

Coordination Chemistry

B.Sc.-III Chemistry(H/S)

Inorganic Chemistry

Paper-VI

Lecture-03



Estd. - 1962

By

Dr. Supriya kumari

J.L.N College, Dehri-on-Sone (Rohtas)

V.K.S.U, Ara

supriyachemu@gmail.com

Coordination Chemistry

Crystal field theory (CFT) :

- Defines the electrostatic approach to the bonding in complexes.
- Applied to ionic type crystalline substances.
- Consider the metal ion M^+ placed in the Centre and the ligand L surrounding it in electrostatic field.
- Predicted the properties such as structures, colours and magnetism

Coordination Chemistry

Crystal field stabilization energy (CFSE)

- Crystal field stabilization energy in terms of $10 dq$ or Δ_o due to the presence of electrons in t_{2g} and e_g level of octahedral complexes.
- It was assumed that the sum of the energies of the five d orbitals in the free state must be equal to the sum of the energies of the five d orbitals in the free state must be equal to the sum of the energies of the five d-orbitals in the octahedral configuration.
- Splitting occurs in such a way that there is no net change in energy

Coordination Chemistry

Merits Of CFT:

- This theory can be used to predict the most favourable geometry of the complex
- This theory can be used to predict the certain four co-ordinated complexes are square planer and others are tetrahedral.
- This theory can be used to explain the fact that certain ligands form outer orbital complexes and others form inner orbital octahedral complexes
- This theory can be used to explain the fact that outer and inner orbital complexes correspond to high spin and low spin Complexes
- This theory can be used to predict the magnetic properties of the complexes
- This theory can be used to predict the color of transition of the complexes
- This theory can be used to predict the spectral properties of transition metal complexes

Coordination Chemistry

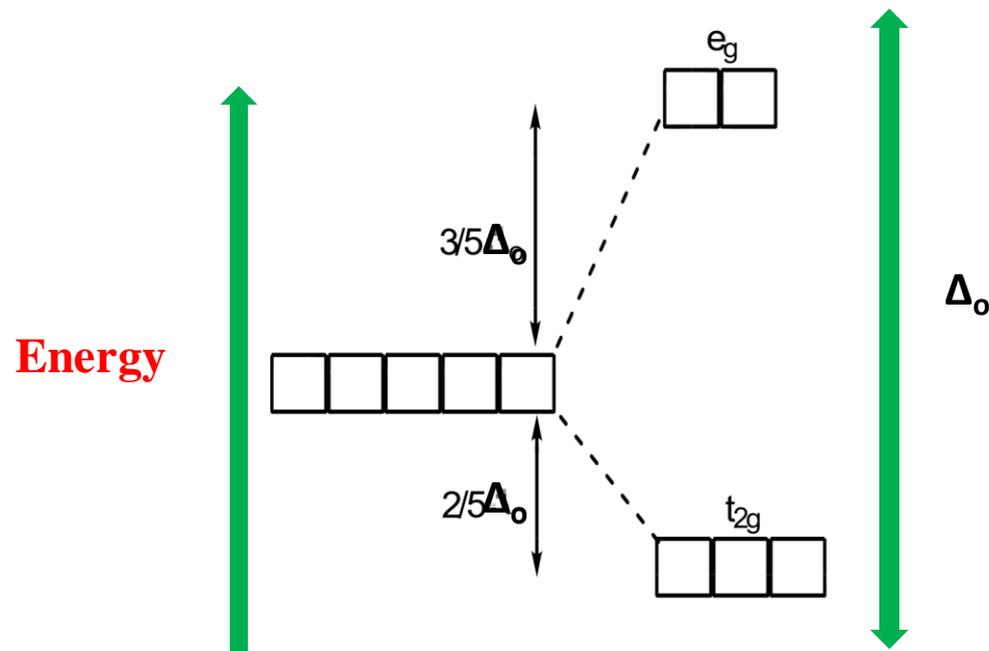
Octahedral Field

The higher t_{2g} set of orbitals = dz^2 and dx^2-y^2

The lower energy e_g set of orbitals = dxy , dyz and dxz

The energy separation between the two levels = Δ_o or $10 Dq$

The e_g orbitals are repelled by an amount of $0.6 \Delta_o$ and t_{2g} orbitals to be stabilized to the extent of $0.4 \Delta_o$.



