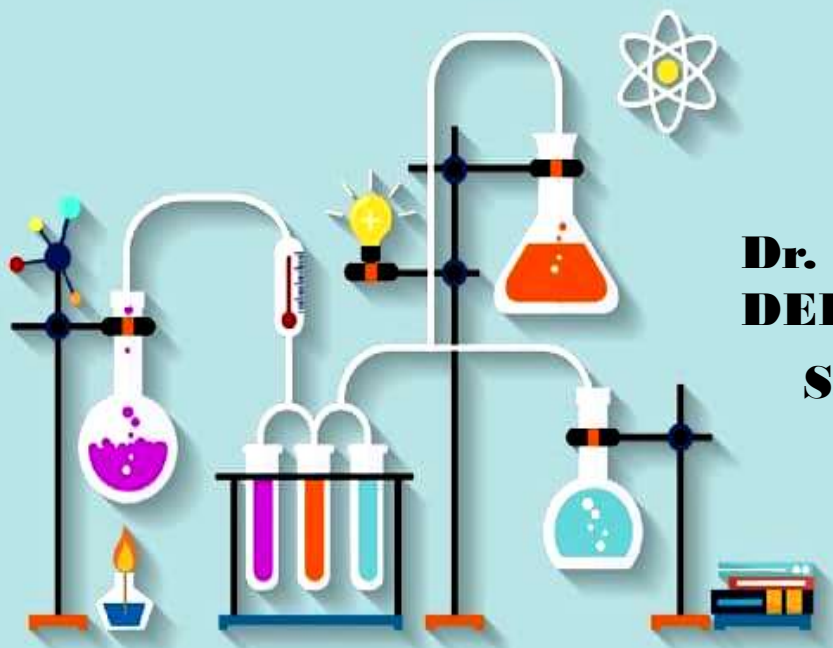


CRYSTAL FIELD THEORY **IN OCTAHEDRAL** **COMPLEXES**



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INTRODUCTION



- Crystal field theory was developed by physicists Hans Bethe & John Hansbrouck Van Vleck in 1930s.
- Crystal field theory assumes that the interaction between the metal ion d-orbitals & ligands surrounded by it is purely electrostatic.
- It explains many important properties of transition metal complexes including their colours, magnetism, structures, stability etc.

POSTULATES



- **The metal ion and the ligands are considered as point charges or point dipoles .**
- **The metal d-orbital electrons maintain their wave mechanical properties .**
- **The interactions between the metals and ligands are purely electrostatic; the electrostatic field they generate is known as crystal field .**
- **In the presence of crystal field the degeneracy of d-orbitals may be perturbed & the degeneracy is lifted to stabilise the co-ordination compound .**

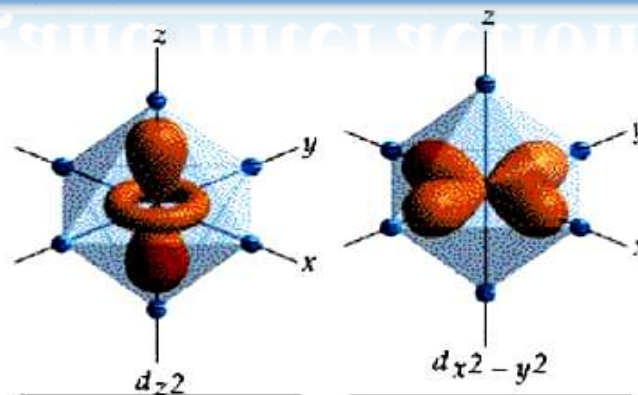
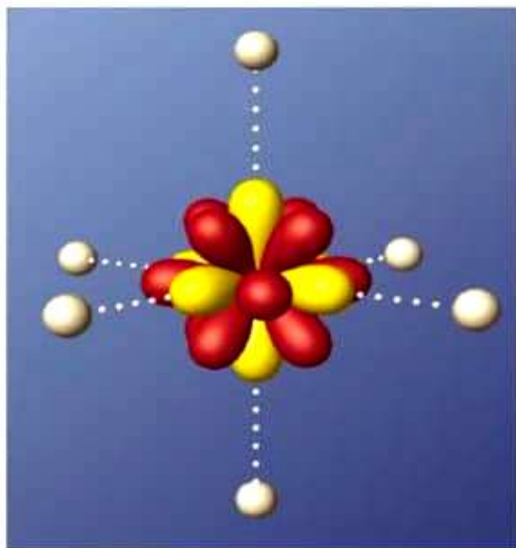
CRYSTAL FIELD SPLITTING IN OCTAHEDRAL COMPLEXES

