CHAPTER - I

INTRODUCTION

The branch of chemistry dealing with co-ordination complexes is advancing very rapidly. Since Tassert isolated the orange compound, Co.CI₃.GNH₃, in 1798, this chemistry has invaded many fields and disciplines. Chemists still hold the chemical tools to decide the geometry, behaviour and utility of the complexes.

Factors controlling the bond formation

Characteristic behaviour of the complexes depend on the nature of both the participating metal and ligand. The controlling factors are:

a) Charge and size of both metal and ligand.

b) Orbital symmetry and vacant orbitals available for bonding.

c) Polarizability or basicity of the ligands which influences the effective accumulation of negative charge on the metal-ligand bonds.

d) Stereochemistry of ligands.

e) Steric effects and

f) Chelate effect.

Co-ordination number and stereochemistry

Co-ordination number gives the basic idea regarding the stereochemistry of a molecule. It is the number of donor sites acquired by a metal through dative bonding. The idea regarding the co-ordination number was first originated by Sidgwick who prescribed the outdated and outmodelled "effective atomic number theory".
Wybollm's "lone-pair bond-pair interaction theory" seems to be more plausible and is accepted by the co-ordination chemists today.

Co-ordination numbers vary from 2 to even 9 or 10, depending upon the metal ions involved and many other factors. The most common co-ordination numbers among the transition elements are 4 and 6.

With the same co-ordination number, a number of structures may be possible for a metal ion. For example, Ni(II)(d^2) with co-ordination number 4, gives rise to square planar and tetrahedral structures. With co-ordination number 5, it gives rise to trigonal bipyramidal and square pyramidal structures and with co-ordination number 6, octahedral and trigonal bi-prismatic structures are possible. Intermediate structures are rather more common than an absolute geometry. They are governed by the symmetry of the metal and ligand, Wybollm's rule of interactions and Jahn-Teller distortions.

**Bonding**

Lewis and Sidgwick's theory of electron pair bonding was modified later and extended to explain the donor-acceptor character of the co-ordinate link.

Pauling used this approach in his "valence bond theory" which was quite successful in describing and predicting most of their magnetic behaviours, stereochemistry, kinetics, and other physical and chemical properties.

**Valence bond theory**

This theory was developed largely from a quantum mechanical treatment of co-ordinate bond. According to this theory, the association results from the overlap of an orbital of the ligand containing unshared pair of electrons with the available orbitals of the metal. It deals with the electronic structure of the ground...
state of the central metal ion and is concerned mainly with the ste­
reochemistry and magnetic properties of complexes. The strength of
the bond formed is illustrated by the effective overlap of bond or­
bital{s}, thus bringing in spatial characteristics of the bonds. It is
calculated by taking into considerations the various canonical attra­
ctive and repulsive parameters contributing to the formation of the
bonds.

Crystal field theory

Valence bond theory assumes the ligand electrons to be par­
tially donated to the metal orbitals, thus forming a covalent bond,
whereas, crystal field theory considers bonding to be entirely elec­
trostatic.

It was first proposed by Bethe\(^2\) from the study of the
effect of symmetry and strength of the crystal field upon the elec­
tron levels of gaseous metal ions, Its application to magnetism of
transition metal ions was made by Schlapp and Penny\(^3\) and VanVleck.\(^4\)
Ilse and Hartmann\(^5\) explained its effect on d-d spectra and Orgel\(^6\)
interpreting used it for\(\)the stability of co-ordination compounds.

The theory considers the ligand to be a point charge and
the five degenerated \(d\)-orbitals of the metal splits up with the
electrostatic field of the former. The set of orbitals lying in the
direction of the ligands are raised in energy, while those lying away
from it are lowered in energy. The lower lying orbitals are prefer­
entially filled and the gain in bonding energy thus achieved is cal­
led the crystal field stabilization energy (C.F.S.E.).

Mulliken\(^7\) used the group theoretical notations necessary
for designating one-electron wave functions and their associated
energy states. Hence a regular octahedral complex has \(e_g\) and \(t_{2g}\).
orbital sets. The difference between the two states is usually called $\Delta Dq$ or $\Delta$. A divalent metal of first transition series has $\Delta Dq \approx 10,000 \text{ cm}^{-1}$ (i.e., 23.6 Kcal) and for the trivalent ions it is $\approx 20,000 \text{ cm}^{-1}$. In going to 2nd and 3rd transition series it increases by about 50% and 100% respectively.

Jorgenson$^3$ arranged the various ions and ligands in a series of increasing $\Delta Dq$. It is called as the spectrochemical series. C.F.S.E. contributes only to about 5-7% of the total bonding energy ($\approx 500-1000 \text{ Kcal mole}^{-1}$). It is obvious that other factors determining the bond strength will be much more significant than the C.F.S.E. in fixing co-ordination number, geometry etc. But, although the C.F.S.E. is small compared to total bonding energy, it is clearly large enough to be chemically significant.

**Molecular orbital theory**

Even though Crystal Field Theory successfully explains the absorption spectra of complexes, theoretical and experimental evidences suggest that some mixing of metal and ligand orbitals exist to a certain degree. This can be illustrated by ESR and NMR spectra of iridium chloride indicating electron delocalization. Increase of intensity of d-d transition spectra and decrease of Russell-Saunders states on complexation may be explained as the result of the overlap of the extended electron cloud of the metal with the ligand.

