

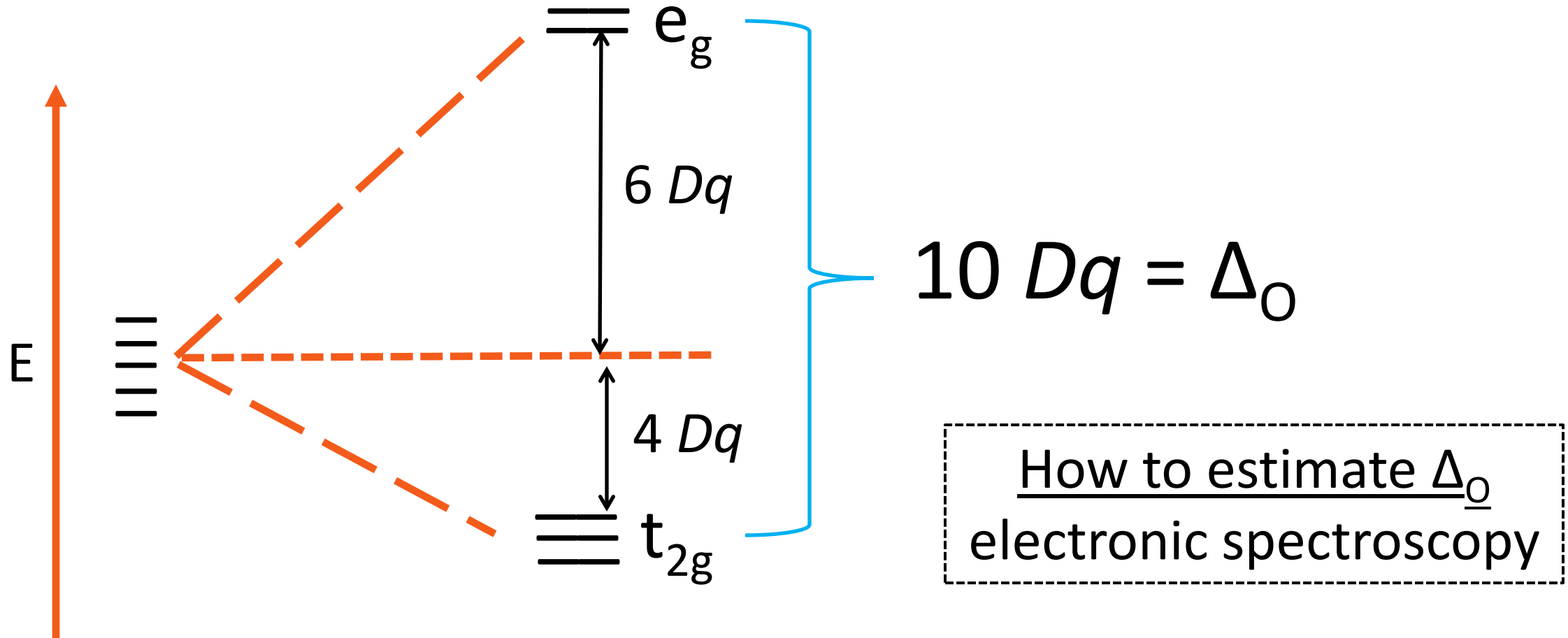


CHEM F111 : General Chemistry

Semester II: AY 2017-18

Lecture-23, 16-03-2018

Summary of lecture 22



$$6 Dq = 0.6 \Delta_O \text{ and } 4 Dq = 0.4 \Delta_O$$

Summary of lecture 22



(1) Nature of the Ligands:

Spectrochemical Series: Strength of the Ligands

Halide donors < O donors < N donors < C donors

Weak Field Ligands

Strong Field Ligands

(2) Nature of Metal cation:

Different Charges on the cation of the same metal:

$$\Delta_o \text{ for } [\text{Fe}(\text{H}_2\text{O})_6]^{2+} = 10,400 \text{ cm}^{-1}$$

$$\Delta_o \text{ for } [\text{Fe}(\text{H}_2\text{O})_6]^{3+} = 13,700 \text{ cm}^{-1}$$

Metal cation with a higher oxidation state has a larger value of Δ_o than that with lower oxidation state.

Summary of lecture 22



Different charges on the cation of different metal:

Two different cation with the same number of d-electrons but with different charge (metals within a same period):

$$\Delta_o \text{ for } [\text{V}(\text{H}_2\text{O})_6]^{2+} = 12,400 \text{ cm}^{-1}$$

$$\Delta_o \text{ for } [\text{Cr}(\text{H}_2\text{O})_6]^{3+} = 17,400 \text{ cm}^{-1}$$

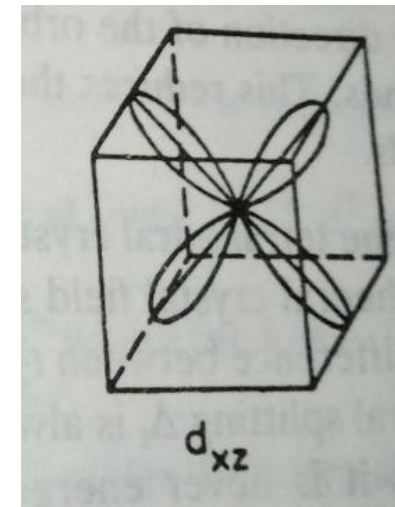
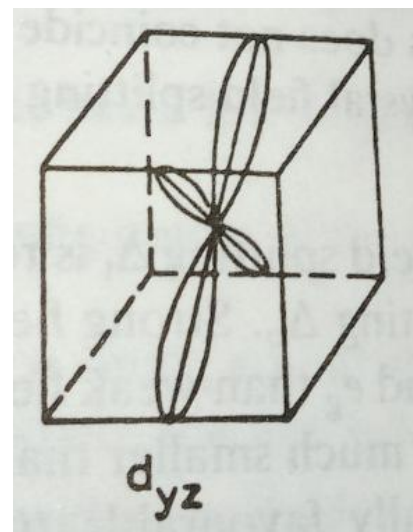
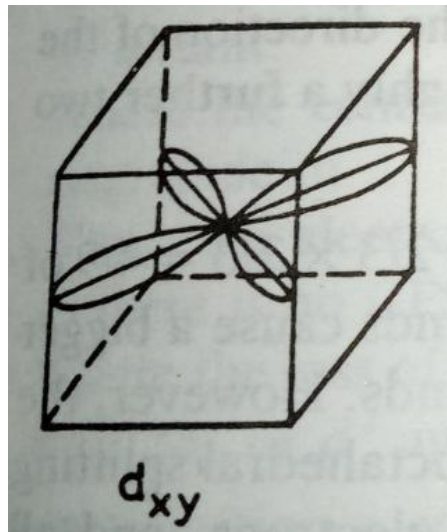
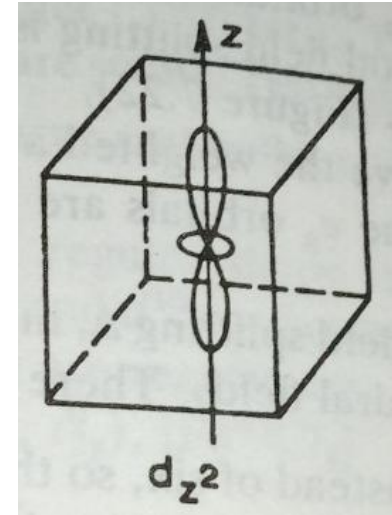
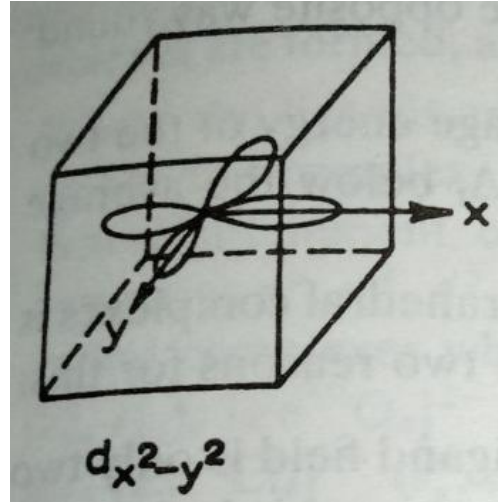
Oxidation state $\propto \Delta_o$

