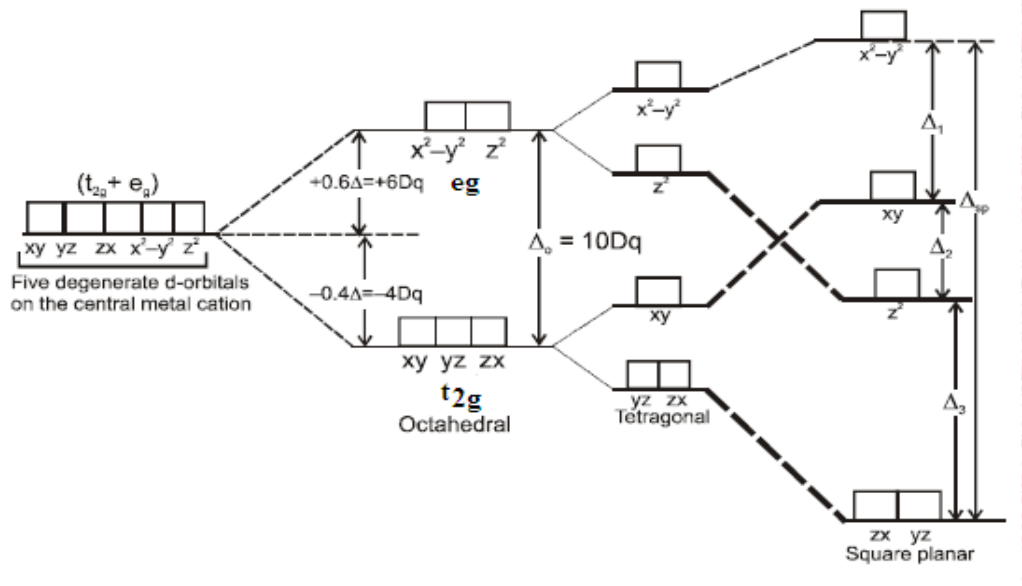
Metal-Ligand Bonding in Transition Metal Complexes

(Lecture-4)

B.Sc. 5th Semester (Pass Course)

INORGANIC CHEMISTRY

(As per MDU, Rohtak Syllabus)



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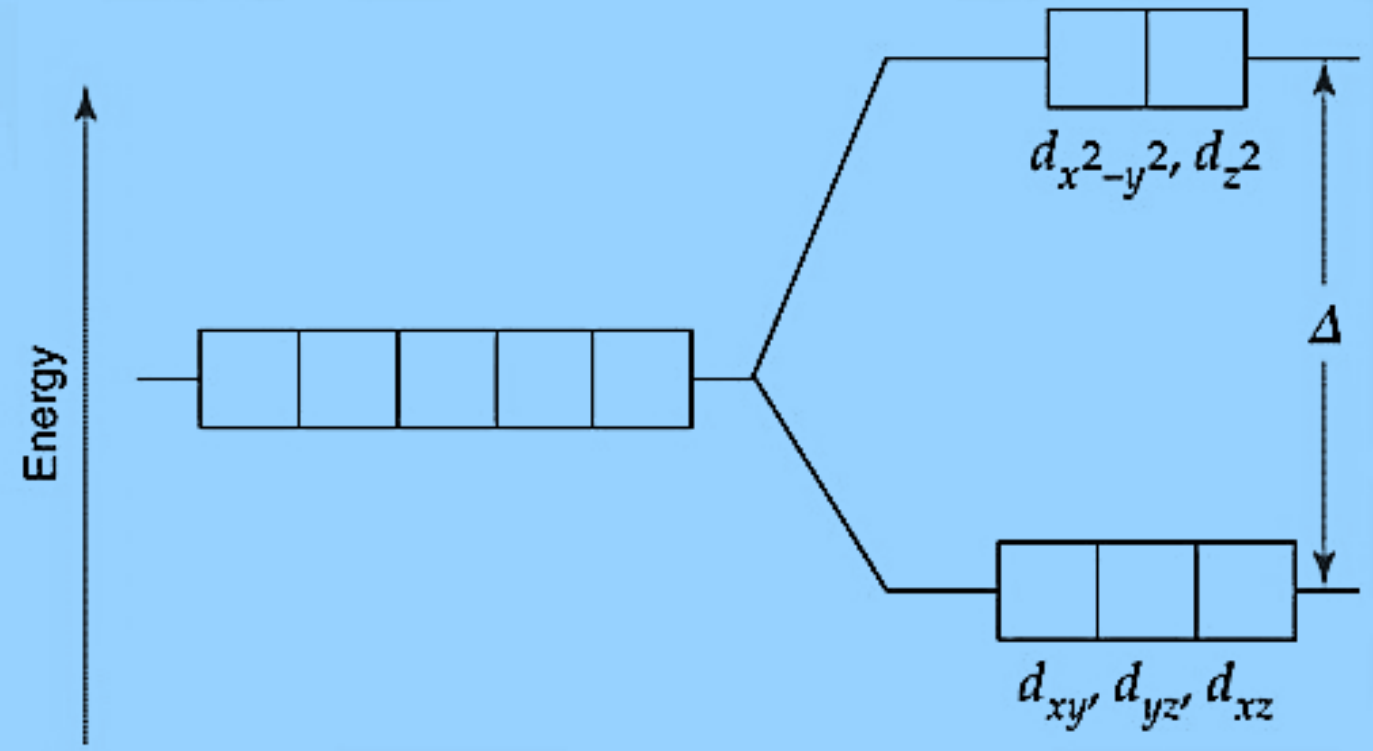
CONTENT

