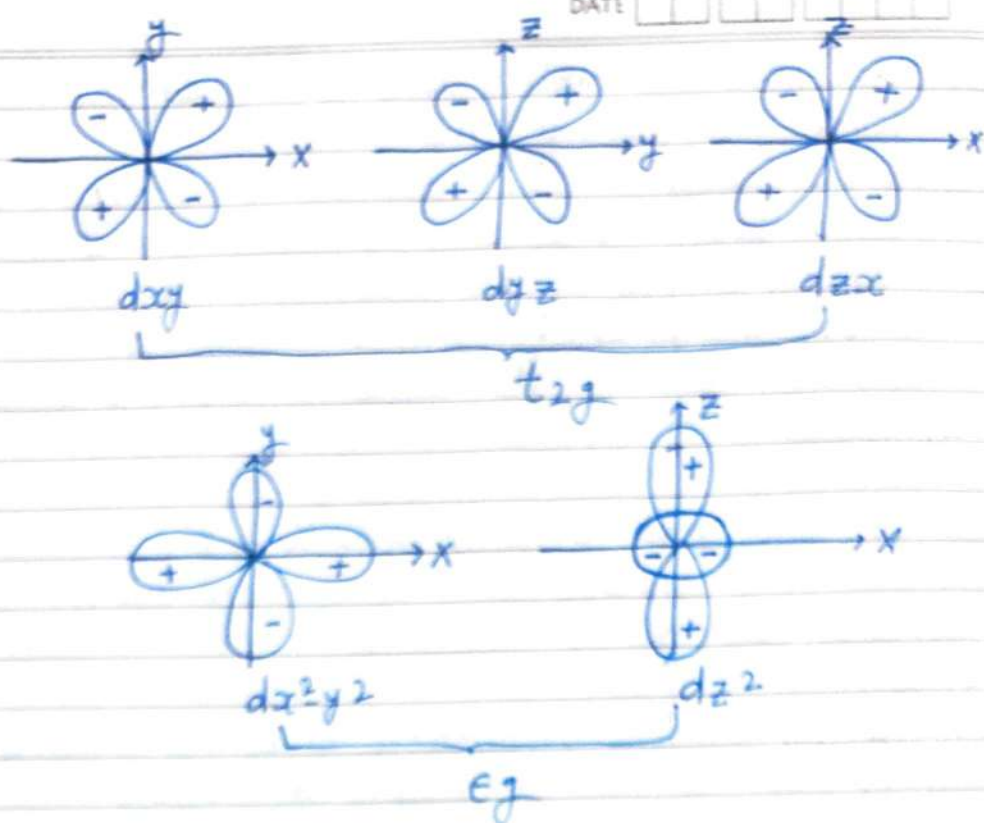


Crystal field Theory (CFT) :

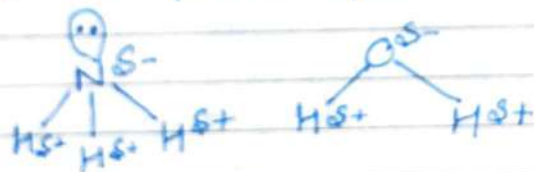
- Developed by H. Bethe and van Vleck
- Originally, crystal field theory was applied to transition metal ions in ionic crystals.
- That is why, the theory is called crystal field theory.

According to CFT bonding between a central metal (ion) and ligands arises from purely electrostatic interactions.



Assumptions of CFT:

1. Ionic ligands are treated as point charges and the neutral ligands such as NH_3 , H_2O etc are regarded as point dipole.



Ligands $\rightarrow$ -ve point charges (Cl^- , OH^- , Br^- etc)
 , Neutral $\rightarrow$ dipole (NH_3 , H_2O etc)