It is therefore necessary that crystal field theory should be interpreted on the basis of molecular orbital theory. First approach in this direction was made by Van Vleck.$^4$ This modified theory is
called "Ligand Field Theory." The energetic calculations are made in the same manner as in M.O. theory. It no longer assumes point charges but overlap of orbitals, whenever symmetry permits (from no overlap (electrostatic approach) to maximum overlap of orbitals by linear combinations). It uses the same orbitals of the central ion as employed by Pauling and also the available orbitals of the coordinating ligands directed towards the central atom. A localized orbital, "M.O.,” is formed holding two electrons in a chemical bond. Half of M.O's are bonding, more stable than the original A.O's. The others are weak and antibonding.

The LCIO method of constructing orbitals of the complex arises from the equation,

$$\psi = \lambda \psi \left( \psi \right) + \beta \sum \alpha_i \psi_i,$$

when $\psi \left( \psi \right)$ is the wave function of the central atom, $\sum \alpha_i \psi_i$ is a linear combination of the ligand wave functions, and $\lambda$ and $\beta$ are the mixing coefficients ($\lambda^2 + \beta^2 = 1$). In bonding M.O's $\lambda$ and $\beta$ are both positive, whereas, they are different in antibonding orbitals.

One-electron Hamiltonian is used to calculate the energetics, where

$$Q_A = \text{Coulomb integral} = \int \phi_A \phi_A \, d\tau,$$

and $\beta = \text{Exchange integral} = \int \phi A \phi B \, d\tau$.

Mulliken proposed this integral $\beta$ to be roughly proportional to the corresponding overlap integrals. Hence,

$$\int \phi_A \phi_B \, d\tau = C \phi a u \phi u = C \phi a u \int \phi_i \phi_0 \, d\tau,$$

where $C$ is a numerical constant and $\phi_a u$ is either taken as an arithmetic or geometric mean of the energies of $\phi_A$ & $\phi_B$.

The M.O's are labelled by group theory symbols and $\alpha$ and $\pi$
bonding cases too are also considered. In an octahedral $d^2sp^3$ bonding, where the metal forms 6 bonds, the orbitals are classified by symmetry and degeneracy, as:

$$t_{lu} = 4p_x, 4p_y, 4p_z$$
$$e_g = 3d_z^2, 3d_{x^2-y^2}$$
$$a_{1g} = 4s$$

forming linear combinations according to symmetry conditions. For a $\sigma$ bond the metal may use $d^3p^3$ hybrid orbitals and the symmetry classifications for these orbitals are:

$$t_{2g} = 3d_{xy}, 3d_{xz}, 3d_{yz}$$
$$t_{1u} = 4p_x, 4p_y, 4p_z$$

Thus, it gives the $4p$ ($t_{1u}$) orbitals to be capable of forming both $\sigma$ and $\pi$ bonds.

It is a formidable task to calculate energy of the M.O.'s and the value of mixing coefficients. Modern computing technique can only be done to approximate extent. Nonempirical (Hartree-Fock self-consistent field) and semiempirical (Pariser, Parr, Pople, Mulliken, Dewar and others) as well as Wolfberg and Helmholtz VSIP methods are currently used for this calculation.

The reasonable approximations for the various coulomb and exchange integrals may be summarized as:

1. The order of coulomb energies is taken to be

$$\sigma (L) < \pi (L) < 3d < 4s < 4p.$$  

2. The amount of mixing of A.O.'s in the M.O.'s is proportional to the A.O. overlap and inversely proportional to their coulomb energy difference.
3. Other things being approximately equal $\sigma^b$ M.O.
is more stable than $\pi^b$ M.O. and $\sigma^\pi$ M.O. is
correspondingly less stable than $\pi^\pi$ M.O. 2.
Ligands like $CN^-$ have $\pi$ systems of their own with $\pi^b$ (filled) and
$\pi^\pi$ (empty) orbitals. Interaction of metal d-electrons with ligand
$\pi$ orbitals stabilises the M.O. mainly based on the metal. Such
interaction is conveniently called $\pi$ back-bonding (or $\pi$ back-dona-
tion) and such ligands are referred to as $\pi$-acceptor ligands.

$M-L \sigma^-$ bonding increases $\Delta$, because $e_g(\sigma^-)$ is raised
and $M-L \pi$ bonding ($L \rightarrow M$ type) decreases $\Delta$, because $t_{2g}(\pi^\pi)$ is
raised. However, $\pi$ back-bonding ($M \rightarrow L$ type) increases $\Delta$ because
$t_{2g}(\pi^\pi)$ is lowered in energy.

With this idea the present spectrochemical series may
be explained. Magnetic and chemical phenomena are explained quite
easily with the help of M.O. theory. The quantitative absolute
bonding energetics are obtained by empirical methods. The effect
of interelectronic repulsions are taken care of by assuming that
each electron moves in an average field of all other electrons.

Nickel(II) complexes

Nickel(II) has been well-studied in the last few years.
It has d$^8$ configuration and can, therefore, yield both spin-free
and spin-paired complexes in both medium and higher ligand fields.
It exhibits various geometries under co-ordination numbers 4, 5
and 6.

Co-ordination number 6 is more common among the
Ni(II) with both inner-orbital ($sp^3d^2$) and outer-orbital
($d^2sp^3$) complexes. It exhibits a spectrum of colours rang-
ing from violet to green for the former type of complexes.
depending upon the ligand field. For example, Ni(H₂O)⁶²⁺ having 10Dq ≈ 9000 cm⁻¹ is green in colour and Ni(en)³⁺ with 10Dq=11000 cm⁻¹ is light violet or purple. However, the molar absorbance is low (about 1-100).

