cite{syamal1992} reinvestigated the magnetic and spectral properties of both benzoyl, and Salicyol hydrazone complexes of Cu(II) by cryomagnetic study and proposed a dimeric structure involving hydrazide (enolic) oxygen bridge and supported the magnetic data of Kubo et al. \cite{kubo1987}.
Naranga and Aggarwal have prepared series of complexes with Salicyol hydrazones and have shown that one of the hydrogen bonding (involving C=N and Co groups in enol form) formed with the azomethine N, is retained in the complexes. The Cu(II) complex with this ligand is shown to be square planar.

Trivalent Mn(III) and Co(III) complexes with benzyolhydrazones of o-hydroxyaldehyde or ketones were synthesised by Rastogi et al. On the basis of magnetic moment IR and electronic data, they have suggested dimeric five and six coordinated structure respectively. Mn(III) complexes \((\text{MnLX})_2\) involved phenolic oxygen bridge whereas Co(III) complexes \([\text{CoLOH(H}_2\text{O)})_2\] involved the hydroxyl bridge.

T.R.Rao et al. reported Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) complexes of acetone (N-benzoyl)glycylhydrazone of the type \(\text{M}\left(\text{B}_2\text{AGH}\right)_n\text{Cl}_2\) \((\text{M} = \text{Mn(II)}, \text{Co(II)}, \text{Cu(II)}, \text{Zn(II)} n = 1)\) and \(\text{M}\left(\text{B}_2\text{AGH-2H}\right)_2\text{3H}_2\text{O}\) \((\text{M} = \text{Co(II)}, \text{Ni(II)}, \text{Cu(II)})\) and \(\text{B}_2\text{AGH} = \text{acetone(N-benzoyl)glycylhydrazone}\) have been synthesized and characterized on the basis of their elemental analysis, molar conductance, magnetic susceptibility electronic and IR spectral data. High spin octahedral geometry for Co(II) and Ni(II) complexes and square planar distorted octahedral geometry for Cu(II) complexes have been assigned.

C.R.Pand et al. reported furfurylidene arylamine complexes of
Dioxouranium(II) chloride and thiocyanate form diamagnetic, non-electrolytic complexes of the type $[\text{UO}_2(\text{SB})_2X_2]$ where SB denote bidentate Schiff base prepared in situ of 2-furoncarboxyaldehyde with equivalent amount of aromatic amines. IR data shows the co-ordination of the ligand through the furon ring oxygen and the azomethine N. The thiocyanate group are N-bonded in a terminal manner.

\[ R = \text{H, m-Cl, o-, m-, p-me, o-, p- Ome, } p-\text{OEt} \]

\[ R = \text{H, m-Cl} \]
\[ \text{o-, p-me} \]
\[ \alpha-p, \text{ Ome, p-OEt}. \]
Two types of complexes of acetone-2-furylhydrazine i.e. (a) VO(LH)SO₄ . Cu(LH)Cl₂ H₂O and M(LH)₂Cl₂ [M = Mn(II), Co(II), Ni(II), Zn(II), Cd(II) and Hg(II)] and (b) compounds of type M(L)₂.2H₂O [M = VO(II), Mn(II), Co(II), Ni(II), Cu(II) and Zn(II)] have been reported. These complexes were prepared by the reaction of appropriate metal salts and the ligand in neutral and alkaline medium for the (a) and (b) complexes respectively. Tetrahedral coordination around Hg(II), Cd(II), Zn(II) and square pyramidal around VO(II) and octahedral around Mn(II), Co(II), Ni(II), Cu(II), have been reported. ESR spectra indicate that unpaired electron in Cu(L)₂.2H₂O is present in dₓ²₋ᵧ² orbital. IR, spectra indicates co-ordination of the ligand through corboxyl oxygen in Zn(II), Cd(II) and Hg(II) complexes and bidentate co-ordination through carbonyl oxygen, and azomethine N in the remaining complexes.
Aim of Research

Schiff bases containing a variety of donor sites have attracted much attention, because of their versatile stereochemical behaviour, and ease with which they form complexes, with various transition and non-transition metal ions $^{17,18}$. They are also known to possess tubercuostic $^{40}$ and bacteriostatic $^{42}$ activities, and are useful in therapy $^{39}$. They are also used as potential models, in the study of energy transfer system.

