CHAPTER I

INTRODUCTION
Complex compounds may be defined as substances formed by the combination of components which are already saturated according to the classical concepts of valency. When a metal ion combines with an electron donor, the resulting substance is said to be a complex compound. According to Werner the neutral molecules or oppositely charged ions or groups are coordinated around a central atom or ion in the first sphere of attraction. The number of groups attached about the central ion is called the coordination number and groups themselves are known as ligands. Complex compounds of coordination number 2 - 8 are known. Ligands may be of various types. If they occupy only one position in the complex compound they are known as monodentate ligands whereas if they occupy two, three or four positions in the complex compound they are known as bidentate, tridentate or quadridentate ligands. Normal complexes are formed with monodentate ligand, whereas ring formation always results with bidentate, tridentate or quadridentate ligands. This type of ring formation was named by Morgan and Drew, 'chelation'.

A number of amino acid, cyclic complexes were reported by Ley in 1904, which he named inner complex salts. The term inner indicated ring formation, complex indicated the presence of coordinate linkage whereas salt denoted the primary bond formation between the metal and the negative carboxyl group. Thus inner complexes are special classes of chelates. The structures of hydrates, double salts, and metal
ammonia compounds were known and much discussed even before the 19th century, that is, the history of ammonates can be traced from the work of Tassaert as early as 1793. The earlier theories of the structure of complex compounds although of historical importance and also helped to promote much experimental work in this sphere, do not give plausible explanation for the complex formation. Some of the earlier theories, such as
1. Berzelius Conjugate Theory.
2. Graham's Ammonium Theory.
need not be discussed here.

With the background provided by the above theories, Werner in 1901 published a paper on coordination theory.

**Werner's Coordination Theory:**

Werner suggested that the atom does possess a certain number of valence bond, but the valence force is exerted over the whole surface of the atom. This valence force can be divided into several units of varying strength depending on the demands of the atoms which unite with it.

**Fundamental Postulates:**

The fundamental postulate in Werner's coordination theory is stated in the following way: 'Even when, to judge the valence number, the combining power of certain atoms is
exhausted, they still possess in most cases the power of participating further in the construction of complex molecules with formation of very definite atomic linkages. The possibility of this action is to be traced back to the fact that, besides the affinity bonds designated as principal valencies, still other bonds on the atoms, called auxiliary valences, may be called into action. Thus Werner gave an idea about primary and secondary valence forces. In terms of Werner theory the secondary valences of atom must be satisfied. The relationship between primary and secondary valencies became closer and closer in the mind of Werner. He reached the conclusion from various experimental data that each element has only a certain number of secondary valences, groups attached to the central element by these valencies are said to be coordinated to it. The coordination number of an atom or ion is the number of groups which can be coordinated to it. Werner’s theory was largely criticised by Jorgensen on a number of points, for example (1) the entrance of a negative group into the complex ion should lower the valence of the complex, (2) that Werner’s theory predicted the existence of many compounds which were then unknown, such as the ‘violeo’ and the ‘flavo’ compounds of cobalt, (3) that all of the coordinated groups do not occupy equivalent positions in the complex, contrary to the postulate of Werner.

These criticisms thus led to the discovery of many more compounds, a theory of rearrangements was devised, the relationship between the primary and secondary valences was
clarified and the octahedral structure of the hexacoordinated complexes was firmly established by the resolution of many compounds into their optically active isomers.

**Coordination and electronic theory of valency:**

Sidgwick assumed that two electrons were present in each coordination bond of such compounds and in many cases the total electron shells of the inert gases are thereby attained.

<table>
<thead>
<tr>
<th>Element</th>
<th>Atomic Number</th>
<th>Electron lost in ion formation</th>
<th>Electron gained in coordination</th>
<th>Total shell</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe(ous)</td>
<td>26</td>
<td>2</td>
<td>12</td>
<td>36</td>
</tr>
<tr>
<td>Co(ie)</td>
<td>27</td>
<td>3</td>
<td>12</td>
<td>36</td>
</tr>
<tr>
<td>Cu(ous)</td>
<td>29</td>
<td>1</td>
<td>8</td>
<td>36</td>
</tr>
<tr>
<td>Zn</td>
<td>30</td>
<td>2</td>
<td>8</td>
<td>36</td>
</tr>
<tr>
<td>Mo</td>
<td>42</td>
<td>4</td>
<td>16</td>
<td>54</td>
</tr>
<tr>
<td>Pd</td>
<td>46</td>
<td>4</td>
<td>12</td>
<td>54</td>
</tr>
<tr>
<td>Ir</td>
<td>77</td>
<td>3</td>
<td>12</td>
<td>86</td>
</tr>
<tr>
<td>Pt</td>
<td>78</td>
<td>4</td>
<td>12</td>
<td>86</td>
</tr>
</tbody>
</table>