Tetrahedral complex

innovate

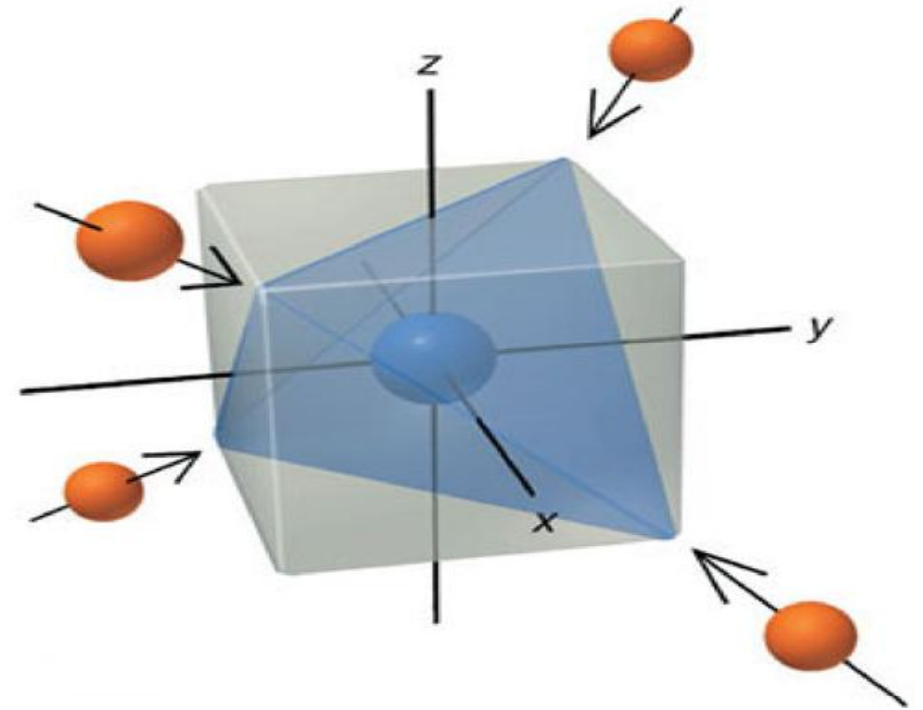
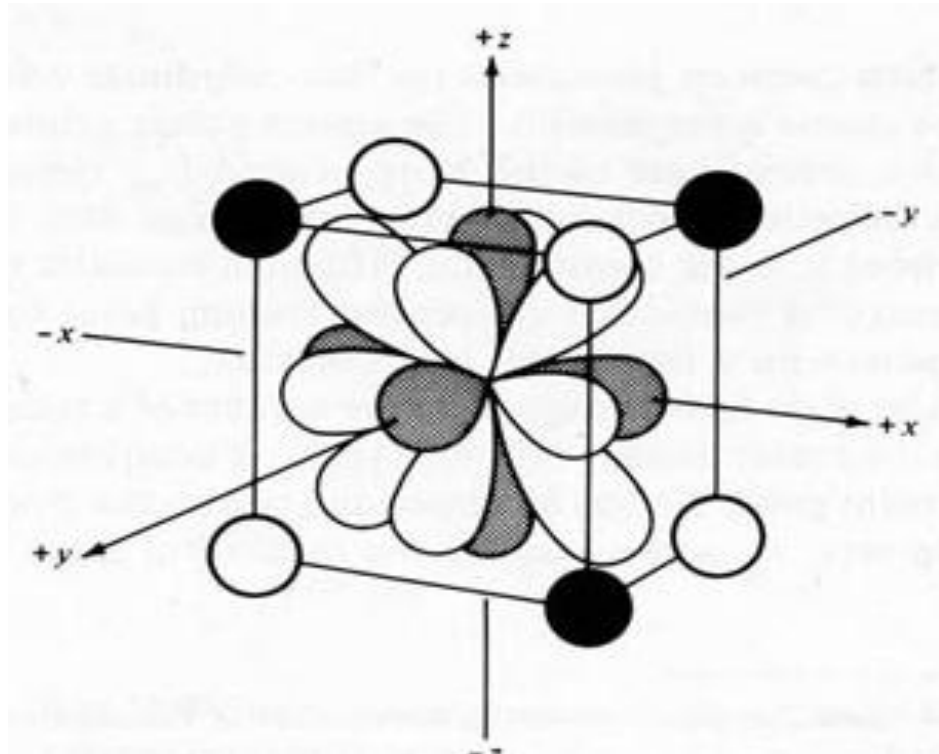
achieve

