B.Sc. Part-II (H), Paper-IIIB, Unit-3 (Gr-A)

⇒ Theories of Coordination/Complex Compounds (By Birendra Kumar)

Bonding and properties of complex/coordination compounds have been explained by different theories:
1. Werner's coordination theory 2. Valence bond theory 3. Crystal field theory 4. Molecular orbital theory 5. Ligand field theory.

1. Werner's Coordination theory: In 1893, Alfred Werner first gave a theory to explain the bonding in complex compounds, known as Werner's coordination theory. The main postulates of the theory are:

(i) Central metal in coordination complex/ion possesses two types of valencies: (a) Primary valencies (b) Secondary valencies.

(ii) Primary valencies are those which a metal exercises in the formation of its simple salts. e.g., In $CoCl_3$, primary valency of Co is +3. They are satisfied by anions only. They are ionisable (ionic). They are equal to oxidation state of the central metal. They are also known as principal or ionisable valencies. It is shown by ···· (dotted line)

(iii) Secondary valencies are those which a metal exercises in the formation of complex ions/compds. e.g., In $CoCl_3 \cdot 6NH_3$, secondary valency of Co^{3+} is 6 (satisfied by NH_3). They are satisfied by neutral polar molecules, anions containing one or more lone pairs. They are non-ionisable (coordinate covalent bonded). They are equal to coordination no. of central metal, and also called auxillary valency. It is shown by — (bold line)

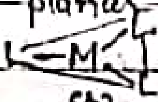
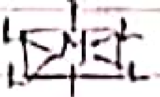
(iv) Every element or metal tends to satisfy both its primary & secondary valencies. A negative ion (i.e., anion) may satisfy both primary & secondary valencies. Thus, properties of Co(III) amines, e.g., $CoCl_3 \cdot 6NH_3$, $CoCl_3 \cdot 5NH_3$, $CoCl_3 \cdot 4NH_3$ & $CoCl_3 \cdot 3NH_3$ can be explained on the basis of the above postulates. In all the amines, Co shows secondary valency, i.e., C.N. 6 and primary valency, i.e. oxidation state +3.

(v) Primary valency is due to outer sphere of attraction (i.e., outside coordination sphere) whereas secondary valency is due to inner sphere of attraction (i.e., coordination sphere).

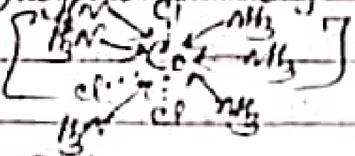
(vi) Secondary valency is usually twice the primary valency.

(vii) Ligands get arranged around the central metal atom/ion in a fixed geometry. Consequently the complex compounds/ions have fixed

Shape & structure or geometry.

C.No.:	2	3	4	4	6
Shape :	Linear	Triangular planar	Tetrahedral.	Square planar	Octahedral
Geometry:	L–M–L				
Hybridisation of Central metal:	sp	sp^2	sp^3	dsp^2	sp^3d^2 or d^2sp^3

Thus, on the basis of Werner's coordination theory, hexaammine cobalt(III) chloride $[CoCl_3 \cdot 6NH_3]$ cobalt has primary valency +3 & secondary valency 6 since there are 6 ammine (NH_3) ligands & o.state of Co is +3. The complex can be represented as



Valence bond theory (VBT)

VBT proposed to explains the bonding & some properties of complex or coordination compounds. The main postulates of this theory are—

1. The central metal atom provides a number of empty orbitals equal to its coordination numbers for the formation of coordinate covalent bonds with ligand orbitals.
2. The empty orbitals of the central metal hybridize to give an equal numbers of hybrid orbitals of equivalent energy.
3. The central metal atom or ion can use $(n-1)d$, ns, np, nd orbitals for hybridisation to give square planar (dsp^2), tetrahedral (sp^3) or octahedral (d^2sp^3 or sp^3d^2) geometry.
4. These hybrid orbitals then overlap with filled orbitals of ligands, which can donate an electron pair for bonding ~~[illegible]~~ $M \leftarrow L$ bond.
5. The nonbonding metal electrons present in the inner orbitals do not take part in chemical bonding.
6. If the complex contains unpaired electrons, the complex is paramagnetic in nature whereas, if it does not contain unpaired electrons, the complex is diamagnetic in nature.
7. Under the influence of a strong ligand (e.g., NH_3, CN^-, CO etc), the electrons can be forced to pair up against the Hund's rule of max^m spin multiplicity.

Limitations: VBT could not explain: (i) The colours of transition metal complexes (ii) The optical absorption spectra. (iii) The detailed magnetic properties (iv) Certain experimental facts regarding geometry of complexes