In other elements which form complexes often very stable ones the total number of electrons may either not attain or may even exceed the number in the inert gas shell, for example:
<table>
<thead>
<tr>
<th>Element</th>
<th>Atomic Number</th>
<th>Electron lost in ion formation</th>
<th>Electron gained in coordination</th>
<th>Total shell</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr</td>
<td>24</td>
<td>3</td>
<td>12</td>
<td>33</td>
</tr>
<tr>
<td>Fe(ie)</td>
<td>26</td>
<td>3</td>
<td>12</td>
<td>35</td>
</tr>
<tr>
<td>Co(ox)</td>
<td>27</td>
<td>2</td>
<td>12</td>
<td>37</td>
</tr>
<tr>
<td>Ni</td>
<td>28</td>
<td>2</td>
<td>12</td>
<td>33</td>
</tr>
<tr>
<td>Cu(ie)</td>
<td>29</td>
<td>2</td>
<td>9</td>
<td>35</td>
</tr>
<tr>
<td>Zn</td>
<td>30</td>
<td>2</td>
<td>12</td>
<td>40</td>
</tr>
</tbody>
</table>

The tendency is not, therefore, merely to attain the inert gas structure, although this appears to be significant; it is also necessary to produce a symmetrical structure (planar, tetrahedral, octahedral or cubic) irrespective of the actual number of electrons involved.

In order to consider more precisely the nature of the bonds present, the group \([\text{Co(NH}_3\text{)}_6]\) may be written, using the Main Smith notation, as follows:

One \(\text{NH}_3\) being written more fully than the others to assist in the summation of charges, when the charges on each atom are summed, the following results are obtained:

\[
\begin{array}{ccc}
\text{H} & \text{N} & \text{Co} \\
\text{Charges due to shared electrons} & -1 & -4 & -6 \\
\text{Charges due to unshared electrons} & 0 & 0 & 0 \\
\text{Core charge} & +1 & +5 & +3 \\
\text{Resultant charge} & 0 & +1 & -3
\end{array}
\]
The grouping is, therefore, as below (II), carrying a resultant charge of \( +6 - 3 = +3 \). Each \( \text{NH}_3 \) group may be considered to combine with the cobalt ion by virtue of its lone pair of electrons and the grouping may accordingly be written as (III) below:

![Diagram II and III showing bonding](image)

This type of bonding the semi-polar bond (Sugden) or the coordinate link (Sidgwick) is common in practically all such compounds containing groups capable of independent existence, i.e. it may in a sense be regarded as a subspecies of covalent link.

Sugden considered that in such compounds the octet rule should not be abandoned, that valency shells larger than the water most group of eight \( ^{\text{th}} \) inert gases should not be pre-supposed. He therefore formulated such compounds with single electron links, and considered that such representation gave a more plausible distribution of electronic charges. These views have met with no general acceptance.
Atomic orbital theory:

When two atoms are brought together so that the electronic field of one can interact with that of the other, an electron bond may be formed, when (1) there electrons in the two orbitals have opposite spins and (2) the electronic orbitals of the two bonding electrons overlap. In complex compounds the number of bonding orbitals available are usually less than those of the atoms. It is, therefore, supposed that in atoms or ions in which several of the outer electronic levels differ slightly in energy, the normal quantization can be changed or broken down and new equivalent bonding orbitals can be formed. This process is known as hybridization and hence the bonding orbitals are called hybrids. The theory of hybridization thus gives four equivalent orbitals directed toward the corner of a tetrahedron or square, or six towards the corner of an octahedron. According to Pauling the hybridized bonds are much stronger than the normal bonds.