lead



Tetrahedral complexes

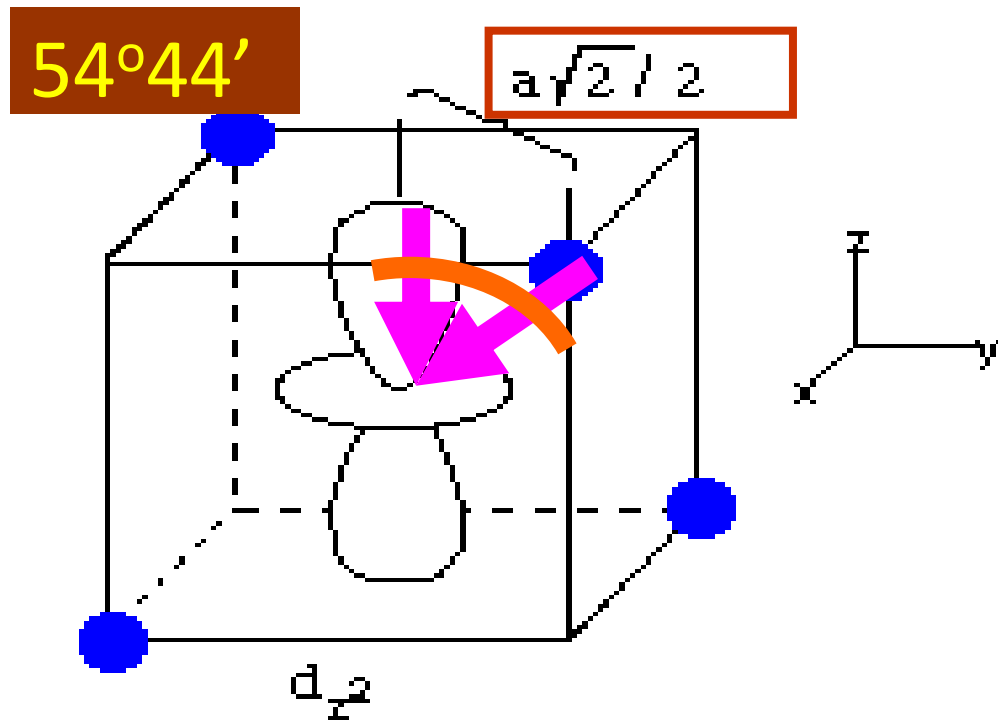
The direction of approaching ligands coincides with neither e_g nor t_{2g} orbitals.



Tetrahedral complexes

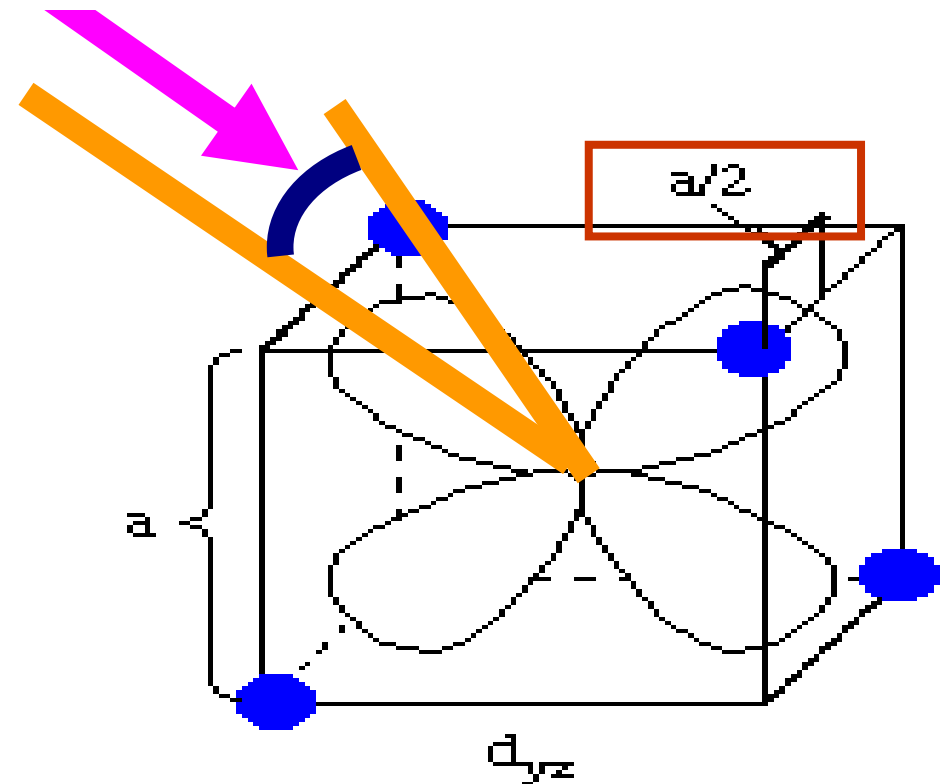
\angle axial orbital – metal-ligand = $109^\circ 28' / 2 = 54^\circ 44'$

Distance between axial orbital and ligand = $0.707a$ (a=edge length) (Face of the cube)



\angle non-axial orbital – metal-ligand = $35^\circ 16'$

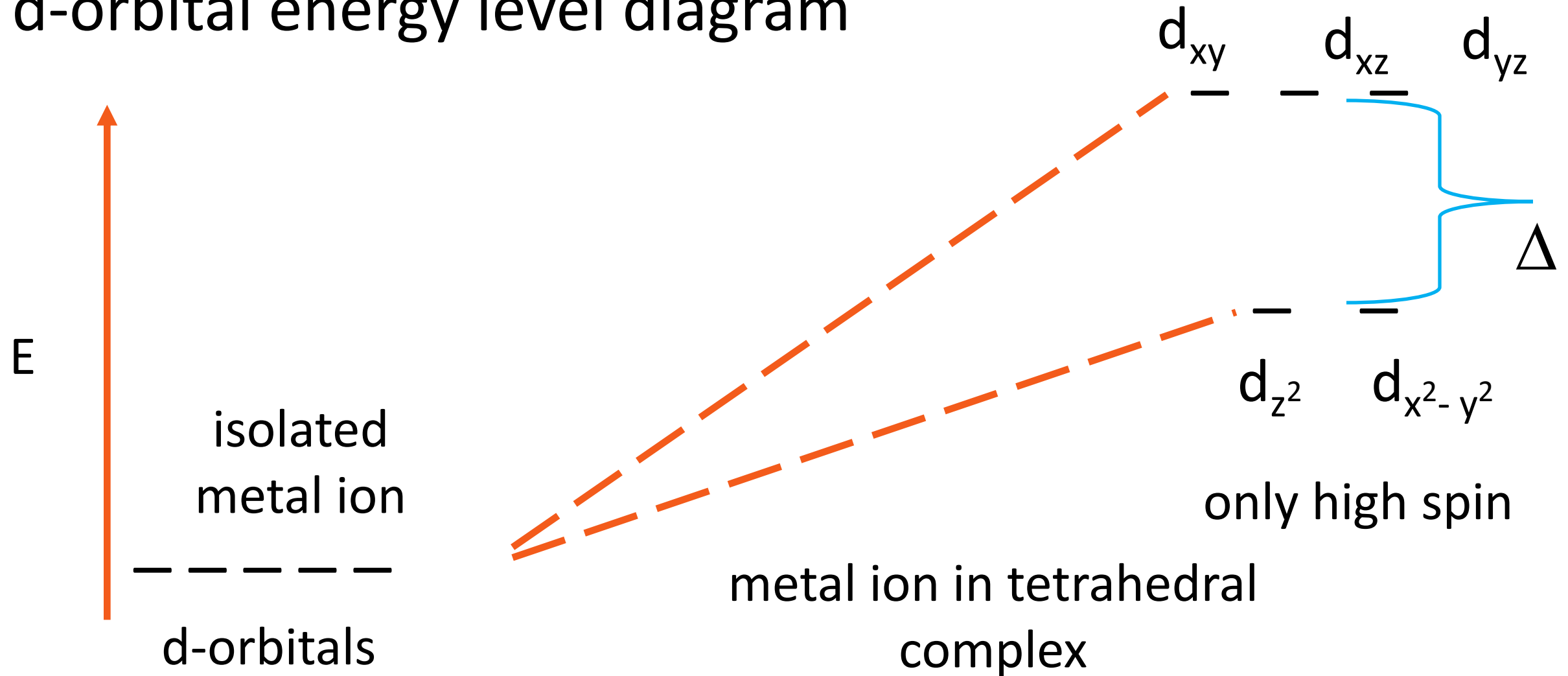
distance between non axial orbital & ligand = $0.5a$ (a= edge l)



