

CHEMISTRY -THEORY

(CYI 101)

Inorganic Chemistry

Instructor: Dr. R P John

Department of Chemistry & Chemical Biology

Evaluation and Study Material

Examination/Class tests/others

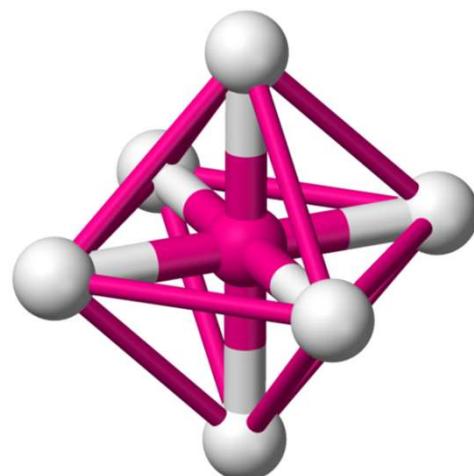
- See Academic Calendar
- Will be informed time to time

Course Material

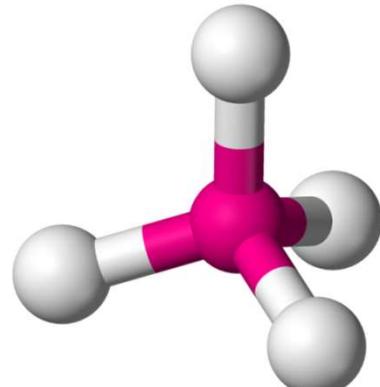
- What the instructor teaches!
- Books: *Inorganic chemistry: Huheey, Keiter and Keiter*
Inorganic Chemistry: Housecroft and Sharpe
Shriver Atkin's Inorganic Chemistry: Atkins, Overton, Rourke, Weller and Armstrong

Crystal Field Theory

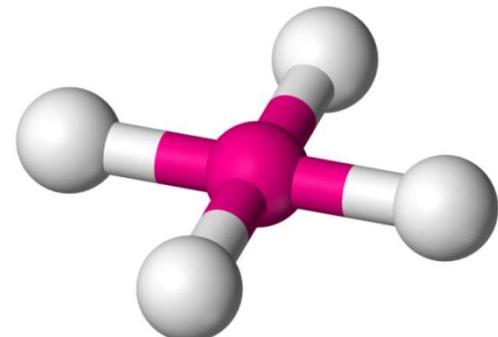
1. This is an electrostatic model for transition metal complexes.
2. Ligands are considered as point charge.
3. The CFT does not provide for electrons to enter the metal orbitals, i.e. it does not consider any orbital overlap.
4. Predicts the pattern of splitting of d-orbitals.
5. Used to rationalize spectroscopic and magnetic properties.



Octahedral complex (O_h)

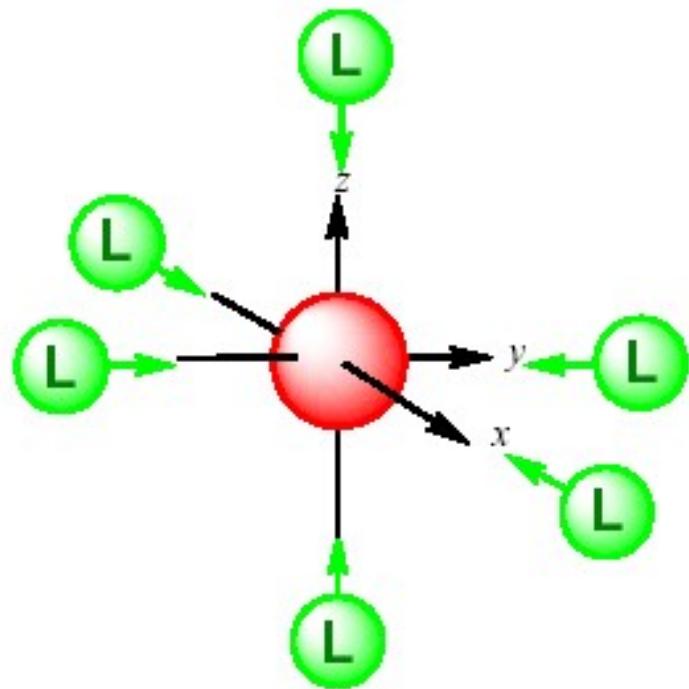


Tetrahedral complex (T_d)



Square planer complex (Sp)

Octahedral Field



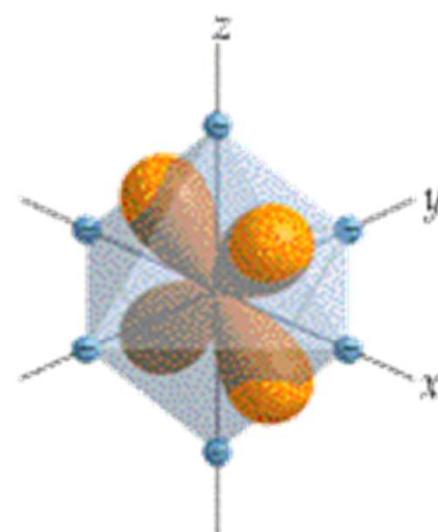
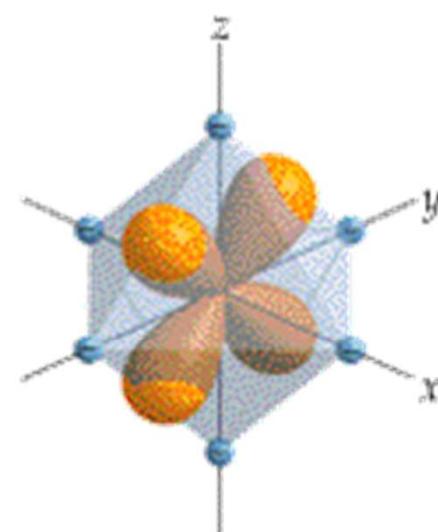
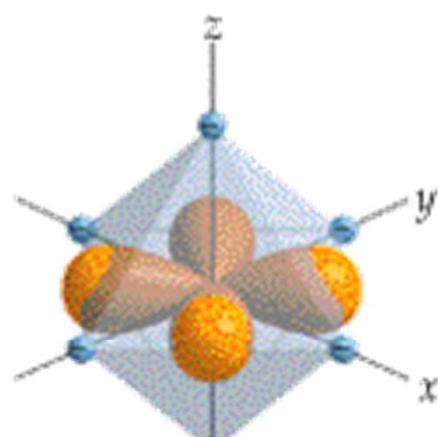
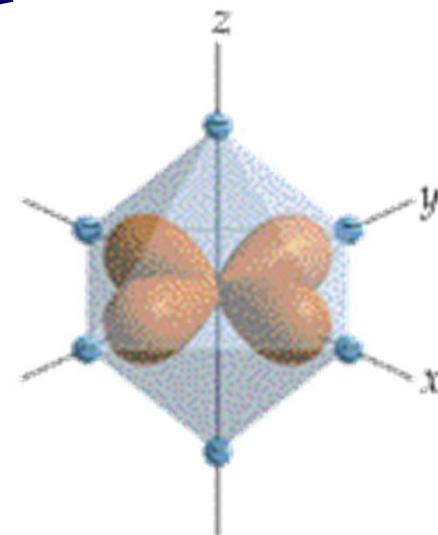
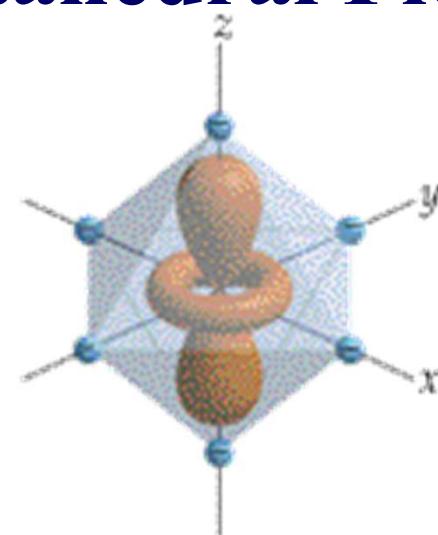
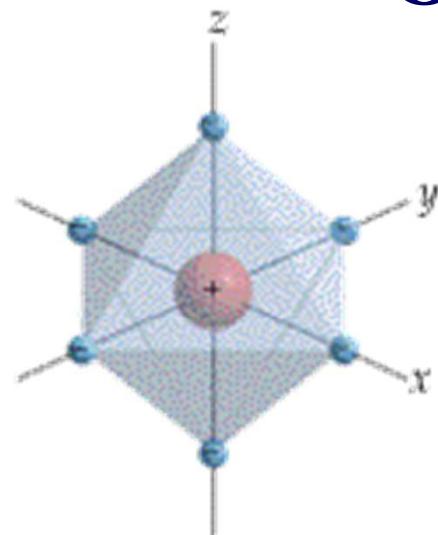
- Six point negative charges (Ligands) representing the ligands are placed in an octahedral array around the central metal ion.
- The ligand and orbitals lie on the same axes.
- These charges interact strongly with the central metal ion.