The transitions observed in visible region of the spectrum are: \( \gamma_1, 3A_{2g}(t_{2g} e_g^2) \rightarrow 3T_{2g}(t_{2g} e_g^3) \); \( \gamma_2, \rightarrow 3T_{1g}(F)(t_{2g} e_g^3) \) and \( \gamma_3, \rightarrow 3T_{1g}(P)(t_{2g} e_g^4) \) in \( \Omega_h \) symmetry with bands appearing at ~10,000, ~16,000, and ~30,000 cm⁻¹. The ratio \( \gamma_2/\gamma_1 \approx 1.6 \). The Racah (B) and Naphalaxotic \( (\beta_{3g}) \) parameters are obtained from the triplet \( 3F-3F \) energy differences. The free ion term, \( B_0 \), is usually taken as 1040 cm⁻¹ in medium fields. These values for the free ions are the highest, giving maximum influence of the effective nuclear charge on the outer electrons. The shielding of the effective nuclear charge through complexation and delocalisation of \( \sigma^- \) and \( \pi^- \) electron density of the metal and ligand reduce them considerably. This reduction is given in terms of the ratio \( B/B_0 = \beta \), which measures the covalency of the metal-ligand bond. A fully ionic ligand like \( F^- \) gives \( \beta \) close to one, while with a \( \pi^- \) contributor like sulphur-donor ligand, it reduces to about 0.29. A difference between spin-allowed value \( (\beta_{3g}) \) and the spin-forbidden ones, \( \beta_{3g} \) (in \( e_g \)) and \( \beta_{5g} \) (in \( t_{2g} \)), measures the \( \sigma^- \) and \( \pi^- \) contributions to the bonds respectively. The weak bonds due to spin-forbidden singlet-triplet transitions are, therefore, important and occur sometimes at ~1200 cm⁻¹ \( (3A_{2g}(F) \rightarrow 1E_g(D)) \) and ~18,000 cm⁻¹ \( (3A_{2g}(F) \rightarrow 1A_{2g}(G)) \).

Perfect \( \Omega_h \) complexes are rare excepting PtCl⁶²⁻. Nickel(II) always suffers from a Jahn-Teller contribution and hence, distortion from octahedral geometry is always present to varying degrees. Two major forms of distortions observed are trigonal and tetragonal distortions.
In a trigonal distortion, the octahedron is either extended or compressed along the threefold axes and the geometry looks like a trigonal antiprism. Under such trigonal distortion, the transitions in an octahedral complex suffer from a split (tending towards an approximate $D_{4h}$ symmetry$^{10}$) to a host of bands:

$$
2B_{1g} \rightarrow 3E_g(F) (~8,500 \text{ cm}^{-1}), \rightarrow 3B_{2g}(F) (~12,000 \text{ cm}^{-1}), \rightarrow 3A_{2g}(F) (~14,500 \text{ cm}^{-1}), \rightarrow 1A_{1g}, 1B_{2g}(1D) (~13,000 \text{ cm}^{-1}), \rightarrow 3E_g(F) (~17,500 \text{ cm}^{-1}) \rightarrow 3A_{2g}(F) (24,500-27,000 \text{ cm}^{-1}) \text{ and } 3E_g(P) (~27,500 \text{ cm}^{-1}) .
$$

The splitting of the $\gamma_1$ band to $3B_{2g}$ and $3E_g$ is taken as a measure of the relative influence of the axial and planar ligands.

Planar $D_{4h}$ symmetry is an extreme case of tetrahedral distortion, where the two trans-axial ligands are separated much farther to be out of the influence of the metal nucleus. The complexes in this symmetry are either orange or red in colour and have two sharp and distinct bands in the visible region, one between 15,000 and 25,000 cm$^{-1}$ ($\gamma_1$, 80-500) and the other between 23,000 and 30,000 cm$^{-1}$ with much higher extinction coefficient. Besides, these two characteristic bands, a host of other bands also appear.

As a distinction, the $D_{4h}$ type compounds have no bands below 10,000 cm$^{-1}$. The transitions observed are $e_g \rightarrow b_{2g}(\gamma_1)$, $e_g \rightarrow a_{1g}(\gamma_2)$ and $e_g \rightarrow b_{1g}(\gamma_3)$. With further increase in distortion to $D_{4h}$, the bands $\gamma_1$ and $\gamma_2$ approach each other and finally $\gamma_1$ becomes more than $\gamma_2$.

A $\sigma^*$ bonded complex gives clear bands with $\gamma_1$ and $\gamma_2$ lying close together and separated from $\gamma_3$ by about 13,000 cm$^{-1}$. In a complex involving contribution from both $\sigma$ and $\pi$, the $e_g$ orbitals split. The metal ligand bonds are assumed to lie along $x$ and $y$ axes and the 1ODq is calculated from the one electron energy separation from $b_{2g}$ to $b_{1g}$. This measures the C.F.S.E. for the planar complexes.
Free ion Octahedral Tetragonal distortion

$3d$

$d_{z^2}$ $t_{2g}$

$d_{xy}$ $b_{2g}$

$d_{yz}$ $e_g$

$e_g$

$a_{1g}$
Fig. 1.1

The main transitions of Ni(II) in tetrahedral (T2) symmetry are 3T1 → 3T2, → 3A2 and → 3T1(P). The first two bands occur far below 10,000 cm⁻¹ with low intensities (ε < 20 cm⁻¹ mole⁻¹). The third band is sharp (but usually split), with ε ~ 200 1 cm⁻¹ mole⁻¹, occurs at ~15,000 cm⁻¹ and is responsible for the characteristic deep blue colour of the complex. The spin-forbidden transitions are 3T₁ → 1E(~12,000 cm⁻¹), → 1D(~14,500 cm⁻¹), → 1G(18,000 cm⁻¹) and → 1T₂(~21,000 cm⁻¹) which often occur as weak or very weak bands.

