PART I
SYNTHESIS AND CHARACTERIZATION

INTRODUCTION

PART I

SYNTHESIS AND CHARACTERIZATION
CHAPTER I
INTRODUCTION

Co-ordination Chemistry, precisely, is the Chemistry of metal atoms "co-ordinated" by atoms or molecules. Co-ordination Chemistry has always been a challenge to the Inorganic Chemist. Chemistry of Schiff bases have been intensively investigated in recent years owing to their co-ordination properties and diverse applications.

The synthesis and structural investigation and reaction of transition metal Schiff bases have received a renewed attention in recent years because of their biological activities as anti tumoral, antifungal and antiviral activities.

The modern study of metal complexes begins with the work of two men, Alfred Werner and Sorphus Mads Jorgenson. Co-ordination Chemistry has grown from a readily defined and limited topic in to what is now the most active research area in inorganic Chemistry encompassing a great variety of subjects and phenomena. Reason for this advancement can be attributed to the formulation of excellent theories of electronic structure of metal ions in coordination compounds such as ligand field and molecular orbital theories and the availability of modern sophisticated instruments which are powerful tools for structure determination.
Complexation reactions are used in qualitative as well as in quantitative analysis. There are some selective and sensitive organic reagents for the determination of metal ions. For example, dimethyl glyoxime is a good precipitating reagent for the gravimetric analysis of nickel and palladium, while EDTA is a good reagent for the volumetric analysis of calcium, magnesium, zinc etc.

The role of co-ordination compounds in colorimetric, spectrophotometric and polarographic analysis is also significant.

Transition metal complexes act as catalyst in many industrial processes like Wacker process, Oxoprocess, Monsanto process etc. Many enzymes contain a small prosthetic group, which is usually a complexed metal ion. Haemoglobin, myoglobin, chlorophyll and cytochromes are some of the most important complex compounds in living systems.

Co-ordination compounds find use in analytical chemistry for the identification and extraction of metal ions in cation exchange resins and in solvent extraction for the preparation of radioactive metals.

Schiff base ligands

Schiff bases constitute an important class of nitrogen donor ligands and occupy a prominent position amongst the recent achievements in the field of coordination Chemistry. Schiff bases contain the azomethine group and are
usually formed by the condensation of a primary amine with an active carbonyl compound. They have the general structure RN = CR'. Where R and R' are aryl, alkyl, cycloalkyl or heterocyclic groups, which may be variously substituted. The synthesis and properties of Schiff bases are widely reviewed. Works on bidentate ligands have been reviewed exclusively by Holmetal. A number of other reviews have also appeared on the chemistry of Schiff bases and their metal complexes.

The bonding ability of ligands depends on the nature of atoms, which act as co-ordination sites, their electro negativity and steric factors. The possibility of having a lone pair of electrons in either a π or sp² hybridised orbital or trigonally hybridised nitrogen in the >C=N group is of the fundamental, chemical and biological importance. If the co-ordinating ligand bears a functional group usually –OH or –COOH sufficiently near to the site of condensation, then a very stable five or six membered chelate ring can be formed. Tridentate Schiff base ligands forming two annulated rings form comparatively stable complexes.

Schiff base ligands and their complexes are known to possess tuberculostic, bactericidal, fungicidal, antimicrobial, and anticancer activities. The possibility of using them in chemical analysis selective separation and enrichment of certain metals catalysis and gas
chromatography\textsuperscript{29,30} and also in stabilizing poly olefins against oxidation and u.v. light deterioration\textsuperscript{31} is being explored.

Among the numerous selective and specific complexing agents, the Schiff base ligands derived from dibenzoyl methane, benzoylaceton, camphor and heterocyclic amines like o-aminophenol, o-aminothiophenol and amino acids like histidine, glycine etc. deserve special mention due to many outstanding features of the complexing system that they provide.

**Metal chelates of Schiff bases derived from β-diketones: A review**

β-Dicabronyl compounds constitute a class of the most important ligands which have been employed very widely from the outset of this century.\textsuperscript{32,33} They are very versatile and exhibit a great variety of coordination modes besides the usual bidentate behaviour of monoanions.\textsuperscript{34}

The metal chelates of β-diketones and their corresponding imines undergo a variety of electrophilic substitution reactions which are characteristic of aromatic systems. The chemical reactivity of these chelates has been ascribed to their pseudo or quasi aromatic character. On the basis of electronic spectra of β-diketonates, Barnum\textsuperscript{35} has suggested that there may be significant bonding between the metal and the ligand. This suggestion has however been questioned by Cotton and Holm\textsuperscript{36} and McGarvey\textsuperscript{37} on the basis of symmetry and energy of the metal orbitals available for \(\pi\)-bonding.
Although the nature of the metal-ligand bonding in these chelates seems to be controversial, it has been established that the coordinated chelate ring possess quasi-aromatic character.

The versatility with which acetylacetone and related ligands coordinate with metal ions yields numerous classes of chelated and open chain complexes in which the ligand occurs variously as

(i) a monomeric bidentate oxygen donor in the enol form
(ii) a neutral bidentate oxygen donor in the keto form.
(iii) a monoanionic ligand coordinating through the methine carbon atom
(iv) a $\pi$-allylic donor
(v) a monoanionic monodentate oxygen donor in the enol form
(vi) a bridging ligand of various types.