A large number of workers have tried to justify that coordination can stabilize both common and uncommon valence states of a metal, by the atomic orbital theory e.g., the relative stabilities of the 2 and 3 states of cobalt have been explained repeatedly in terms of atomic orbital theory. But the theory is not free from deficiency e.g., it can not interpret the spectra or can not give relative energies of different structures and of different coordination numbers. Due to this lack of precision in quantitative interpretation,
this theory has been criticised by some workers.

**Molecular orbital theory:**

This theory deals with the formation of a molecule in terms of the positions of the electrons when they form a molecule. If two factors (1) the energy sequence of the molecular orbitals and (2) the shape or symmetry properties of electron allowed are known, then the molecular structure can be formed similar to that of the structure of atom. The molecular orbitals will then be filled by the electrons in turn, beginning with the orbitals of lowest energy; consider for example A and B, a dye, atomic molecule in which A and B may be like or unlike atoms. When two atoms are brought very close to each other, the potential and kinetic energy of the electron of an atom is very little affected by the presence of the other. Hence the molecular orbital $\gamma_M$ of the composite molecule will be identical to those of the separate atoms or $\gamma_M = \gamma_A \pm \lambda \cdot \gamma_E$ where $\lambda$ depends on the overlap of atomic wave functions.

When each pair of atomic orbital combines in this way, it will give a new molecular orbital. If the energy of the molecular orbital is less than those of atomic orbitals as represented by $\gamma_M = \gamma_A + \lambda \cdot \gamma_E$, it will constitute a bonding orbital whereas if $\gamma_M = \gamma_A - \lambda \cdot \gamma_E$, it will describe an antibonding orbital. The net effect when the atom unites to form a molecule is determined by the
resultant force of the bonding and the antibonding orbitals. The orbitals which are perfectly quantized do not take part in the molecular framework and so are called nonbonding orbitals. If the overlap integral is very small i.e. the internuclear distance is minimum λ will be very small and the molecular orbital \( \psi_m \) will not be very much different from \( \psi_A \) or \( \psi_B \) i.e. the atomic orbitals.

Atomic orbitals can unite to form a molecular orbital when,

1. the separate atomic wave functions are comparable in energy,
2. their electron charge clouds overlap to a maximum state in the region between the nuclei,
3. the atomic wave functions have the same symmetry with respect to the line joining the nuclei.

If the line joining the nuclei is taken as the \( x \) direction then three characteristics are possible for the atomic wave functions,

(a) axial symmetry in the region of overlap, as for the \( 3s, 3p_x \)\& \( 3d_{xz}, 3d_{yz} \) atomic orbitals,
(b) one nodal plane as for \( p_y \) or \( d_{xy} \) orbital and
(c) two nodal planes for \( d_{yz} \) orbitals.

These symmetry are preserved in the resulting molecular orbitals, which are known as \( \sigma, \pi \) and \( \delta \) -orbitals as compared with 0, 1 and 2 nodal planes of atomic orbitals respectively. The electronic configuration and the shape of
the molecule is thus known.

This theory, although in principle, able to calculate actual energies as well as relative changes in energy due to perturbations, is unable to do so in practice for any but the simplest systems. The importance of molecular orbital theory lies in explaining chemical, stereochemical, optical and magnetic properties of complex compounds.

There is a relationship between the orbitals used for the complex formation and the spatial arrangement of bonds in complex compounds, e.g., with coordination number 4, so³ or sd³ orbitals will give rise to a tetrahedral model and d⁶e² orbitals, a square planar geometrical configuration, and so on.

Ligand field theory:

In the field free space the d orbitals have five directions, but in an electrical field they are no longer of equal energy. A field of cubic symmetry splits the d levels into two group i.e. (a) d_y orbitals and (b) d_e orbitals, where d_y orbitals signifies d_{x^2} and d_{x^2-y^2} orbitals and d_e, the d_{xy}, d_{yz} and d_{xz} orbitals. The d_e orbital is of lower energy than the d_y orbital. The d_y pair have the property of combining with s and p orbitals to give bonding hybrid orbitals whereas d_e forms the π bonding with atoms at the vertices of the octahedral.
Π bonded complexes can be formed by the ligands in two ways,

(1) if it is possible to write a resonance structure with a vacant p orbital on a ligand atom, then dπ - pπ bond may be formed.

(2) if the atoms have d level vacant which can act as acceptors then dπ - dπ bonds are formed.