Although the stereochemical investigations of metal complexes of monovalent bidentate, have been the subject of intensive research $^{17,18}$ those of the tridentate dibasic and tetradentate complexes have received relatively, little attention which we have seen by the survey of previous work. A detailed study of the effect of the nature of the central metal atom and the geometry of tridentate ligands on co-ordination of chelation behaviour is possible $^{145}$ if one can vary the molecular structure of these ligands by changing, (a) the ligand fragments, adjacent to the immediate environment of the metal atom, (b) the electron donating atoms (O, S, N and Se) for the same ligand fragments of metal atom(s) or (c) the metal atom for the same ligands. Such study will provide the information about the structural property relations of metal chelates and the tendency of these ligands towards complex formation with metal ions.
With vast development in synthesis of new complexes and establishing their structure, on the basis of different spectral studies it has become quite essential to study their biological applications to use them, not only as that analytical reagents but most effective drugs in irradiating burning problems like cancer and other diseases. In this direction we wished to synthesise complexes which can have biological importance, rather than their structural aspects.

Since the discovery that CisPt(NH$_3$)$_2$Cl$_2$ has antitumor activity, research on improvement or effectiveness of this compound by modifying the methods of its application and by reducing its side effects has outmighed research on the development of new co-ordination compounds that may be more effective and less toxic. It has been recently suggested that the requirement for a protential antitumour co-ordination compounds are (a) a pair of strongly covalently bonded ligands with nitrogen being the donor atom the two ligands should occupy two cis position in the complexes (b) a pair of moderatery labile ligands and (c) a soft acid type metal atom. Substituted pyridines provide strong covalant bonds to heavy metal atoms, especially when they behave as chelating agents. Moreover possible substitution on the pyridine ring makes it possible the modification of the lapid and water solubility of ligands and their complexes. Substitution on the pyridine ring
also provides a means of modifying the electronic environment of the metal atom. We therefore set out to synthesise a series of complexes of Schiff bases derived from 2-aminopyridine and 2,6-diaminopyridine with arylaldehydes and complexation of these ligands with heavy metal, like U(VI) and Th(IV), Tin(IV) as well as IIB group metals and transition metals like Co(III), Ni(II) and Cu(II) in order to screen them for their antibacterial and antifungal activity, and to evaluate insecticidal and pesticidal properties. Curaim was also to carry out preliminary studies on toxic effect of these compounds on the protein content of liver of amphibians.

Hydrazones have been investigated and proved to be promising chelating agents for number of transition elements. Hydrazone complexes are of special interest in recent years due to the biological importance. Aroylhydrazone of pipermot(3,4-methylenedioxybenzaldehyde) form metal chelates with novel structural and magnetic properties. In support of this a good number arylhydrazone complexes with sub-normal magnetic moments have already been reported in literature.

Biological importance of hydrazone in general and less study in the salicylidene-2-furylhydrazone complexes created an interest in the author to study some complexes of Zn(II), Cd(II), Hg(II) with salicyliden-2-furylhydrazone and vanillinidene-2-furylhydrazone and obtain their structural information with help of spectral and analytical data. Author is much interested in studying the biological importance of these hydrazone complexes.
REFERENCES