The $\beta$-dicarbonyl compound generally exists as an equilibrium mixture of the tautomeric keto and enol forms. The rate of spontaneous interconversion between these forms is rather slow at room temperature\textsuperscript{38} and their simultaneous NMR spectroscopic observation is possible. For instance the $^1$H NMR spectrum of neat acacH is composed of OH, CH, CH$_2$ and CH$_3$ signals in accordance with the following equilibrium.
The enol tautomer is stabilized at least partially by the intramolecular hydrogen bond, and since the internally hydrogen bonded molecule, the enol form is favoured by nonpolar solvents.

Literature reveals that unlike the reactions of coordinated β-diketonates, the reactions of coordinated Schiff bases are not much attempted. This may be probably due to the fact that β-ketoimines are more susceptible to acid hydrolysis\textsuperscript{39,40} than metal β-diketonates. Although the Schiff bases are quite susceptible to hydrolysis, their metal chelates, particularly those of Cu(II), Ni(II) and Pd(II) are quite stable towards hydrolysis.

Among the various γ-CH substitution reactions of β-ketoimines, the nitrosation and amine exchange reactions are quite unique and have interesting features.
Keto-enol tautomerism of $\beta$-ketoimines

Schiff bases derived from the 1:1 condensation of $\beta$-dicarboxyls and primary monoamines are capable of existing in any of the three tautomeric forms, the Schiff base (a) the ketoamine (b) and the enolimine (c).

The interchange between the last two tautomers involves a small displacement in the equilibrium position of the acidic proton. The observed composition of the solutions was found to be insensitive to, solvent acidity, polarity and to substituent effects at the carbonyl carbon.

For many condensation products the most direct method of investigating tautomeric equilibria is proton magnetic resonance. Recent p.m.r. investigation of a wide variety of species capable of existing in any or all of the three tautomeric forms, has led to the general conclusion that, the chelated ketoamine form predominates to the extent of $> 95$ mole $\%$ in nonpolar solvents.$^{41-42}$
Kishita et al.\textsuperscript{43} who prepared copper(II) chelate of N-acetyl-acetone-o-hydroxy aniline, called attention to its subnormal magnetic moment. Direct Cu-Cu interaction in the solid state resulting from dimerisation was presumed. Its dimeric nature was confirmed through determination of crystal structure by Barclay et al.\textsuperscript{44} The copper atoms are bridged by the phenolate oxygen atom of the ligands. Each copper atom of the dinuclear complex has identical arrangements, but has different environments. One copper atom forms a distorted square pyramid with an oxygen atom while the other forms a square planar structure.

Recently, the above structural data have been reinterpreted in terms of a tetrameric structure.\textsuperscript{45} A similar copper(II) complex of benzoylacetone-o-hydroxy aniline was also reported.\textsuperscript{46}

An important consequence of this is to introduce competition of O- or N-coordination of the oxiimino group of the same ligand. Since the oxiimino group can bond to the metal using either of its donor atoms, it is said to be 'ambidentate'. The monovalent bidentate ligand(III) therefore offers interesting possibilities of producing a variety of chelate linkage isomers.
Coordination of a donor atom of the oxiimino group and the imine nitrogen, \( =C=NR \) can be expected to form three chelate linkage isomers represented by \( M(II)-NNNN, M(II)-NONO \) and \( M(II)-NNON \) bonding.

\[ \text{\beta-Ketoimines provide fairly similar complexing system as that of salicylaldimines. Both types bearing the ON donor set, form six membered metal chelate rings. The following structural types (IV) and (V) are the most important.} \]

In (IV) \( R_2 = R_1 = R = \text{CH}_3, M = \text{Cu}(II), n = 2. \)

In (V) \( R_2 = \text{CH}_3, R_1 = \text{C}_6\text{H}_5, B = \text{CH}_2\text{CH}_2 \) and \( M = \text{Ni}(II) \)

Of these 2 types type (IV) forms bidentate ON donor group.
Nyholm and coworkers\textsuperscript{47} for the first time isolated, bis(oximinoacetylacetoneimino)nickel(II) using sodium nitrate in presence of ammonium acetate. However, the possibility of linkage isomerism of the oximino group was not considered either by these authors or by the subsequent investigators.\textsuperscript{48,49} Around 1970, both Bose et al.\textsuperscript{50} and Dixit\textsuperscript{51} independently proposed the structure (VI) for the nitrosated complex obtained by Nyholm et al. and other authors.

![Diagram of complex VI](image)

It is significant to note that in (VI) one of the ligands is coordinated via O-, while the other via N- of the oximino group. The formulation of the interesting bonding mode as in (VI) led to the extensive studies on the coordination behaviour of the oximino group of the oximino-\(\beta\)-ketoimines in their nickel(II) complexes and palladium(II) complexes in a few instances. It has been shown the bonding mode of the oximino group is unique as in (VI) in all the nickel(II) complexes.\textsuperscript{52} However the factors modifying the ambidentate co-ordination of the oximino group are still open for further investigation.
Similarly the electrophilic substitution reactions of transition metal complexes of monovalent \(\beta\)-diketone are quite well studied\(^{47}\). The corresponding analogous reactions of bivalent tetradentate metal \(\beta\)-ketoiminates are not known, except for the bromination and nitration of 4,9-dimethyl-5,8-diazododeca-4,8-diene-2,11-dionato copper(II)\(^{48}\) and the mononitrosation of bivalent quindentate Schiff base metal chelates derived from \(\beta\)-diketones and 1,2-diamines namely \([Men/iPn(Al)2]\) where \(M = \text{Ni(II)}, \text{Cu(II)}\) or \(\text{Pd(II)}\) etc.\(^{49}\) An interesting feature of the latter monosubstitution products display an intermolecular chelate linkage isomerism (ambidentate coordination).