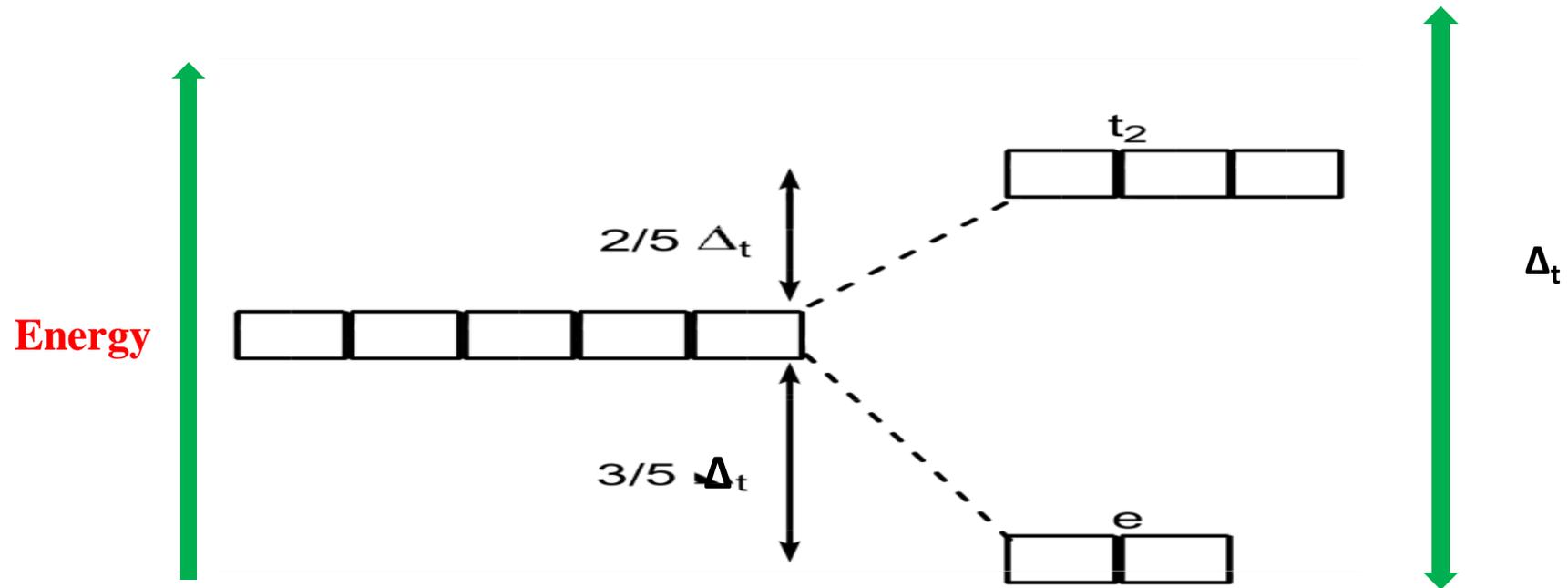
Coordination Chemistry

Tetrahedral Field

The crystal field splitting in the tetrahedral field is smaller than in the octahedral field $\Delta_t < \Delta_o$