- Crystal field splitting energy
- Crystal field stabilization energy
- Factors affecting value of Δ_{oct}
- Spectrochemical series

Crystal field splitting energy

Octahedral field Splitting Pattern:



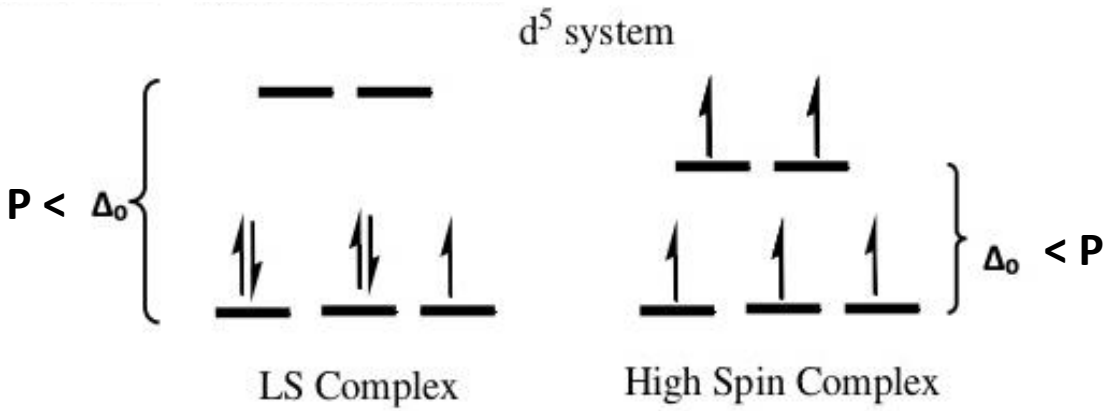
The energy gap is referred to as Δ (10 Dq) , the crystal field splitting energy.

Crystal field stabilization energy (CFSE)