In this respect, it may be mentioned that the hetero group \(\gamma\)-CH substitution in both the chelate rings can change the coordination of the already present ambidentate substituent at \(\gamma\)-CH. For instance, to examine the factors modifying the ambidentate coordination of the isonitroso group and thereby the changes manifested in the quasiaromatic character of the mononitrosated \(\beta\)-ketoimine chelate rings, reactions like facile bromination of a series of monosubstituted nickel(II) and palladium(II) complexes were studied. These reactions yielded a series of interesting heterogroup \(\gamma\)-CH substituted products. Similar studies, however appear to be quite meagre in the case of copper(II) complexes of bivalent tetradentate Schiff base chelates.\(^{48,49}\)
Isonitrosoacetylacetone (HIAA) i.e., 4-imino-2,4-pentanedione-3-oxime and related β-keto ligands are versatile chelating agents manifesting various modes of bonding to the metal ions. The isonitroso moiety (>C=NH) also referred to as a hydroxyimino group is particularly ambidentate chelating functionality, having coordination ability either through nitrogen and/or oxygen whereby inter and/or intramolecular chelate linkage isomers are produced.

According to Mehta et al.55 N-acetylacetoneethanolamine formed 2:1 complexes with copper(II), zinc(II), palladium(II) and cadmium(II) ions. Since the ligand is presumed to act as monobasic bidentate in these complexes, these authors represented the ligand as monobasic tridentate in iron(II), cobalt(II) and nickel(II) complexes. Through crystallographic studies, copper(II) complex of this ligand was shown to be a tetramer.56 By the same method copper(II) complex of N-acetylacetonepropanolamine was shown to be a dimer, in either of these cases the ligands act as dibasic tridentate. A novel series of acetylacetoneanthranilic acid adducts of Cu(II) have been prepared and characterised based on spectral data.57

Furthermore, biologically important reactions such as amination, transamination and deamination involve intermediate formation of Schiff bases =C=NR. Such reactions frequently involve coordination of the grouping to a metal ion.58 While the amine exchange reactions of
bis(salicylaldehyde)copper(II) complexes have been studied in detail,\textsuperscript{59,60} reports of such reactions with β-ketoimine complexes are very few.

They offered synthetic routes to obtain new coordination compounds. They also have played an important role in the synthesis of linkage isomeric complexes. A variety of known reactions of coordinated β-ketoimimates are listed in Table 1.1.

Metal chelates of β-ketoimines and other tridentate Schiff bases possessing ONO donor sites are given in Table 1.2.

**Stability constants of various Schiff bases and their metal chelates**

The experimental methods, which give the highest accuracy in the determination of complexing constants in an unknown system are those which are used to measure the concentration of individual species. Polarography, potentiometry and spectrophotometry are the different types of methods to find out the stability constants.

Stability of Schiff base complexes depends primarily on the strength of the C=N bond, basicity of the imino group, density of the Schiff base and steric factors.\textsuperscript{81}

The stability constants of various transition metal complexes of bi and tridentate Schiff bases have been reported.\textsuperscript{18,82-92}
Between N-acetylacetone-o-aminobenzenesulphonic acid and N-acetylacetoneanthranilic acid, the more ionised sulphonic acid ligand has been reported to yield the less stable complexes, as expected. Stability of metal complexes of these ligands determined pH-metrically, showed the order of stability with respect to metal ions as $\text{UO}_2^{2+} > \text{Cu}^{2+} > \text{Ni}^{2+} > \text{Co}^{2+} > \text{Zn}^{2+} > \text{Cd}^{2+}$, which is in agreement with Irving-Williams stability order.

The thermal stability of complexes depends primarily on which bonds of the complexes break first at elevated temperatures. If decomposition begins with fission of the bond between the central metal atom and the donor atom, the thermal stability will depend on the strength of this bond i.e., on the stability of the complex. Thermal stability will be effected by the structure of the complex molecule, by steric factors or by the substituents, as these factors change the strength of the coordinate bond. Decomposition of this type occurs with complexes containing volatile ligands (examples - amine, pyridine and aquocomplexes).
TABLE 1.1
Reactions of Coordinated Metal Schiff bases and Keto imines