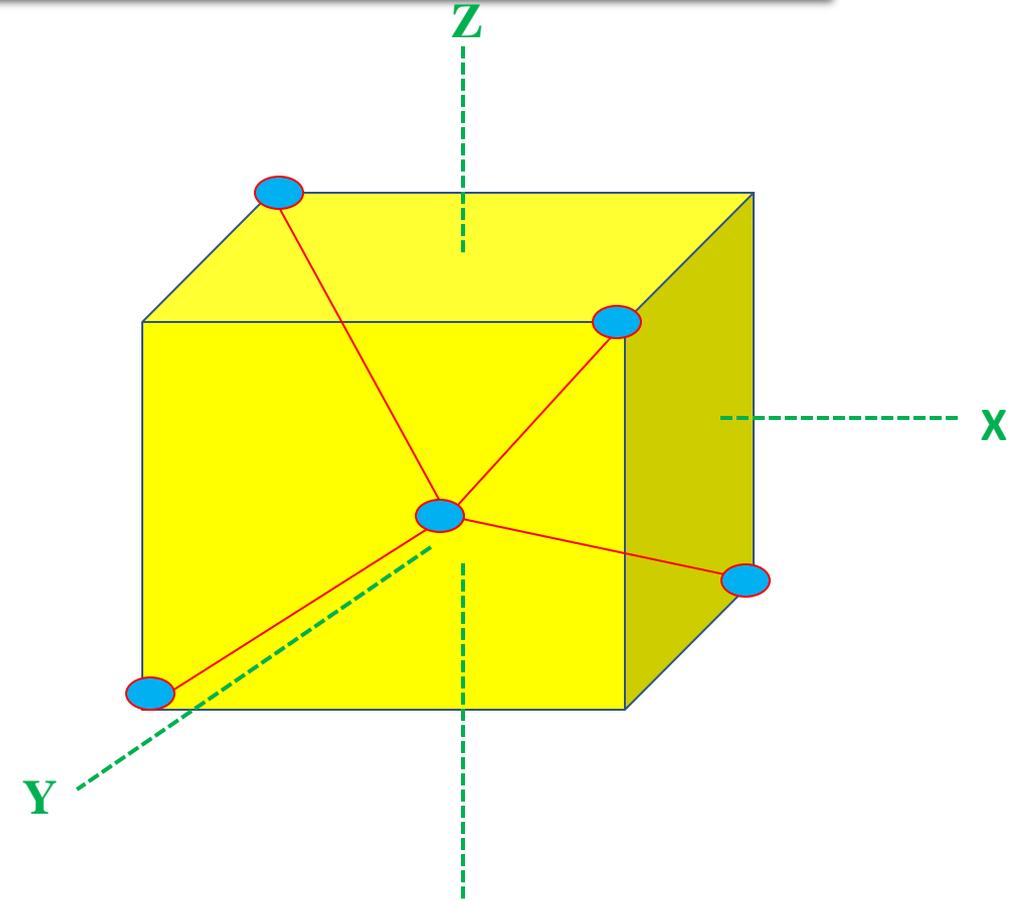
The relationship may be represented as $\Delta_t = 4/9\Delta_o$

The higher energy set t_{2g} (dxz, dyz, dxy) and the lower energy set e_g are designated as (dz^2 and dx^2-y^2)