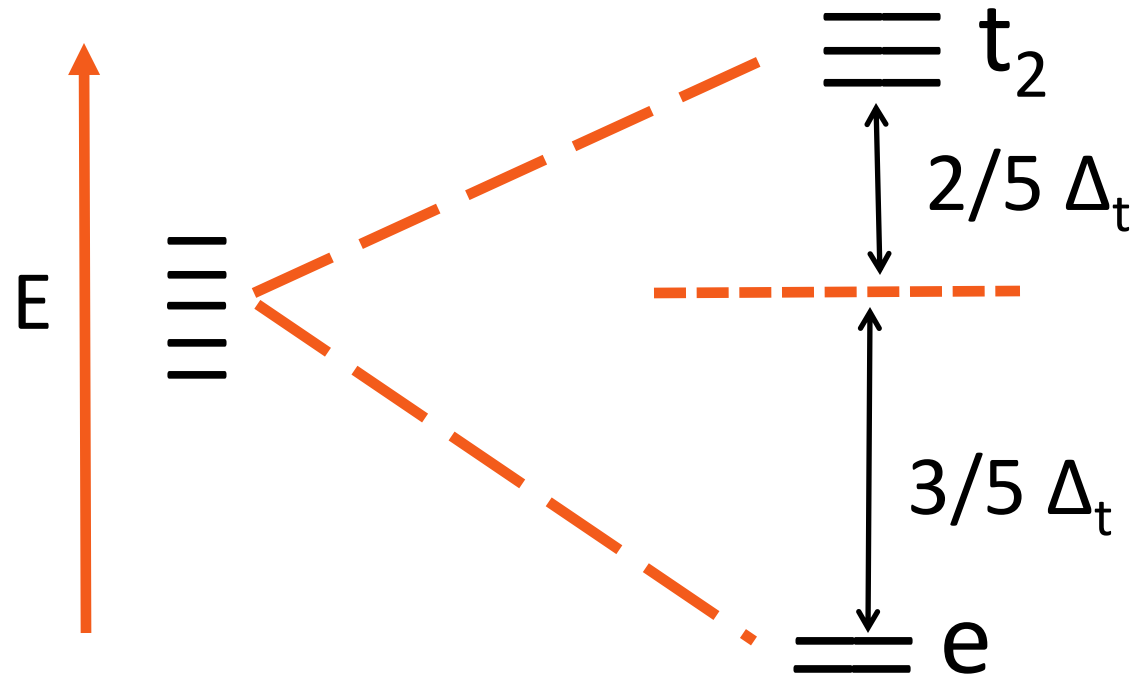
Splitting in tetrahedral complex



d-orbital energy level diagram



Tetrahedral complexes



- t_2 orbitals are in higher energy as opposed to octahedral field.
- Since there is no centre of symmetry in tetrahedron the parity subscript g is omitted.
- The total tetrahedral splitting is Δ_t

Tetrahedral complexes



In general $\Delta_t < \Delta_o$,

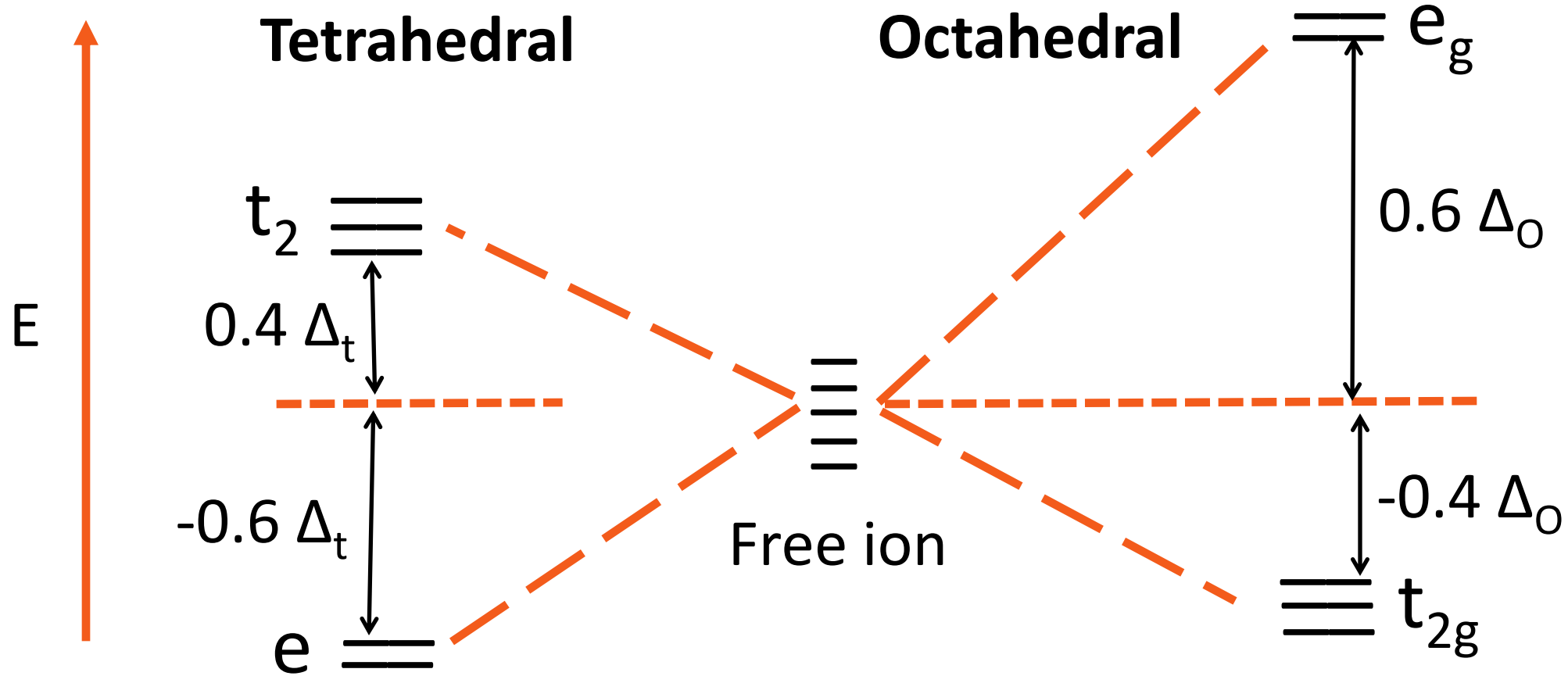
- Since there are only 4 ligands compared to 6 in octahedron; this gives 2/3 reduction from the octahedral crystal field splitting.
- d-orbitals do not coincide with the direction of M-L bonds; this gives another 2/3 reduction.