<table>
<thead>
<tr>
<th>Reaction type</th>
<th>Metal ion</th>
<th>Ligand</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Halogenation</td>
<td>Cr(III), Co(III)</td>
<td>N-arylacetylimine. Both β-diketones and ketoimines</td>
<td>61, 62</td>
</tr>
<tr>
<td></td>
<td>Cu(II), Ni(II)</td>
<td>N,N-ethylene bis(acetylacetonate)</td>
<td>63</td>
</tr>
<tr>
<td>2. Halogenation cum nitration</td>
<td>Pd(II)</td>
<td>N-substituted β-ketoimines</td>
<td>64</td>
</tr>
<tr>
<td>3. Nitration</td>
<td>Co(III)</td>
<td>N',N-ethylene bis(salicylaldehyde acetylacetonate)</td>
<td>65</td>
</tr>
<tr>
<td>4. Amine exchange</td>
<td>Pd(II), Cu(II), Ni(II)</td>
<td>Isonitrosoethylacetate</td>
<td>66, 67</td>
</tr>
</tbody>
</table>
TABLE 1.2

Metal Chelates of Tridentate Schiff bases derived from \(\beta\)-ketoimines

(R = phenyl, naphthyl, pyridyl and substituted phenyls)

<table>
<thead>
<tr>
<th>(R_\alpha)</th>
<th>(R_\gamma)</th>
<th>(R)</th>
<th>Metal</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH(_3)</td>
<td>CH(_3)</td>
<td>C(_6)H(_5)</td>
<td>Cr(III), Co(II), Ni(II), Cu(II), Th(IV)</td>
<td>61, 68-74</td>
</tr>
<tr>
<td>CH(_3)</td>
<td>CH(_3)</td>
<td>CH(_2)C(_6)H(_5)</td>
<td>Cr(III), Ni(II)</td>
<td>61, 69</td>
</tr>
<tr>
<td>CH(_3)</td>
<td>CH(_3)</td>
<td>o-C(_6)H(_4)CH(_3)</td>
<td>Cr(III), Ni(II)</td>
<td>61, 69</td>
</tr>
<tr>
<td>CH(_3)</td>
<td>CH(_3)</td>
<td>m-C(_6)H(_4)CH(_3)</td>
<td>Cr(III), Ni(II)</td>
<td>61, 69</td>
</tr>
<tr>
<td>CH(_3)</td>
<td>CH(_3)</td>
<td>p-C(_6)H(_4)CH(_3)</td>
<td>Cr(III), Ni(II)</td>
<td>61, 68, 69</td>
</tr>
<tr>
<td>CH(_3)</td>
<td>CH(_3)</td>
<td>p-C(_6)H(_4)CH(_3)</td>
<td>Co(II), Cu(II), Th(IV)</td>
<td>73</td>
</tr>
<tr>
<td>CH(_3)</td>
<td>C(_6)H(_5)</td>
<td>C(_6)H(_5)</td>
<td>Ni(II)</td>
<td>75</td>
</tr>
<tr>
<td>CH(_3)</td>
<td>C(_6)H(_5)</td>
<td>C(_6)H(_5)</td>
<td>Cu(II)</td>
<td>75, 71</td>
</tr>
<tr>
<td>C(_6)H(_5)</td>
<td>C(_6)H(_5)</td>
<td>2-C(_6)H(_4)N</td>
<td>U(VI)O(_2)</td>
<td>76</td>
</tr>
<tr>
<td>CH(_3)</td>
<td>CH(_3)</td>
<td>o-C(_6)H(_4)OH</td>
<td>[TiL(_2)], [TiL(OEt)(_2)]</td>
<td>77</td>
</tr>
<tr>
<td>CH(_3)</td>
<td>CH(_3)</td>
<td>o-C(_6)H(_4)COOH</td>
<td>[CuL(_2)]</td>
<td>78</td>
</tr>
<tr>
<td>CH(_3)</td>
<td>C(_6)H(_5)</td>
<td>o-C(_6)H(_4)OH</td>
<td>[CuL(_2)]</td>
<td>79</td>
</tr>
<tr>
<td>CH(_3)</td>
<td>C(_6)H(_5)</td>
<td>o-C(_6)H(_4)OH</td>
<td>[TiL(_2)]</td>
<td>80</td>
</tr>
</tbody>
</table>
Metal Chelates from Schiff bases derived from Amino acids

The world of Schiff bases is very wide, but the works on amino acid Schiff bases are very few. Relevant work reported in this area is on the condensation of amino acids with salicylaldehyde, pyridoxal, o-vanillin and hydroxy naphthaldehyde. This review has been restricted to transition metal complexes of tridentate ONO- and tetradentate ONNO-type donor ligand, since only such ligands are pertinent to the present investigation. The work done in the field of complexation of Schiff bases is very few, but the parent amino acids were found to form complexes with almost all metal ions. Amino acid complexes have been attracted by the biochemists, because of its vast application. In ceruloplasmin histidine residues are involved in copper ion bonding where as in ferritin, and transferin, tyrosine is bonded to Fe(III).

The study of tridentate Schiff bases of salicylaldehyde with aliphatic amino acids are in the forefront now. N-salicylidene glycine and similar ligands have been reported to form dinuclear nickel(II) complexes. In these complexes, metal ion acquires octahedral environment through two coordinated water molecules per metal ion. Dutta and Ray in 1977 reported the preparation and characterization of Mn(II) complexes derived from the condensation products of glycine, β alanine and L-leucine with
salicylaldehyde, and its derivatives. These complexes, similar to Ni(II) complexes mentioned above, have been formulated as [MnL(H₂O)₂]₂.

