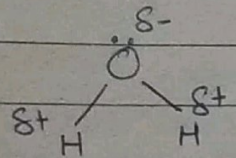
Chapter - III

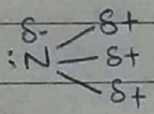
Date

Crystal field Theory :-

This Theory was given by H. Bethe and V. Vleck in 1935. The main postulater of this theory are:

1. The complex is a combination of central metal ions and ligands.
2. The negatively charged ligands such as $F^{\ominus}$, $Cl^{\ominus}$, $Br^{\ominus}$, $OH^{\ominus}$, $CN^{\ominus}$ etc. are regarded as -ve point charges and the neutral ligands such as H_2O, NH_3, pyridine are regarded as point dipoles because there ligands are dipolar.
3. The bonding between the central metal ion and ligand is purely electrostatic.
4. In the case of negative ligands, the attraction between them and central. metal ion is like attraction between two oppositly charged ions and in case of complex having neutral ligands, the negative end of the dipole is directed towards the metal ion.





5. When the ligands approaches towards central metal ion there occurs repulsion between the electrons of the ligands and those of the central metal ion which causes the splitting of d orbitals of central metal ion into two sets t_{2g} (triply degenerate) and e_g (doubly degenerate).

6. The first set of d-orbitals i.e. t_{2g} are d_{xy}, d_{yz} and d_{zx} while second set of d-orbitals i.e. e_g are $d_{x^2-y^2}$ and d_{z^2}. This splitting of d-orbitals into two sets of orbitals having different energies is called Crystal field splitting.

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Shape of d- orbitals

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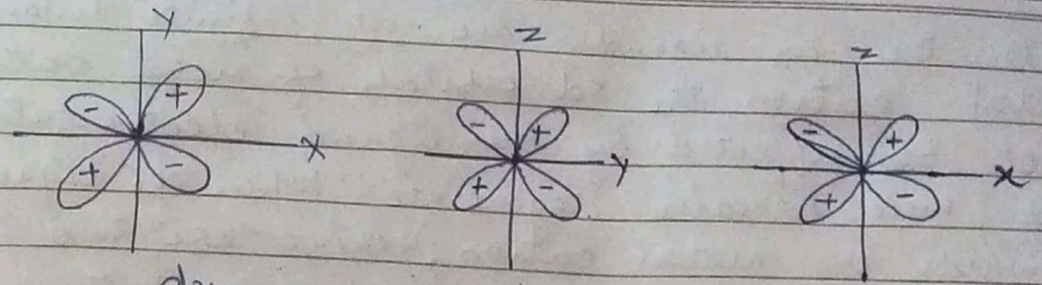
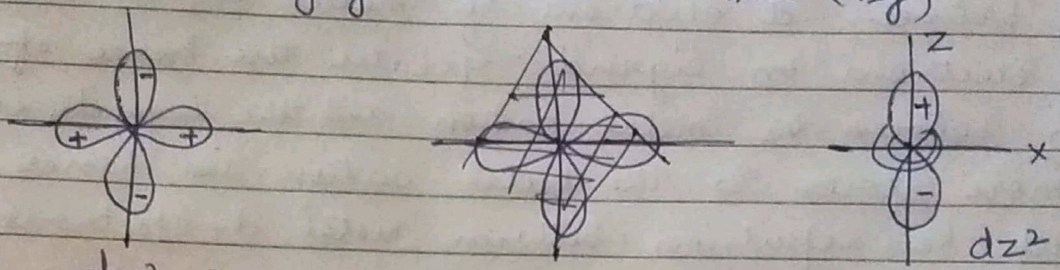


dxy dyz dzx

lobes lying between the axis (t_{2g})

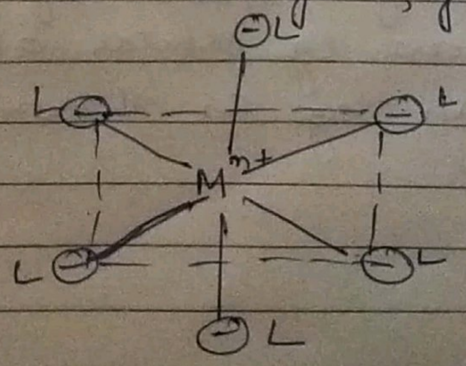


dx^2-y^2 dz^2

lobes lying along the axis (e_g).

⇒ Crystal field splitting in Octahedral complexes :-

In a free or isolated metal cation all five d-orbita are degenerate (i.e. having same energy). In an Octahedr complex say $[ML_6]^{n+}$, the metal cation is placed at th centre of Octahedron and six ligands are at six corn There six ligands are directed along the Cartesian coordinates i.e. along x, y & Z-axes.