So for the same ligand and same metal ion

$$\Delta_t = (4/9)\Delta_o \text{ (approximately)}$$

Due to this low Δ_t values almost all the tetrahedral complexes are **High Spin** (No pairing).

Octahedral vs. tetrahedral

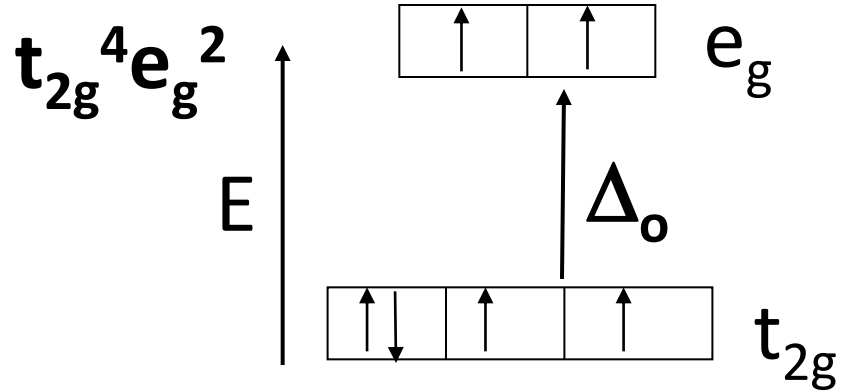


So for the same ligand and same metal ion
 $\Delta_t = (4/9)\Delta_o$ (approximately)

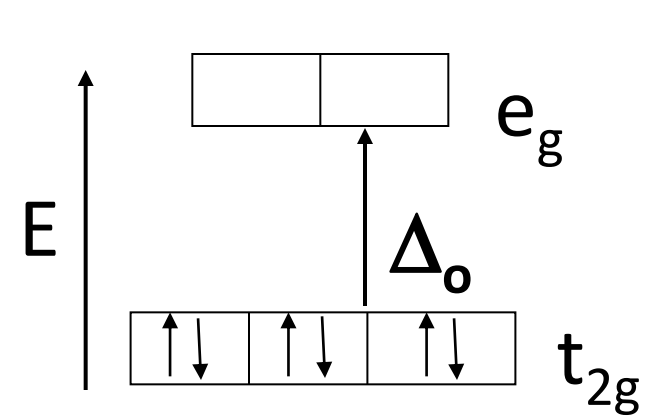
d⁶ configuration



Weak



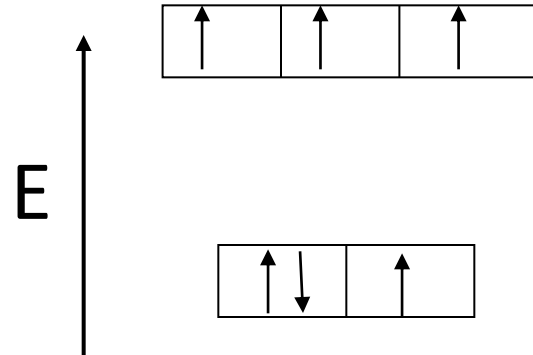
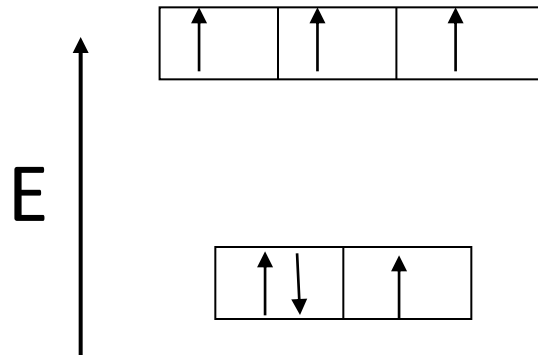
Strong



$t_{2g}^6 e_g^0$

Octahedron

$e^3 t_2^3$



$e^3 t_2^3$

Tetrahedron

Crystal Field Stabilization Energy



In the d^1 system, one electron is $0.4 \Delta_o$ below Bari Centre. OR this electron is stabilized wrt spherically symmetric field.

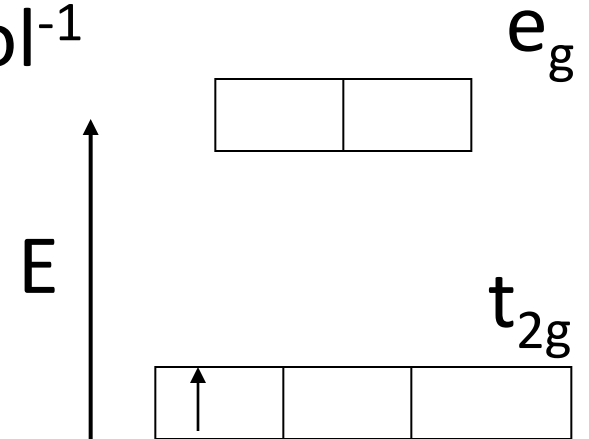
For an octahedral geometry:

$$\text{Crystal Field Stabilization Energy} = \text{CFSE} = (-0.4n_{t_{2g}} + 0.6n_{e_g}) \Delta_o ;$$

n = no. of electrons

$$[\text{Ti}(\text{H}_2\text{O})_6]^{3+} : \text{CFSE} = -0.4 \times 1 \times \Delta_o = -0.4 \times 243 = -97 \text{ kJmol}^{-1}$$

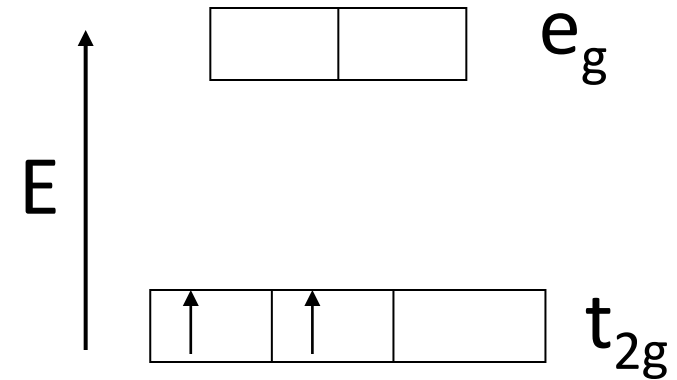
NOTE: This stability is w.r.t. Bari Centre.