Monomeric 1:1 complexes of type [MLX] of Fe(II) with Schiff bases derived from salicylaldehyde and the amino acid, β alanine or anthranilic acid have been synthesized¹⁰⁹,¹¹⁰ Co(II), Ni(II), Zn(II), and Cd(II) may also form complexes with same ligand. Complex of Ni(II) with Schiff bases, derived from the condensation with the bidentate amino acids β alanine, DL-2-aminobutyric acid and the potential tri dentate amino acids like DL- aspargines and L-glutamine have been prepared and characterised.¹¹¹ Crystalline complexes of Cu(II), Co(II), and Fe(II) complexes of pyridoxylidene amino acids have been reported.¹¹² According to Holm, pyridoxylidine amino acids possess catalytic property.¹¹³ Copper(II) complexes¹¹⁴ having the formula [CuL(H₂O)].nH₂O with salicylaldehyde, and amino acids like alanine, valine, leucine, iso leucine, phenyl alanine, phenyl glycine and serine were reported. Cu(II) readily forms a coloured complex with salicylaldehyde and glycine.¹¹⁵ Hamalainen and coworkers¹¹⁶ reported the synthesis and characterization of copper chelate of Schiff base derived from phenyl alanine. Anionic complexes of iron and cobalt having the formula [FeL₂]⁻ and [CoL₂]⁻ obtained from their salts by salicylaldehyde - aminoacid (ligand) replacement.¹¹⁷ Mixed ligand complex of Ni having the formula [NiL(Py)₂]₁¹⁸ have been prepared, where, LH is the Schiff base...
derived from N-salicylidene amino acids and Py is pyridine. Oxovanadium(IV) which form stable complexes with ligands derived from amino acids and [VOL(H₂O)] type complexes of N-salicylidene amino acids (glycine, alanine, leucine) have been prepared and characterized.¹¹⁹ By similar methods, mixed ligand complexes of oxovanadium(IV) have been obtained from anthranilic acid.¹²⁰ A series of oxovanadium(IV) and oxovanadium(V) complexes with 2-hydroxy-l-naphthalidene amino acids have been reported by Syamal et al.¹²¹ Dimeric Mn(II)¹²² complex of 5-nitro and 5-chloro salicylidene amino acids having the formula [MnL(H₂O)₂]₂nH₂O are reported. These are prepared with 5-bromo salicylidene glycine, 3,5-dibromo salicylidene glycine and 5-nitro salicylidene glycine. Mixed ligand complexes of copper having the formula [CuLA] have been prepared where LH is the Schiff base derived from the above ligand and A is pyridine or α picoline or γ picoline. Oxovanadium (IV) can form stable complexes with ligands derived from amino acids [VOL(H₂O)] type complexes of N-salicylidene amino acids have been prepared and characterized. Salicylidene amino acids and 2 hydroxy naphthalidene amino acids have also found to form complexes with Cu(II).¹²³

A series of new poly crystalline Cu(II) complexes with N-nicotinyl amino acids ligand were prepared.¹²⁴ A notable piece of work have been reported by Jessy et al.⁵⁷,¹²⁵-¹²⁸ on a novel series of metal chelates of
vanillidene anthranilic acid and its 5-bromo derivatives with almost all metal ions of first transition series and some lanthanide ions. Co(II), Ni(II), Zn(II) and Cu(II) complexes of two Schiff bases citronellal anthranilic acid and citronellal-5-bromo anthranilic acid have also been synthesized\(^{129}\) by Rehina. Shanti et al.\(^{130}\) prepared octahedral Cr(II) complexes of N-salicylidene amino acids of type K[Cr(Sal.aa)\(_2\)].nH\(_2\)O. Isolation and characterization of VO(II) complexes of Schiff bases of anthranilic acid with salicylaldehyde, 5-bromo salicylaldehyde and 2-hydroxy-1-napthaldehyde have been reported by Mohanty et al.\(^{131}\) Chakravarthy and Coworkers\(^{132}\) have studied the transition metal complexes of vanilline anthranilic acid. In 1974 Shivahare and Rao\(^{133}\) have synthesized Ni(II), Fe(II) and Co(II) complexes of salicylaldehyde 5-bromo anthranilic acid. Nakao et al.\(^{134}\) reported synthesis and characterization of thirteen Cu(II) complexes of Schiff bases derived from some amino acids, having the formula [CuL(H\(_2\)O)]. N-salicylidene anthranilic acid and N-salicylidene β alanine forms a non planar dimeric bridged structure\(^{135}\) with Cu(II) ions with no direct spin change. Salicylidene amino acids and 2-hydroxy napthalidene amino acids have found to form complexes with Cu(II).\(^{136}\)

Solid state chelates of Fe(II), Co(II) and Ni(II) with a tri dentate ligand of 5-bromo salicylidene anthranilic acid have been synthesized and characterized.\(^{137}\) Chandra et al.\(^{138}\) have reported Mn(II) complexes of Schiff
bases derived from salicylaldehyde and β alanine or anthranilic acid or 2-
hydroxy naphthaldehyde and anthranilic acid of the type MnL₂. In this the
reaction of the ligand H₂L with [Mn(OAc)₃·2H₂O] affords [KMnL₂·H₂O],
which upon chemical or electro chemical oxidation in methanol gave MnL₂ in
high yield, and among this, the structure of β alanine complexes was detected
by X-ray crystallography. Preparation and oxygenation of Mn(II) complexes
of imines derived from salicylaldehyde and amino acids (L-alanine, L-valine,
L-phenyl alanine, L-histidine and glycine) of the type [MnLₙQ] have been
reported³³, where Q is H₂O or EtOH. Most of these compounds are stable
towards dry air but absorb oxygen readily in many organic media to the extent
of O₂/ Mn, equal to 1 or 0.5.