The charges on the ligand which are negative dipoles are directed towards the central atom and thus set up an electrostatic field. The ligand field theory deals with the idea that the electrons of the central ion should avoid those regions of space in which the field due to the attached negative ion is the largest.

If the ligands set up a weak field, its effect is balanced by the repulsion between the dγ and dε orbitals. If however the ligands set up a strong field, the energy of an electron may be raised so much that the electrostatic repulsion between electrons in dγ and dε state is overcome.

The ligand field theory approach has thus proved useful and suggestive, not only for the treatment of complex formation, but also for problems of ionic crystal which, for some purposes, can be regarded as infinite polynuclear complexes.

The only defect of this theory is that it does not take into consideration directed covalent or electron pair
bonds between the ligand and the central atom. As a result of this the theory fails to explain the formation of complexes, \( \pi \) bonding, and also the resolution of asymmetric complexes into their optically active modifications.

Stability of coordination compounds:

The stability of the chelates which form a special class of coordination compounds, depend mainly on two factors and (1) the nature of the chelating agent (2) the nature of metal ion.

Nature of chelating agent:

The factors which normally influence the stability of the chelate and are characteristic of the ligand, are briefly discussed below:

Size of chelating ring:

Ley\(^2\) while working on amino acid chelates gave a convincing evidence that the most stable chelates have five and six membered rings. Four membered chelate rings are much less in number. Information is generally lacking about the relative tendencies for the formation of five and six membered rings. It has been noticed by Pfeiffer\(^10\) that five membered ring generally is more stable when the ring is entirely saturated, but the six membered ring is favoured when one or more double bonds are present, although the exceptions to this can not be ruled out. It can, therefore, be said that the
chelates obtained from the aliphatic ligands form structures in which the five membered rings are more stable than the six membered ones, while if the ligands are aromatic compounds, the six membered rings are more stable. The greater stability of five membered rings is mainly due to the enthalpy of formation and not due to the entropy as is evident from the thermodynamic data.

**Number of rings**

It has been known since long that an increase in the number of rings within a particular chelate structure confers a greater stability to the chelates. But the quantitative data regarding the number of rings to prove greater stability have been only recently provided. Contribution to this aspect has been provided by the work of Calvin and Bailes, Schwartenbach and large number of other workers.

**Entropy effect**

When two or more donor groups are tied together to form an additional chelate ring without materially altering the donor groups, the increased stability of the chelate as is evident from the increase in the formation constant, is due almost entirely to an increase of entropy. This effect has been pointed out by Calvin.
Resonance effect:

Calvin and Wilson has shown effectively the importance of resonance in conferring stability on complexes. The subject has been further studied by a large number of workers, Pauling, Brockway and Cross, Chatt, Fischer and Hearn. Hearn while discussing histidine chelates proposed double bond resonance as an explanation of the higher stability, as histidine combines more strongly with cobalt and similar transition metals than other natural amino acids with the exception of cysteine.

Nature of donor atom:

It is difficult to present a clear picture about the nature of the donor atom on the stability of chelates as the changes in the donor element are associated with many other effects such as size of ring, resonance, steric factors, basic strength etc., but the most important of these factors is the change in the basic strength. If we restrict ourselves to organic compounds in which the donors are O, N, and S atom, as the chelate of these groups have been much studied, then according to Sidgwick, the metals forming chelates with oxygen and nitrogen can be divided into three classes, but consideration such as size of ring, influence of substituents on acidity etc., are also to be taken into account.
\[ \varnothing > N \quad \text{Mg, Ca, Sr, Ba, Ca, In, Ti, Ti, Zr, Th, Si, Ge,} \\
\varnothing > N \quad \text{Sn, V(V), V(IV), Cr(V), Ta(V), Mo(V), U(VI), U(IV),} \\
\varnothing > N \quad \text{Fe(III), Co(II).} \\
\varnothing \geq \quad \text{Be, Cr(III), Fe(II), Platinum metals.} \\
\varnothing > \varnothing \quad \text{Cu(I), Ag(I), Au(I), Cu(II), Cd, Hg, V(III), Ni(II).} \\

Although \( S \) and \( O \) bear similarity to each other in many ways, their chelate forming tendency is not the same. This can be seen from the following comparisons given by Sidgwick:

\[ S > O \quad \text{Cu(I), Ag(I), Au(I), Hg(I).} \]
\[ O > S \quad \text{Be, Cu(II), Au(III) and most other metals.} \]

