

The nature of the Co-ordination Linkage

There are three major approaches to the study of the co-ordinate linkage:

- ① Valence Bond Theory (VBT) (1930-1950)
- ② Crystal Field Theory (CFT)
- ③ Molecular Orbital Theory (MOT)

Of these VBT propounded by Pauling is the oldest and is based on the conception of hybridization of suitable orbitals of the metal ion. The VBT has served inorganic chemists very well during two decades (1930-1950) and provided a useful understanding of the valence and structure of the co-ordination complexes. After 1950 the quantitative inadequacy of the theory was gradually realised and CFT gained ground. CFT assumes the ligands as dipoles or ions and examines the effect that these dipoles or ions force on the ordering of the d-orbitals of the transition metal ions. MOT largely considers a good overlap of the orbitals of the ligands and the metal ions so that the bonding turns out to be largely covalent.

VBT: According to VBT

- (a) The metal M first loses requisite number of electrons to form the ion, the number of electrons thus lost being the valency of the resulting cation.
- (b) The metal ion will make available a number of orbitals equal to its co-ordination number for the formation of covalent bonds with the ligands. Since metal ion complexes attain certain definite stereochemical directions, metal ion orbitals must be so disposed that they point to such stereochemical directions.
- (c) There occurs an overlap of a filled ligand orbital and an empty hybrid orbital of the metal ion (M←L).
- (d) The regrouping of electrons is achieved obeying Hund's rule, that is, with maximum possible unpaired electrons.

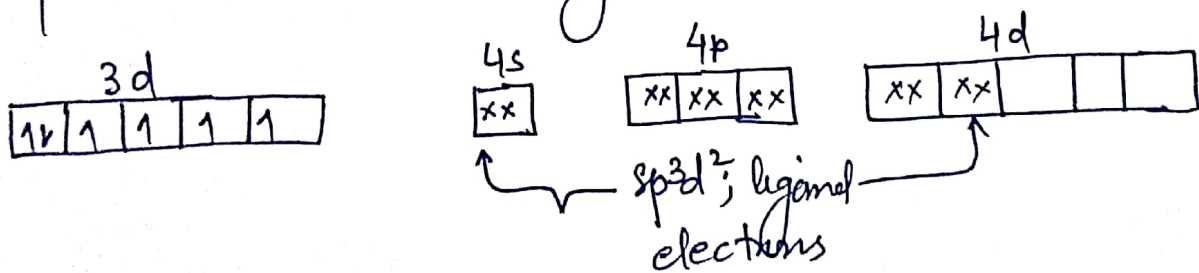
⊙ Example: Atomic no. of Co = 27. A Co(III) ion will have

only 24 electrons.

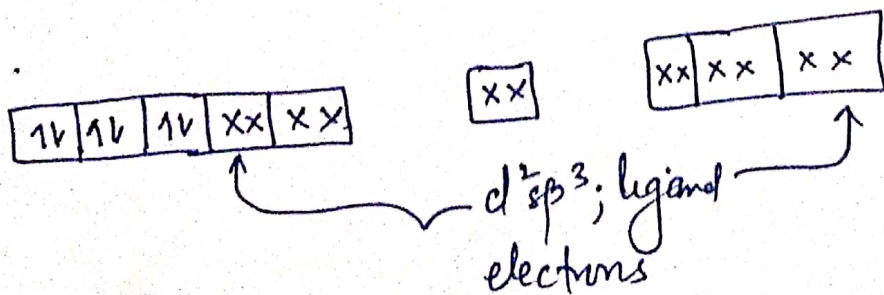
Co(III) ion = $1s^2 2s^2 2p^6 3s^2 3p^6 3d^6$; it is simply a $3d^6$ ion.

Co (III) ion forms 6 equivalent linkages to six N donor atoms of 6 NH₃ groups. Valence bond gives 6 equivalent bonds via sp³d² or d²sp³ hybrid orbitals using the outer orbital d (i.e. 4d) or inner orbital d (i.e. 3d). These hybrid orbitals will be occupied by ligand lone pair of electrons. The metal ion will then be forced to rearrange the pairing of its own electrons in the available d orbitals. So for the two cases electron arrangement will be as shown below:

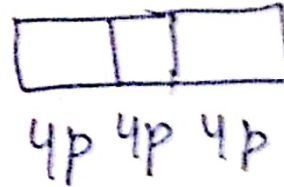
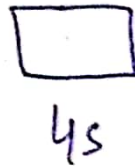
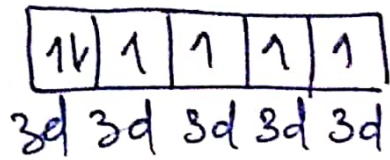
sp³d² Co(III) with ligand electrons (marked x):



d²sp³ Co(III) with ligand electrons (marked x):



Compare these two distributions with that of $\text{Co}(\text{III})$ ion:



$\text{Co}(\text{III})$:

Experimentally, hexammine Cobalt (III) chloride is found to be diamagnetic i.e. with all spins paired.

Therefore we have to accept the inner orbital hybridisation in this complex i.e. d^2sp^3 hybridisation.