Eleven Fe(III) complexes of tridentate di basic salicylidene/substituted
salicylidene aminoacids were prepared by Ray.⁴⁰ They are represented by
general formula [FeL(H₂O)₂]₂.(OH)₂. All Fe(III) complexes possess dimeric
pseudo octahedral structure. These are characterized by elemental analysis,
magnetic moment studies and TGA. IR spectra of these complexes are super
impossible with those of Ni(II), Co(II), Mn(II) and Zn(II) complexes.
Thermal studies on Co(II), Ni(II) and Cu(II) complexes of Schiff bases
derived from salicylaldehyde and glycine were carried out by Nathmala.⁴¹
Physico chemical investigations on complexes of Mn(II), Fe(II), Co(II),
Ni(II), Cu(II) and Cd(II) with N-5-bromo salicylidene, 5-bromo anthranilic
acid have been carried out.\textsuperscript{142} Octahedral Ni(II) complexes with Schiff bases derived from serine and salicylaldehyde have been prepared and characterized.\textsuperscript{143} Li Taishan \textit{et al.}\textsuperscript{144} reported the synthesis and properties of five Schiff bases obtained by the reaction of salicylaldehyde with glycine, DL-valine, L isoleucine, L leucine and L phenyl alanine. Analysis of IR, $^1$H NMR and electronic spectra indicate that the tautomeric equilibrium between the enol imine and keto enamine exist in the Schiff bases. A review with five references includes a listing of the odour properties of methyl anthranilate based Schiff bases commonly employed in perfume industry.\textsuperscript{145} Ruthenium salicylaldehyde amino acid complexes were synthesized and their reaction with $\pi$ accepter ligands such as 2, 2' bi pyridine and 1, 10 phenanthroline have been studied by Kureshy and Khan.\textsuperscript{146} Dimeric complexes of Cu(II) anthranilate, benzoate acetate and oxalate derived from Schiff bases were prepared.\textsuperscript{147} Salicylidene amino carboxylate complexes of Cu(II), [Cu(X-SA)]L$_2$nH$_2$O], where SA is salicylidene glycinate and salicylidene anthranilate, X is substituents on the salicylidene moiety (X = H, 5-bromo, 3,5-dibromo, 5-nitro, 3,5-dinitro) and L = monoamines (pyridine, picoline, quinoline and triethyl amine) and diamines like ethylene diamine, O-phenanthroline have been prepared.\textsuperscript{148} Cinnamaldehyde complexes of Mn(II), Fe(II), Co(II), Ni(II) and Cu(II) with anthranilic acid were synthesized and analysed.\textsuperscript{149,150}
Synthesis and characterization of N-salicylidene amino acids Zn(II) complexes of the type ZnL(H₂O) have been reported. Crystal studies, molecular structure and spectroscopic properties of oxovanadium complexes with salicylidene aminoacids have been studied by Cavaco et al. Some new Cu(II) and Zn(II) complexes of Schiff bases derived from ortho vaniline and glycine, DL alanine, DL valine, DL methionine, L leucine, L phenyl alanine were synthesized and characterized by Wang et al. The Schiff bases are bivalent anions with tri denatate ONO donors derived from carboxylate O, imino N and phenolic O. Cai Dongmei et al. have synthesized and characterized monodentate germanium(IV) complexes of Schiff bases derived from amino acids and salicylaldehyde. Condensation of equimolar quantities of salicylaldehyde and amino acids (glycine, alanine, valine, leucine, phenyl alanine, serine, cysteine) in absolute MeOH-KOH gives amino acid Schiff bases as their potassium salts. From this germanium tetra chloride adducts having the formula GeCl₄(Sal.aa)₂ were prepared and characterized by elemental analysis, conductance measurement, IR,¹H-NMR spectra and electronic spectra. Synthesis, spectral and electro chemical studies of mixed ligand complexes of ruthenium(III) chiral Schiff base complexes with nitrogen donors have been reported. Eighteen mixed ligand complexes of ruthenium having the formulae [RuL(PPh₃)Y] and [RuL(PPh₃)(H₂O)Y] type were prepared. where LH is the Schiff base derived from L alanine, L valine,
L serine, L cysteine, L arginine or L aspartic acid with salicylaldehyde and, Y is 2-2' bi pyridine or 1,10 phenanthroline. According to Jursik and his coworker\textsuperscript{156} Co(III) complex derived from salicylaldehyde- amino acid help to elucidate the iron binding site in transferrins. Nathmala et al\textsuperscript{157} have reported Cu(II) complexes of salicylidene amino acid Schiff bases of the type [Cu(Sal.aa)H\textsubscript{2}O].nH\textsubscript{2}O. The activities of these were tested towards the decomposition of H\textsubscript{2}O\textsubscript{2} at 40\textdegree over a pH range 6-11. Disproportionation of H\textsubscript{2}O\textsubscript{2} catalyzed by these complexes at 40\textdegree at pH 9 are reported. Synthesis and anti tumor activity of Schiff base coordination compounds containing Cu, Ni, Zn and Co synthesized from salicylaldehyde, 2,4 di hydroxy naphthaldehyde, with glycine and L alanine have been reported.\textsuperscript{158} Potentiometric determination of equilibrium constants and species distribution of Schiff base complexes in aqueous solution involving salicylaldehyde and tri dentate \(\alpha\) amino acids with metal ions, Cu(II), Ni(II) and Zn(II) were reported.\textsuperscript{159}