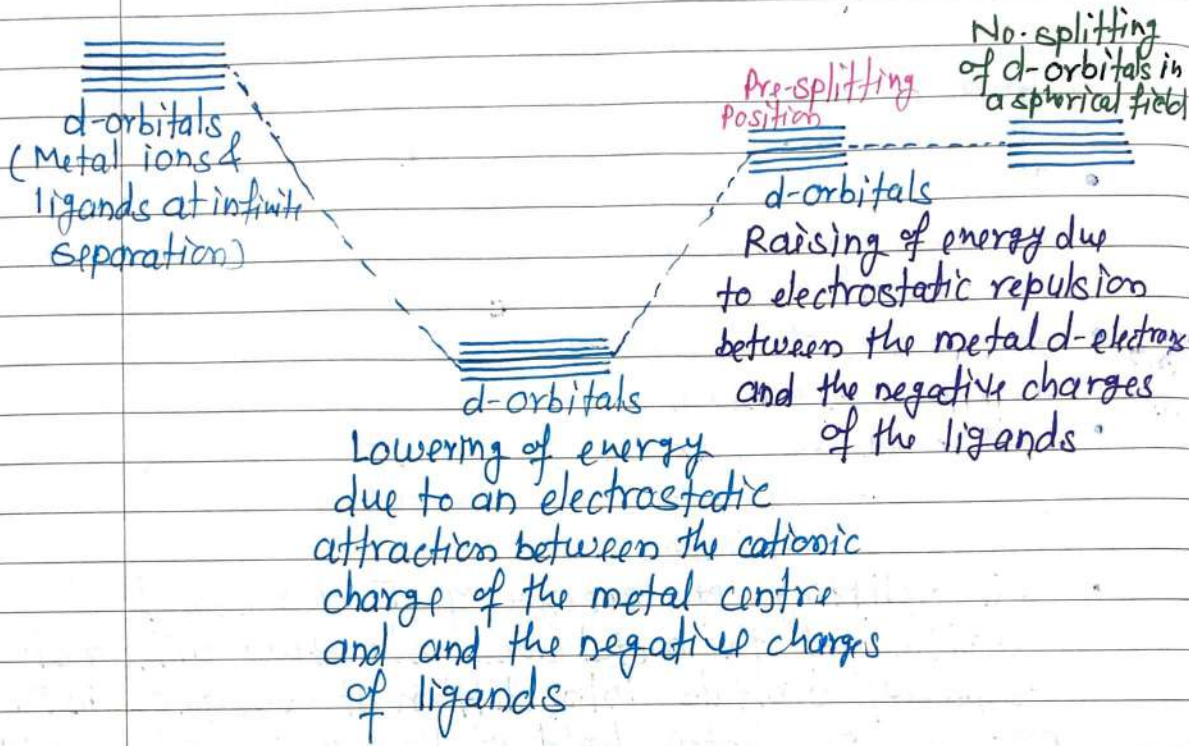
2. There is no interaction between metal orbitals and ligand orbitals.
3. All the five d-orbitals of the isolated gaseous metal atom all have the same energy. These 5 d-orbitals of the gaseous atom possessing the same energies are called **degenerate orbitals**.

If a spherically symmetric field of negative charges is placed around the metal (ion), all the 5-d orbitals of the metal will be raised in energy as a repulsion between the negative field and the negatively charged electrons of the orbitals.

- In brief, the energy of the orbitals is raised because of the repulsion between the field and the electrons on the metal.
- However, the energy of the 5-d orbitals will still remain degenerate.
- When a complex is formed, the ligands destroy the degeneracy of 5d-orbitals i.e. 5d-orbitals now have different energies.
- The splitting of energy of 5-degenerate d-orbitals of the metal (ion) into two different sets of orbitals into different energies in the presence of electric field of ligands is called crystal field splitting.

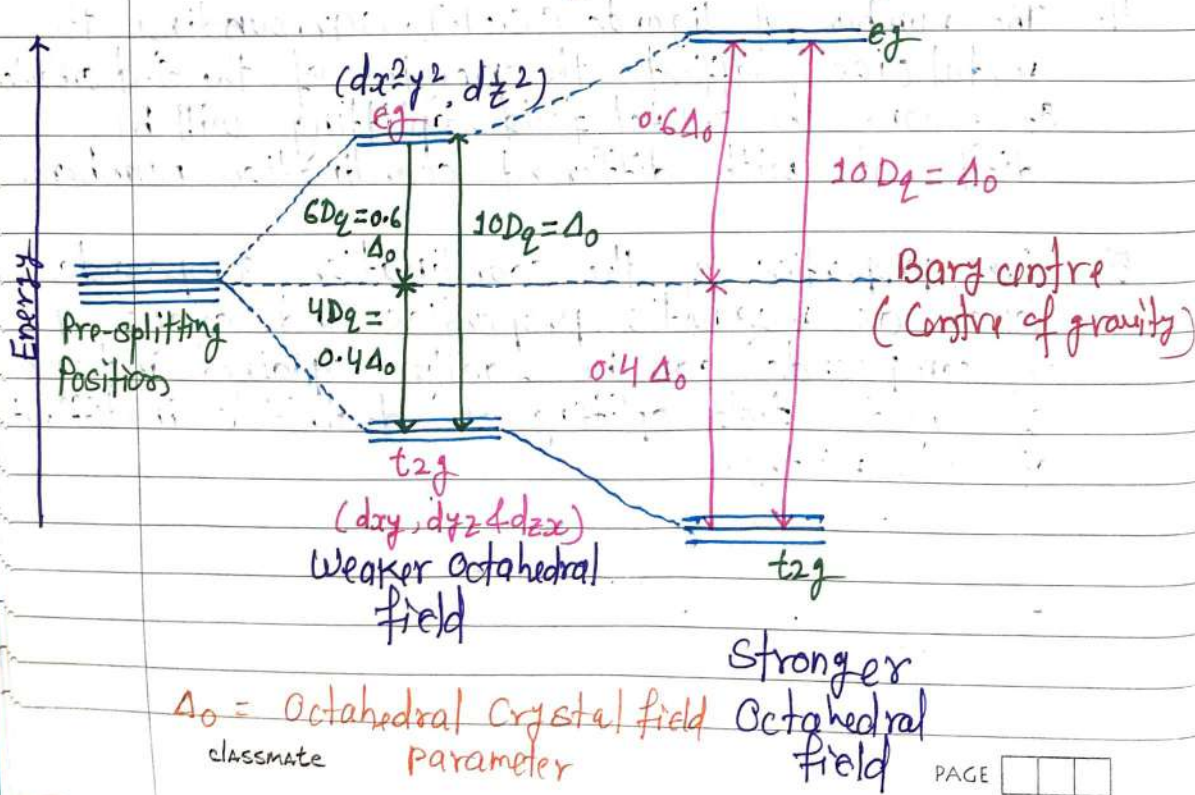
4. The number of ligands (C.N.) surrounding the metal (ion) affects the energies of the 5-d orbitals. It means the crystal field splitting will be different with different coordination numbers.