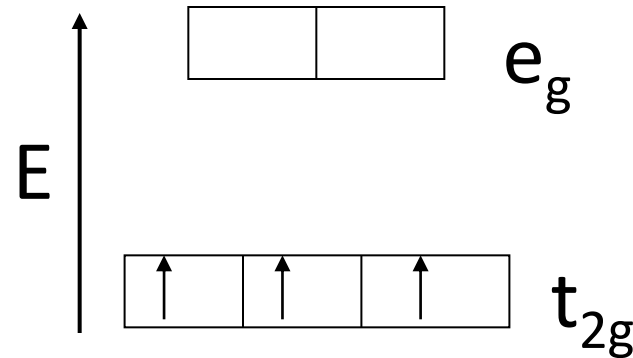
CFSE for d-electron



Similarly, $V^{3+} = d^2 = t_{2g}^2$ So $CFSE = -0.8 \Delta_o$

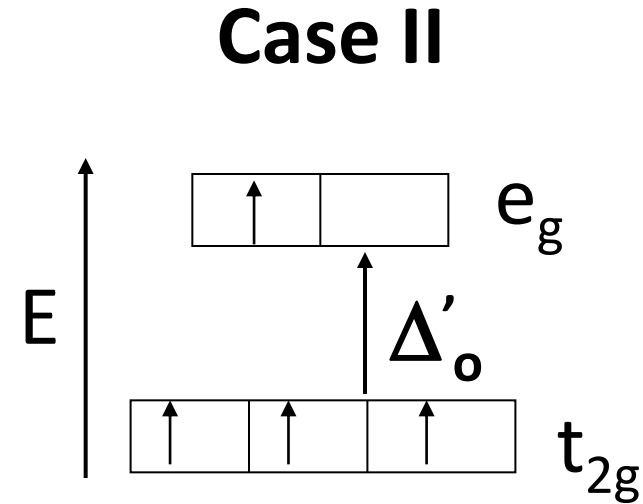
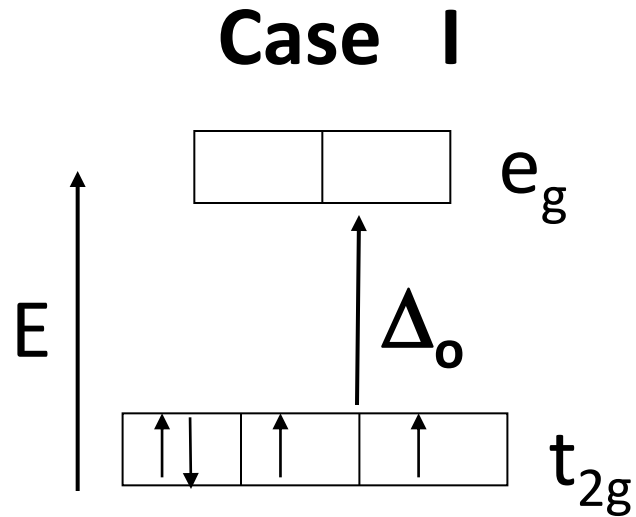


$Cr^{3+} = d^3 = t_{2g}^3$ $CFSE = -1.2 \Delta_o$



Due to Hund's rule of maximum multiplicity the electrons are going to different orbitals

CFSE of d^4 configuration



Case I: involves pairing which requires energy input

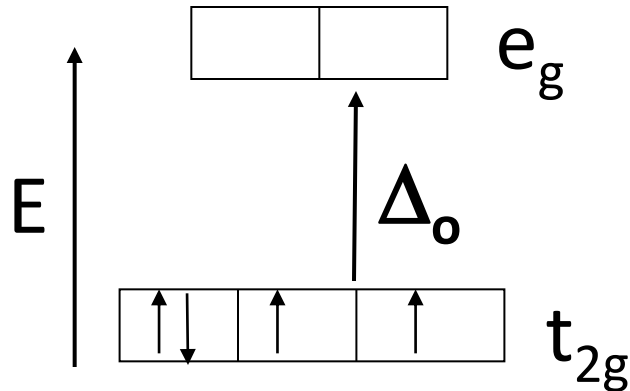
Case II: electron is placed in high energy e_g orbital

Note: In both the cases the fourth electron placement raises the energy of the system

CFSE of d^4 configuration

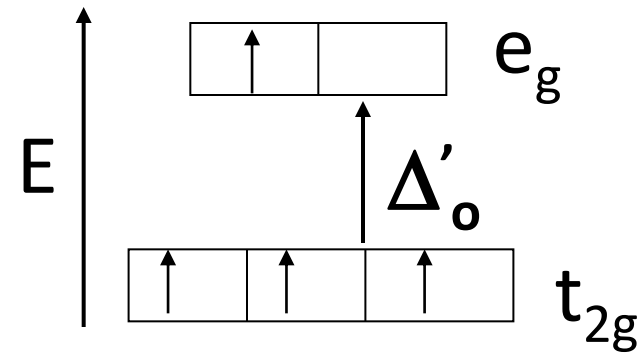


Case I



$$\Delta_o \gg \Delta'_o$$

Case II



Case I

Pairing energy $\ll \Delta_o$
Low spin complex;
Spin paired complex;
Strong ligands

Case II

$\Delta'_o \ll$ Pairing energy;
high spin Complex;
spin free complex;
Weak ligands

CFSE for Octahedral complexes



Weak Field Ligand				Strong Field Ligand		
d^n	Configuration	Unpaired electrons	CFSE Δ_o	Configuration	Unpaired electrons	CFSE Δ_o
d^1	t_{2g}^1	1	-0.4	t_{2g}^1	1	-0.4
d^2	t_{2g}^2	2	-0.8	t_{2g}^2	2	-0.8
d^3	t_{2g}^3	3	-1.2	t_{2g}^3	3	-1.2
d^4	$t_{2g}^3 e_g^1$	4	-0.6	t_{2g}^4	2	-1.6
d^5	$t_{2g}^3 e_g^2$	5	0.0	t_{2g}^5	1	-2.0
d^6	$t_{2g}^4 e_g^2$	4	-0.4	t_{2g}^6	0	-2.4
d^7	$t_{2g}^5 e_g^2$	3	-0.8	$t_{2g}^6 e_g^1$	1	-1.8
d^8	$t_{2g}^6 e_g^2$	2	-1.2	$t_{2g}^6 e_g^2$	2	-1.2
d^9	$t_{2g}^6 e_g^3$	1	-0.6	$t_{2g}^6 e_g^3$	1	-0.6
d^{10}	$t_{2g}^6 e_g^4$	0	0.0	$t_{2g}^6 e_g^4$	0	0.0

Tetrahedral complexes



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

$$\text{Tetrahedral CFSE} = (-0.6n_e + 0.4 n_{t_2}) \Delta_t$$

In octahedral cases, CFSE = 0 for d^0 , $d^5(\text{weak})$ and d^{10} cases;

In Tetrahedral cases, CFSE = 0 for d^0 , d^5 and d^{10} cases irrespective of strong or weak field ligands.

