Crystal Field Theory (CFT)

1. Introduction

- Crystal Field Theory explains the electronic structure, colour, magnetic and other properties of coordination compounds on the basis of the electrostatic interaction between the metal ion (central ion) and the surrounding ligands (point charges).
- In CFT, ligands are considered as negative point charges or dipoles which create an electric field around the central metal ion. This field removes the degeneracy of the d-orbitals and causes splitting of their energy levels.
- It is a model (not a complete theory) but it gives a good explanation of many properties of coordination compounds.

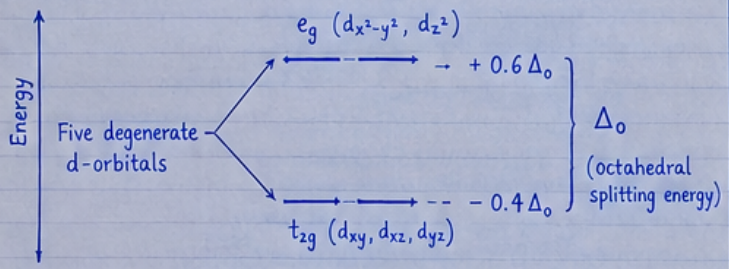
2. Basic Assumptions of CFT

① Ligands are treated as point charges (or dipoles).
② The metal ion is considered to be in a spherical field created by the ligands.
③ The d-orbitals are degenerate in the absence of ligands.
④ On coordination, the d-orbitals split due to the electrostatic repulsion between metal and ligands.
⑤ The relative magnitude of splitting depends on the nature of ligand and geometry.

3. Splitting of d-orbitals in an Octahedral Field

In an octahedral complex (ligands along x, y, z axes), the five d-orbitals split into two sets:

- t_{2g} (d_{xy}, d_{xz}, d_{yz}) → lower energy
- e_g ($d_{x^2-y^2}$, d_{z^2}) → higher energy

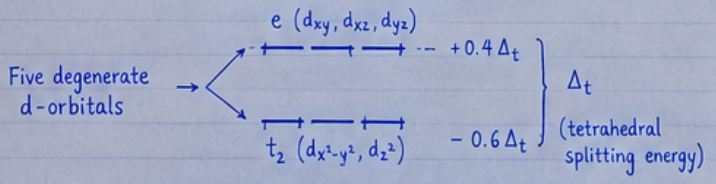


- The energy difference between the two sets is called crystal field splitting energy (Δ_o).
- e_g set is higher in energy because the ligands approach directly along the axes, so the repulsion is greater.
- t_{2g} set is lower in energy because the ligands approach between the axes, so the repulsion is less.

4. Splitting in a Tetrahedral Field

In a tetrahedral complex, the splitting is much smaller than in octahedral field and the order of energy levels is reversed:

- e (d_{xy}, d_{xz}, d_{yz}) → higher energy
- t_2 ($d_{x^2-y^2}$, d_{z^2}) → lower energy



$\Delta_t \approx \frac{4}{9} \Delta_o$ (i.e. Δ_t is about $\frac{4}{9}$ times Δ_o)

5. Effect of Ligand Field Strength

- Ligands can be classified as strong field or weak field ligands based on their ability to cause splitting.
- Strong field ligands → large Δ_o → pairing of electrons (low spin complex).
- Weak field ligands → small Δ_o → no pairing (high spin complex).

Examples:

Strong field ligands: CN^-, CO, NH_3, en, NO_2^-, bpy (cause large Δ_o).

Weak field ligands: F^-, Cl^-, Br^-, I^-, H_2O, NH_3 (in weak field), etc. (cause small Δ_o).

6. High Spin and Low Spin Complexes

- If Δ_o < pairing energy (P) → electrons do not pair → high spin complex.
- If $\Delta_o > P$ → electrons pair in t_{2g} before occupying e_g → low spin complex.

7. Crystal Field Stabilisation Energy (CFSE)

CFSE is the extra stabilisation energy gained by the complex due to the splitting of d-orbitals.

(a) Octahedral Complex

$$CFSE = (-0.4 \times n_{t_{2g}} + 0.6 \times n_{e_g})\,\Delta_o$$
$$= (0.4\, n_{t_{2g}} - 0.6\, n_{e_g})\,\Delta_o$$

where,
$n_{t_{2g}}$ = number of electrons in t_{2g}
n_{e_g} = number of electrons in e_g

For high spin: n_{e_g} is larger
For low spin: n_{e_g} is smaller

(b) Tetrahedral Complex

$$CFSE = (-0.6 \times n_{t_{2g}} + 0.4 \times n_e)\,\Delta_t$$
$$= (0.6\, n_t - 0.4\, n_e)\,\Delta_t$$

8. Magnetic Moment (μ)

- It depends on the number of unpaired electrons (n).
- Formula:

$$\mu = \sqrt{n(n+2)}\ \text{BM}$$ (n = number of unpaired electrons)

- If n = 0 → diamagnetic ($\mu = 0$)
- If n > 0 → paramagnetic ($\mu > 0$)

9. Colour of Complexes

- Colour arises due to d-d transitions (movement of electrons between t_{2g} and e_g levels).
- The energy of light absorbed = Δ_o (or Δ_t).
- The complementary colour is observed.
- Higher Δ_o → absorbs higher energy (shorter wavelength) → appears in the visible region as different colour.

10. Summary Tables

Geometry	Splitting pattern	Order of energy levels	Δ value
Octahedral	$t_{2g} < e_g$	t_{2g} (lower) e_g (higher)	Δ_o
Tetrahedral	$t_2 < e$	t_2 (lower) e (higher)	$\Delta_t \approx \frac{4}{9}\Delta_o$

Ligand type	Field strength	Δ_o	Spin state
Strong field	Large	Large	Low spin
Weak field	Small	Small	High spin

Remember: More Δ_o → more pairing → low spin → diamagnetic
Less Δ_o → less pairing → high spin → paramagnetic