1. The stability of the complex in large part from this attractive interaction between opposite charges.

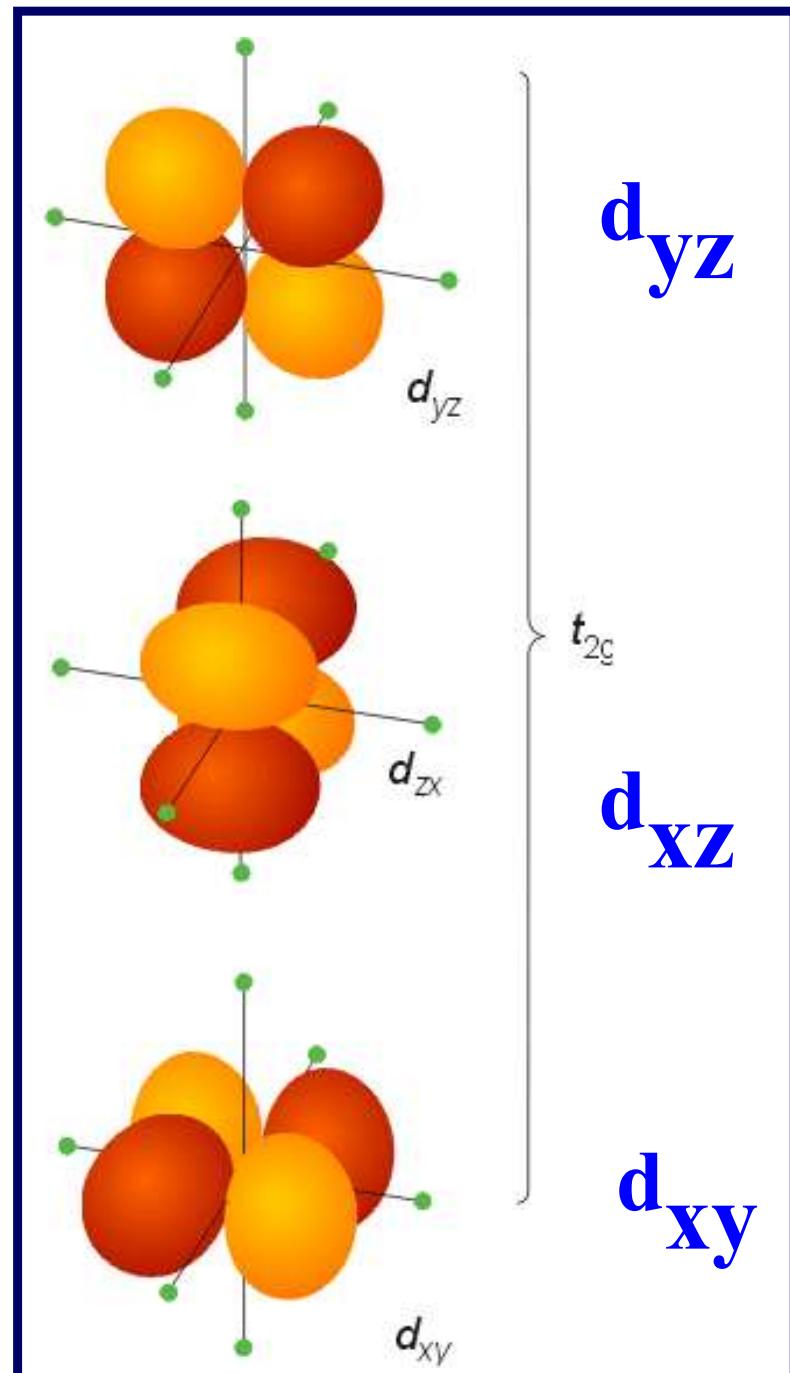
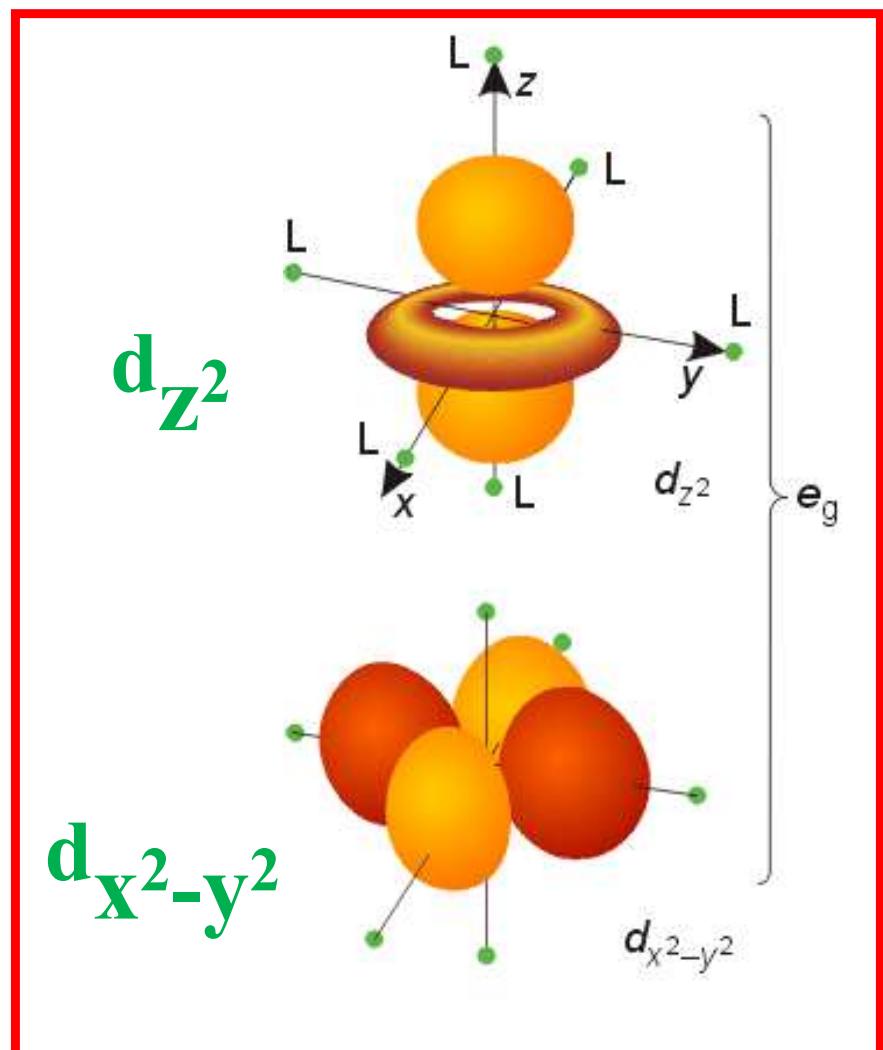
2. There is a much smaller but very important secondary effect arising from the fact that electrons in different d orbitals interact with the ligands to different extents.

❖ Although this differential interaction is little more than about 10 per cent of the overall metal-ligand interaction energy, it has major consequences for the properties of the complex.