1. A.E.Martell and M.Calvin,

2. F.P.Dwyer and D.P.Mellor,

3. H.J.Emeleus and A.G.Sharpe,

4. B.E.Douglas and D.H.McDaines,

5. F.A.Cotton and G.Wilkinson,

6. R.S.Nyholm,

7. D.M.Adams,
8. M. Mikami, I. Nakagawa and T. Shimanouchi,

9. J. C. Bailer and D. H. Busch,

10. F. Basalo and R. C. Johnson,
    "Co-ordination Chemistry", W. A. Benjamin INC and Amsterdam (1964).

11. E. W. Benson, R. E. Khormann and D. X. West,

12. R. T. Sanderson,

13. H. S. Ahuja, S. C. Jain and R. Revest,

14. R. S. Drago,

15. M. Riederer and W. Sawodny,
16. R.J.H. Clarke,
H.J. Emeleus, R.S. Nyle and A.F.T. Dickencon, Fergamen Press,

17. L. Sacconi,
Experientia Suppl. 9, 148 (1964),

18. S. Yamada,

19. B.O. West,
"New Pathways in Inorganic Chemistry", Eds. B.A.V. Ebsworth

20. R.S. Nyholm,

21. M.J.M. Campbell,

22. A. Shulman and F.P. Dwyer and D.P. Mellor (Eds.),
"Chelating Agents and Metal Chelates", Acad. Press. New York

23. David R. Williams,
24. R. Lontie and R. Witters,

25. B. Reinhammer,

26. N. Beinert,

27. C. Hilegg and K. Lerch,

28. S.W. May, R.S. Phillips, P.W. Mueller and H.H. Herman,

29. K. Kanda, M. Nekamore, H. Okawa and S. Kido,

30. A.B.P. Lever, B.S. Ramaswamy, S.R. Pikkens,

31. M.M. Rogi and T.R. Demmin,
"Aspects of Mechanism and Organometallic Chemistry", Ed.

32. S.M. Nelson,
33. S. E. Groh, Israel,  

34. G. I. Solomor,  

35. S. Yamada, E. Chno, Y. Kunge, A. Takeuchi and K. Yamanouchi,  
K. Iwasaki,  

36. N. D. Hobday and T. D. Smith,  

37. H. S. Maslen and T. N. Waters,  

38. U. Caselleto, P. A. Vigato and M. Vidali,  

39. E. M. Hodnell and W. J. Duny,  

40. L. Muslin, W. Roth and H. Erlenmeyer,  

41. W. M. Farrow, H. Calvin and F. H. Schucler,  
42. Shin, Ichiro and Takase,

43. F. Liene and K.V. Martin,

44. G.T. Morgan and F.H. Brustall,

45. M.R. Litzow, L.F. Power and A.M. Tait,

46. Y. Mutto,

47. N.S. Biradar and V.B. Mahale,

48. N.S. Biradar, T.R. Goudar, V.B. Mahale and V.H. Kulkarni,
J. Karn. Univ. (Sc), 18, 19 (1973).

49. P. Bamfield,

50. N. Dunasky and T.H. Crawford,
51. R.C. Paul, S.K. Vasista, S.K. Nehru and D. Singh,

52. V.H. Kulkarni, B.K. Prabhakar and B.R. Patil,

53. D.K. Rastogi and P.C. Panchari,

54. G.O. Dudek and E.P. Dudek,
J. Amer. Chem. Soc., 86, 4283 (1964);
J. Chem. Soc. B. 1356 (1971);

55. J.J. Charette,

56. N.M.D. Brown and D.C. Nonhebel,
Tetrahedron, 24, 5655 (1968).

57. N.G. Voronkov, G.G. Skavortsova, E.S. Domnina,
Yu. N. Ivlev. N.F. Chernor N.N. Chipanna,
V.R. Voronkov and D.D. Taryashinova,

58. N.S. Biradar and V.B. Mahale,
59. V.B. Mahale,
Ph.D. Thesis, Karnatak University, Dharwad.

60. N.S. Biradar, T.R. Goudar, V.B. Mahale and V.H. Kulkarni,
J. Karn. Univ. (Sci), 18, 19 (1973).

61. a. N. Iwasaki, K. Sone and H. Ojima,

b. E.D. McKezzia, R.E. Paine and S.J. Selvey,

62. Thabet, S. and Tabibian, O.

63. D.St.C. Black and Hartshorn,

64. M.A. Goodwin,

65. H.A. Goodwin and F. Lions,

66. D.H. Bush and J.C. Bailor Jr.,
67. F. Lion and K.V. Martin, 

68. M. Branca, P. Checconi and B. Pispisa, 

69. P.R. Blum, R.M.C. Wei and S.C. Cummings, 

70. J.V. Dubsky and A. Sokol, 

71. a. A. Syamal and V.D. Ghankar, 
Current Science, 45, 547 (1976).