5. The properties of the coordination compounds such as magnetic properties and colour of the compounds can be easily explained in terms of crystal field splitting of d-orbitals in different stereochemistry.



Crystal field splitting in Octahedral complexes:

Δ_o = Differential of quanta



Significance of t_{2g} and e_g :

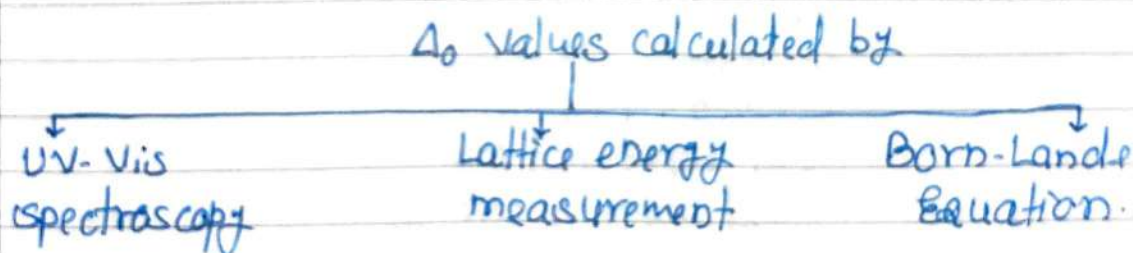
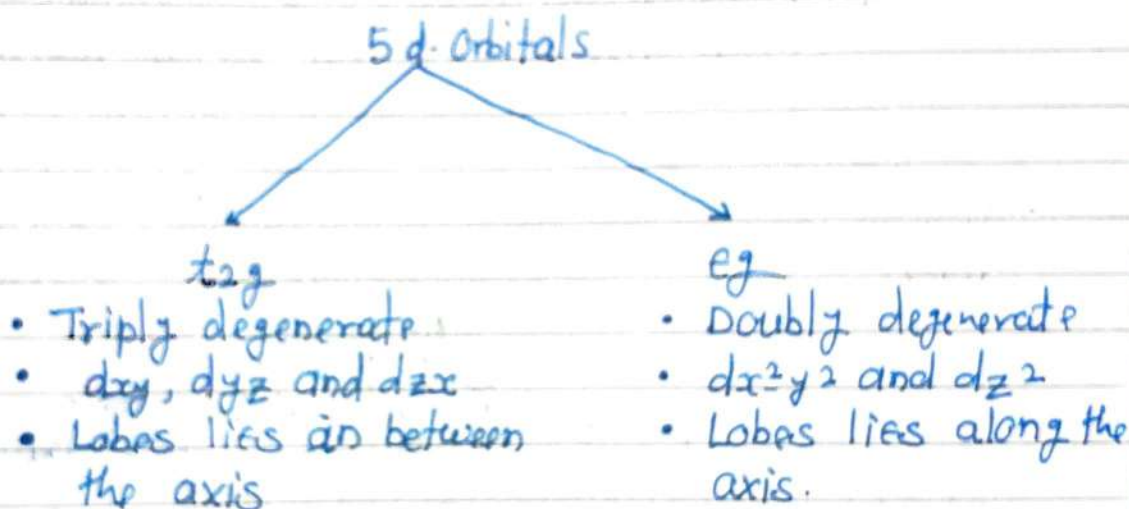
t_{2g} = triplet orbital degeneracy

e_g = doublet orbital degeneracy

g = gerade (even)

Symbol 'g' denotes the presence of centre of inversion (i.e. centre of symmetry).

- In octahedral complex having the 6 identical ligands, the metal centre lies at the centre of inversion and with respect to this centre of inversion, the d-orbitals maintain the same sign of the wave functions in the opposite lobes (i.e. the opposite lobes bear the same signs).



$$\text{CFSE for } Oh = [-0.4x + 0.6y] \Delta_o + nP$$

where x = no. of e^- s in t_{2g} orbitals

y = no. of e^- s in e_g orbitals

$n = 0, 1, 2, 3, \dots$

classmate P = Pairing energy

Crystal field splitting in Tetrahedral Complexes:

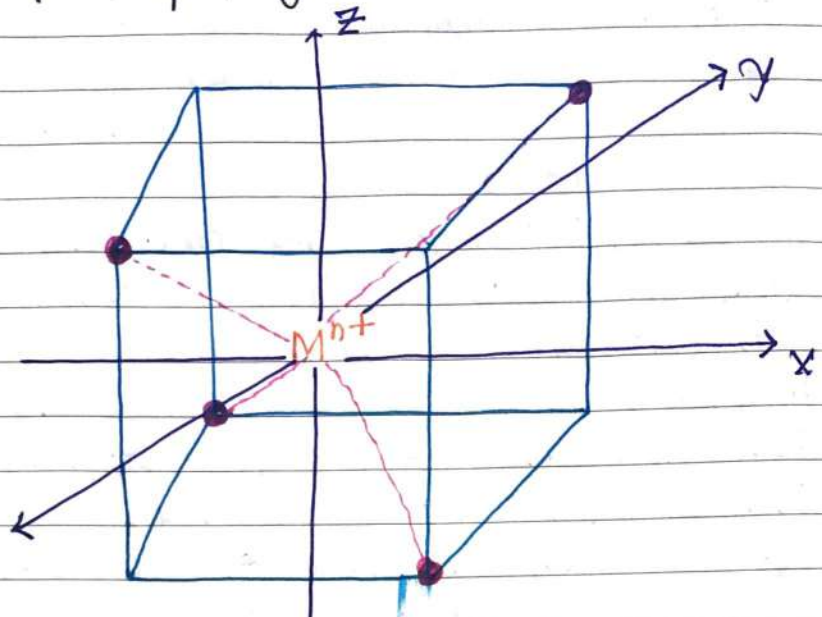


Figure: Td arrangement of four ligands around the central metal (ion).

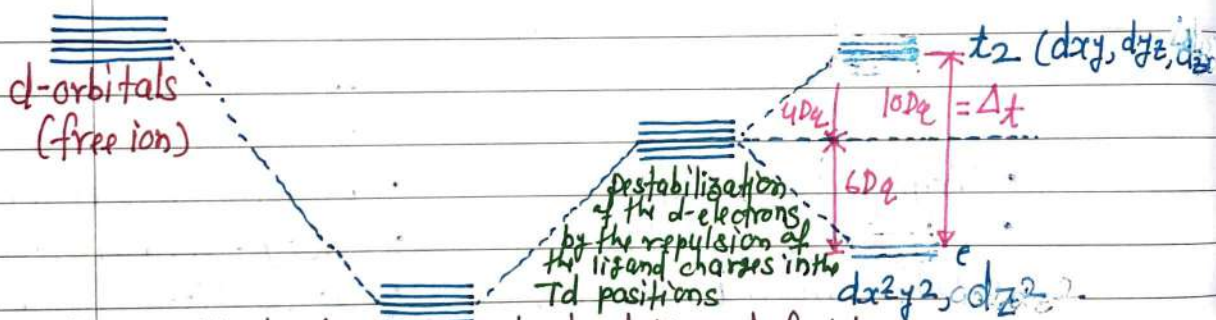
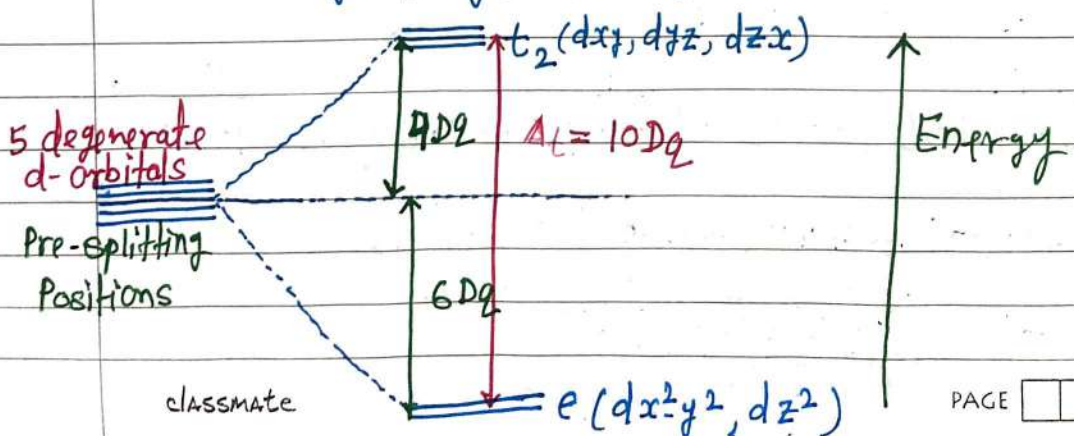


fig: Effect of the tetrahedral ligand field

stabilized due to the electrostatic attraction between the cationic metal centre and the ligand negative charges



Note: The subscript 'g' does not appear because in the tetrahedral field - there is no centre of symmetry.

$$\Delta_t = 10Dq_t = \frac{2}{3} \times \frac{2}{3} \Delta_o = \frac{4}{9} \Delta_o (= 10Dq_o)$$

- The magnitude of the crystal field splitting (Δ_t) in tetrahedral complexes is considerably less as compared to octahedral complexes.
- There are two reasons for this:
- There are only four ligands instead of 6, so the ligand field is only $\frac{2}{3}$, hence the ligand field splitting is also only $\frac{2}{3}$.
 - The direction of the orbital does not coincide with the direction of the ligands. This reduces the crystal field splitting by roughly a further $\frac{2}{3}$.
- $\Delta_o \gg \Delta_t$. Thus it is never energetically favourable to pair electrons and all Td complexes are high spin.