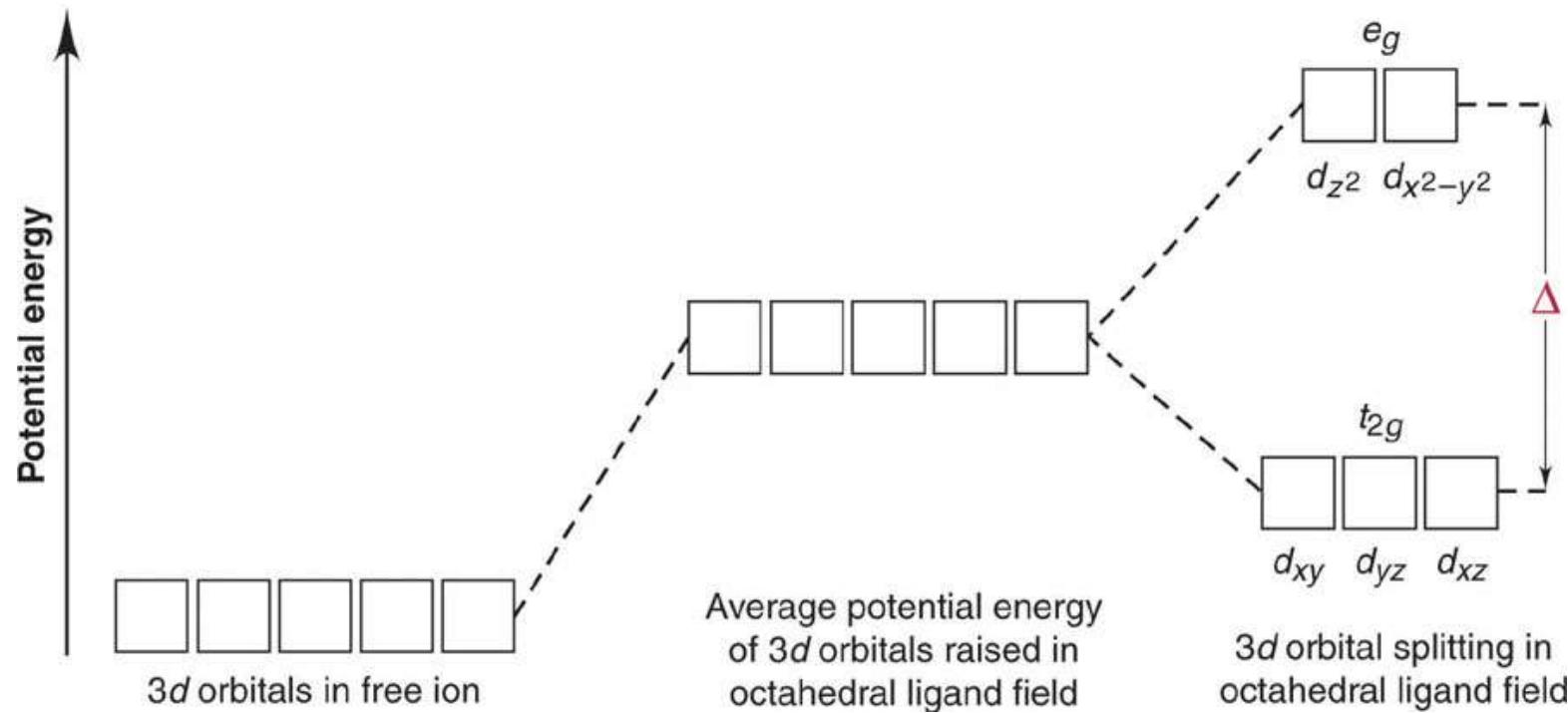
Octahedral Field



Octahedral Field

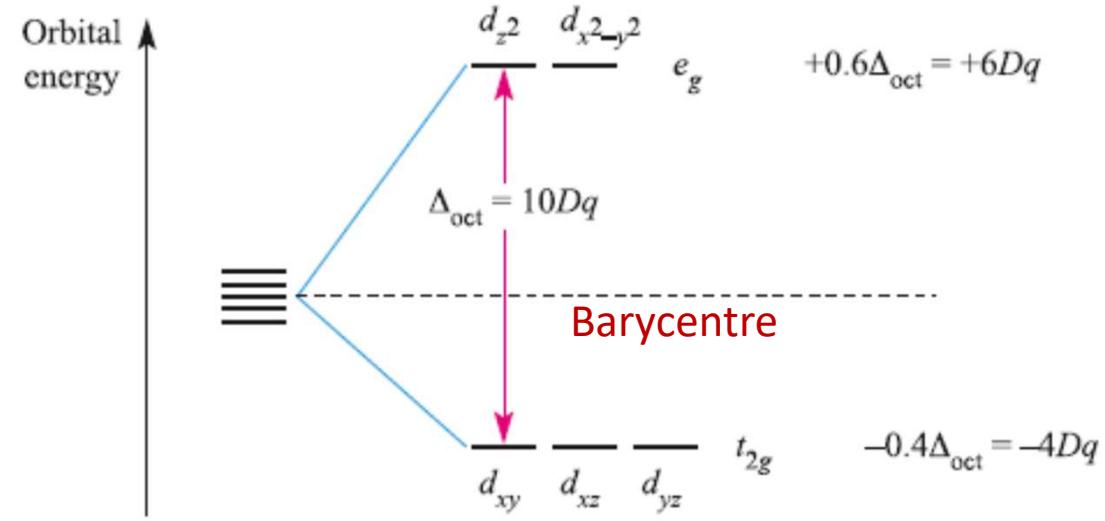
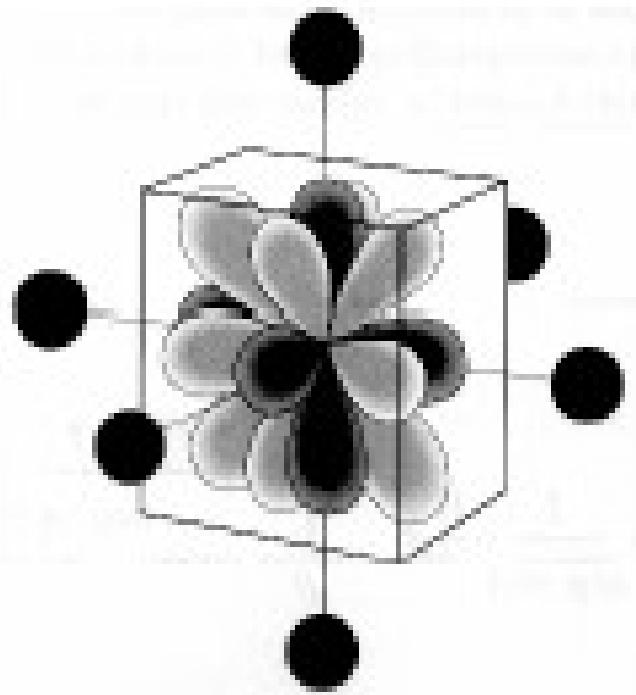


Splitting of *d*-orbital energies in an octahedral field of ligands.



The *d* orbitals split into two groups. The difference in energy between these groups is called the ***crystal field splitting energy***, symbol Δ_o .

Octahedral Field



- The overall stabilization of the t_{2g} orbitals equals the overall destabilization of the e_g set.
- Thus, the two orbitals in the e_g set are raised by $0.6 \Delta_o$ with respect to the **Barycentre** while the three in the t_{2g} set are lowered by $0.4 \Delta_o$.
- The magnitude of Δ_o is determined by the strength of the crystal field, the two extremes being called weak field and strong field.

$$\Delta_o \text{ (Weak field)} < \Delta_o \text{ (Strong field)}$$

Factors influencing the Magnitude of Δ_o for Octahedral complexes

1. The nature of metal cation:

i) Oxidation state of the metal ion

$[\text{Ru}(\text{H}_2\text{O})_6]^{3+}$	28600 cm^{-1}
$[\text{Ru}(\text{H}_2\text{O})_6]^{2+}$	19800 cm^{-1}

ii) Different charges on the cation of different metals

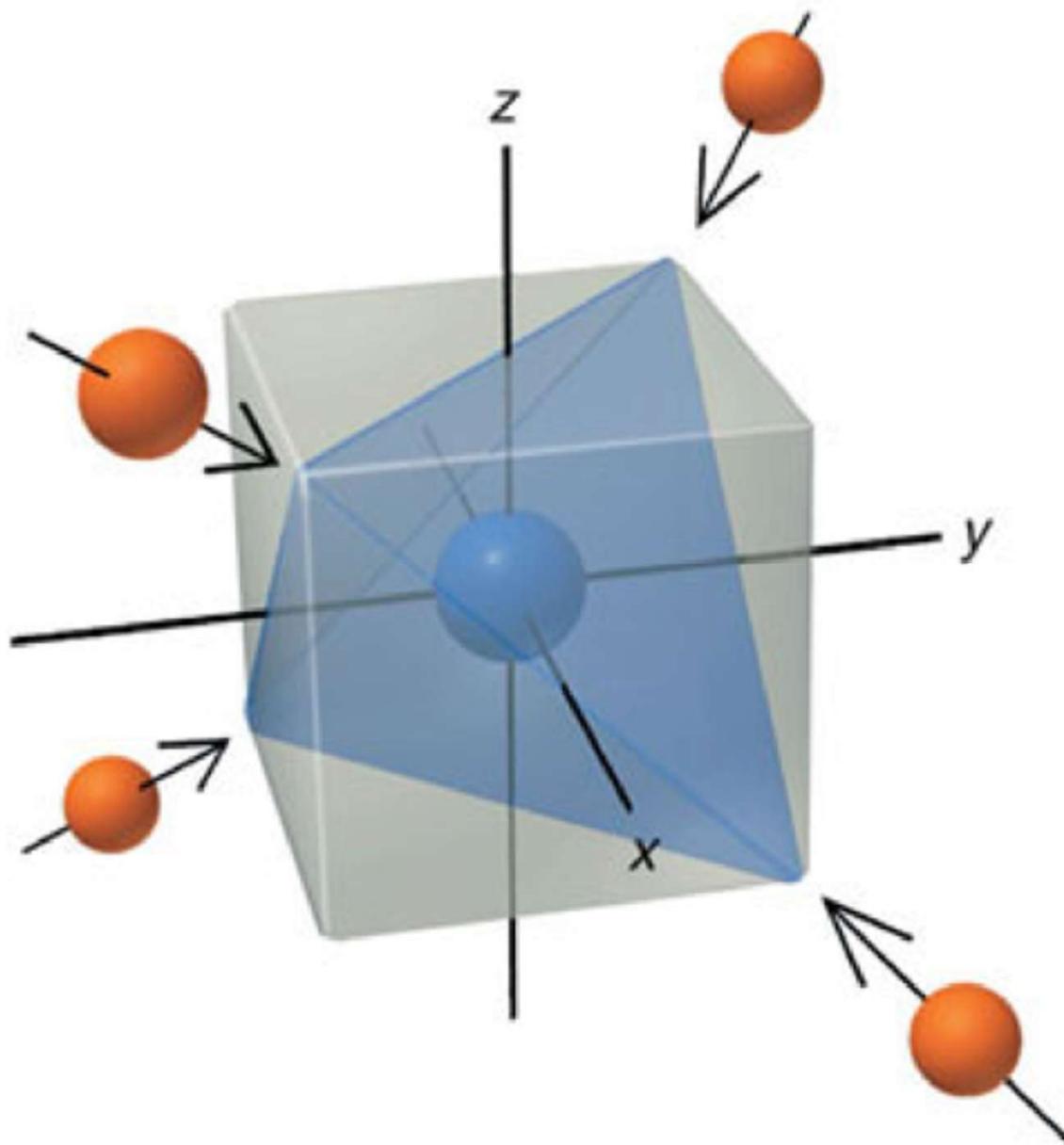
$[\text{V}(\text{H}_2\text{O})_6]^{2+}$	12400 cm^{-1}	$3d^3$
$[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$	17400 cm^{-1}	$3d^3$

iii) Quantum number (n) of the d- orbitals of the central metal ion.

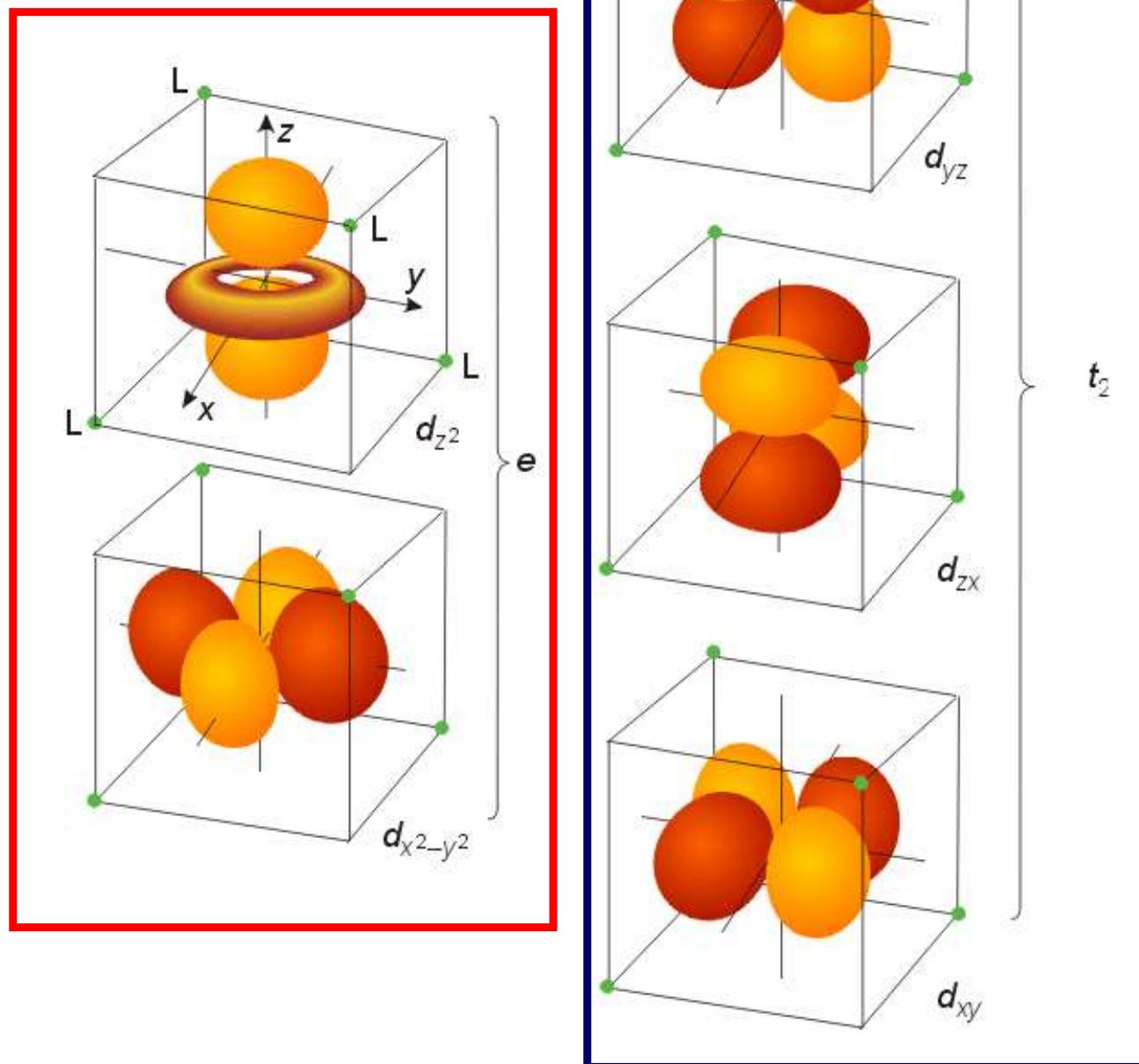
$[\text{Co}(\text{NH}_3)_6]^{3+}$	23000 cm^{-1}	$3d^6$
$[\text{Rh}(\text{NH}_3)_6]^{3+}$	34000 cm^{-1}	$4d^6$
$[\text{Ir}(\text{NH}_3)_6]^{3+}$	41000 cm^{-1}	$5d^6$