- In an octahedral co-ordination compound, there are six ligands surrounding the metal ion.
- There will be repulsion between the electrons in metal d-orbitals & electrons of ligands

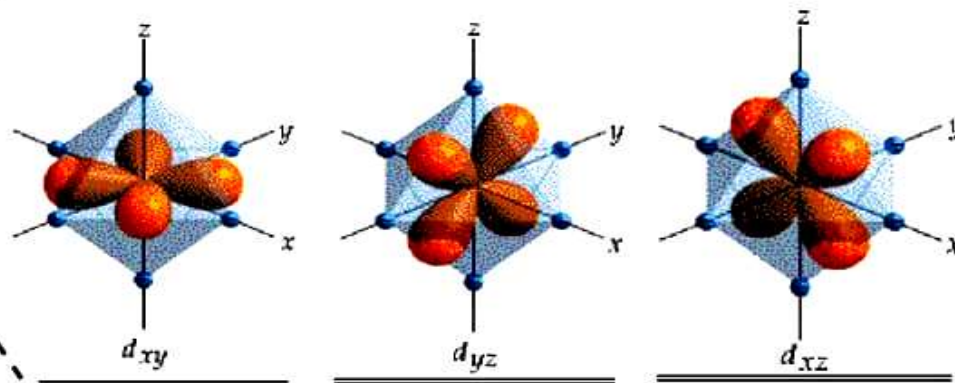
Thus dx^2-y^2 & dz^2 orbitals (e_g set) which point towards the axes along the direction of ligands experience more repulsion and will be raised energy and the d_{xy} , d_{yz} & d_{xz} orbitals (t_{2g} set) which are directed between the axes will be lowered in energy. This is to maintain the barycentre .

d-orbital electron & ligand interaction :

Ligands with their pair of electrons approach the metal along the X, Y and Z axes for an octahedral complex formation



d-orbitals having lobes pointing directly at x,y and z axis are repelled most by electron-electron repulsion