b. R.N. Kapoor and V.S. Rajpurohit, 

72. R.V. Singh and J.P. Tandon, 

73. a. R.L. Dutta and M.M. Hossain, 

b. A. Shahani and A. Athor and N. Ahmad, 
74. a. A.N. Sundram and G.P. Prabhakaran,

   b. R.C. Elder and M.C. Hill,

75. K.K. Deshamukh, A.M. Hundekar and D.N. Sen,

76. a. Barbieri and R.H. Herber,

   b. S.S. Biradar and V.H. Kulkarni,

77. G.S. Stocco, G. Alanzo, N. Bertazzi and F.D. Bianca,

78. J.N. Ruddick and J.R. Sams,

79. Pfeiffer,

80. R. Cefalu, F. Maggic, L. Pellerito and V. Rumano,
81. S.N. Poddar and N.S. Das,

82. N.S. Biradar, V.H. Kulkarni and N.N. Sirmokadam,

83. a. R. Barbieri and R.H. Herber,

b. R.V. Singh and J.P. Tandon,

84. T. Tanaka and S. Kono,

85. L.E. Warren, S.M. Horner and W.E. Hatfield,

86. R.C. Elder,

87. N.S. Biradar, M.D. Patil and T.R. Goudar,

88. M. Vidali, P.A. Vigato and U. Casellato,
89. M. Vidali, P.A. Vigato, U. Casellato, 
E. Toudello and O. Traverso, 

90. N.S. Biradar and S.D. Angadi, 

91. Tayim, Hassan A. Molakion, Artint, Bikhazi Anwin, B. 

92. Balch, Alan, L. Parks John E., 

93. Dombrowski, Lawerence J. Partt. Edward L., 
Anal. Chem. 43 (8), 1042 (1971).

94. Packam, Donald, I., Hydron J.C. 

95. D. Brodaki and G. Pannetier, 

96. D.K. Rastogi, P.C. Pachauri, K.C. Sharma and M.P. Teotia, 

97. Rana Vidya B. Singh, Mrs. Prabha Singh, Dharma P. Teotia, 
Mahendra P., 
98. Paoluci, G. Stelluto S, Sitron S.

99. Nathan Lawernce C. Doyls, Christine A. Mooring,
Anne. M. Zapien Donald C. Larsen Scott. K.,
Pierpont Cortland G.

100. DeCola L. Smailes, D.L. and L.M.Vallarnio,

101. V.S.Shrivastava, C.P.Bhasivi and G.C.Saxena,

102. Nishida Yuzo, Sumita, Akira Kida Sigeo,

103. R.G.Vijay, and J.P.Tondon,

104. N.S.Biradar and V.B.Mahale,

105. N.S.Biradar, V.H.Kulkarni and N.N.Sirmokadam,
J. Karnatak Univ., 17, 14 (1972).
106. N.S. Biradar and T.R. Goudar,

107. S.N. Poddar and N.S. Das,

108. N.S. Biradar, V.B. Mahale and B.R. Havinale,

109. J. Czaszar, and J. Balog,

110. D.K. Rastogi and P.C. Pachauri,

111. Dash, Kailash C. Mohanta, Hradananda,

112. Arun Syamal and Om Praksh,

113. Ranganathan, Hemalatha, Ramaswamy D. and M. Santappa,

114. Mohamed R. Mohamoud, El-Haty. T. Mohamed,


57

b. N.B. Mallur,

124. H. Ohta,

125. J.R. Merchant and D.S. Chothia,

126. Gerhard Bahr and D. Thiele,

127. P. Heizmann and K. Ballschmiter, Fresenius,

128. L. El-Sayed and M.F. Iskander,

129. J.F. Alcock, J.R. Baker and A.A. Daimantis,

130. H. Ohta,

131. K.K. Narang and Miss A. Aggrawal,
132. M.D. Revenko and N.V. Gerbelu,

133. D.K. Rastogi, V.B. Rana and Duo,

134. A. Syamal and K.S. Kale,

135. N.S. Biradar and B.R. Havinale,

136. K. Ueno and A.E. Martell,

137. S. Satyapathy and B. Sahoo,

138. S. Yameda, E. Ohno, Y. Kuge, A. Takeuchi
K. Yamanouchi and K. Iwasaki,

139. U.L. Ray, K.B. Pandeya and R.P. Singh,

140. M. Kubo, Y. Muto, Y. Kuroda and M. Kishita,
141. A. Syamal and K.S.Kale,

142. D.K.Rastogi, S.K.Sahm, V.B.Rana and S.K.Dua,

143. T.R.Rao,

144. a. C.R.Pand, S.C.Nayak, V. Charkarvorthy and K.C.Dash,

b. J. Scientific and Industrial Research,
Vol. 44 No. 12, 635 (1985).

145. V.V.Zelentsovj O.A.Osipov and Burlow,

146. B. Rosenberg, L. Van Camp and T. Drigas,

147. D.R.Williams,