Effect of substitution on the ligand:

The tendency for chelation can be affected in one of the two ways if a group of the chelating agent is substituted:

1. The acidity of the donor group may change or the resonance of the chelate ring may increase or almost it may get affected.
2. Mainly due to steric influences the groups added to the ligand by substitution may prevent the ligand from acquiring the orientation about the central metal ion most favourable for chelation. Thus substitution is not always without effect on the behaviour of chelate compounds.
Steric effects:

In some cases the classification of groups on two coordinated ligands will result in a distortion of bond angles and decrease in stability. This is the phenomenon of F-strain, described by Brown, as applied to complex compounds. By means of steric strain a number of experimental data can be correctly interpreted. Several workers who studied the thermodynamic stability of \( N^2 \) and \( N^1 \), \( N^1 \)-alkyl substituted ethylenediamines, observed that the stability of the complex decreased when the alkyl groups were substituted for hydrogen atoms on the nitrogen. This can be explained as due to steric factors. Much work has been done on this such as by Smirnoff, Willink and Wibaut, Irving, Butler and Ring, Berg, etc.

Basicity of the ligand:

The stability of the chelate compound is greatly influenced by the basicity of the ligand, since hydrogen and metallic ions behave similarly in complex formation. The result is that the strongly basic ligand which possesses a larger affinity for a proton may show a similar behaviour towards metallic ions. If the localisation of the negative charge on the coordinating ligand increases by any factor, then according to Riley, the electrons become more readily available with the result that the capacity of the base to coordinate increases. Larsson has given a linear relationship between the basic strength of the ligand and its complex.
forming affinity, although this idea met with criticism by
a few workers, it gives very good conclusions, when
systems of sufficient structural similarity are compared
and a linear relationship between pK complex and pK base
is obtained. The work on diketones, amino carboxylates,
amines and silver amino complexes by Brushman and Verhoek
have supported this view. The stability of the complex is
greater, with the larger number of points of attachment of
the ligand with the central metal ion.

Nature of metal ion:

The stability and other properties of the chelate
also depend on the nature of the central metal ion, some
important features of which are given below:

Chelate forming metals:

Most of the metals of the periodic table form
chelates and complex compounds but this tendency is present
particularly in transition metals which act as strong electron
donors. In general it can be said that chelation takes place
more or less with all positive metal ions. Two factors appear
to be responsible to cover the relative tendencies for a metal
ion to form a coordination compound.

(1) the charge in the radius of the metal ion,
and (2) the tendency to form homopolar bond's in an electron
donor.
as a generalisation, it can be said that elements of the periodic table with vertical symmetry possess the capacity to form complexes, whereas the rare earths and the metals of the 8th group possess this tendency for which horizontal similarity appears to apply.

**Stability constants and periodic classification of metals:**

The following order seems to appear in the stability of the complexes as was observed by Kellor and Malsey.

\[
Pd > Cu > Ni > Pb > Co > Zn > Cd > Fe > Mn > Mg
\]

With the increasing basicity of the metal, the stability decreases which indicates that the availability of the metal to form homopolar bonds is a criterion of the bond strength of the chelates. The greater the strength of homopolar bonds formed by the metal, the greater will be the stability of the chelate.

**Influence of charge and radius of metal ion:**

The alkali metals and the alkaline earths which give chelates mainly of the ionic type show that the strength of chelation increases with increasing ionic charge of both the metal ion and the donor and also increases with the decrease of ionic radius of the metal ion. The reagents which give nearly a normal order of stability constants have lesser number of donor groups and hence form a less highly chelated
structure. If the chelate bonding is ionic, the chelate formation tendency increases with the increase in charge radius ratio.

Competition between metals:

The chelates of copper and other metals with EDTA were shown by Pfeiffer and Schmitz to have a stability which depended largely on the nature of the remaining positive ion in the solution. Copper disodium chelate was found to be stable with caustic soda, but when sodium ions were replaced by Ca and Mg ions, copper hydroxide was precipitated. The interference of Ca and Mg ions was shown not to be due to the replacement of Cu ion, as similar effect was observed in the presence of Ba, Sr, Be, Mg ions. It was concluded by Pfeiffer that interaction with the complex anion preferably does not involve compound formation, but is great enough to weaken the chelate considerably.
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