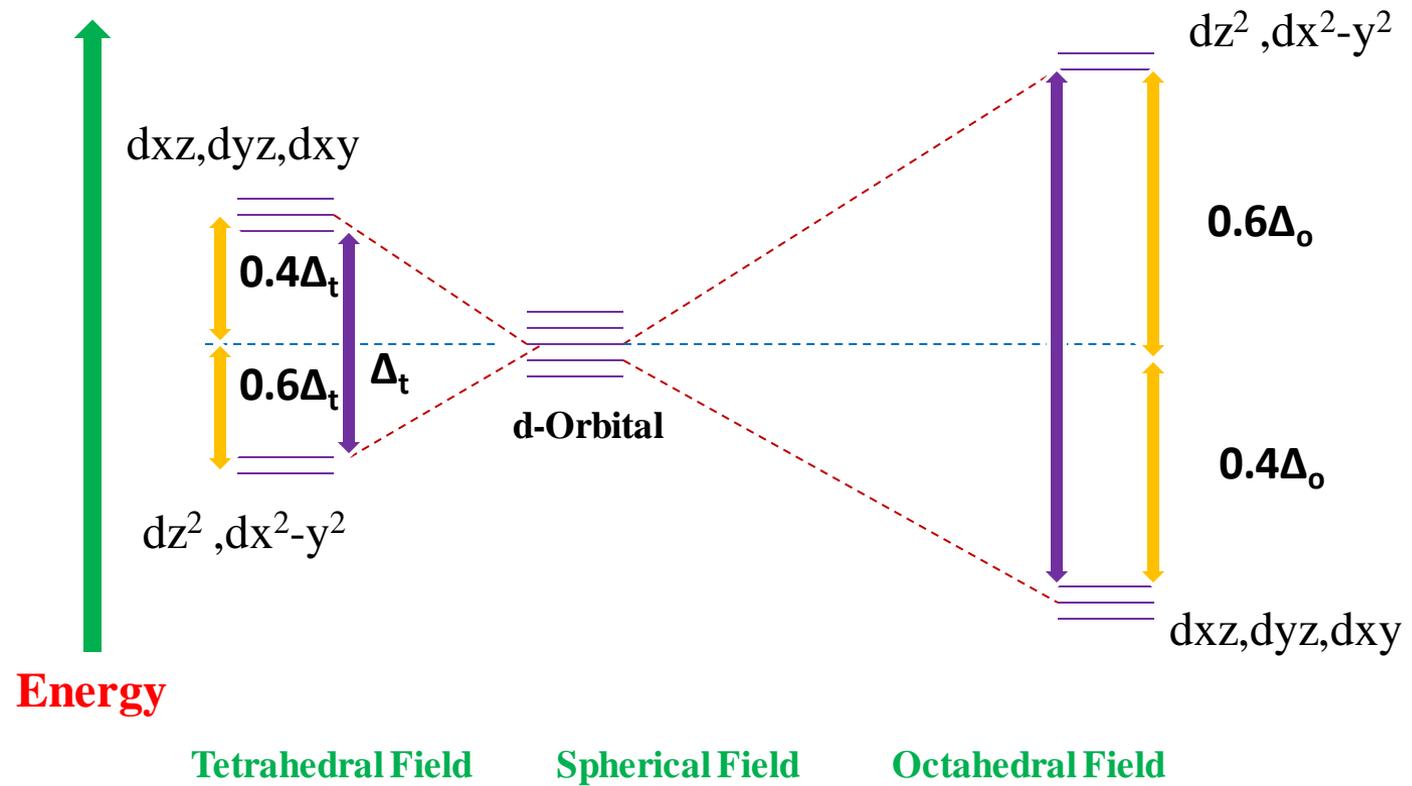


Coordination chemistry

Tetrahedral Geometry



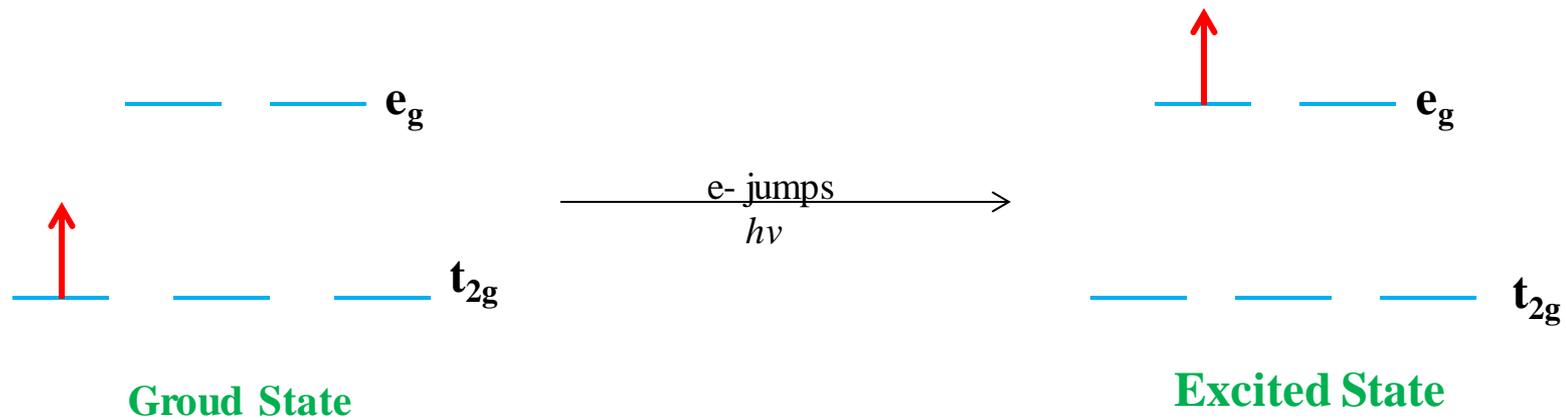
Coordination Chemistry



Coordination Chemistry

[Ti(H₂O)₆]⁺³ Complex

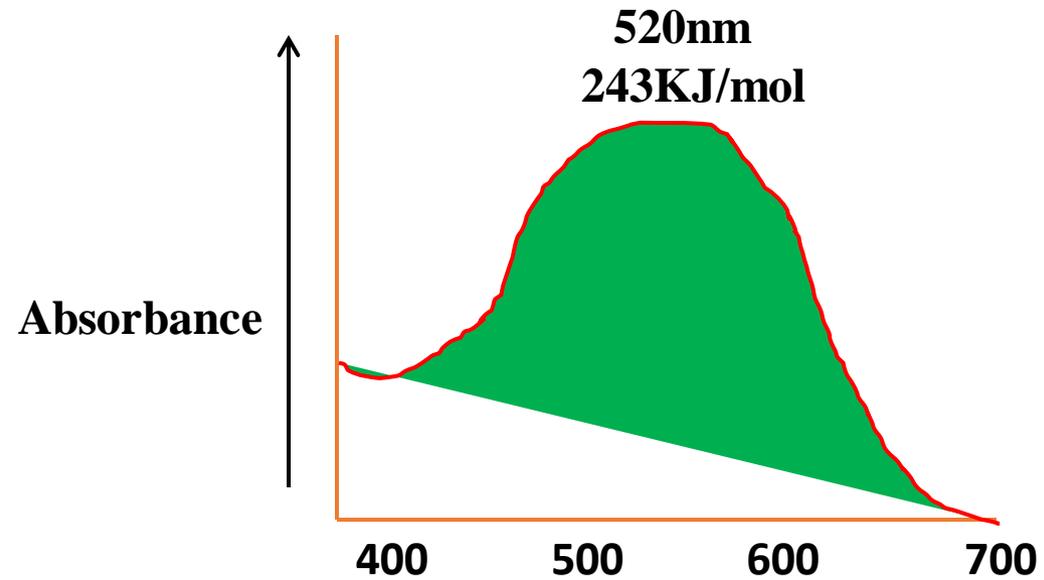
Here, Ti⁺³ = 3d¹(3d²,4s²)



Coordination Chemistry

G.S t_{2g} orbital (4926\AA^0) absorb energy and get excited $[\text{Ti}(\text{H}_2\text{O})_6]^{+3}$ eg orbital.

In case of $[\text{Ti}(\text{H}_2\text{O})_6]^{+3}$, this corresponds to 520 nm ($20,300\text{ cm}^{-1}$).



Coordination Chemistry

Factors Affecting the Magnitude of Δ_0

1. Higher oxidation states of the metal atom correspond to larger Δ_0

$[\text{CoII}(\text{NH}_3)_6]^{2+}$	$\Delta_0 = 10,200 \text{ cm}^{-1}$
$[\text{CoIII}(\text{NH}_3)_6]^{3+}$	$\Delta_0 = 22,870 \text{ cm}^{-1}$
$[\text{FeII}(\text{CN})_6]^{4-}$	$\Delta_0 = 32,200 \text{ cm}^{-1}$
$[\text{FeIII}(\text{CN})_6]^{3-}$	$\Delta_0 = 35,000 \text{ cm}^{-1}$

2. In groups, heavier analogues have larger Δ_0 as we moved down in the group

Eg: Hexaammine complexes $[\text{M}^{\text{III}}(\text{NH}_3)_6]^{3+}$:

$\Delta_0 = 22,870 \text{ cm}^{-1}$	(Co)