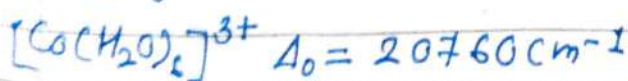
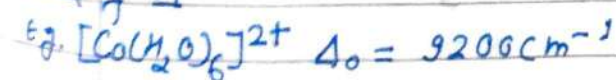
Oh CFSE > Td CFSE

- Octahedral complexes are more stable and more common.

Factors Affecting Crystal Field Splitting (Δ):

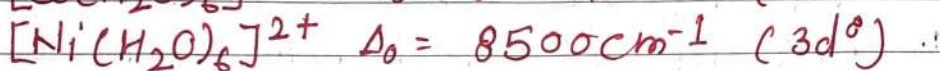
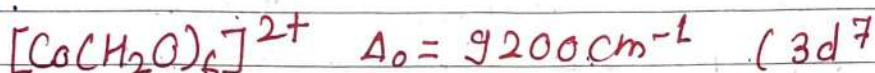
1. $\downarrow$ O.S. of the metal (ion)	2. $\downarrow$ Same O.S. of the metal (ion) but the no. of d electrons is different	3. $\downarrow$ Principal Q.N. (n)	4. $\downarrow$ Nature of Ligands	5. $\downarrow$ Number of ligands	6. $\downarrow$ Geometry of the complex
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Higher the O.S. of the metal (ion) the greater the value of Δ



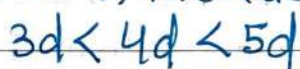
2. Same Oxidation state of the metal (ion) but the number of d-electrons is different:
- Δ_o decreases with increase of number of d-electrons.
 - It is due to fact that the higher number of d-electrons prevents the ligands to come closer to the metal (ion).

e.g.



3. Principle Quantum Number (n):

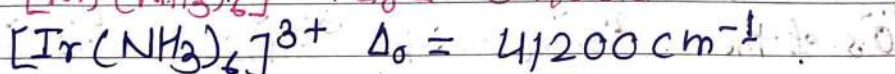
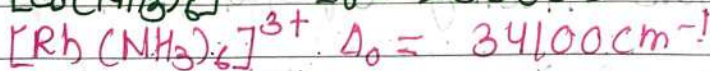
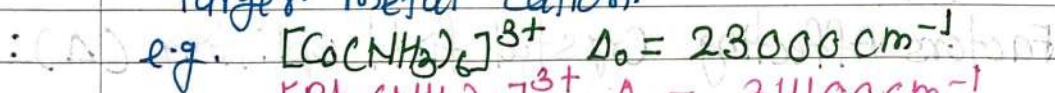
As the n increases Δ_o and Δ_t both increases.



Reasons:

(i): On moving 3d to 4d and 4d to 5d, the size of the d-orbitals increases and electron density decreases in them. Therefore the ligands can approach the metal cation with larger d-orbitals more closely.

(ii): There is less steric hindrance round a larger metal cation.



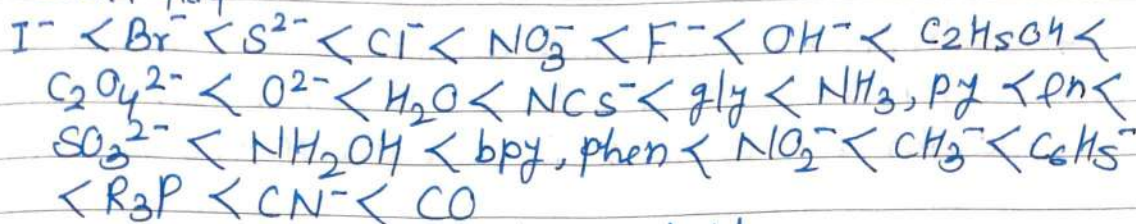
4. Nature of Ligands:

Weak field
cause smaller degree
of crystal field splitting

classmate

Strong field
cause large degree of
crystal field splitting

Weak field



Strong field

This order is called as **spectrochemical series**.