Sacconi, Furlani and Ciampolini are the pioneers who made extensive study on penta co-ordinated complexes using S, N, P & As donor systems with various geometry of the ligands. Work of Chakravorty school¹³ may also be given importance who made use of N and O donor systems in deriving penta co-ordinated complexes of Ni(II).
The spectra of (Sal₂·dptn)Ni and (5-Cl·Sal·en·N₂Et₂)₂Ni in chloroform have been taken and they are found to exhibit bands at 8850 (26), 9800 sh, 11,810 (7), 17,000 (29), 10,000 (26), 12,740 (18), 16,130 (44) respectively (figures in parentheses are extinction coefficients). They explain the splits under trigonal bipyramidal and square pyramidal geometry. The theoretical scheme for the split may be given below.

Fig. 1.2

Energy levels of metal ions trigonal bipyramidal (D₃h) and square pyramidal (C₄v) fields.

Zacharias¹³ has worked on penta co-ordinated complexes of Ni(II) with idealised geometry of trigonal bipyramidal and square pyramidal structures using Ni(Sal)(Sal·Na₂) and analogous compounds.
The splitting of the Russell-Saunders states may be given as:

\[
\begin{array}{ccc}
\text{Free ion} & \text{C}_{4v} & \text{C}_{4v} \\
3P & 3\text{A}_{2g}(e_{g}^{2}) & 3\text{B}_{1}(b_{1a}) \\
E & 3\text{T}_{2g}(t_{2g}e_{g}) & 3\text{B}_{2}(b_{1b}) \\
 & 3\text{E}(a_{1g}) & 3\text{A}_{2g}(b_{1b}e) \\
 & 3\text{A}_{2g}(b_{1b}e) & \\
3P & 3\text{T}_{1g}(t_{2geg}) & 3\text{E}(b_{2e}) \\
& 3\text{E}(b_{2e}) & \\
& 3\text{A}_{2g}(e_{g}^{3}) &
\end{array}
\]

The transitions occurring at \(\sim 7,500 \text{ cm}^{-1}\) for \(3\text{B}_{1}(F)(b_{1d}) \rightarrow 3\text{E}(F)\) \(b_{1e}\), \(\sim 11,000 \text{ cm}^{-1}\) for \(3\text{A}_{2}(F)(b_{1b}e) \rightarrow 3\text{B}_{2}(F)\) \(a_{1b}l\) and \(\sim 16,500 \text{ cm}^{-1}\) for \(3\text{B}_{2}(F)(b_{1e}) \rightarrow 3\text{A}_{2}(F)\(b_{1e}\)) are responsible for square pyramidal geometry with spin-forbidden bands at \(\sim 11,500 \text{ cm}^{-1}\).

Some amount of work has been reported on the trigonal biprismatic structures of cis-cis-tach complexes of Ni(II) and Co(II), where tach = \(1\), \(3\), \(5\) - triamino cyclohexane. The metal ion is encapsulated into the fixed array of the donor atoms. Enough work and proper theoretical study has not yet been made on this type of complexes.

The magnetic moment observed for Ni(II) complexes are within 2.9 - 4.2 B.M., where 2.9 - 3.3 B.M. are usually exhibited by octahedral complexes and 3.3 - 4.2 B.M. by the tetrahedral complexes. Low C.F.S.E. \((30\text{Dq})\) value in the tetrahedral geometry \(\Delta t \approx 4/9 \Delta_{Q}\) brings in large orbital contribution to the spin only.
value, thus making the magnetic moment large. A very high ligand field in the planar complexes exceeds the spin pairing energy making the complex dimagnetic. An octahedral complex with a medium ligand field, experiences a smaller contribution to the magnetism. An outer orbital complex, formed with high promotion energy, where the ligand electrons are made to occupy $d^2sp^3$ hybrid orbitals, are dimagnetic. Examples of complexes of this type are $\text{Ni(diars)}_3(C1O_4)_2$, $\text{Ni(Ind)}_4X_2$ etc.

**Copper(II) complexes**

Copper(II) ion with $d^9$ configuration is equivalent to one hole in 3d system and hence, seems to be one of the simplest ions. But, in fact, its chemical behaviour and spectra are quite complex. A large spin-orbit coupling coefficient (-830 cm$^{-1}$), inter-electronic repulsion parameter and significant Jahn-Teller effect make it to possess a highly distorted geometry.

An octahedral complex of Cu(II) has usually a narrow XY plane and long trans-Z axis. The ligands are susceptible to such a large separation in the Z axes that the complex preferentially takes up a planar geometry. The octahedral $e_g$ and $t_{2g}$ states split with increasing tetragonal components of the crystal field. The $2A_1$ state increases in energy with distortion and crosses over the $2E$ and $2E_2$ states, thus making the three bands often unresolved in the spectrum.