Some new diphenyl tin(IV) complexes having the general formula Ph\textsubscript{2}SnL where LH, the Schiff bases derived from the condensation of 2-hydroxy-1-napthaldehyde with amino acids have been synthesized and characterized.\textsuperscript{160} A series of Schiff bases of \(\alpha\) and \(\omega\) amino acids with salicylaldehyde was synthesized and their hydrolysis constants at pH 6, 7 and 8 were determined.\textsuperscript{161} Synthesis and characterization of complexes of Cu(II) with N salicylidene-phenyl alanine and N salicylidene alanine have been
carried out by Shen wiang\textsuperscript{162} \textit{et al.} There are reports\textsuperscript{163} on synthesis of N salicylidene leucine 3d metal complexes and their studies on thin layer chromatography and ultra violet spectra studies. Seven complexes of Co(II), Ni(II), Zn(II) and Cd(II) by metal ion template condensation of amino acids and aldehyde/ketone (salicylaldehyde ortho hydroxy naphthaldehyde, ortho vanillin, isatin) have been reported by Sharma \textit{et al.}\textsuperscript{164}

Thermo chemical behavior of salicylidene - valine and its complexes with Co(II) and Ni(II) of molecular formula [Co(HL)(H\textsubscript{2}O)\textsubscript{2}Cl] and [Ni(HL)Cl] were characterised by Emam \textit{et al.}\textsuperscript{165} Four kinds of Schiff base complexes of Cu(II), Zn(II) and Ni(II) derived from ortho vanillin and alanine, leucine and phenyl alanine were reported.\textsuperscript{166} A review with 46 references is given on the synthesis, structure, and reactions of chiral metal complexes with Schiff bases derived from amino acids.\textsuperscript{167} Another set of 41 references based on Schiff base complexes of salicylidene amino acid were published. Their properties and application in many region such as fluoroescene, chromatographic behavior, anti bacterial, anti cancer, and catalysis study has also been summarized in it.\textsuperscript{168} Abdel and coworkers have synthesized\textsuperscript{169} Co(II) and ternery Ni(II), Cu(II) complexes of salicylidene amino acids (Sal.aa) with imidazole or substituted imidazole. Christensen prepared crystalline complexes of Fe(II), Co(II) and Cu(II) with pyridoxylidene amino acids.\textsuperscript{170} Cu(II) complexes of Schiff base derived from
amino acids were prepared and studied. Singh have characterized Co(II), Ni(II) and Cu(II) complexes of Schiff base derived from amino acids. Octahedral and tetrahedral Ni(II) complexes were reported with Schiff base derived from serine and salicylaldehyde. Bertrand and Eller in their broad review have reported that amino acids on deprotonation shows an increased tendency to chelate and to form additional bond and bridge with metal ions. According to Butler manganese(II) form complexes with 5-bromo or 5-chloro salicylidene anthranilic acid. Similar complex formation have been reported with vanillin anthranilic acid. Sharma and Dubay have synthesized and characterized Fe(II) complexes with N-salicylidene and N-(2-hydroxy-1-naphthaldehyde)-amino acids. Solid state chelates of some inner transition metal ions with a tridentate ligand of anthranilic acid have been reported. Some square planar complexes of Ni(II) with N-naphthylidene amino acids have been isolated by Mohmoud and coworkers. Successful synthesis and characterization of transition metal complexes of hydroxy naphthaldehyde - anthranilic acid were carried out. Physicochemical studies and thermal decomposition kinetics of Co(II), Ni(II), Cu(II) and Zn(II) complexes of camphor anthranilic acid and camphor 5-bromo anthranilic acid have been reported. Coenzyme behavior of Schiff bases of pyridoxal 5'-phosphate and 5'-deoxy pyridoxal with leucine in pure water and aqueous solution containing, different amounts of surfactants have
been studied.\textsuperscript{182} Synthesis characterization and antitumour studies of N-(2-hydroxy naphthylidene)-Gly-K Schiff base and its Cu(II) and Ni(II) complexes were carried out.\textsuperscript{183} Formulas of these compounds are $[K(C_{13}H_{12}NO_4)], [Cu(C_{13}H_{11}NO_4)]$ and $[Ni(C_{13}H_{13}NO_6)]$. Cu(II) complex had one molecule of coordinated water and it showed 27.5\% anti tumor activity. Recently detailed studies like antibacterial activity, stability constants etc. of N-salicylidene amino acids and their 3d metal complexes have been reported.\textsuperscript{184}

