Crystal Field Theory

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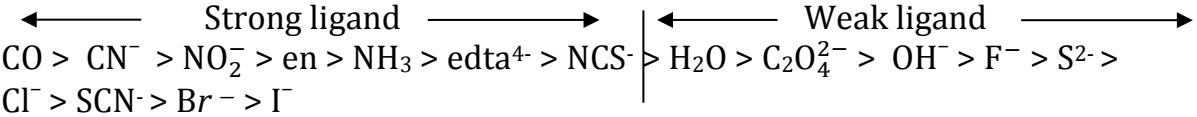
* According to crystal field theory, the bonding between a central metal ion and a ligand is purely electrostatic.
* In an octahedral field s-orbital (because of no degeneracy) and *p*-orbitals (because of their shape) are not affected, but the degeneracy of *d*-orbitals is lifted because all d-orbitals are not spatially equivalent.
* The valence electrons of metal are repelled by the negatively charge ligands, so that they occupy those d-orbitals which have their lobes away from the direction of ligands.
* The effect of ligands is particularly marked on d-electrons and it depends on the number of electrons.

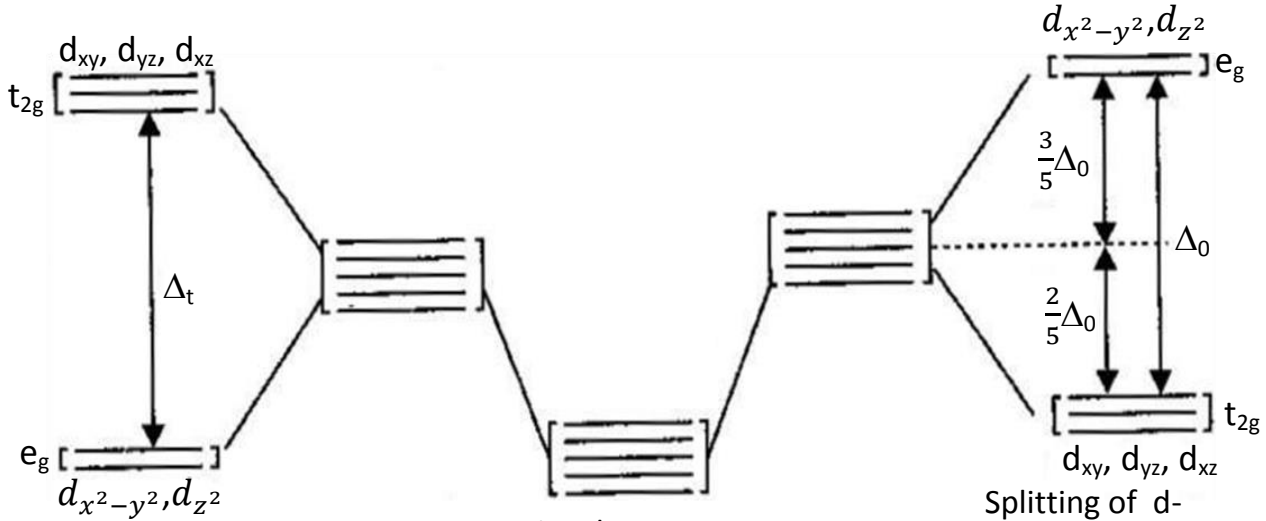
Crystal Field Splitting of d-orbitals.

* The five *d*-orbitals can be classified into two sets as follows:
* Three of *d*-orbitals i.e., *dxy*, *dyz* and *dzx* which are oriented in between the co-ordinate axes are called t_{2g}- orbitals.
* The other two *d*-orbitals i.e., $dx^2 - y^2$ and dz^2 oriented along the axes are called e_g orbitals.
* In the case of free metal ions, all the five *d*-orbitals degenerate, i.e., they have equal energy. But their interactions form the one pair of ligands and their energies also become deficit. This splitting of five *d*-orbitals of metal ions under the influence of approaching ligands is called crystal field splitting. It is designated by Δ and is called crystal field splitting energy.
* The ligands which cause greater crystal field splitting are termed as strong ligands while those which cause lesser crystal field splitting are weak ligands.
* **Spectrochmeical Series:**

The decreasing order of field strength among some of the ligands are:



* The above series is known as Spectrochemical series.



Splitting of d-orbitals in an tetrahedral crystal field.

Five degenerate d-orbitals in free metal ion.

Splitting of d-orbitals in an octahedral crystal field.

Figure- Splitting of d-orbitals in tetrahedral and octahedral ligand fields.

- In octahedral complexes the six ligands approach the central metal ion along the co-ordinate axes is the axes $dx^2 - y^2$ and dz^2 orbitals. Consequently, the e_g set of orbitals has higher energy than t_{2_g} of orbitals.
- In tetrahedral complex, four ligands may be imagined to occupy the alternate corners of the cube and the centre ion at the centre of the cube. In this situation, the t_{2_g} set of orbital lie relatively nearer to the approaching ligands and therefore t_{2_g} set of *d*-orbitals have higher energy than e_g, set of orbitals.
- Relationship between Δ_t and Δ_0 is given as $\Delta_t = \frac{4}{9}\Delta_0$

Limitations of Crystal Field Theory:

(i) The assumption that ligands are point charges is not practically true because anionic ligands should have strong field but actually many of them are not.

(ii) It does not take in account the covalent character of bonding between the ligands and the central atom.