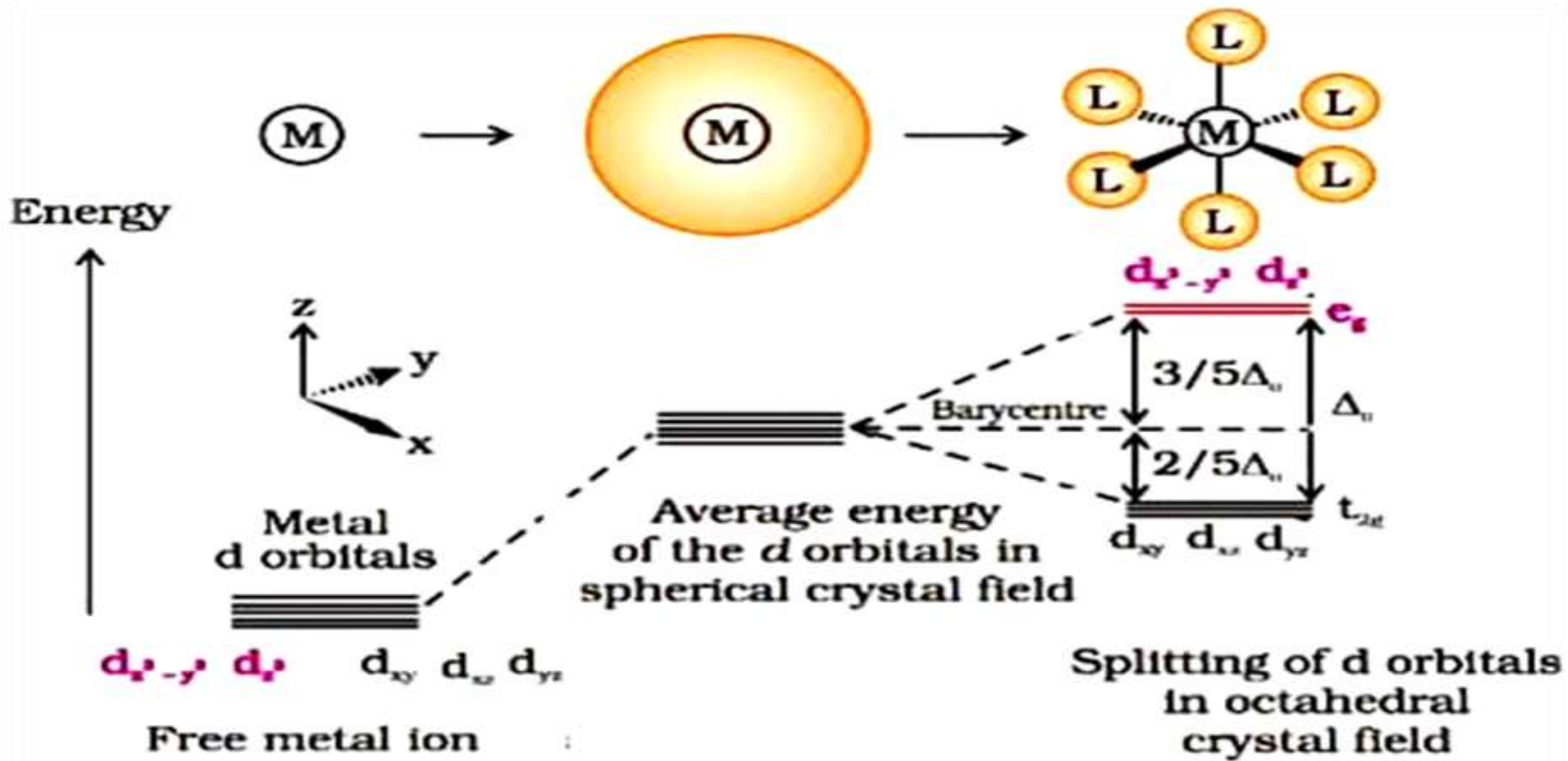


d-orbitals not pointing directly at x, y and z axis are stabilized to maintain the overall energy same

Splitting Of d-orbitals :

- **The degeneracy of d-orbitals is removed because of metal electron & ligand electron in octahedral complex produce three orbitals of lower energy (t_{2g} set) and two orbitals of higher energy (eg set) .**
- **This splitting of the degenerate levels due to the presence of ligands in a definite geometry is called crystal field splitting.**
- **The energy separation is denoted by $10Dq$.**
- **The energy of two eg orbitals will increased by $0.6 Dq$ & that of t_{2g} will decreased by $0.4 Dq$.**

Thus the eg set of orbitals destabilised while the t_{2g} set of orbitals are stabilised to maintain the barycentre .



d- Orbital splitting in octahedral field

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APPLICATIONS OF CFT

1. COLOUR OF COMPLEXES

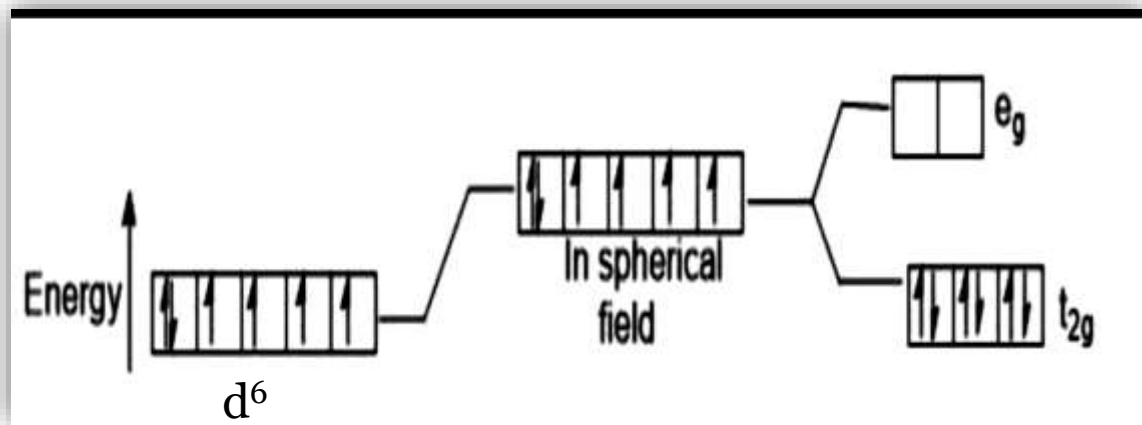
Crystal field theory explains why certain metal complexes exhibit vivid colours .

- **When the transition metal ion is in solution being surrounded by solvent molecules, the degeneracy is destroyed . The distorted degeneracy bring about colour change .**
- **The non-degeneracy causes energy different between the non-equivalent d-orbitals in metal complex. As a result of which the excitation of an electron from a lower to higher level takes place by absorption of visible light & the compound imparts colour .**

Ex : $K_4[Fe(CN)_6]$ appears pale yellow because the low spin complex absorbs higher energy violet photons .