$34,100 \text{ cm}^{-1}$	(Rh)
$41,200 \text{ cm}^{-1}$	(Ir)

Coordination Chemistry

3. Geometry of the metal coordination unit affects Δ value greatly.

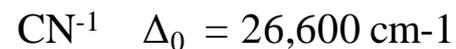
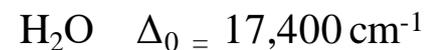
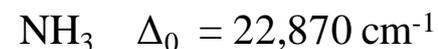
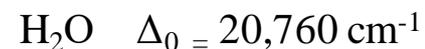
Tetrahedral complexes ML_4 have smaller Δ than octahedral ones ML_6 :



4. Nature of the ligands: weak field ligand have low CFSE as compared to strong field ligand

Weak field ligand F^-, I^-, Br

Strong field ligand H_2O, CN^-



Coordination Chemistry

Spectrochemical Series

The ligand are arranged according to their increasing splitting ability in the Spectrochemical Series.

Weak field ligand– $I^- < Br^- < SCN^- < Cl^- < N_3^- < F^- < NCS^- < NH_2^- < OH^- < ox^{2-} < O^{2-} < H_2O < NCS^- < py < NH_3 < en < bpy < phen < NO_2^- < CH_3^- < C_6H_5^- < CN^- < CO$ – **Strong field ligand**

Electronic spectroscopy of many oh complexes gives a relative ranking of the crystal field strength of ligands called the spectrochemical series

Coordination Chemistry



Net energy decrease is called crystal field stabilization energy (CFSE)