CFSE for an Octahedral Complex

$$CFSE = -0.4 \times n(T_{2g}) + 0.6 \times n(E_g)\ \Delta_o$$

Where, n is the no. of electrons



HS Complex

$t_{2g}^{3}e_g^{2}$

CFSE = {-0.4(3)+ 0.6(2)}Δ_o

= 0 Δ_o

LS Complex

$t_{2g}^{5}e_g^{0}$

CFSE = {-0.4(5)+ 0.6(0)}Δ_o+2P

= -2.0 Δ_o+ 2P

Calculation of CFSE for d^5 (HS+LS) octahedral Complex

d^n	High-spin = weak field		Low-spin = strong field	
	Electronic configuration	CFSE	Electronic configuration	CFSE
d^1	$t_{2g}^1 e_g^0$	$-0.4\Delta_{oct}$		
d^2	$t_{2g}^2 e_g^0$	$-0.8\Delta_{oct}$		
d^3	$t_{2g}^3 e_g^0$	$-1.2\Delta_{oct}$		
d^4	$t_{2g}^3 e_g^1$	$-0.6\Delta_{oct}$	$t_{2g}^4 e_g^0$	$-1.6\Delta_{oct} + P$
d^5	$t_{2g}^3 e_g^2$	0	$t_{2g}^5 e_g^0$	$-2.0\Delta_{oct} + 2P$
d^6	$t_{2g}^4 e_g^2$	$-0.4\Delta_{oct}$	$t_{2g}^6 e_g^0$	$-2.4\Delta_{oct} + 2P$
d^7	$t_{2g}^5 e_g^2$	$-0.8\Delta_{oct}$	$t_{2g}^6 e_g^1$	$-1.8\Delta_{oct} + P$
d^8	$t_{2g}^6 e_g^2$	$-1.2\Delta_{oct}$		
d^9	$t_{2g}^6 e_g^3$	$-0.6\Delta_{oct}$		
d^{10}	$t_{2g}^6 e_g^4$	0		

Crystal field stabilisation energy for high spin d^4 octahedral complex is

A. $-1.8\ \Delta_o$

B. $-1.6\ \Delta_o + P$

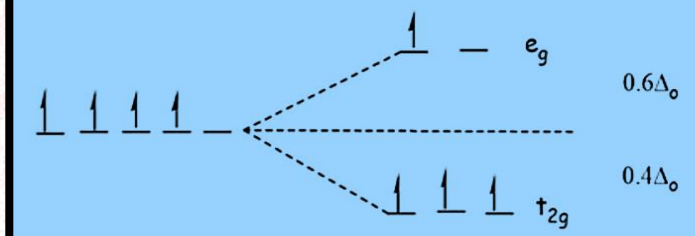
C. $-1.2\ \Delta_o$

D. $-0.6\ \Delta_o$

D. $-0.6\ \Delta_o$

In the case of high spin complex Δ_o is small. Thus, the energy required to pair up the fourth electron wit the electrons of lower energy d- orbitals would be higher than that required to place the electrons in th higher d -orbital. Thus pairing does not occur.

For high spin d^4 octahedral complex,



Factors affecting magnitude of Δ_{oct}

1. Nature of metal ion (row to which it belongs) Going from the first row to second row there is an increase in Δ_o : Larger the metal → larger is the Δ
2. Oxidation state of the metal ion (higher the oxidation state more is the Δ_o
3. Number of ligands and shape of complex (Octahedral, tetrahedral, square planar....)
4. Relative strength of the ligand (Spectrochemical Series)

1)Nature of metal ion:

a) Same metal ion with different charge

e.g. $[Co(H_2O)_6]^{3+}$ Co^{3+} $\Delta o=18,200\ cm^{-1}$ > $[Co(H_2O)_6]^{2+}$ Co^{2+} $\Delta o=9,300\ cm^{-1}$

b) Different metal ion with same charge

e.g. $[Co(H_2O)_6]^{2+}$ Co^{2+} (d^7) $\Delta o=9,300\ cm^{-1}$ > $[Ni(H_2O)_6]^{2+}$ Ni^{2+} (d^8) $\Delta o=8,500\ cm^{-1}$.

c) Different metal ion with different charge but same number of d – electrons

e.g. $[Cr(H_2O)_6]^{3+}$ Cr^{3+} (d^3) $\Delta o= 17,400\ cm^{-1}$ > $[V(H_2O)_6]^{2+}$ V^{2+} (d^3) $\Delta o= 12,400\ cm^{-1}$

d) Different metal ion with same charge but different principal quantum number.