Billing and Underhill suggested an expression for obtaining approximate $10Dq$ values for such distorted octahedral complexes as:

$$\text{Billing and Underhill suggested an expression for obtaining approximate } 10Dq \text{ values for such distorted octahedral complexes as}$$
where the transitions are $^2B_1 \rightarrow ^2E \rightarrow ^2B_2$ and $^2A_1 \rightarrow ^2E$.13

**Fig. 1.3**

Energy levels of copper(II) ion under octahedral and tetragonal fields.

Trigonally distorted compounds are also known, e.g., tris (bipyridyl) and tris (o-phenanthroline) compounds with bands at $\sim 6,000$ and $\sim 15,000$ cm$^{-1}$.

Penta co-ordinated Cu(II) compounds are not uncommon. $[\text{Co(NH}_3)_6][\text{CuCl}_6]$ compound shows bands at 8,300 and 10,200 cm$^{-1}$ for $e'$ and $e''$ to $a_1^*$ transitions in trigonal bipyramidal geometry. Cu(ter-Py)Cl$_2$ and $[\text{Cu(diPy)}_2]^+$ have also been known to show a similar geometry. The diaquo(acetylacetonato)copper(II) picrate and the pyridine and similar other amine adducts of bis(acetylacetonato)copper(II) and bis(salicylidimino)copper(II) have square-pyramidal geometry.

In finding out a decision regarding the above two structures Zacharias and Balundgi13 used the ESR spectra where the $g$ values obtained are quite diagnostic. For a trigonal bipyramidal
structure, one of two \( g \) values is lesser than 2.03 and the other one more. But in a square pyramidal geometry the two values are above 2.04 and further, \( G = \frac{E_n - E_2}{E_1 - E_2} \) is \( \approx 4 \) in absence of extensive exchange coupling. These are in good agreement in Cu(Sal)(NR$_2$Sal) type of complexes.

A tetrahedral complex of copper(II) is characterised by the absence of any band within 20,000-10,000 cm$^{-1}$. Jahn-Teller effect is prominent in this type complex and often distorts the \( T_d \) symmetry to a flattened tetrahedral, \( D_{2d} \) symmetry, with \( ^2T_2 \) ground state. The magnetic moment is usually the highest (\( \gtrsim 3.5 \mu_B \)) owing to strong spin orbit interaction \( ^{22} \) influenced mostly by the above effect. In distorted tetrahedral complex of copper(II), the band usually appears at \( \sim 5000 \) cm$^{-1}$.

As already mentioned, planar complexes are common for Cu(II). With the approach planar form from tetrahedral one, the ligand field band shifts to visible region. For example, in Cu(Sal-1.Pt)$_2$ which has a pseudo tetrahedral structure, the bands are observed at 3500 and 12,500 cm$^{-1}$\( ^{23,24} \). In a completely planar compound \([\text{Pt(NH$_3$)$_4$}][\text{CuCl$_4$}]\) these bands occur at 10,200 and 14,300 cm$^{-1}$\( ^{25} \).

Large number of bridged complexes are known in various forms. Superexchange through single and poly-atoms are observed in those complexes. When there is a single atom bridge through oxygen atom (e.g., acetylacetone mono-(o-hydroxyl) Copper(II)\( ^{26} \) and N-N' -salicyledene ethylenediamine copper(II)\( ^{27} \)) superexchange quenches the magnetic moment to varying extent. Delocalisation of the metal electron through oxygen is not effective in quenching such magnetic moment when the metal atoms are separated by
more than one atom (e.g., azido and imidazolato complexes of copper(II)).

Direct exchange is prominent in $[\text{Cu}_2(\text{CH}_3\text{COO})_4\cdot\text{H}_2\text{O}]^{2+}$ and also in the monochloroacetate complexes. The former has a dimeric octahedral structure with Cu-Cu distance 2.64 Å. The metals being sufficiently close to each other a lateral overlap of 3d$_{xy}$ orbitals cause σ-bonding overlap and hence, large quenching in magnetic moment. Such interaction does not occur when the H$_2$O is replaced by amines or phosphine oxides, or when acetate is replaced by formate or benzoate. This overlap is maximum in diazoaminobenzene complexes of copper(II) causing a completely spin-coupled metal-metal bond.

Besides the formation of the general bimetallic compounds, both tetra- and polymetallic copper(II) compounds have also been reported. The polymetallic antiferromagnetism proves a π superexchange mechanism for the observed quenching in their magnetic moment.

Ferromagnetic interactions in copper(II) complexes are rare. However, the anionic adducts in the polymetallic dimethylglyoximato complexes of copper(II) are good examples of this category.

**The M$_2$C$_y$ Co-ordination Sphere**

Ligands having both nitrogen and oxygen co-ordinating donor sites occupy a key position in the co-ordination chemistry. The complexes formed and the peculiarities shown are many. These chelating ligands are usually 2-aryl azoephens, triazine 1-oxide, 8-hydroxyquinoline, aminalcohols, aminophenols, 2-hydroxyamidines,
\(\text{-17-}\)

\(\text{L-}\text{-aminoacids, schiff bases etc. Schiff bases of particular interest are those derived out of salicylaldehyde, acetylacetone and the type, because of the wide variety of substituted products they yield to give co-ordination compounds of different structural, physical and chemical behaviours.}\)

A brief review is, therefore, given here on the above type of compounds with a greater demonstration of the schiff-base complexes. This thesis relates mainly the schiff-base complexes. The most illustrated, labile and critical metals, Cu(II) and Ni(II), are being given stress. This review does not cover all the papers published on the subject, but typical and outstanding works have not been omitted.