Metal chelates of tridentate Schiff bases derived from pyridoxal and aminoacids were isolated by Wrableski and Long.\textsuperscript{185} Baddiley\textsuperscript{186} synthesized and characterized Cu(II) complex of the Schiff base derived from pyridoxal and valine. Mn(II) complexes having the formula Mn(HL)$_2$ with the above ligand was also synthesized.\textsuperscript{187} Cu(II) chelate of Schiff base was deduced from phenyl alanine by Bentley and coworkers.\textsuperscript{188} Pyruvic acid amino acids, glyoxalic acid - amino acids and 3-(hydroxy methylene) camphor amino acids have been found to form complexes with Cu(II).\textsuperscript{189-191} Some work has been reported on the complexation abilities of benzoin anthanilic acid with Cu(II), Co(II), Ni(II), Zn(II), Cd(II) and Hg(II).\textsuperscript{192} A notable piece of work have been reported by Mohan on metal chelates of hydroxy naphthaldehyde amino acid and N acetyl acetone amino acids with almost all metal ions of first transition series. Preparation and X-ray diffraction studies were reported for two novel
N-salicylidene tryptophanato di aquo Cu(II) complexes.\textsuperscript{193} Mg(II) chelate\textsuperscript{194} of N-salicylidene glycine alkyl ester when heated under reflux in methanol gave 3-amino coumarin and the same chelate yielded an amine on treatment with sodium methoxide in methanol. N-salicylidene glycine esters have been reported to undergo transesterification and aminolysis reactions.\textsuperscript{195} Studies on model systems utilizing N-pyridoxylidene amino acids and their metal complexes have been carried out and the results have been reviewed.\textsuperscript{196-198} The complexes formed between transition metal ions and the Schiff bases synthesized from salicylaldehyde, 2, 4 dihydroxy naphthaldehyde and aminoacids were isolated and their anti tumor activity were studied by Zhao et al.\textsuperscript{199} The order of antitumor activity of compounds is Ni>Cu>Zn>Co. Some transition metal complexes of amino acid Schiff base were synthesized and their purity was confirmed by Li Huaina and coworkers.\textsuperscript{200} Blue crystalline mixed ligand complex of Cu(II) having the formula Cu[L(Py)$_2$] where H$_2$L is salicylidene L valine and Py is pyridine was synthesized and its structure determined by single crystal X ray diffraction method.\textsuperscript{201} The synthesis and X ray crystal structure of Schiff bases prepared from salicyldehyde and di amino acids were studied.\textsuperscript{202} Cluster complexes of salicylidene glycine and salicylidene anthranilic acid complexes of Cu(II) with metal halides and perchlorates were isolated.\textsuperscript{203} Das and coworkers have prepared and characterized a series of planar or octahedral complexes of salicylidene amino
1:2 chelates of 2 hydroxy naphthaldehyde-anthranilic acid were isolated in solid form and analysed by electronic, spectral, and thermal studies. Synthesis and properties of Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) complexes with amino acid Schiff bases have been reported by Tian et al. Complexes of N salicylidene anthranilic acid, 2 bromo salicylidene anthranilic acid and N-(2 hydroxy benzyl) anthranilic acid with Cu(II) were prepared and characterized. A series of transition metal complexes with two Schiff bases, fluorenone anthranilic acid and anthracene carboxaldehyde anthranilic acid were prepared and characterized on the basis of physico chemical studies. Solid state complexes of L-histidine with first row of d-block was separated and studied.

The review reveals that while the coordination chemistry of N-salicylidene amino acids, N-pyridoxylidine amino acids and N-(2 hydroxynaphthylidene) amino acids has received considerable attention in recent years, that of dibenzoyl methane amino acids, benzylacetone amino acids and camphor amino acids received only scanty and sporadic attention.

Scope of Present Investigation

Even though extensive studies were done on metal complexes of Schiff bases derived from various aldehydes and ketones, the importance of transition metal complexes of Schiff bases derived from amino acid with
dibenzoyl methane and benzoyl acetone is yet to be studied. In the present investigation aromatic Schiff base ligands, dibenzoyl methane-L-histidine (DBMH), dibenzoyl methane-glycine (DBMG), benzoyl acetone-glycine (BAG), benzoyl acetone L-histidine (BAH), dibenzoyl methane O-amino phenol, (DBM. AP), dibenzoyl methane O-amino thiophenol (DBM-ATP) and camphor-L-histidine have been synthesized and characterized. Their complexes with many transition metal ions have already been isolated. Generally used metal ions during the current course of studies are Mn(II), Co(II), Ni(II) Cu(II), Zn(II) and Cd(II).

The solid complexes were characterized by various physicochemical methods like IR, electronic spectra, molar conductance and magnetic moment data. The thermal decomposition character of certain representative complexes in air have been studied by TGA technique so as to understand their general thermal stabilities and decomposition pattern. Crystalline state of few of the complexes of Mn(II) and Ni(II), complexes of benzoyl acetone L-histidine. and Cu(II) complex of benzoyl acetone-glycine, and Ni(II) complex of camphor L-histidine were established empirically by indexing its X-ray powder diffraction pattern.