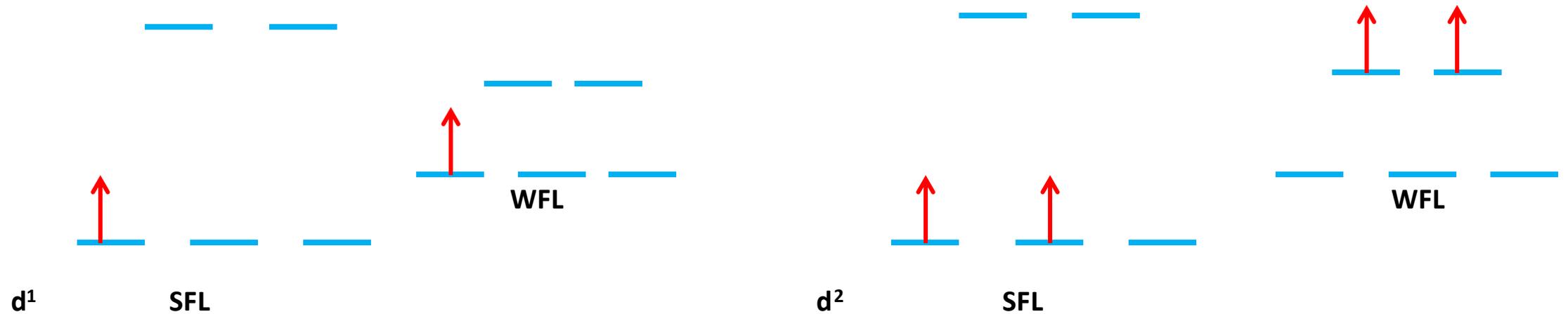
SFL strong field ligand

WFL weak field ligand

Coordination Chemistry

CFSE

Net energy decrease is called crystal field stabilization energy (CFSE)



SFL : Strong field ligand

WFL: Weak field ligand

$$d^1 \text{ CFSE} = 1 \times 0.4 = 0.4 \Delta_o$$

$$d^2 \text{ CFSE} = 2 \times 0.4 = 0.8 \Delta_o$$

Coordination Chemistry

Distribution of electron in Octahedral geometry

	<u>High-spin</u>		<u>Low-spin</u>	
d₁	t _{2g} ¹ e _g ⁰	0.4 Δ _o	t _{2g} ¹ e _g ⁰	0.4 Δ _o
d₂	t _{2g} ² e _g ⁰	0.8 Δ _o	t _{2g} ² e _g ⁰	0.8 Δ _o
d₃	t _{2g} ³ e _g ⁰	1.2 Δ _o	t _{2g} ³ e _g ⁰	1.2 Δ _o
d₄	t _{2g} ³ e _g ¹	0.6 Δ _o	t _{2g} ⁴ e _g ⁰	1.6 Δ _o
d₅	t _{2g} ³ e _g ²	0.0 Δ _o	t _{2g} ⁵ e _g ⁰	2.0 Δ _o
d₆	t _{2g} ⁴ e _g ²	0.4 Δ _o	t _{2g} ⁶ e _g ⁰	2.4 Δ _o
d₇	t _{2g} ⁵ e _g ²	0.8 Δ _o	t _{2g} ⁶ e _g ¹	1.8 Δ _o
d₈	t _{2g} ⁶ e _g ²	1.2 Δ _o	t _{2g} ⁶ e _g ²	1.2 Δ _o
d₉	t _{2g} ⁶ e _g ³	0.6 Δ _o	t _{2g} ⁶ e _g ³	0.6 Δ _o
d₁₀	t _{2g} ⁶ e _g ⁴	0.0 Δ _o	t _{2g} ⁶ e _g ⁴	0.0 Δ _o

Coordination Chemistry

- Weaker ligands give high-spin complexes, whereas stronger ligands give low-spin complexes

$$\text{For } d^{10}, \text{CFSE} = (6 \times 0.4) - (4 \times 0.6) = 0.0 \Delta_o$$

- There are only 4 ligands in tetrahedral and whereas in octahedral complexes 6 ligands.
- 1/3 decrease in the number of ligands decreases the Δ_t value to some extent from the Δ_o value