**Complexes of Aminoacids**

The aminoacids are the basic parts of proteins and enzymes. The complexes of amino-acids in biological, as well as, in analytical systems are not yet completely understood. It will, therefore, be inappropriate to produce a detail review on the subject in the present thesis. For brevity the discussions are limited to simple aminoacids, e.g., glycine (\(\text{Hgly}\)) and alanine (\(\text{Hala}\)), and pseudo aminoacids, e.g., anthranilic acid (\(\text{Haa}\)).

In \(\text{L-}\text{-aminoacids the amine and carboxylate groups are properly separated to give rise to five-membered chelate rings (Structure I.1) of remarkable stability. The earliest of such complexes, (gly)\(_2\)Cu.H\(_2\)O\(_3\) (structure I.2) was known to exist in two forms.}\) The structure of the cis-form has been known definitely to be with two planar chelate rings having a water of crystallisation at the axial co-ordination position. A distorted octahedron around Cu(II) is formed with weak interaction of a carboxylate oxygen from a neighbouring molecule. Zn(II) and Cd(II) form basically similar compounds.\)
(L-α-ala)₂Cu, forms with trans-CuN₂O₂ coordination sphere having two long axial Cu...O (the oxygen atom belonging to carboxyl group of neighbouring molecule). The (D-α-ala)₂Cu gives both trans- and cis-isomers with the latter involving in axial coordination by groups of neighbouring molecules.

The crystal structures of several aminoacid chelates of copper(II) are known. The basic structural patterns remain grossly planar (trans-CuN₂O₂) with axial coordination of water of crystallization (if present) and/or by carboxylate oxygen of neighbouring molecules. The ligand field spectra are generally observed within 15,000-17,000 cm⁻¹. The EPR spectra of some of the chelates and also some ORD and ligand field absorption spectra have also been reported.

(gly)₂Ni(H₂O)₂ has a trans octahedral structure with triplet ground state giving rise to typical ligand field spectrum. The anhydrous compound, (gly)₂Ni, is also paramagnetic and it undoubtedly involves intermolecular carboxylate bridges.

The stepwise formation constants of the complexes of various amino acids have been extensively studied. Their stability would be expected to depend on the size of...
the chelate ring. Boyd et al.\textsuperscript{46} have reported $\Delta H^0$ and $\Delta S^0$ values for the glycinate and $\beta$-alaninate complexes of Co(II), Ni(II) and Cu(II). The $\beta$-alanine complexes give rise to six-membered chelate rings (Structure I.3), and were found to be uniformly less stable, primarily due to an entropy effect. The complex trans-bis ($\beta$-amino-3-butyrate) copper(II) is known from X-ray data to contain six-membered chelate rings.\textsuperscript{47} The $\gamma$, $\delta$- and $\epsilon$-amino acids do not generally form chelate rings with metal ions.\textsuperscript{48}

Cobalt(III) oxide reacts with glycine to form a mixture of two isomers of (gly)$_2$Co.\textsuperscript{49} Electronic spectra could only establish much later that the red $\beta$-form and the violet $\alpha$-form are respectively the cis and trans isomers.\textsuperscript{50} (Structure I.4 and I.5)
Both cis- and trans-forms exist as enantiomers, viz, \( \text{L-D}, \text{L-L}, \beta-D, \) and \( \beta-L \). Resolution of these isomers could only be partially achieved by selective adsorption on quartz.  

**Complexes of Schiff bases**

Schiff bases have occupied an ever expanding realm of chemistry and have been adopted in different fields of activities of physical sciences. Large number of comprehensive reviews have appeared on this aspect of co-ordination chemistry and many attempts have been made to understand the generalised behaviour of their complexes. The present discussion is limited to a brief outline to illustrate their general behaviour with particular reference to the complexes of copper(II) and nickel(II). They invite a continuing interest in this field because of the ease of synthesis of a host of ligands, their diverse properties and use as a biological and stereochemical model. Our interest is focussed only on those derived from salicylaldimine type of Schiff bases.

The diverse properties of these salicylaldimine complexes may be seen through their colours in solid state and in solution, variation in dipole moment and magnetic moment. These observations derive interest towards molecular structure, electronic states and variation in co-ordination number brought about by polymerisation or solvation.

Holm used the term \( \Theta, \phi, \beta, S, \) and \( \sigma^{-} \) etc. to illustrate the geometry of the Schiff base complexes. According to him the donors of the chelate bite the metal atom with an angle \( \beta \) (bite angle) at the metal atom (NMO). The metal index axis \( (Z) \) makes a dihedral angle, \( \Theta \), with the co-ordination or the chelate plane (NMO).
In tetrahedral compounds this $\theta$ remains essentially $109^\circ$ and in planar, $0^\circ$. $\beta$ is $90^\circ$ in a perfectly planar compound and decreases when it tends towards a tetrahedron. The ligand plane (1) and the metal planar axes in $\text{Mg}_2\text{O}_2$ do not always coincide. In a molecular folding the step (S) is given as an algebraic sum of the half steps ($\delta$) 

\[ S = \delta_1 + \delta_2 \] 

(Structures I.8 to I.10). In an umbrella type complex this is given in restricted sense.

