2. Theories of Co-ordination Compounds

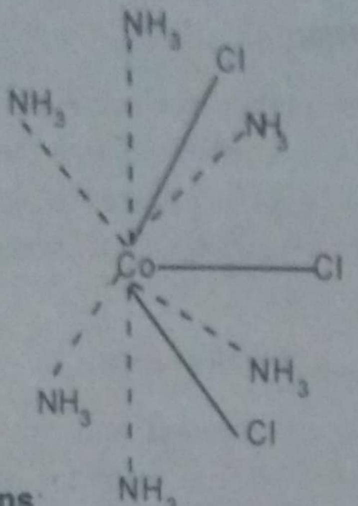
WERNER'S THEORY

Alfred Werner in 1893 put forward his famous co-ordination Theory to represent the structure of complex compounds such as $CoCl_3 \cdot 6NH_3$, $K_4[Fe(CN)_6]$ etc.

Postulates:

1. There is a central metal atom around which other atoms or groups are arranged or co-ordinated. Neutral molecules or oppositely charged ions are co-ordinated to the central atom.
2. The maximum number of atoms or groups, which can be co-ordinated to central metal ion, or atom is known as its co-ordination number (CN). The co-ordinated groups are called ligands.
3. Each metal has a fixed CN.
4. Metals possess two types of valencies
   a) Primary or ionisable valency
   b) Secondary or non-ionisable valency
   Primary valency corresponds to the oxidation state of the metal. It is always satisfied by negative ions.
   Secondary valencies correspond to the CN. of the metal. It is satisfied by negative groups or neutral molecules or even by positive groups.
5. The sphere enclosing the central metal ion and the co-ordinated groups is called the co-ordination sphere.
6. The secondary valencies are directed in space about the central metal ion. Thus, for metals with C.N.6 the six ligands are arranged at the six corners of the regular octahedron with the metal ions as center. For metals with co-ordination number 4, four such ligands may be arranged either in square planar or tetrahedral fashion.
   The complex compounds are capable of exhibiting the phenomenon of isomerism.
7. Every element tends to satisfy both its primary and secondary valencies. To meet this requirement a negative ion often shows a dual behavior, i.e., it may satisfy both primary and secondary valencies.
8. The net charge on the co-ordination complex is the resultant of the charges borne by the central metal ion and the ligands.

E.g. $Fe^{3+} + 6CN \longrightarrow [Fe(CN)_6]^{3-}$



$[Co(NH_3)_6Cl_3]$ gives $3Cl^-$

Applications:

On the basis of this theory Werner assigned the following structure to $CoCl_3.6NH_3$ representing primary,valencies with solid lines and secondary valencies with dotted lines.

The primary valency (i.e., oxidation state of +3) is satisfied by three Cl^- ions which have been shown by solid lines and are kept outside the co-ordination sphere; As all the three Cl^- ions are loosely bound, they are immediately precipitated as AgCl on the addition of $AgNo_3$ solution.

Treatment with HCl at 100°C, effects no removal of ammonia. This shows that all the six ammonia molecules are unionisable and are held to metal ion in the co-ordination sphere, Werner formulated this complex as $[Co(NH_3)_6]Cl_3$

Other example: $CoCl_3$ $5NH_3$, $CoCl_3$ $4NH_3$ and $CoCl_3$ $3NH_3$ may be written as follows $[Co(NH_3)_5Cl]Cl_2$, $[Co(NH_3)_4Cl_2]Cl$ $[Co(NH_3)_3Cl_3]$ etc.,

In the molecule $CoCl_3$ $5NH_3$ which is formulated $[Co(NH_3)_5Cl]Cl_2$ one Cl^- ion does the dual function, since it satisfies both primary and secondary valencies. This Cl^- ion being non ionic is not precipitated as AgCl by Ag^+ ions. Hence it is placed along with five NH_3 molecules and central metal ion in the co-ordination sphere. The other two Cl^- ions being ionic, are precipitated as AgCl by Ag^+ ions.

The molecule $[Co(NH_3)_4Cl_2]Cl$ contains only one ion Cl^- ion which gets precipitated as AgCl by $AgNO_3$ solutions.

The molecule $[Co(NH_3)_3Cl_3]$ has no ionic Cl^- ionic and hence it behaves as a non electrolyte.