- Δ_o increases about 30% to 50% from $3d^n$ to $4d^n$ and from $4d^n$ to $5d^n$.
- Increase down a group reflects the larger size of the 4d and 5d orbitals compared to compact 3d orbitals and the consequent stronger interactions with the ligands.

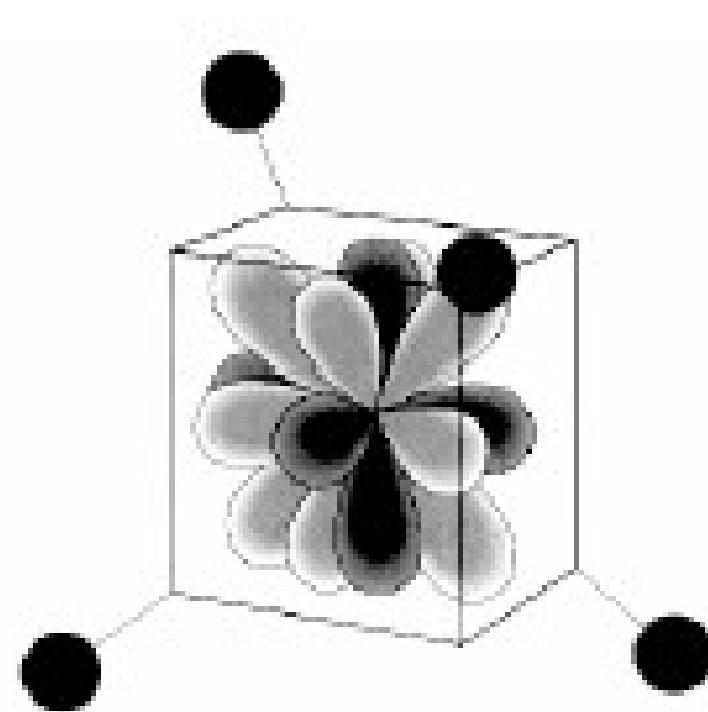
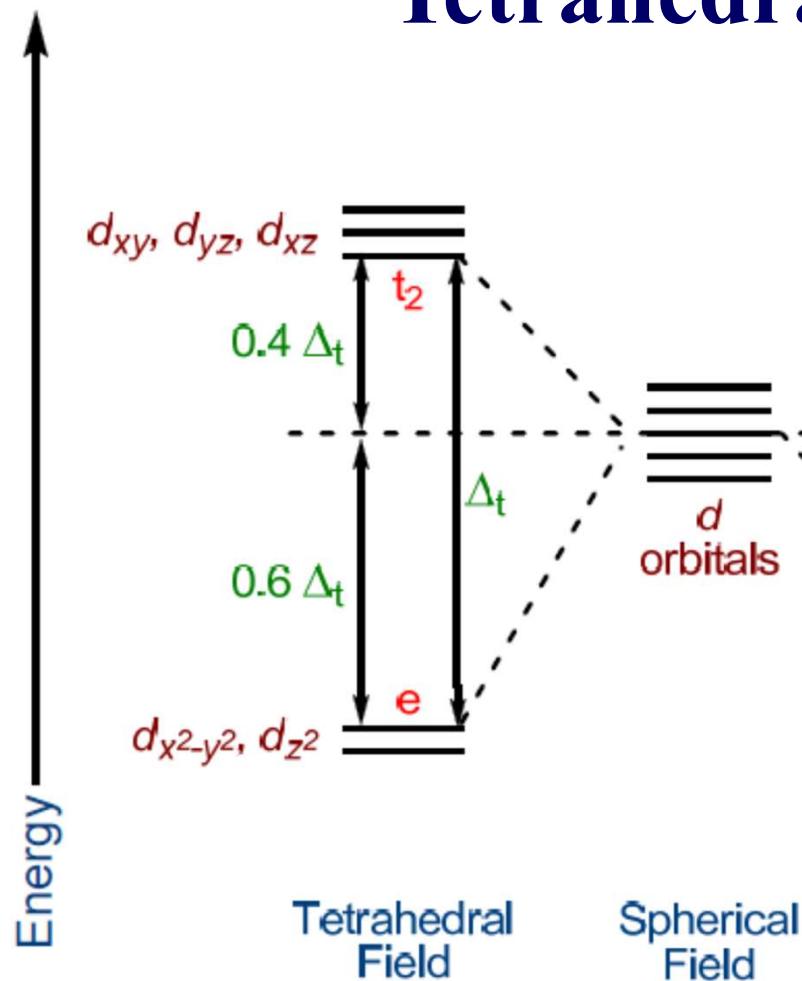
Tetrahedral Field



Tetrahedral Field



Tetrahedral Field



$$\Delta_t < \Delta_o$$

$$\Delta_t = 0.45 \Delta_o$$

For the same metal and ligands and the same internuclear distances

Strong and weak ligands: Spectrochemical Series

Weak Field

$\text{I}^- < \text{Br}^- < \text{S}^{2-} < \text{SCN}^- < \text{Cl}^- < \text{NO}_3^- < \text{F}^- < \text{C}_2\text{O}_4^{2-} <$
 $\text{H}_2\text{O} < \text{NCS}^- < \text{CH}_3\text{CN} < \text{NH}_3 < \text{en} < \text{bipy} < \text{phen} < \text{NO}_2^-$
 $< \text{PPh}_3 < \text{CN}^- < \text{CO}$

Strong Field

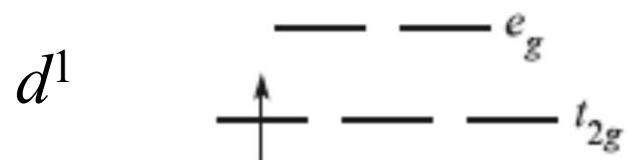
Spectrochemical series is the arrangement of ligands in the increasing order of their ability to split d –orbitals in a crystal/ligand field.

Crystal Field Stabilization Energy (CFSE)

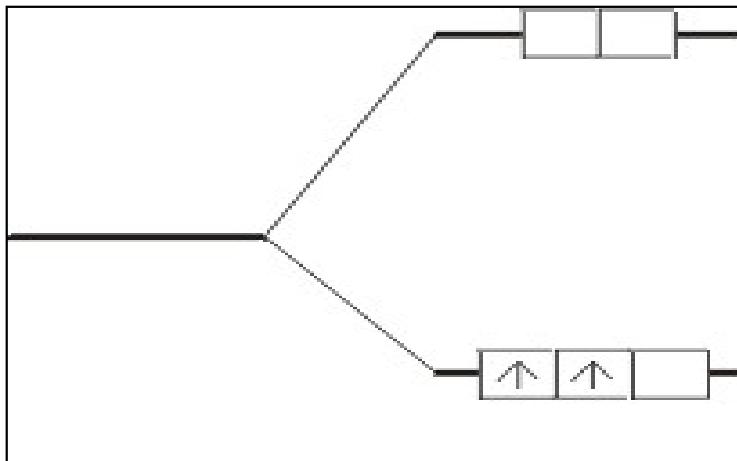
- In Octahedral field, configuration is: $t_{2g}^x e_g^y$
- Net energy of the configuration relative to the average energy of the orbitals is:

$$= (-0.4x + 0.6y)\Delta_O$$

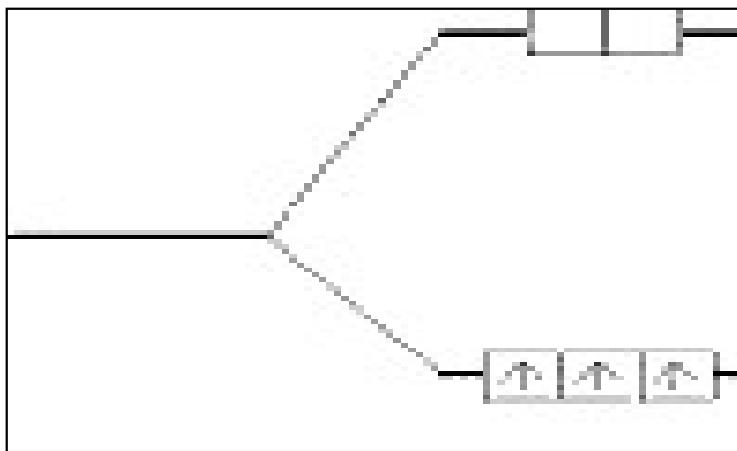
$$\Delta_O = 10 \text{ Dq}$$



Crystal Field Stabilization Energy (CFSE)