Octahedral structure of $[ML_6]^{n+}$ complex ion

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When all the six ligands are at infinite distance from metal cation, the 5d orbitals of metal cation will not be affected by the ligand electrostatic field and will remain degenerate. When the ligand move towards the metal cation, there are two electrostatic forces, One is the attraction between metal cation and ligands and second is electrostatic repulsion between d electrons of metal cation and lone pair of electrons on ligand. Greater the force of attraction between the metal cation and the ligands, ligands will be more closer to the metal cation and hence more will be repulsion between metal d-electrons and lone pair of $\bar{e}$s.

Since t_{2g} orbitals (d_{xy}, d_{yz}, d_{xz}) are oriented between coordinate axes, whereas e_g orbitals ($d_{x^2-y^2}$ & d_{z^2}) are lying along the coordinate axes. When the six ligand approaches towards the central metal ion in an octahedral configuration along x, y and z axes, the e_g orbitals lying in a direction directly towards the Incoming ligands, therefore the e_g orbitals experience a greater repulsion than t_{2g}. Consequently, the energies of these two sets of d-orbitals no longer remain the same and these d-orbitals undergoes splitting into two sets of d-orbitals of different energy. During this process, e_g orbitals attains a higher energy state than t_{2g} as shown in figure

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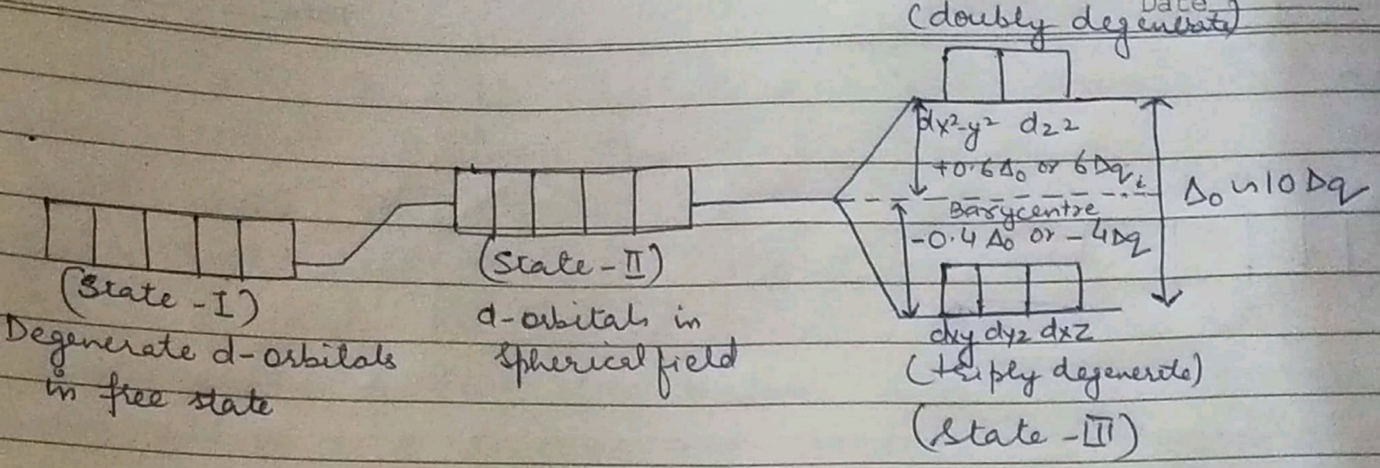

Fig: Splitting of d-orbital in Octahedral complex.

The splitting of five degenerate d-orbitals under the influence of approaching ligands into two sets of orbitals having different energy is called Crystal Field Splitting. The energy difference between two sets of orbitals which arise from an Octahedral field is measured in terms of parameter Δo or 10Dq where 'o' in Δo stands for octahedral.

Since the energy of Barycentre remains constant, the total energy decrease of t_{2g} set must be equal to total energy increase of eg set. Therefore there are two eg orbitals and they must increase by 0.6 Δo or 6Dq and three t_{2g} orbitals must decrease by 0.4 Δo or 4Dq per electron. The decrease in energy of t_{2g} orbital stabilizes the complex by 0.4Δo and increase in energy of eg orbital destabilizes the complex by 0.6 Δo.