Halide donors < O-donors < N-donors < C-donors

5. Number of Ligands: As the number of ligands increases Δ value increases.

6. Geometry of the Complex:

$$\Delta_t < \Delta_{sp} < \Delta_o$$

$$\Delta_t = \frac{4}{9} \Delta_o$$

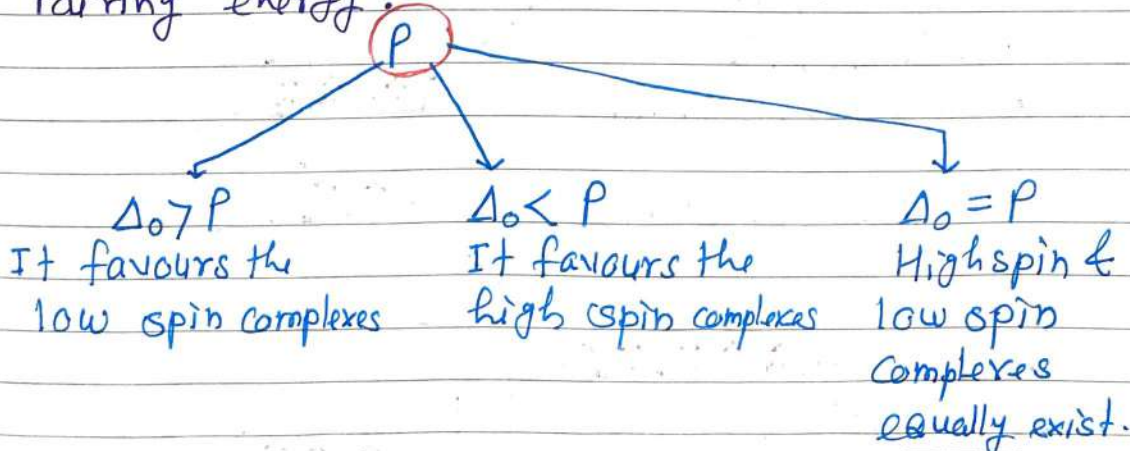
$$\Delta_{sp} = \Delta_1 + \Delta_2 + \Delta_3$$

$$\Delta_{sp} = 1.3 \Delta_o = 1.3 \times \frac{4}{9} \Delta_t$$

Pairing Energy (P): Energy required to pair-up the electron is called the pairing energy.

→ When more than one electrons are paired, P becomes the mean pairing energy.

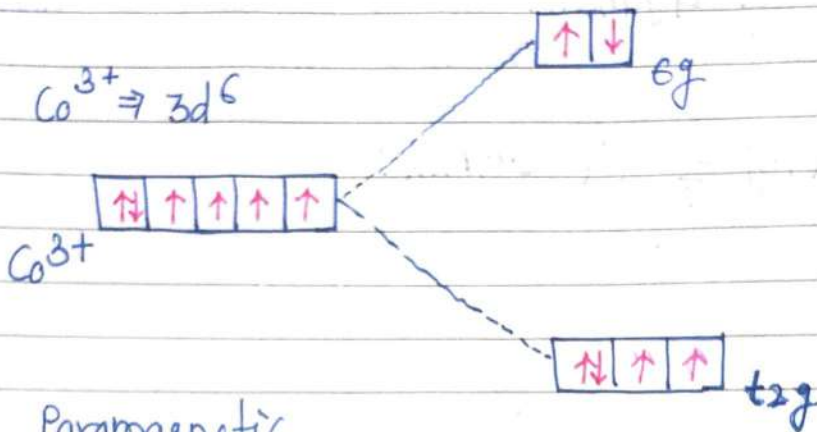
High spin and Low spin complexes on the basis of Pairing energy:



Q. Write the electronic configurations of the following complexes on the basis of CFT and predict whether the complex is paramagnetic or diamagnetic.

1. $[\text{CoF}_6]^{3-}$

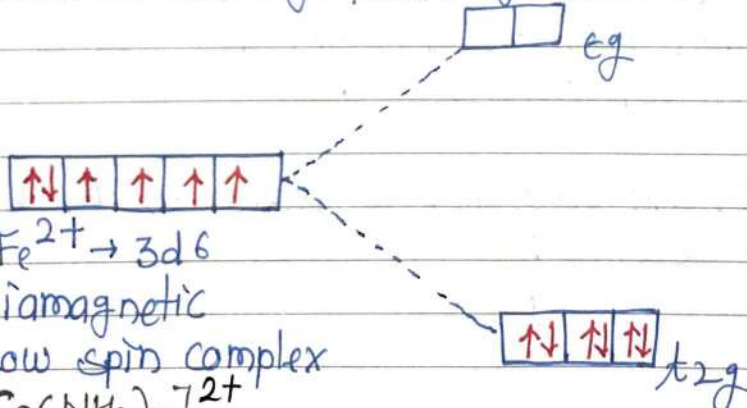
F^- is a weak field ligand
 $\Delta_o < P$ High spin complex



→ Paramagnetic
 High spin complex.

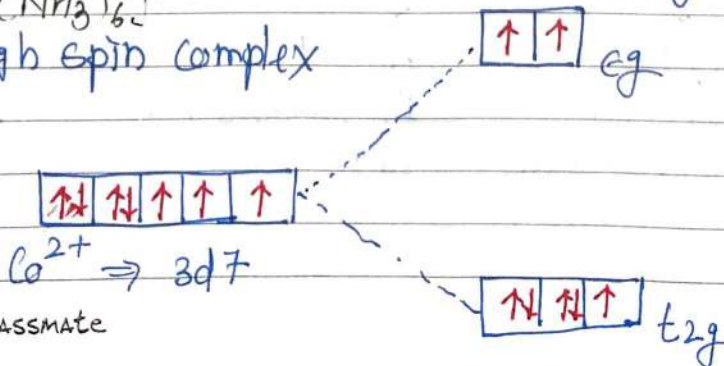
2. $[\text{Fe}(\text{CN})_6]^{4-}$

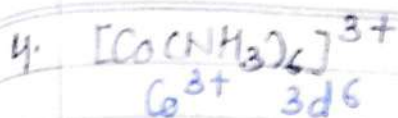
$\text{Fe}^{2+} \rightarrow 3d^6$
 $\text{CN}^- \rightarrow$ strong field ligand



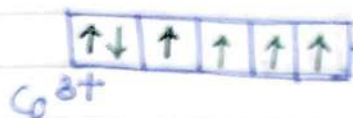
→ Diamagnetic
 Low spin complex

3. $[\text{Co}(\text{NH}_3)_6]^{2+}$
 High spin complex





$\text{NH}_3 \rightarrow$ strong field ligand



- Diamagnetic
- Low spin complex.