Stabilization of oxidation state

(i) $[\text{Co}(\text{H}_2\text{O})_6]^{3+}$: $3d^6$ system, $t_{2g}^4 e_g^2$, CFSE: $-0.4 \Delta_o$

(ii) $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$: $3d^7$ system, $t_{2g}^5 e_g^2$, CFSE: $-0.8 \Delta_o$

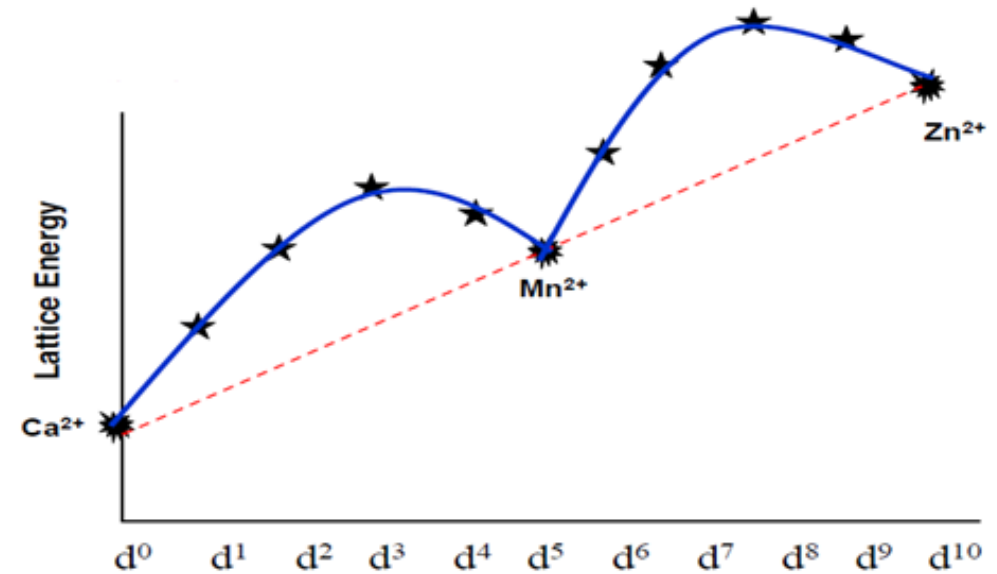
(iii) $[\text{Co}(\text{NH}_3)_6]^{3+}$ (CFSE: $-2.4 \Delta_o$) and $[\text{Co}(\text{NH}_3)_6]^{2+}$ (CFSE: $-1.8 \Delta_o$)

Crystal Field Theory: lattice energy



CRYSTAL FIELD THEORY in explaining variation of Lattice Energy for transition metal chlorides (1st row transition metals)

Excess stabilization (-ve) energy above the line can be from CFSE



d ¹	d ²	d ³	d ⁴	d ⁵	d ⁶	d ⁷	d ⁸	d ⁹	d ¹⁰
Sc ²⁺	Ti ²⁺	V ²⁺	Cr ²⁺	Mn ²⁺	Fe ²⁺	Co ²⁺	Ni ²⁺	Cu ²⁺	Zn ²⁺
-0.4Δ _o	-0.8Δ _o	-1.2Δ _o	-0.6Δ _o	0	-0.4Δ _o	-0.8Δ _o	-1.2Δ _o	-0.6Δ _o	0

Crystal Field Theory: hydration energy

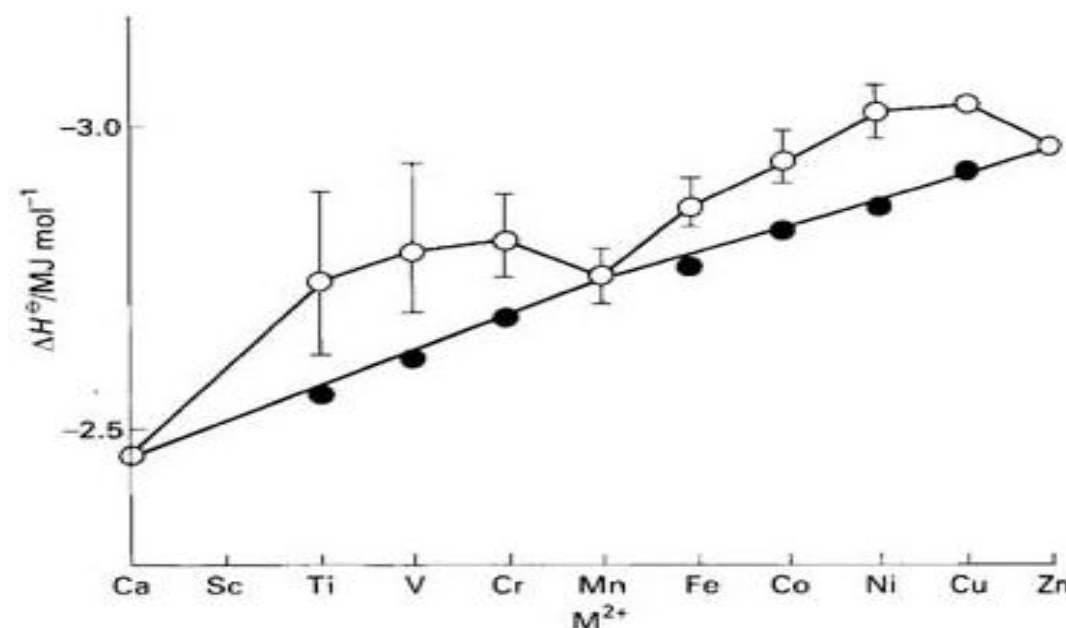


CRYSTAL FIELD THEORY in explaining variation of Hydration Energy



Zero CFSE cases (Spherically symmetric field cases) are d^0 , d^5 (weak) and d^{10} i.e. Ca^{2+} , Mn^{2+} , and Zn^{2+}