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Crystal field splitting in tetrahedral complexes:

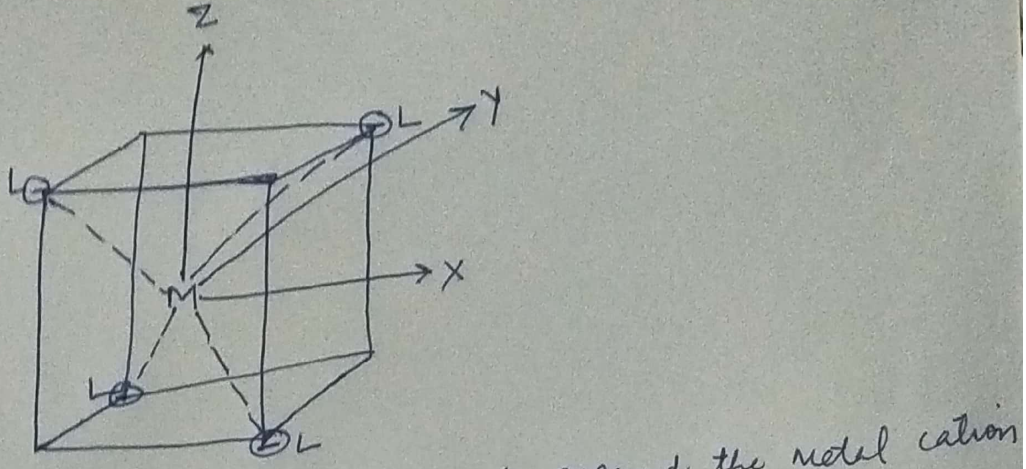
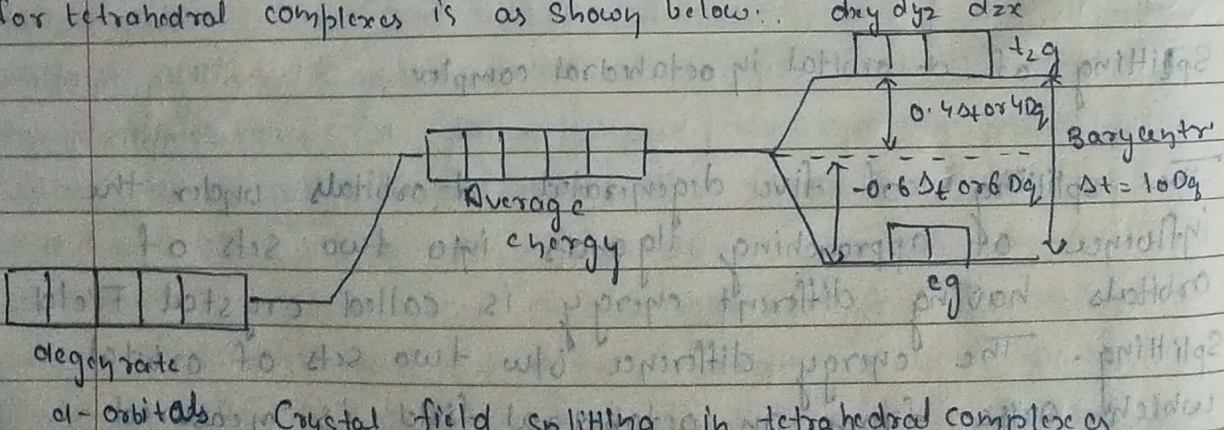


Fig: Tetrahedral arrangement of 4 ligands around the metal cation in a cube.

In tetrahedral ligand field, the four ligands may be imagined to occupy alternate corners of a cube and metal ion at the centre of the cube as shown in fig. The direction of x, y, z axes points to the centre of the face of the cube. The eg orbitals are placed along x, y & z-axis whereas t_2g orbitals are lying in b/w the co-ordinate axis. The direction of the approach of the ligands does not coincide exactly with either eg or t_2g orbitals but t_2g orbitals are somewhat nearer to the direction of the ligands then eg orbitals. Therefore, the approach of the ligands raises the energy of t_2g orbitals more than eg orbitals. Thus t_2g orbitals have more energy than eg orbitals. Thus t_2g orbitals are now of higher energy & eg orbitals are of low energy. The energy difference b/w eg & t_2g orbitals for tetrahedral complexes is as shown below:



Crystal field splitting in tetrahedral complexes

The magnitude of crystal field splitting in tetrahedral complexes is denoted by Δ_t where t stands for tetrahedral. The difference Δ_t is less then that for octahedral field (Δ_o). This is due to no. of ligands as only four ligands are there in the tetrahedral field as compared 6 in the octahedral field. Moreover there are ligands along each axis in octahedral field while there is no ligand along any axis in the tetrahedral field, for a given metal ion & a given ligand. The crystal field splitting Δ_t for tetrahedral complexes is about two third of Δ_o. Infact it has been observed that $\Delta_t = \frac{4}{9} \Delta_o$.