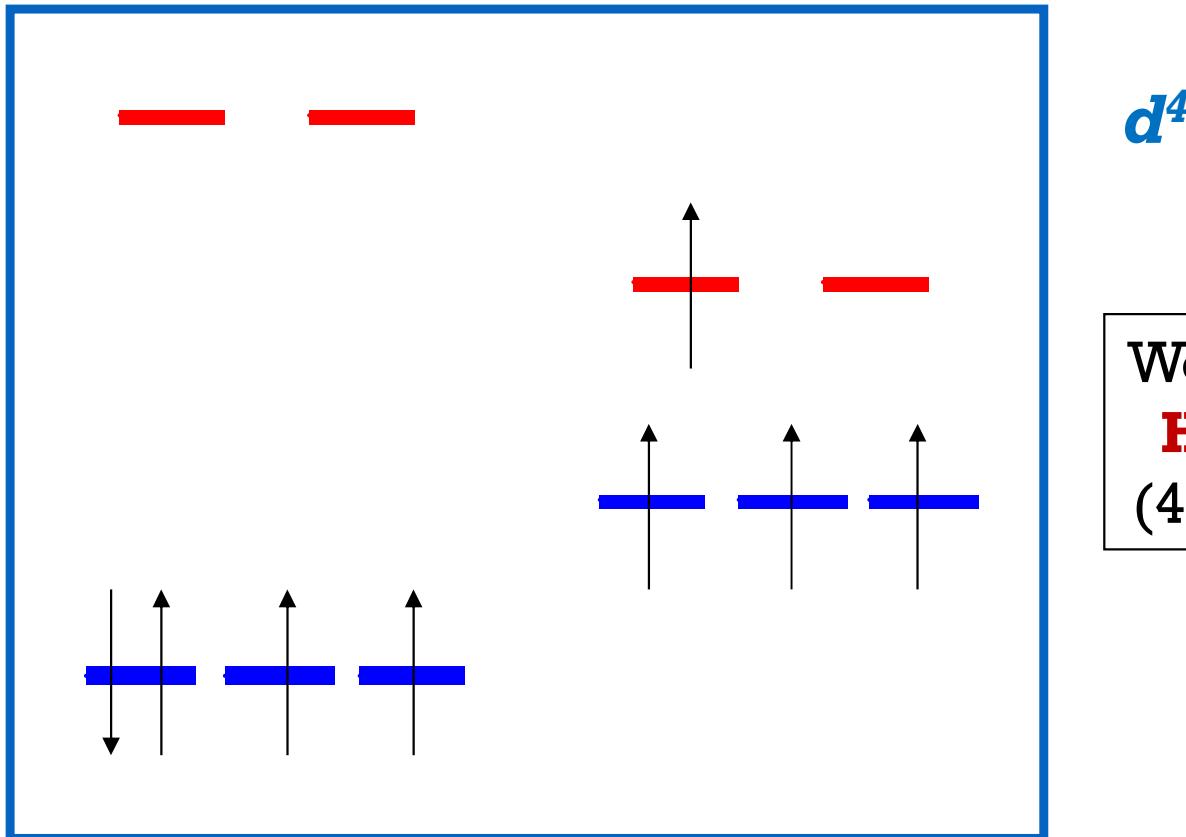


d^2 $\text{Ti}^{2+}, \text{V}^{3+}$



d^3 $\text{Cr}^{3+}, \text{Mn}^{4+}, \text{V}^{2+}$

When the **4th electron** is assigned it will either go into **the higher energy e_g orbital** at an energy cost of Δ_o or be **paired** at an energy cost of **P**, the pairing energy.



Strong field =
Low spin
(2 unpaired)

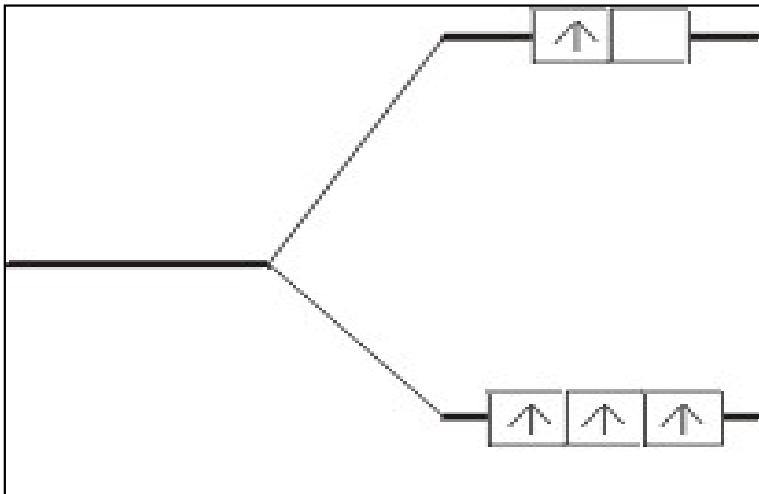
d^4

Weak field =
High spin
(4 unpaired)

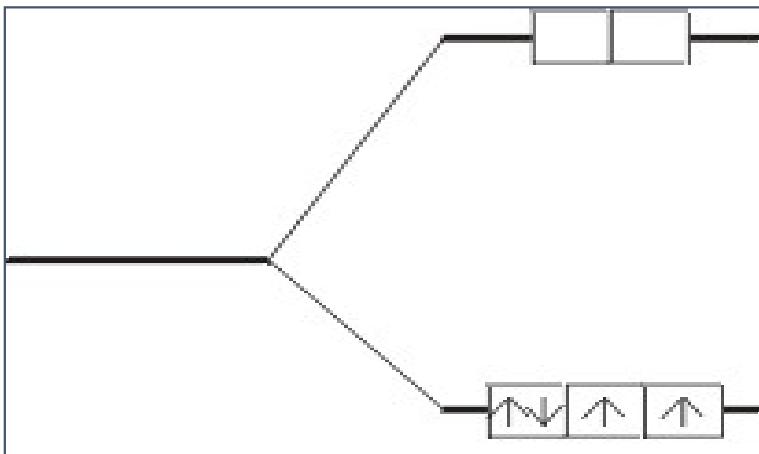
$$P < \Delta_o$$

$$P > \Delta_o$$

Crystal Field Stabilization Energy (CFSE)



Weak field d^4



Strong field d^4



Weak Field Complex

the total spin (S) is $4 \times \frac{1}{2} = 2$

High Spin Complex

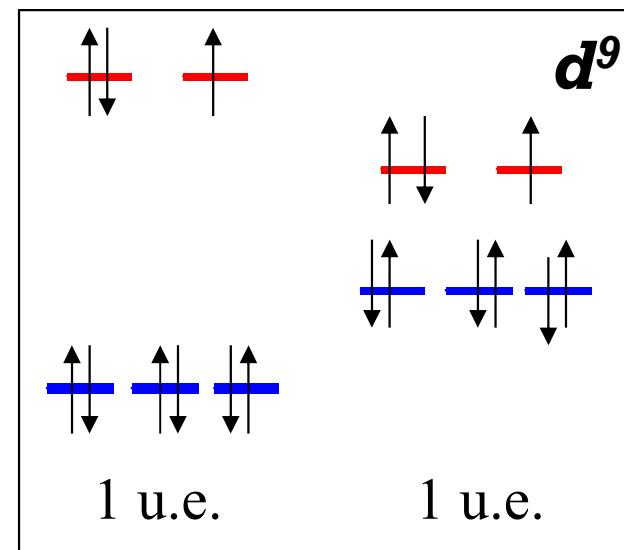
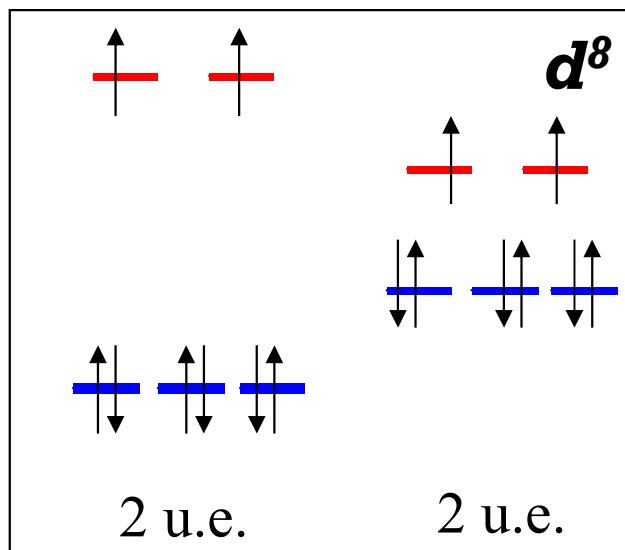
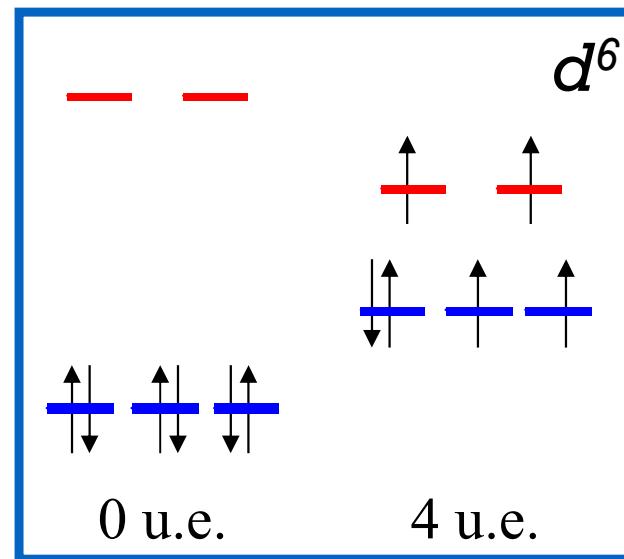
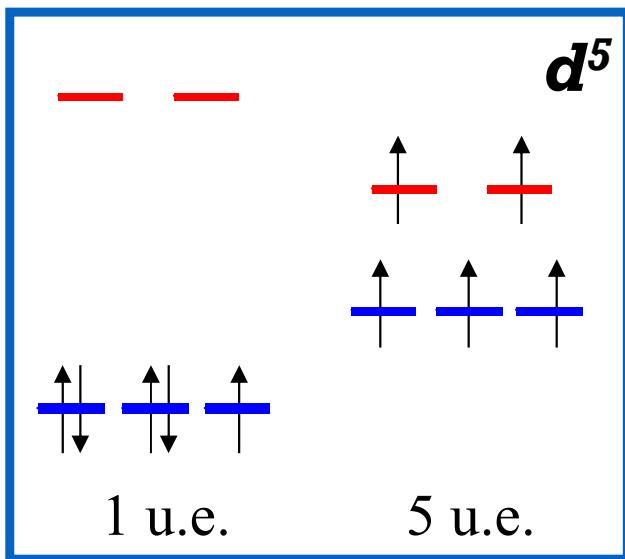


Strong field Complex

total spin (S) is $2 \times \frac{1}{2} = 1$

Low Spin Complex

Placing electrons in d orbitals



What is the CFSE of $[\text{Fe}(\text{CN})_6]^{3-}$?