Crystal Field Stabilization Energy (CFSE) in Octahedral Complexes:

In the presence of Octahedral field, the d-orbitals of the metal (ion) are split into two sets of different energies t_{2g} of lower energy and e_g of higher energy.

- The separation between these two sets is equal to Δ_o .
- The t_{2g} set has an energy of $-0.4 \Delta_o$ and e_g set has an energy of $+0.6 \Delta_o$ relative to the barycentre.
- Minus and plus signs indicate decrease and increase in energy relative to the barycentre respectively.
- The complex ion with one electron in one of the t_{2g} orbitals has an energy of $-0.4 \Delta_o$ relative to the barycentre. This means in a complex ion of d^1 configuration $0.4 \Delta_o$ energy is released. This released energy is called the crystal field stabilization energy (CFSE) of the complex ion.

$$\text{CFSE} = [-0.4x + 0.6y] \Delta_o + mP$$

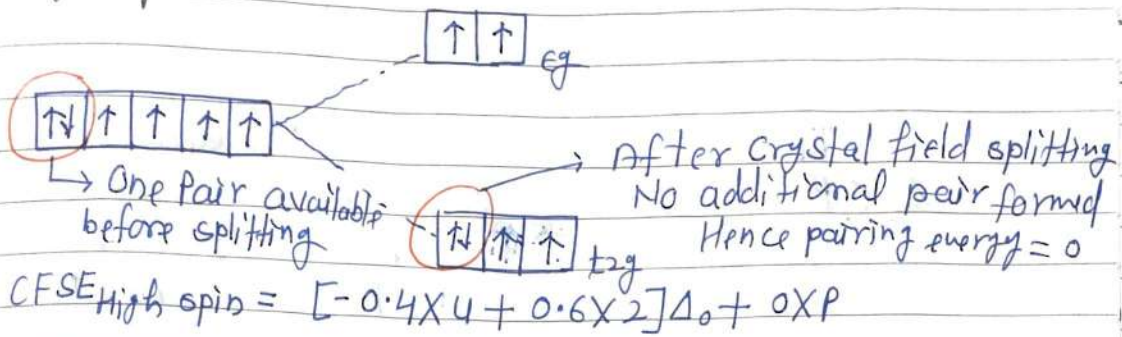
where x = no. of e⁻s present in t_{2g} orbital

y = no. of e⁻s present in e_g orbital

m = no. of pairs of electrons caused by the ligands

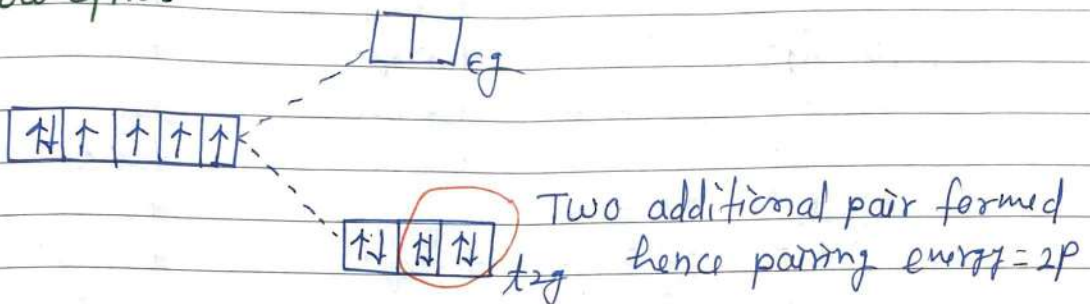
P = mean pairing energy

High Spin:

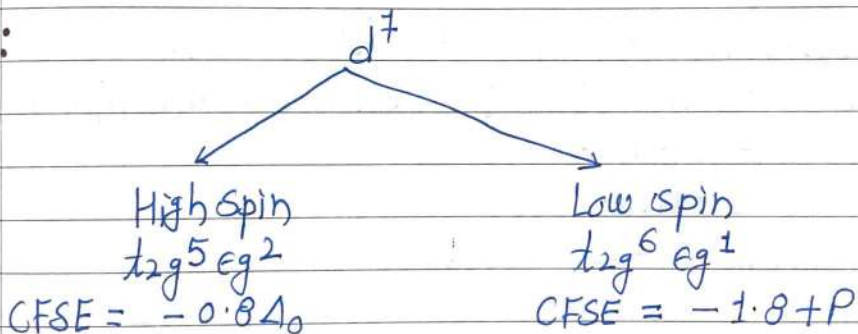


$$\boxed{\text{CFSE}_{\text{High spin}} = -0.4 \Delta_o}$$

Low Spin:



$$\boxed{\text{CFSE}_{\text{Low spin}} = -2.4 \Delta_o + 2P}$$

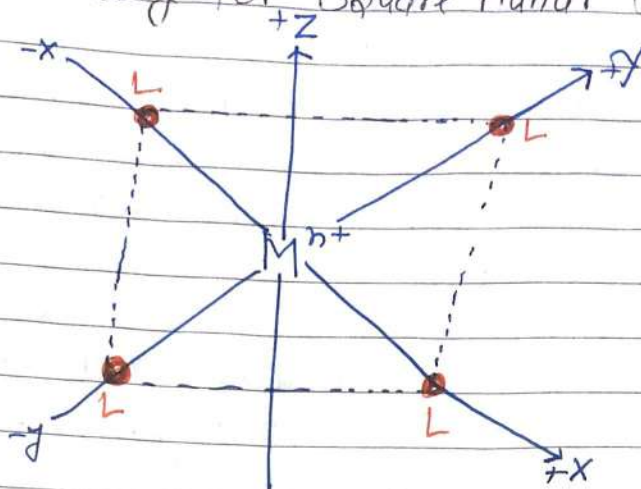
 d^7 :

CFSE in Tetrahedral Complexes:

$$\begin{aligned} \text{CFSE}_{Td} &= [-0.6x + 0.4y] \Delta_t & (\because \Delta_t = \frac{4}{9} \Delta_o) \\ &= [-0.6x + 0.4y] \frac{4}{9} \Delta_o \end{aligned}$$

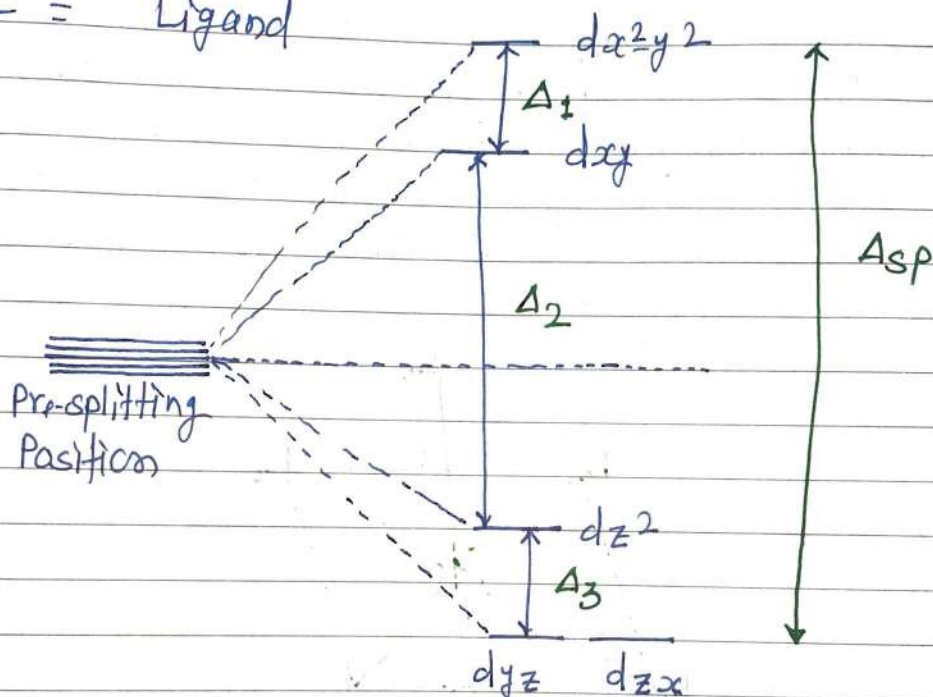
$$\boxed{\text{CFSE}_{Td} = [-0.27x + 0.18y] \Delta_o}$$

Crystal field theory for Square Planar Geometry:



M^{n+} = Central metal ion

L = Ligand



$\Delta_{sp} = \Delta_1 + \Delta_2 + \Delta_3 = 1.3 \Delta_0$

 for square planar complexes of Pd^{2+} and Pt^{2+}

John-Teller Theorem or John-Teller Effect:

In 1937, John and Teller put forward a remarkable theorem to explain why some 6-coordinated complexes (octahedral complexes) undergo distortion and distorted octahedral geometry.

This theorem states that if a molecule/complex possessing any shape (except linear shape) has an unsymmetrically filled

set of degenerate orbitals is unstable and hence undergo distortion.

- This distortion takes place in such a way that the symmetry and energy of the molecule/complex is lowered and hence the molecule/complex becomes more stable.
- This theorem does not say which type of distortion will occur in the molecule/complex.
- According to this theorem, if the electrons in d-orbitals of the central metal ion of a regular octahedral complex are asymmetrically filled, the octahedral shape of the complex will get distorted, since the electrons present in a asymmetrically filled d-orbitals will repel some ligands to greater extent while other ligands will be repelled to lesser extent. The distortion of non-linear system due to John-Teller effect is called John-Teller distortion.