Coordination Chemistry

Distribution of electron in tetrahedral geometry

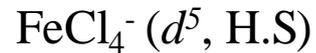
High spin		
d1	e1 t ₂ 0	0.6 Δ_t
d2	e2 t ₂ 0	1.2 Δ_t
d3	e2 t ₂ 1	0.8 Δ_t
d4	e2 t ₂ 2	0.4 Δ_t
d5	e2 t ₂ 3	0.0 Δ_t
d6	e3 t ₂ 3	0.6 Δ_t
d7	e4 t ₂ 3	1.2 Δ_t
d8	e4 t ₂ 4	0.8 Δ_t
d9	e4 t ₂ 5	0.4 Δ_t
d10	e4 t ₂ 6	0.0 Δ_t

Coordination Chemistry

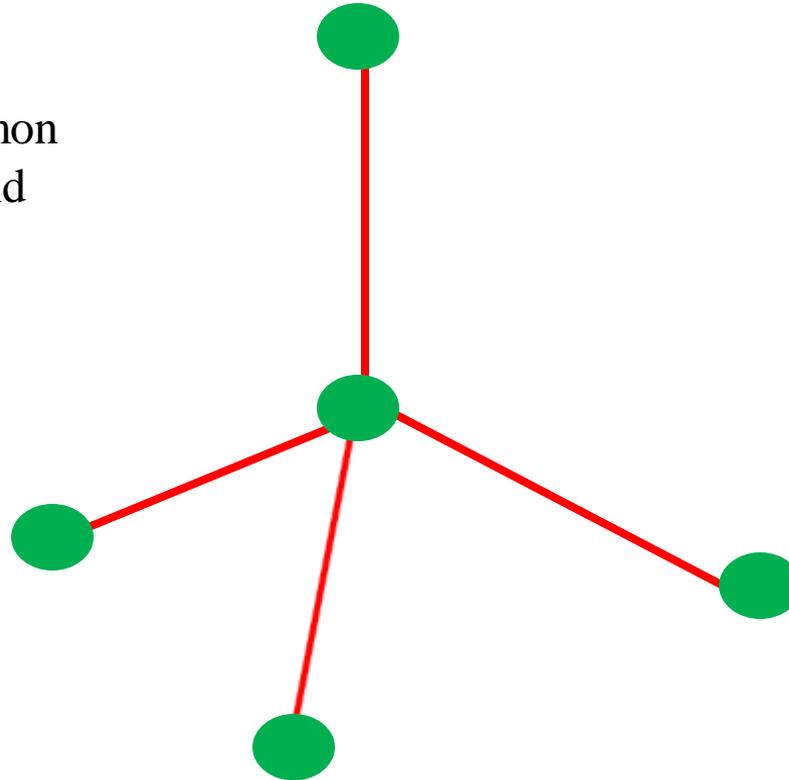
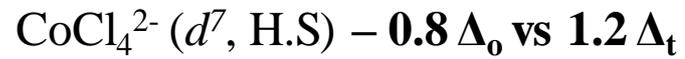
When to expect tetrahedral geometry

Low-spin tetrahedral complexes are not common
If ligands are large; so as to avoid ligand-ligand repulsion

Metal ions with zero CFSE = d^0 , d^5 and d^{10}



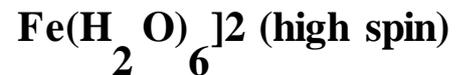
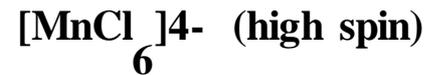
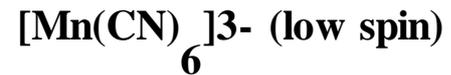
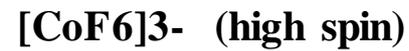
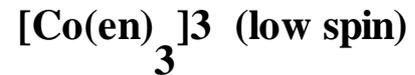
Metal ions with small CFSE (d^2 and d^7)



Coordination Chemistry

Problem for practice:

1. How many unpaired electron are present in the following complexes
2. Also calculate the C.F.S.E



Coordination Chemistry

Problem for practice:

1. The magnitude of Δ_o value depend on

- a) Charge of the central metal ion
- b) Nature of the ligand
- c) Principal quantum number of the d-electron
- d) All the above
- e) None of these

2. The highest CFSE (Crystal field stabilization energy) is:

- a) $[\text{Co}(\text{NH}_3)_6]^{2+}$
- b) $[\text{Co}(\text{NH}_3)_6]^{3+}$
- c) $[\text{Rh}(\text{NH}_3)_6]^{3+}$
- d) $[\text{Ir}(\text{NH}_3)_6]^{3+}$