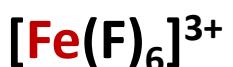
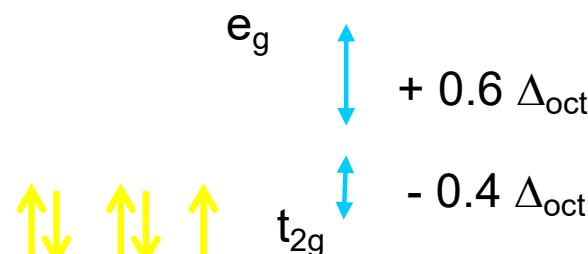
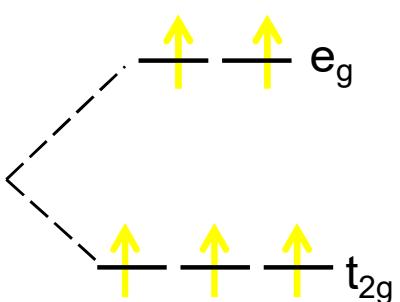
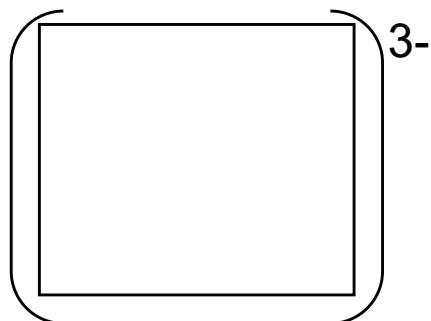
C.N. = 6 ∴ O_h

Fe(III) ∴ d^5

H.S.

L.S.

$\text{CN}^- = \text{S.F.L.}$



$$\text{CFSE} = 5x - 0.4 \Delta_\text{oct} + 2P = -2.0 \Delta_\text{oct} + 2P$$

If the CFSE of $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ is $-0.8 \Delta_\text{oct}$, what spin state is it in?

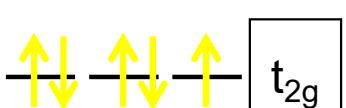
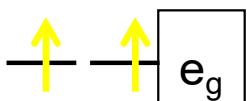
C.N. = 6 ∴ O_h

Co(II) ∴ d^7

H.S.

L.S.

$[\text{Co}(\text{CN})_6]^{2+}$



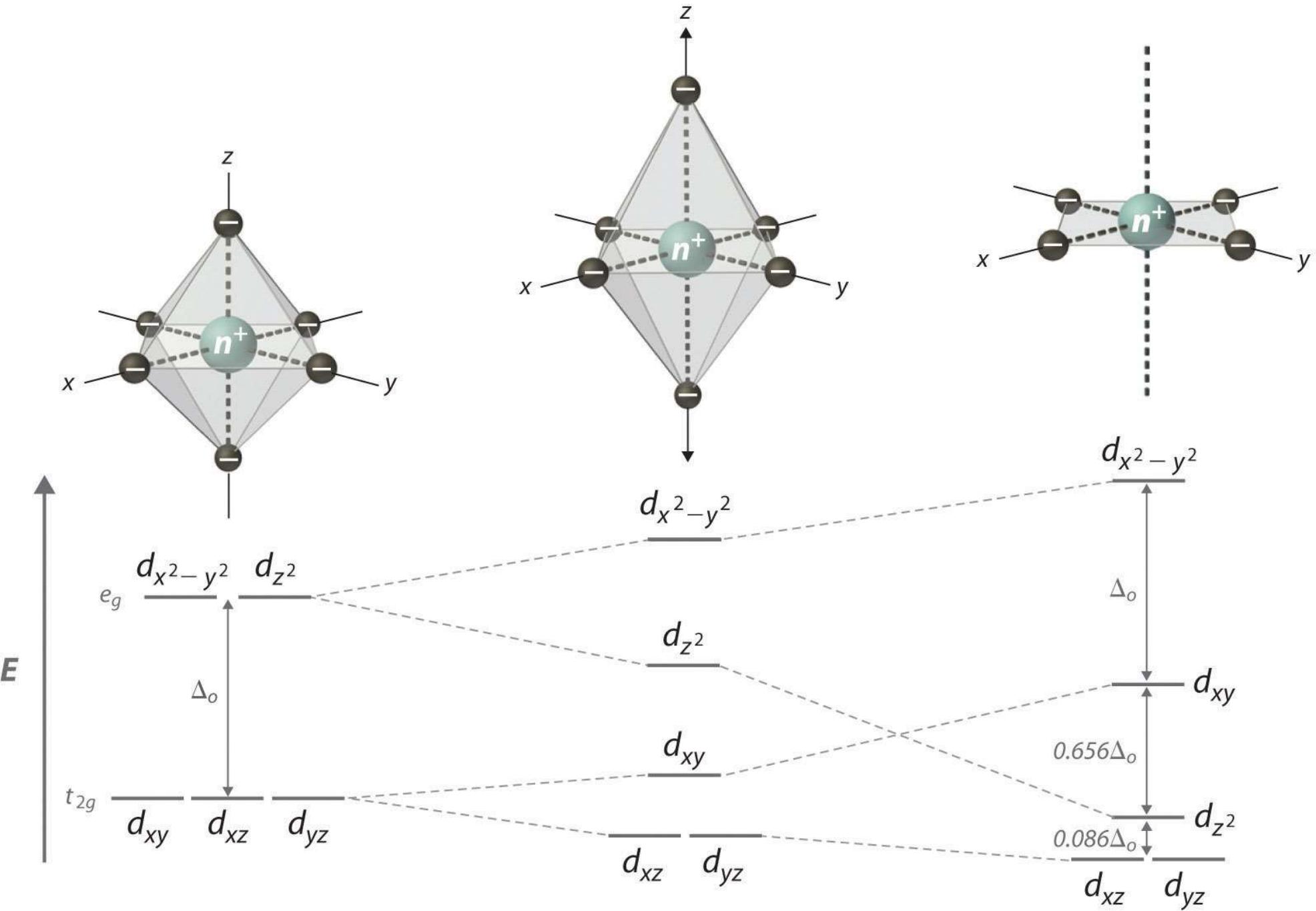
$$\begin{aligned} \text{CFSE} &= (5x - 0.4 \Delta_\text{oct}) \\ &+ (2 \times 0.6 \Delta_\text{oct}) = -0.8 \Delta_\text{oct} \end{aligned}$$

$$\begin{aligned} \text{CFSE} &= (6x - 0.4 \Delta_\text{oct}) \\ &+ (0.6 \Delta_\text{oct}) + P = -1.8 \Delta_\text{oct} + P \end{aligned}$$

Crystal Field Stabilization Energy (CFSE)

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

Distortions of Octahedral Complexes

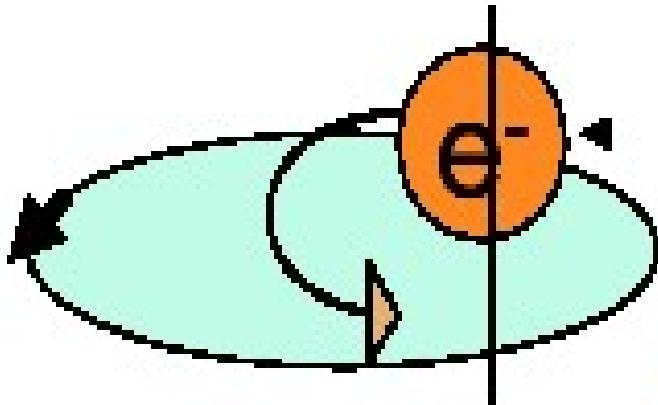


Magnetism

Each electron has a magnetic moment owing to its:

spin angular momentum

orbital angular momentum



Orbital motion of e generates current and magnetic field

Spin motion of e about its own Axis also generates a magnetic field

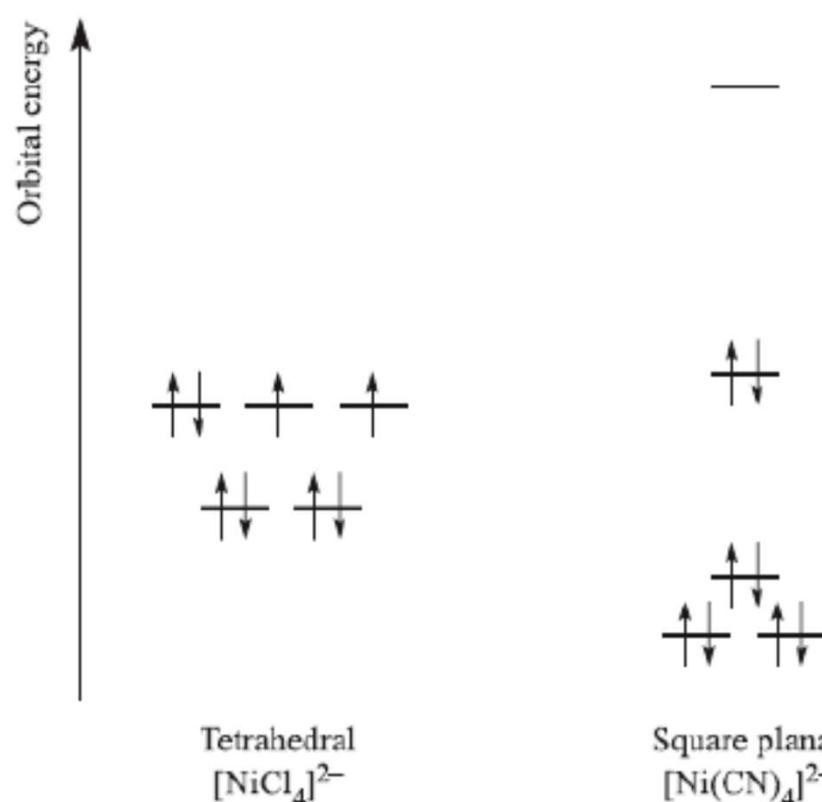
n = no. of unpaired electrons

$$\mu = \{n(n+2)\}^{1/2} \mu_B$$

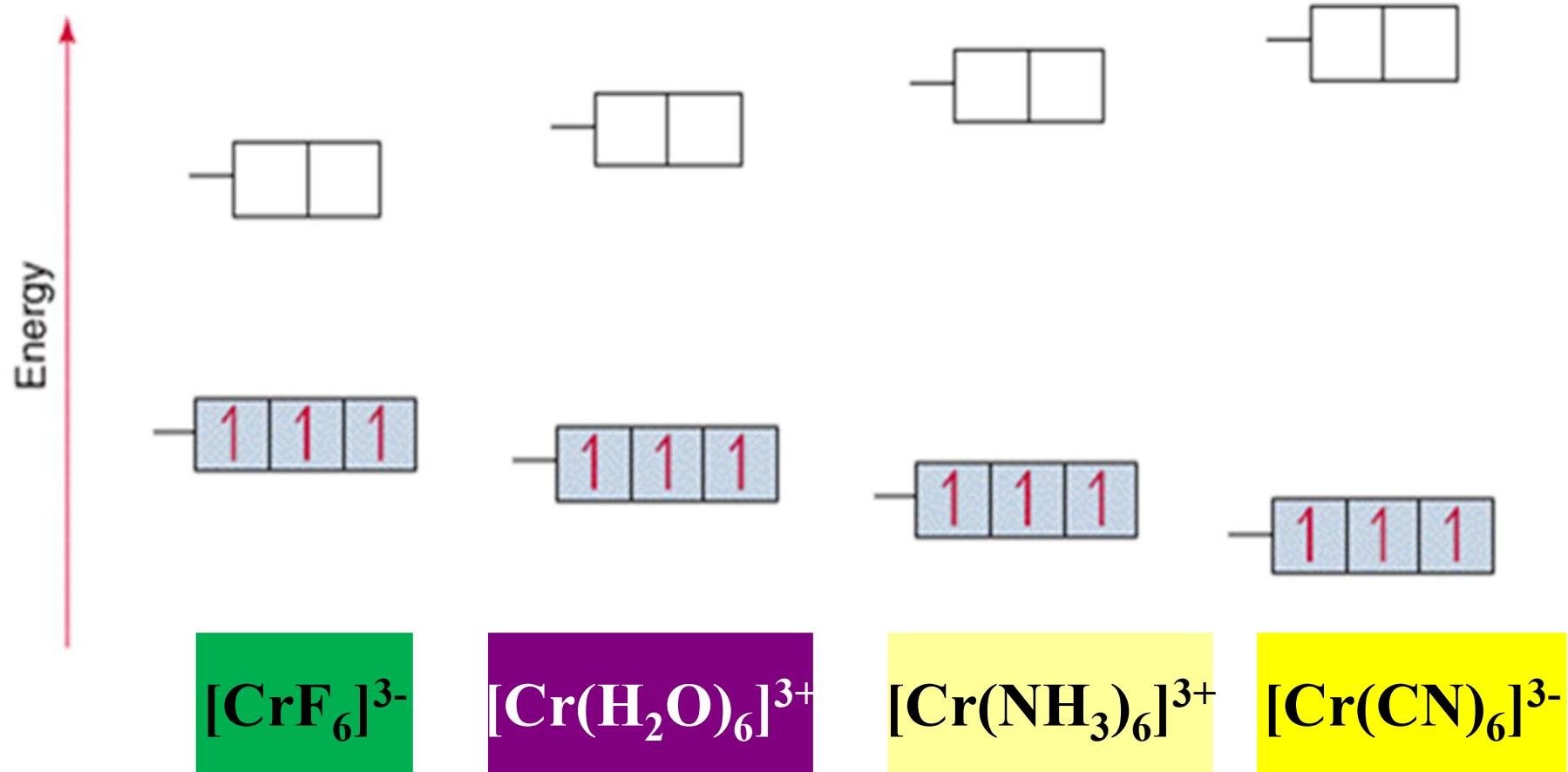
Ion	n	S	μ/μ_B Calculated	Experimental
Ti ³⁺	1	1/2	1.73	1.7 – 1.8
V ³⁺	2	1	2.83	2.7 – 2.9
Cr ³⁺	3	3/2	3.87	3.8
Mn ³⁺	4	2	4.90	4.8 – 4.9
Mn ²⁺	5	5/2	5.92	5.9 - 6.3

**Similar Calculation can be done
for Low-spin Complex**

The d^8 complexes $[\text{Ni}(\text{CN})_4]^{2-}$ and $[\text{NiCl}_4]^{2-}$ are square planar and tetrahedral respectively. Will these complexes be paramagnetic or diamagnetic?



Thus, $[\text{NiCl}_4]^{2-}$ is paramagnetic while $[\text{Ni}(\text{CN})_4]^{2-}$ is diamagnetic.



As Cr^{3+} goes from being attached to a **weak field ligand** to a **strong field ligand**, Δ **increases** and the **color of the complex changes from green to yellow**.

Home work Assignment 1

1. What are the limitations of crystal field theory?
2. Show the filling of electrons in the d-orbitals and calculate the spin only magnetic moments of a) $[\text{MnCl}_6]^{3-}$, b) $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$, c) $[\text{NiCN}_4]^{2-}$ (Sq.planar), d) $[\text{Ni}(\text{CN}_6)]^{3-}$
3. The magnetic moment of a certain octahedral Co(II) complex is $3.87 \mu_B$. What is its electron configuration?
4. The crystal field splitting energy(Δ) for $[\text{CoCl}_6]^{4-}$ is 18000 cm^{-1} . What will be the Δ for $[\text{CoCl}_4]^{2-}$?
5. Predict the spin only magnetic moment of the octahedral complexes formed by the reaction of Mn^{3+} with H_2O and CN^- . Given: the Pairing energy (P) for $\text{Mn}^{3+} = 28,000 \text{ cm}^{-1}$, $\Delta_o(\text{H}_2\text{O}) = 21000 \text{ cm}^{-1}$, $\Delta_o(\text{CN}^-) = 38000 \text{ cm}^{-1}$.
6. Calculate the Crystal field stabilization energy for the octahedral and tetrahedral complexes formed. $[\text{MnCl}_4]^{2-}$, $[\text{Fe}(\text{SCN})_4]^-$, $[\text{Co}(\text{NH}_3)_6]^{2+}$, $[\text{Ru}(\text{NH}_3)_6]^{2+}$, $[\text{FeF}_6]^{4-}$. The Pairing energy for the ions are: $\text{Mn}^{2+} = 25500 \text{ cm}^{-1}$, $\text{Fe}^{3+} = 30,000 \text{ cm}^{-1}$, $\text{Co}^{2+} = 23,800 \text{ cm}^{-1}$, $\text{Ru}^{2+} = 33,000 \text{ cm}^{-1}$, $\text{Fe}^{2+} = 18,200 \text{ cm}^{-1}$, Dq for ligands: $\text{Cl} = 640 \text{ cm}^{-1}$, $\text{NH}_3 = 1560 \text{ cm}^{-1}$, $\text{F}^- = 850 \text{ cm}^{-1}$, $\text{SCN}^- = 550 \text{ cm}^{-1}$.

Limitations of CFT

Considers Ligand as Point charge/dipole only

Does not take into account of the overlap of ligand and metal orbitals

Consequence

e.g. Fails to explain why CO is stronger ligand than CN⁻ in complexes having metal in low oxidation state

Homework assignment 2

CHEMISTRY -THEORY

(CYI 101)