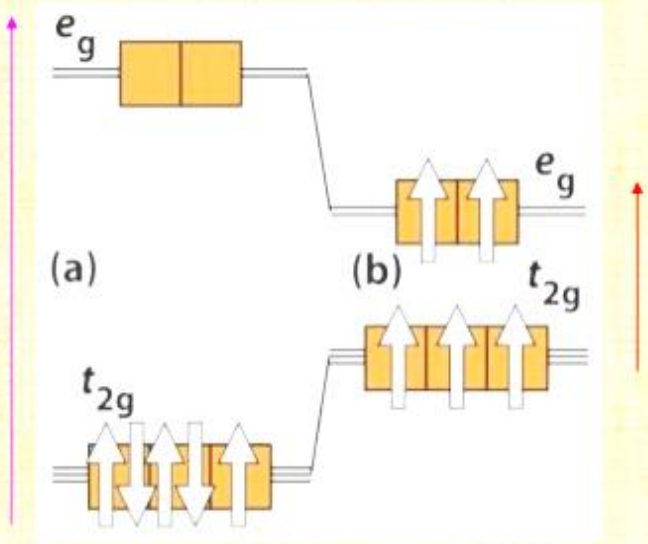
e.g. $[Ir(NH_3)_6]^{3+}$ Ir^{3+} $(5d^6)$ $n=5$; $[Rh(NH_3)_6]^{3+}$ Rh^{3+} $(4d^6)$ $n=4$; $[Co(NH_3)_6]^{3+}$ Co^{3+} $(3d^6)$ $n=3$

$\Delta o= 41,000\ cm^{-1} > \Delta o= 34,000\ cm^{-1} > \Delta o= 23,000\ cm^{-1}$

2)Nature of ligand

a) When the ligands are strong the energy gap between t_{2g} and e_g is more the distribution of electron does not takes place according to Hund's rule. These are Low spin Complexes .

b) When ligands are weak CFSE is relatively small hence five d- orbitals are suppose to be degenerate and therefore distribution of electrons takes place according to Hund's rule. These are High spin Complexes .



Strong field Ligands (violet, low spin)

Weak field Ligands (red, high spin)

• Geometry of complexes

- Order of crystal field stabilization energy according to geometry of complexes is
- Δsp (square planner) > Δo (octahedral) > Δt (tetrahedral)
- 1.73 > 1.23 > 0.43

Spectrochemical Series

Halides < OH^- < $C_2O_4^{2-}$ < H_2O < $\underline{N}CS^-$ < py < NH_3 < en < NO_2^- < CN^- < CO

Weak Field Ligands
Weak Metal Interactions
Small Δ_o

↓

High-Spin Complexes

Strong Field Ligands
Strong Metal Interactions
Large Δ_o

↓

Low-Spin Complexes

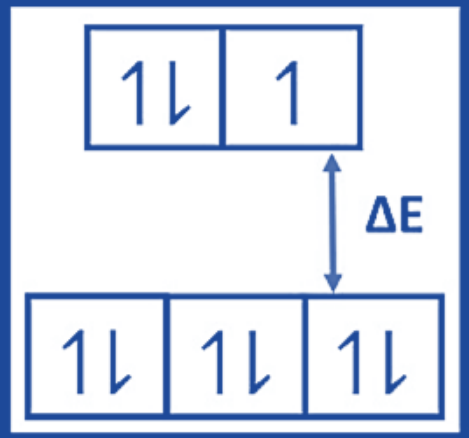
Qualitative Theory on Magnitude of Δ_o

Spectrochemical Series

The spectrochemical series arranges ligands in order of their ability to split d-orbitals in an octahedral complex ion.

$$I^- < Br^- < S^{2-} < Cl^- < F^- < OH^- < H_2O < SCN^- < NH_3 < CN^- \approx CO$$

Increasing splitting of d-orbitals



The greater the splitting, the greater the energy difference (ΔE) between the two sets of d-orbitals.

The Spectrochemical Series

$I^- < Br^- < [NCS]^- < Cl^- < F^- < [OH]^- < [ox]^{2-} \sim H_2O < [NCS]^- < NH_3 < en < [CN]^- \sim CO$

- **σ donor**

Weak field ligands ⟶ **Strong field ligands**

Ligands increasing Δ_{oct}

- **Small Δ**
- **High spin**
- **π donors**

- **Large Δ**
- **Low spin**
- **π acceptors**


THANK
YOU