The simplest bis-chelates, $(\text{H-Sal})_2\text{M}$, are given by $\text{M} = \text{Ni}(\text{II}), \text{Pd}(\text{II}), \text{Cu}(\text{II})$ etc. They have a trans-$\text{Mg}_2\text{O}_2$ co-ordination plane. In the absence of compelling situations, where it forms cis-configuration (Structure I.7), a trans-grossly planar (Structure I.6) complex usually forms. Intra-molecular interactions are quite common in grossly planar salicylaldimine complexes.

The chelate $(\text{Me-Sal})_2\text{Cu}$, is isolated in three different forms: (i) without much inter-molecular interactions ($\beta$-form), 

(ii) with $\text{Cu}...\text{Cu}$ weak interaction ($\delta$-form), and (iii) with $\text{Cu}...\text{O}...\text{Cu}$ bridging ($\gamma$-form) interaction (Structure I.11). The $\delta$ and $\beta$ forms of $(\text{Me-Sal})_2\text{Ni}$ have structures similar to those of the corresponding copper(II) complexes. One or more paramagnetic forms of $(\text{Me-Sal})_2\text{Ni}$ can be obtained by heat treatment of the normal dimagnetic molecules. These paramagnetic species show pseudo octahedral ligand field spectra. Undoubtedly they are polymeric in nature. So also the $(\text{Sal}_2\text{enNi})^+$
complexes have low magnetic moment because of weak Ni-O-Ni bridging in a polymeric structure (Structure 1.12). Copper(II), however, gives dimeric complex with square pyramidal geometry. A similar complex of copper(II), Cu(acac$_2$), is dimeric, but has a trigonal bipyramidal structure. On the other hand, another similar compound, Cu(hap$_2$), is monomeric.
Observations in solution show configuration equilibrium between monomeric planar and polymeric forms for (Me-Sal)$_2$Ni, as well as, for (Ar-Sal)$_2$Ni, which shifts towards planarity with increase in temperature. Such an equilibrium is seen in solution for (i-Pr-Sal)$_2$Ni, but not in (t-Bu-Sal)$_2$Ni, where the latter behaves as completely tetrahedral. It has been explained that branching at $\beta$-carbon atom by bulkier groups hinder molecular association.

\[
\text{Structure I.11} \quad \text{Structure I.12}
\]

Haxton and Waters\textsuperscript{61} bear a serious objection to the current basis of conformational explanations.\textsuperscript{63} Their main points of criticism on the earlier explanations to the
structures are based on the following experimental observations:

1. (i-Pr-Sal)$_2$Ni and (i-Pr, Et-Sal)$_2$Ni are tetrahedral with $\theta = 81.3^0$ and $85.3^0$ respectively, whereas, (i-Pr, 3-Me-Sal)$_2$Ni is planar.

ii. Straight chain groups are non-bulky and hence, favor planar structure.

iii. (St-Sal)$_2$Cu is pseudo-tetrahedral in one polymer ($\theta = 35.9^0$) whereas, (R-Sal)$_2$Cu (where R = Me, n-Pr, n-Bu) are planar.

iv. Explanation through "crystal packing forces" are irrational and vague.

Many of the difficulties disappear if the electronic state of these molecules, as evidenced by X-ray structural data, are considered. This is, however, discussed in detail by Haslem & Waters using such "stereo-electronic view." The explanations are based on the facts that:

(1) Electron flow in a molecule has an overall effect on stereochemistry.

(ii) The extent of the electron input is related to the hyperconjugations present with the substituents.
(iii) The electron redistribution implied by electron shifts is also manifested in small geometrical changes throughout a molecule.

Metal ion forms a delocalised hetero-nuclear \( \pi \) system similar to naphthalene ring in Schiff-base metal chelates. An enhanced electron density is found at the electronegative donor atoms, \( O \) and \( N \) (Structure I.13). By change of substituents in the chelate system a density alteration may be established on the metal atoms and the two donors and this, in turn, would result in electronic and structural consequences. Quantum mechanical calculations showing higher "free valence" at \( C \) and X-ray determinations of similar compounds suggest various canonical forms of the entire molecule.

Structure I.13
Complexes derived from schiff bases of Aminoacids

Schiff bases containing aminoacids belong to the class of bidentate ligands. Because of their complex behaviours large amount of work have been recently pursued by many workers of different fields. The chelates of N-salicylideneaminoacid form simple models for the complicated metal-pyridoxal-aminoacid systems which are intermediates of biological transaminations. The general structure of such chelates is represented in structure I.14.

Structure I.14
Kubo et al. synthesized a variety of complexes of N-salicylidene
glycinato copper(II) in hydrated and anhydrous forms. The most interesting feature is their magnetic behavior. The anhydrous forms obtained from two different hydrates have different subnormal magnetic moments strongly suggesting structure I.16 which makes use of an oxo-bridge for a magnetic quenching by superexchange. But the reason for the difference in magnetic moment of the anhydrous forms is not known. The sesquihydrate has been confirmed by X-ray

<table>
<thead>
<tr>
<th>Compound</th>
<th>Colour</th>
<th>Mode of preparation</th>
<th>Magnetic moment</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuSg.1.5H2O</td>
<td>Bluish-green</td>
<td></td>
<td>1.86 BM</td>
</tr>
<tr>
<td>CuSg.5H2O</td>
<td>Green</td>
<td></td>
<td>1.86 BM</td>
</tr>
<tr>
<td>CuSg</td>
<td>Green</td>
<td>Obtained by heating sesquihydrate.</td>
<td>1.56 BM</td>
</tr>
<tr>
<td>CuSg</td>
<td>Green</td>
<td>Obtained by heating pentahydrate.</td>
<td>1.33 BM</td>
</tr>
</tbody>
</table>

to have a planar structure (Structure I.15) containing the ligand and one water molecule in the coordination sphere.

