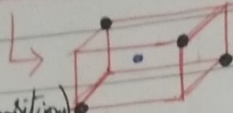


3. Crystal Field Splitting in Tetrahedral complexes:-

here, $\bullet \rightarrow \text{CMA}$

- \rightarrow ligands (at alternate positions)



(choose ^{non} adjacent points or else
repulsion will take place)

- \rightarrow ligands (at alternate positions)
- Approaching ligands do not coincide exactly with either t_{2g} or e_g orbitals

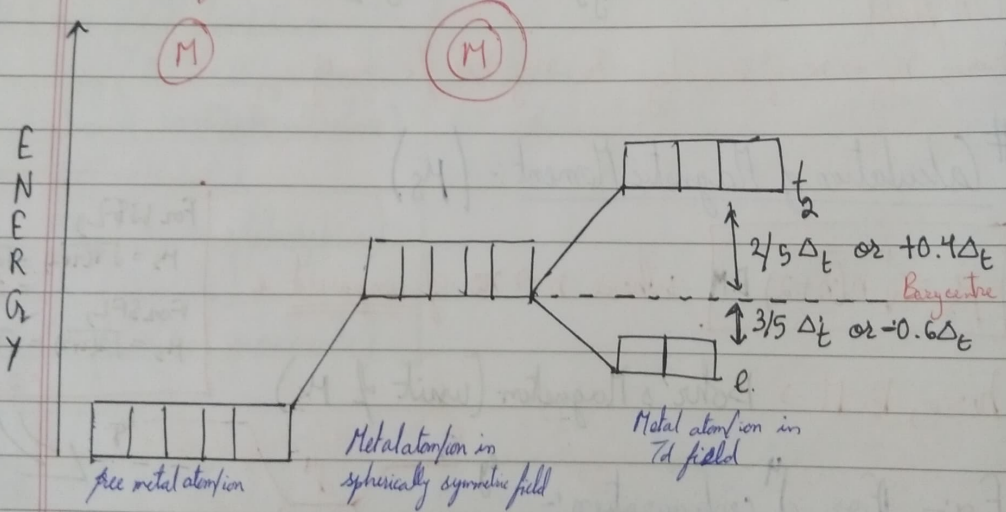
- Approaching ligands do not coarsen \rightarrow
- The angle betⁿ (MA; eg. ligand) = $\frac{1}{2} \times \text{Id angle}$
- $\therefore \frac{2}{10} \times 109.28' (54' = 60' = 60')$
- $\frac{109.28'}{2} = 54.64'$
- $= 54^{\circ} 44'$

- The angle betⁿ CMA; t_{2g} & ligand = 35.16°

Hence, comparing and of E_g & t_{2g} with approaching ligands, the approaching ligands are closer to t_{2g} than E_g orbitals.

Therefore, t_2 orbitals rise in energy from bary centre & e_g orbitals get lowered from Bary centre

CFSE Diagram



* In Td field, we do not write 'g' (gerade) because Td complexes do not have centre of symmetry

In Oh field, we write 'g' because Oh complexes have centre of symmetry.

Magnitude of CFSE (Δ_t) in Td complex is always less than the CFSE (Δ_o) in Oh complex due to 2 reasons:-

(i) Oh complexes \rightarrow 6 ligands
Td complexes \rightarrow 4 ligands $\left(\frac{2}{3}^{\text{rd}}$ of ligands in Oh $\Rightarrow \left(\frac{2}{3} \times 6 \right)$ ligands

\therefore CFSE in Td complex is lowered by $\boxed{\frac{2}{3}^{\text{rd}}}$

(ii) In Tetrahedral field, the approach of ligands does not coincide exactly with either t_{2g} / e_g orbitals. This further reduces CFSE by a factor of $\frac{2}{3}^{\text{rd}}$

$$* \Delta_t = \frac{2}{3} \times \frac{2}{3} \Delta_o \Rightarrow \Delta_t = \frac{4}{9} \Delta_o \quad \text{--- } (*)$$

(i) (ii)

Splitting of d-orbitals in Td complex is less than Oh complexes (*)

Thus, it is never energetically favoured to pairing of e^- in Td complex irrespective of ligand's strength. \therefore All ligands behave as weak field ligands

Calculation of CFSE:- (in Td field)

$$\text{CFSE}_{\text{in Td field}} = [-0.6(n_{e_{t_2}}) + 0.4(n_{e_{t_1}})] \Delta_t$$

* Since pairing is less favoured & splitting is less,

\therefore The e^- can jump to t_2 orbital & hence most of these complexes are paramagnetic