All other ions have additional stability which is CFSE



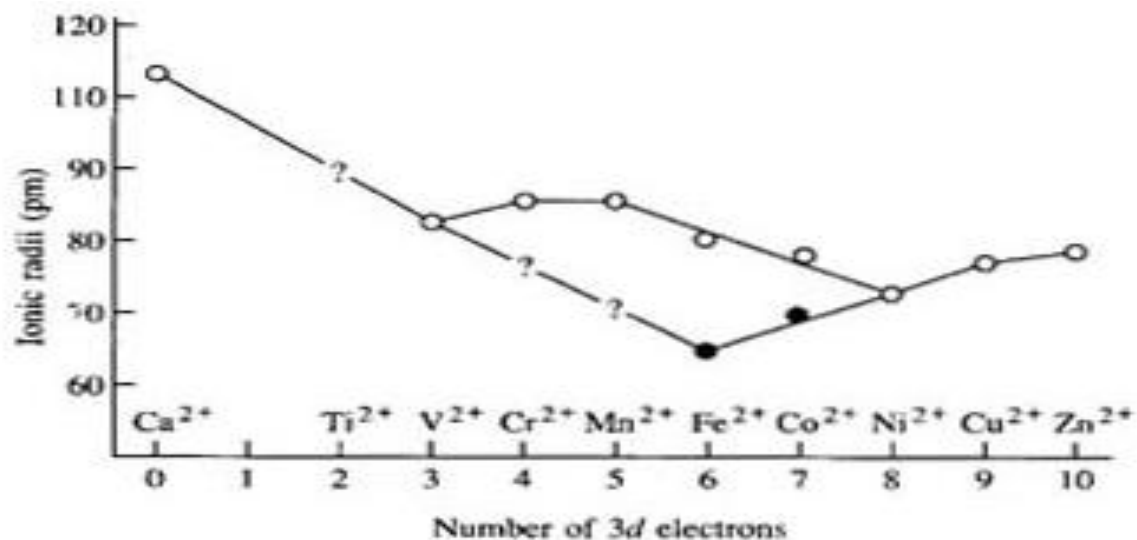
Crystal Field Theory: ionic radii



CRYSTAL FIELD THEORY in explaining variation of Ionic Radii of M^{2+} ions in Octahedral environment

- $Ca^{2+} \rightarrow Zn^{2+}$ nuclear charge increases
- Additional electrons are going to the same shell
- d electron shielding is poor
- Therefore the size of the ions should decrease smoothly
- However, as seen in the following graph the radius change is not smooth

Crystal Field Theory: ionic radii



Ionic radii of the dihalides of the 1st transition series

Dark circles represents low spin anions

t_{2g} electrons : **not oriented** in the direction of metal-ligand bonds. Less repulsion between the ligand and metal d electrons; **closer bonding and the ionic radius decreases.**

V²⁺ → d³ → t_{2g}³ ; nuclear charge is increased, but the additional electron goes to t_{2g} only; hence radius further decreases.

Explanation



$\text{Cr}^{2+} \rightarrow d^4 \rightarrow t_{2g}^3 e_g^1$ (weak field); The fourth electron is now placed in an orbital directly in M-L bond; repulsion and ionic radius increases

$\text{Mn}^{2+} \rightarrow d^5 \rightarrow t_{2g}^3 e_g^2$; one more electron in e_g ; hence radius further increases

Similarly for Fe^{2+} , Co^{2+} , Ni^{2+} (d^6 , d^7 , d^8) the additional electrons go to t_{2g} orbitals and hence the radius decreases

For Cu^{2+} and Zn^{2+} the 9th and 10th d electrons go to e_g orbital and the radius increases

Crystal structure of spinels



Explanation of Crystal Structure of Spinel using CFT:

Spinel, AB_2O_4 : A(II); B(III); O^{2-}

Structure: Cubic Close Packed Structure of Anions and the cations occupy the empty sites.

No. of Tetrahedral sites: $2N$ (N= no. of anions per unit cell)

No. of Octahedral sites: N

In normal Spinel: $(A^{2+}[B_2^{3+}]O_4^{2-})$

A(II) occupy the tetrahedral sites

B(III) occupy the octahedral sites

Crystal structure of spinels



Crystal Structure of Spinel:

In Inverse Spinel: $(B^{3+}[A^{2+}B^{3+}]O_4^{2-})$

A(II) occupy the Octahedral sites

B(III) occupy the Octahedral and Tetrahedral sites

Compare the structures of $Mn^{2+}Mn_2^{3+}O_4$ and $Fe^{2+}Fe_2^{3+}O_4$

	$Mn^{3+} (d^4)$	$Mn^{2+} (d^5)$	$Fe^{3+} (d^5)$	$Fe^{2+} (d^6)$
CFSE (Octahedral weak field)	$-0.60 \Delta_o$	0	0	$-0.40 \Delta_o$
CFSE (Tetrahedral weak field)	$-0.18 \Delta_o$	0	0	$-0.27 \Delta_o$

Crystal structure of spinels



Identify the preferred spinel structure for NiFe_2O_4

Ni is in +2 oxidation state, d^8 configuration

In tetrahedral void, configuration: $e^4 t_2^4$, $\text{CFSE} = -0.8 \Delta_t$ ($0.4 \Delta_o$)

In an octahedral void, configuration: $t_{2g}^6 e_g^2$, $\text{CFSE} = -1.2 \Delta_o$

Fe is in +3 oxidation state, d^5 system

In tetrahedral void, Configuration: $e^2 t_2^3$, $\text{CFSE} = 0$

In octahedral void, configuration: $t_{2g}^3 e_g^2$, $\text{CFSE} = 0$

Hence, Ni^{2+} prefer to stay in the octahedral void

Therefore, **inverse spinel structure, $\text{Fe}^{\text{III}}[\text{Ni}^{\text{II}}\text{Fe}^{\text{III}}]\text{O}_4$**

Discussed topics.....



- ✓ Factors affecting the magnitude of Δ_o
- ✓ Tetrahedral complexes
- ✓ Crystal field stabilization energy in Octahedral geometry
- ✓ CFSE calculation of tetrahedral complexes
- ✓ Uses of CFSE: stabilization of oxidation state, lattice energy, hydration energy, and ionic radii
- ✓ Crystal structure of spinel

CFSE comparison (supporting slide)



When the CFSE is comparable both in octahedral and tetrahedral geometries.

d^0, d^5, d^{10} no CFSE in oct. and tet.

$$\begin{aligned} d^1 \text{ and } d^6 \text{ (weak) has Oct and Tet CFSE difference} \\ = -0.4 \Delta_o - (-0.6 \Delta_t) = (-0.4 - (-0.6 \times (4/9))) \Delta_o \\ = (-0.4 - (-0.27)) \Delta_o = -0.13 \Delta_o \end{aligned}$$

Similarly for d^2 and d^7 cases the difference is
Only $-0.17 \Delta_o$

Nature of metal cation (supporting slide)



Same charge on the cation of different metal but different d-electrons (metals within a same period): (Exceptional, trend is not followed properly, many factors are responsible)

$$\Delta_o \text{ for } [\text{Co}(\text{H}_2\text{O})_6]^{2+} = 9300 \text{ cm}^{-1}$$

$$\Delta_o \text{ for } [\text{Ni}(\text{H}_2\text{O})_6]^{2+} = 8500 \text{ cm}^{-1}$$

Dq values in some octahedral complexes

M ⁿ⁺ /Ligands	6F ⁻ (Dq)	6Cl ⁻ (Dq)	6H ₂ O (Dq)	6NH ₃ (Dq)
Mn ²⁺	780	750	850	--
Co ²⁺	---	690	920	1020
Ni ²⁺	730	750	850	1080