**Werner’s cordination theory:-**

Alfred Werner (considered as the father of coordination chemistry) studied the structure of coordination complexes such as Luteocobalticchloride[ CoCl3.6NH3], Roseoocobalticchloride [CoCl3.5NH3], Psaeocobalticchloride [CoCl3.4NH3 (green)] and Violeocobalticchloride[ CoCl3.4NH3 (violet)].

Originally they thought that these compounds are ammoniates like hydrate salts. But later, it was found that they cannot eliminate ammonia molecules on strong heating or they cannot react with con. H2SO4 to form (NH4)2SO4.

Werner and his co-workers performed the following experiments—

1. They measured the conductivity of the solutions of these compounds and determined the total no. of ions formed per molecule as shown in the table below—



1. They used AgNO3 to precipitate the Cl- ions as AgCl and determined the total no. of free Cl- ions present per molecule in these compounds. They found the ratio of free Cl- ions per molecule in these compounds as 3:2:1:1 respectively.

From their research work, Werner stated as – “Even when, to judge by the valence number, the combining power of certain atoms is exhausted, they still posses in most cases the power of participating further in the construction of complex molecules with 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 called auxiliary valencies, may be called into action.” The various postulates of this statement are given as—

**(i)** Each metal in coordination compound possesses two types of valencies : a) Primary valency or principal valencies or ionisable valencies and (b) Secondary valency or non ionisable valencies.

**(ii)** Primary valencies are satisfied by anions only. The number of primary valencies depends upon the oxidation state of the central metal. It may change from one compound to other. These are represented by dotted lines between central metal atom and anion

**(iii)** Secondary valencies are satisfied only by electron pair donor, the ions or the neutral species. These are represented by thick lines.

**(iv** Each metal has a fixed number of secondary valencies also referred as coordination number. The coordination number depends mainly on the size and the charge on the central atom. The maximum number of ions or molecules that the central atom can hold by secondary valencies is known as coordination number.

**(v)** The ion attached to primary valencies possesses ionising nature whereas the ions attached to secondary valencies do not ionize when the complex is dissolved in a solvent. Anions can exhibit its dual nature i.e.they may satisfy primary as well as secondary valencies of the metal at the same time. Such bonds are represented by ….. lines.

**(vi** Every central metal ion tends to satisfy its primary as well as secondary valencies.

**(vii)** The secondary valencies are directional and are directed in space about the central metal ion. The primary valencies are nondirectional. The presence of secondary valencies gives rise to stereoisomerism in complexes.

Initially, Werner had pointed out coordination number of a metal atom to be four or six. The six valencies were regarded to be directed to the corners of a regular octahedron about the metal ion at centre. For metals having four coordination numbers, the four valencies are either arranged in a planar or tetrahedral nature.

Thus on the basis of werner theory, the CoCl3. 6NH3 is called hexaminecobalt (III) chloride because there are six ammonia ligands and the cobalt is in the +3 oxidation state, i.e. cobalt has three primary valencies and six secondary valencies. According to Werner, there are two spheres of attraction. The outer sphere is satisfied by Primary valencies and inner sphere is satisfied by Secondary valencies. The inner sphere is written within [ ].The Werner’s formulation of the compound CoCl3. 6NH3 is shown as—



In CoCl36NH3, the six secondary valencies and three primary valencies are satisfied by six NH3 and three Cl- ions respectively. Thus, these three Cl- ions are ionizable. Hence the Werner’s formulation of the compound is represented as [Co(NH3)6]Cl3. In CoCl35NH3, one Cl- ion exhibits its dual nature. So, in this compound only two Cl- ions are ionizable and formulated as [Co(NH3)5Cl]Cl2. Similarly, the compound CoCl34NH3 can be formulated as [Co(NH3)4Cl2]Cl.

**Some important definations**:-

**1. Coordination entity:** A coordination entity constitutes a central metal atom or ion bonded to a fixed number of ions or molecules. Example: in K4[Fe(CN)6], [Fe(CN)6]4- represents coordination entity.

2. **Central atom or ion:** In a coordination entity, the atom/ion to which a fixed number of ions/groups are bound in a definite geometrical arrangement around it, is called the central atom or ion. E.g.: in K4[Fe(CN)6], Fe²+ is the central metal ion.

**3. Ligands:** A molecule, ion or group that is bonded to the metal atom or ion in a complex or coordination compound by a coordinate bond is called ligand. It may be neutral, positively or negatively charged. Example: H2O, CN-, NO+ etc.

4. **Donor atom:** An atom of the ligand attached directly to the metal is called the donor atom. For example: in the complex K4[Fe(CN)6], carbon is a donor atom.

5. **Coordination number:** The coordination number (C.N.) of a metal ion in a complex can be defined as the number of donor atoms to which the metal is directly bonded to other atoms, ions or molecules to satisfy its secondary valencies . For example: in the complex K4[Fe(CN)6], the coordination number of Fe is 6.The coordination number is equal to the no.of mono-dentate ligands (ligands having only one donor atom) or twice the no. of bi-dentate ligands present in the complex compound. i.e. CN =∑no.of ligands x denticity of the ligand. The C.N. indicates the geometrical shape of the complex.

6. **Coordination sphere or inner sphere**: The central atom/ion and the ligands attached to it are enclosed in square bracket and is collectively termed as the coordination sphere. For example: in the complex K4[Fe(CN)6], [Fe(CN)6]4- is the coordination sphere.

7. **Counter ions:** The ions present outside the coordination sphere are called counter ions. (i.e. the ions present in the outer sphere) For example: in the complex K4[Fe(CN)6], K+ is the counter ion.

8. **Coordination polyhedron:** The spatial arrangement of the ligand atoms which are directly attached to the central atom/ ion defines a coordination polyhedron about the central atom. The most common coordination polyhedra are octahedral, square planar and tetrahedral. For example: [PtCl4]2- is square planar, Ni(CO)4is tetrahedral while [Cu(NH3)6]3+ is octahedral.

9. **Charge on the complex ion:** The charge on the complex ion is equal to the algebraic sum of the charges on all the ligands coordinated to the central metal ion.

10. **Denticity:** The number of donor (linking) atoms present in ligands which can attach to a metal ion in the formation of complexes is called denticity.

11. **Oxidation number of central atom:** The oxidation number of the central atom in a complex is defined as the charge it would carry if all the ligands are removed along with the electron pairs that are shared with the central atom.