Brown crystalline trihydrate complex of salicylideneanthranilato copper(II) (CuSa.3H2O) has been isolated by Golfer and Savich which decompose on dehydration. But, however, anhydrous forms could be isolated for CuSa and Cu(3-Br,3a)32 using cupric acetate dihydrate in aqueous alcoholic medium.

Definite co-ordination by oxygen of carboxyl group
is proved for the copper(II) complex, CuSa, (structure I.17) from infra-red data. An antisymmetric COO$^-$ stretching vibration in free acid, at 1633-1705 cm$^{-1}$, suffers a shift to lower energy in the complex which produces evidence of a delocalised $\cdot$ structure. A dimeric formulation with an eight-membered delocalised binuclear ring appears necessary to obtain co-ordination number 4.

Structure I.15

Structure I.16
Recently Theriot and coworkers, have made studies on the salicylideneaminoacid complexes of Co(II), Ni(II) and VO(II). Their magnetic studies on tetrametalllic N-salicylidene-L-valinatocopper(II) under varying temperature indicates π-pathway for superexchange using 3d\textsubscript{yz} or 3d\textsubscript{xy} orbitals of copper ion and 2p(\pi) orbitals of the bridging oxygen atom. Studies on Ni(II)\textsuperscript{30} reveals that it has an octahedral arrangement (\(\mu_{\text{eff}} = 3.2\ \text{BM}\)) through a dimeric structure (Structure I.18). Burrows and Bailar\textsuperscript{31} have studied the Fe(III) and Co(III) complexes of the same system.
Behera and Pani have isolated Co(II)Sg compounds in three forms, a dihydrate (pink) and two anhydrous (brown and red). The structures are similar to those of the Ni(II) isolated by Theriot et al.
The acid dissociation constant of salicylideneanthranilic acid and the stability constants of its complexes of Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and UO₂(II) in mixed solvents have been determined potentiometrically by Mehta and Gupta. The stability constant of salicylideneglycine have also been determined by Behera and Pani in dioxane-water medium (log $K_1$ = 10.27 and log $K_{II}$ = 8.90). Bai and Leussing have studied the kinetics of the Ni(II), Cu(II) and Zn(II) chelates of salicylideneaminoacids by pH-stat measurement.

Schiff base complexes are susceptible to polymerisation as discussed earlier. Such behaviour becomes more compelling in the case of tridentate chelating ligands. Examples of this may be seen in Theriot's work on bimetallic and tetrametallic compounds of Cu(II), Ni(II), Co(II) and VO(II), and in the works of Kubo et al and Hishita et al. As already discussed, subnormal magnetic moment is very common in polymerised complexes. This is more prominent in the complexes of schiff bases derived from o-aminophenol and L-aminoalcohol.

These polymeric bonds generally break in the presence of co-ordinating solvents to normal monomer units. This synergic effect is highly prominent in the presence of pyridine (e.g., 5-bromo and 5-nitro salicylideneanthranilato complexes of copper(II) yield monopyridinated derivatives). Balundgi has prepared a number of complexes of Cu(II), Ni(II) & Co(II) with schiff bases formed from salicylaldehyde and o-hydroxyacetophenone with N,N'-di-substituted ethylenediamine. They form adducts with chloroform, pyridine, halogens, as well as, acetylacetone and salicylaldehyde. The compounds exhibit various co-
ordination numbers depending on the nature of hetero-ligand and the mode of bonding.

Dutta and co-workers have prepared the o-phenanthroline adduct of Cu(II). According to them ethylenediamine does not form such adduct, but displaces the aminoacid from the complex forming salicylideneethylenediaminecopper(II).

Cu(II) itself is an interesting metal having high affinity for oxygen donors where it co-ordinates to cis-oxygens and also makes space for co-ordinating homo and hetero metals. Thus the primary complex behaves as a chelating agent to a secondary metal. This brings the secondary metal to such a close range that often considerable direct overlap of metal orbitals or super-exchange through oxygen $\pi$-system takes place making an effective spin pairing and huge quenching in magnetic moment. Many works have been published to assess and establish the magnetic effects of these compounds in bi-, tri- and tetra-metallic forms polymerised in straight chain, angular, zigzag, triangular or quadrilateral geometry.

**Concluding Remarks**

From the foregoing discussions the following general conclusions can be arrived at:

1. When a tridentate dibasic schiff base ligand derived from salicylaldehyde and aminoacids react with metal ions like Cu(II) and Ni(II), the deficiency of co-ordination number is made up by polymerisation and/or solvation.
(ii) The deficiency can be filled up by other ligands to achieve desired stereochemistry. The resulting mixed ligand complex can be neutral or anionic in nature.

(iii) Polynuclear complexes of Cu(II) involving above type of schiff bases and similar or different metal ions may be possible.

(iv) A survey of literature shows that no detailed work has been done on the above type of schiff base complexes of Ni(II) and Cu(II) to make any systematic structural, spectral and other correlations.

In view of the above considerations the present work has been undertaken for more detailed and systematic investigation of Cu(II) and Ni(II) complexes of salicylideneaminocarboxylic acids.

An advance summary of the work is presented in Chapter II.
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