**Here, Fe has +2 oxidation state .
 Fe^{2+} has low spin d-orbital complex
, in the presence of $6CN^-$ strong
field ligands**

POTASSIUM FERROCYANIDE STRUCTURE



Colour of Potassium ferrocyanide

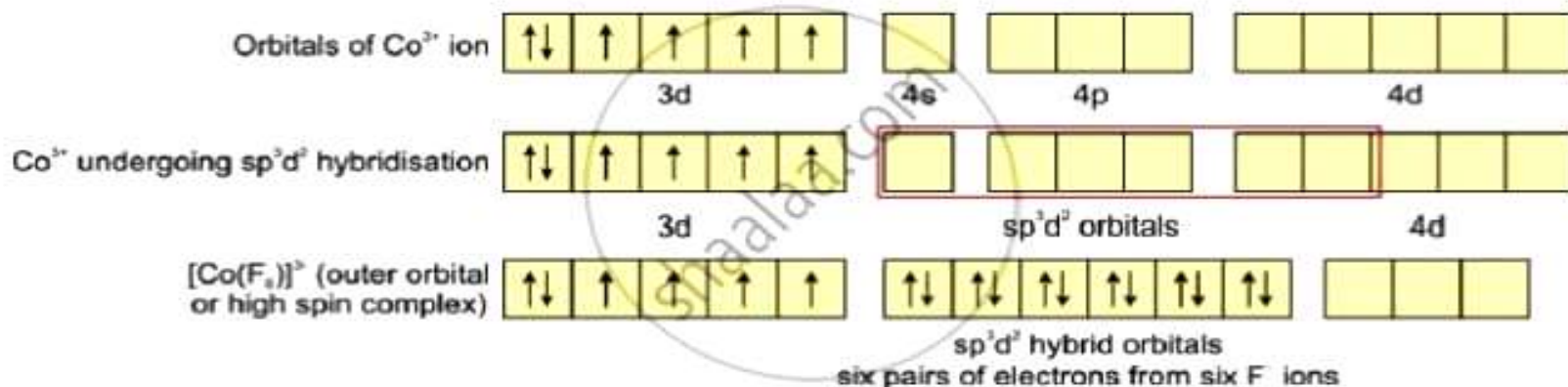
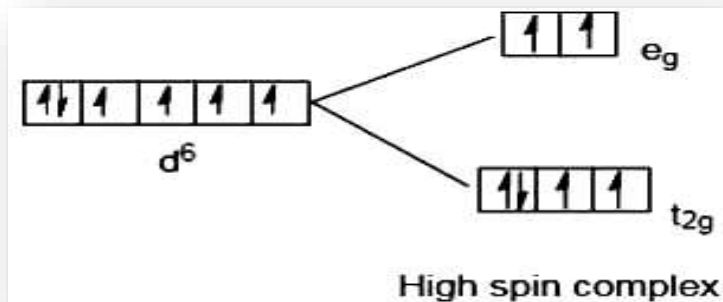
2. MAGNETIC PROPERTY

Crystal field theory helps in determining the magnetic property of metal complex, by analysing the distribution of electrons in the d-orbitals, one can predict if a complex will be paramagnetic (with unpaired electron) & diamagnetic (without unpaired electron).

Ex: $[\text{CoF}_6]^{3-}$ is paramagnetic & contains four unpaired electrons .

It is a high spin outer orbital complex .

Here , Co has +3 oxidation state.



3. STABILITY OF COMPLEX

The stability of a complex is determined by the crystal field splitting energy (CFSE). A higher CFSE value indicates a more stable and kinetically inert complex.

❖ **Some factors that affect the stability of a complex :**

- **Charge on metal ion** A higher charge on metal ion makes the complex more stable.
- **Size of metal ion** The stability of the complex decreases as the metal ion increases.
- **Chelate rings** Chelate rings increase the stability of the complex through the chelate ring.
- **Nature of ligand** The higher the basic strength of the ligand the more stable is the complex.

4. CATALYSIS

- Industrial Catalysts : Many industrial processes involve metal complexes as catalyst . CFT helps in understanding how these catalysts work by providing insights into the electronic structure and reactivity of the metal centre .
- Biocatalysis : In biochemical systems, such as enzyme catalysis CFT can explain the role of metal ions catalysing reactions .

5. ENVIRONMENTAL CHEMISTRY

CFT is used to design processes & materials for the removal or recovery of metal ions from environmental sample such as water treatment system .

LIMITATIONS :

- Ignoring ligand-ligand interactions : CFT primarily focuses on the interaction between the central metal ion & surrounding ligands, without considering interaction between the ligand-ligand themselves.
- CFT treats metal ligand bonding purely in terms of electrostatic interaction , neglecting the covalent character of metal-ligand bond.
- CFT doesnot explicitly address the detailed effects of electron-electron repulsion within the metal ion , which can influence the actual energy levels & electronic configuration.

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THANK

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