Inorganic Chemistry

Instructor: Dr. R P John

Department of Chemistry & Chemical Biology

Evaluation and Study Material

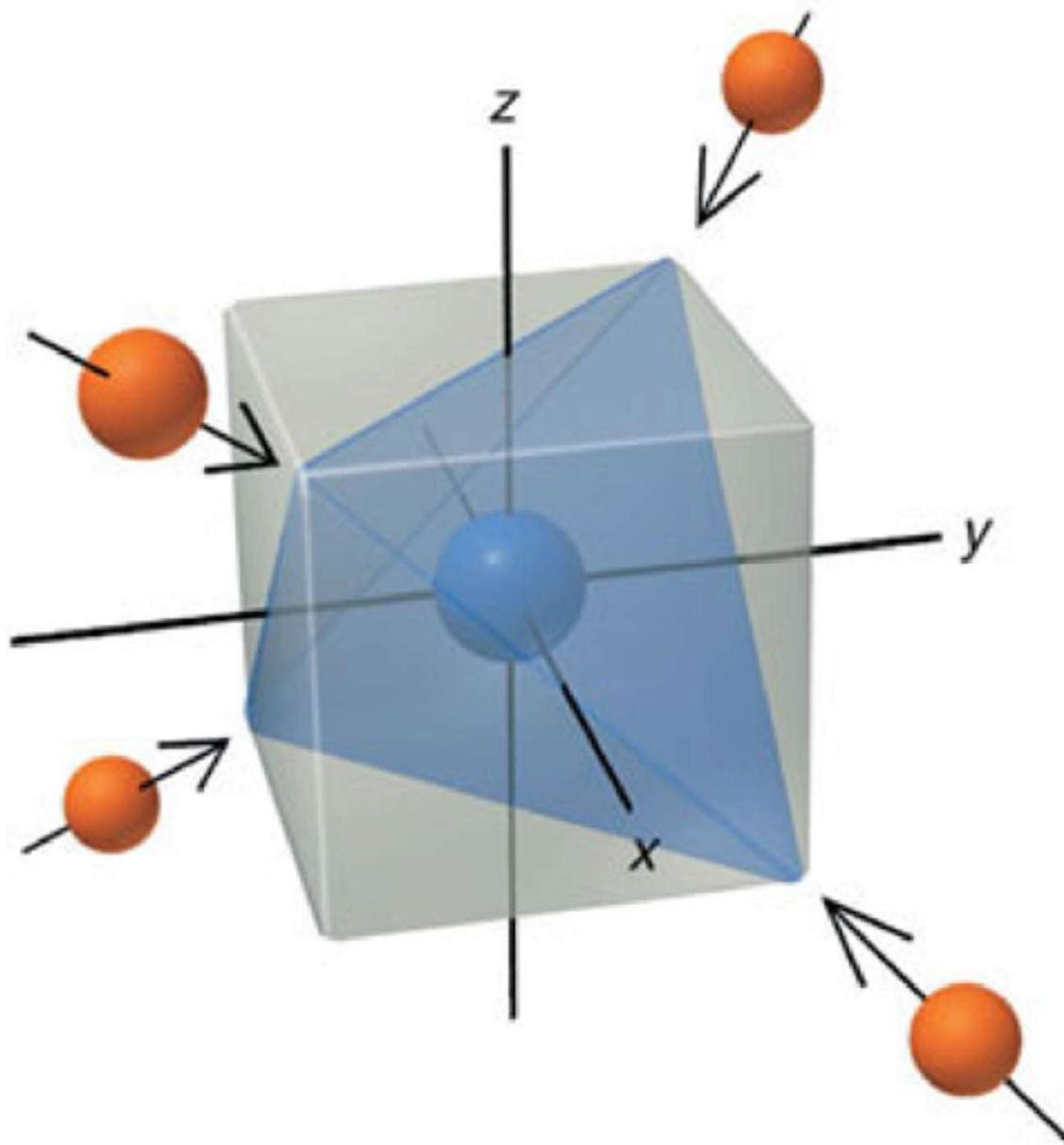
Examination/Class tests/others

- See Academic Calendar
- Will be informed time to time

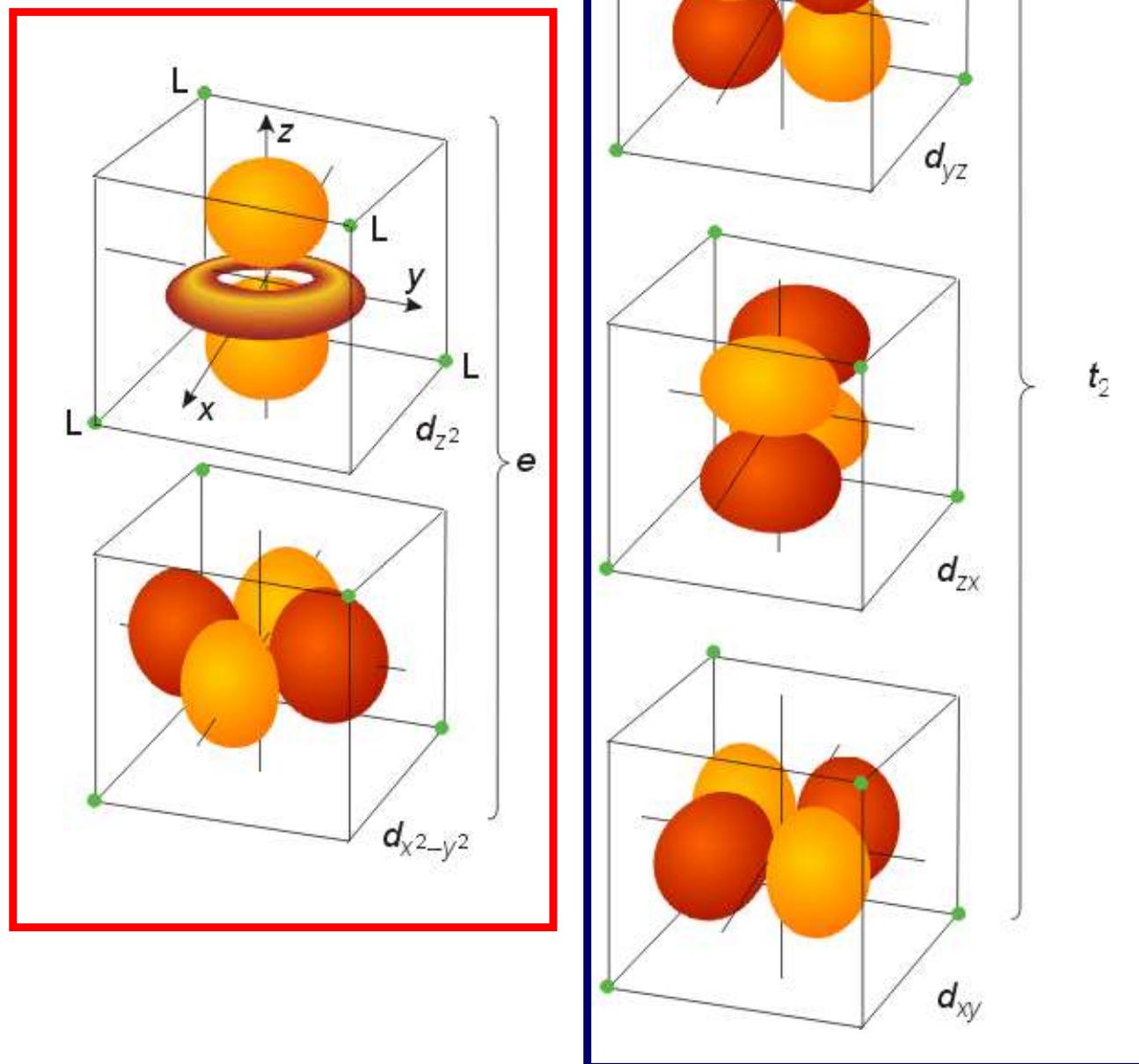
Course Material

- What the instructor teaches and Course materials provided
- **Books:** *Inorganic chemistry: Principles of Structure and reactivity: Huheey, Keiter and Keiter*
Inorganic Chemistry: Housecroft and Sharpe
Inorganic Chemistry: Meissler and Tarr
Shriver Atkin's Inorganic Chemistry- Atkins, Overton, Rourke, Weller and Armstrong

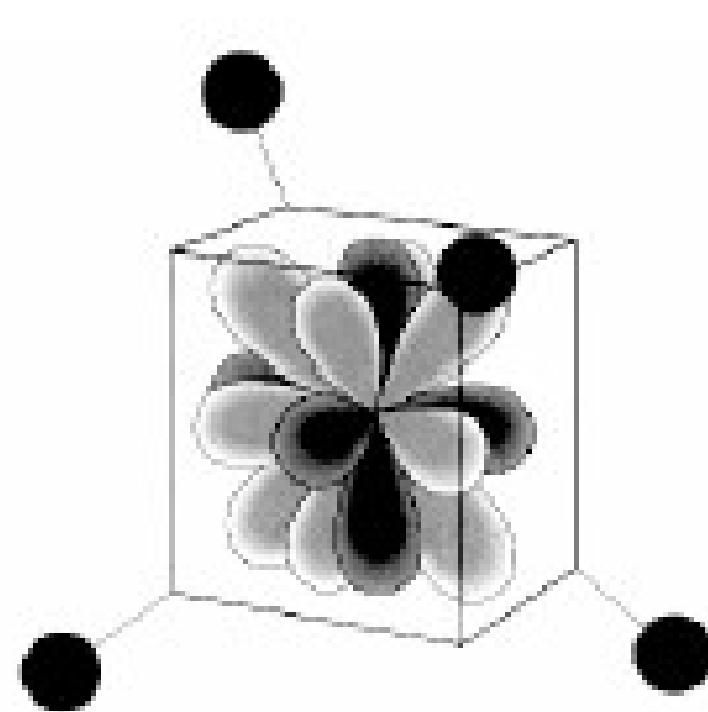
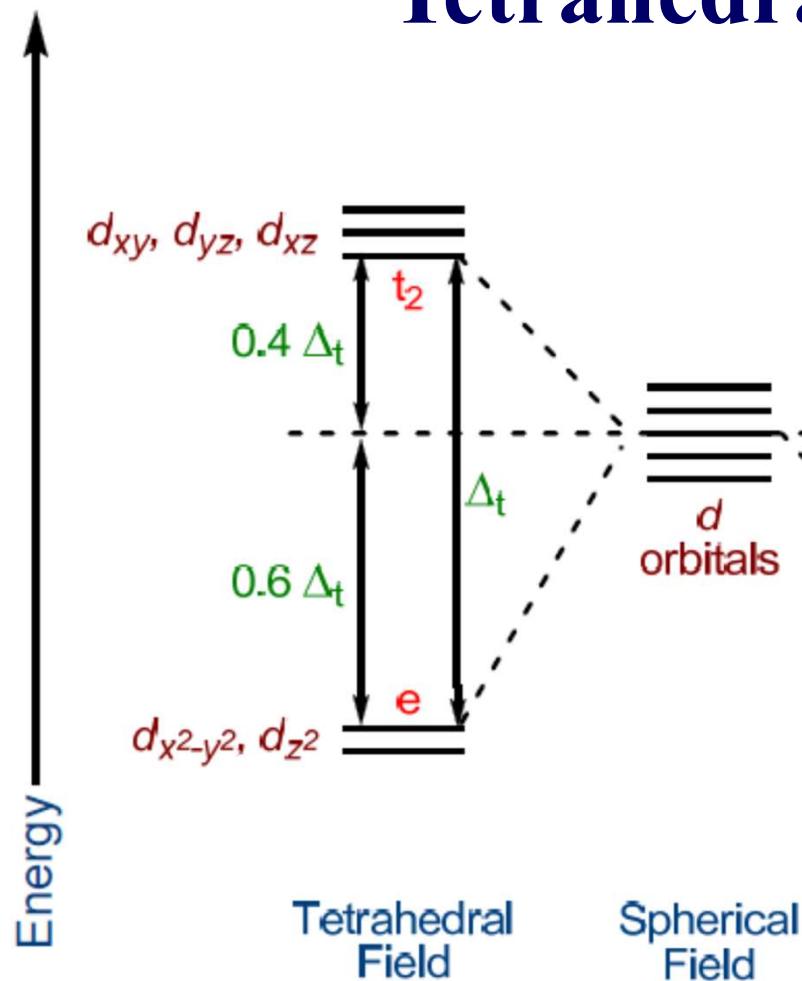
Tetrahedral Field



Tetrahedral Field



Tetrahedral Field

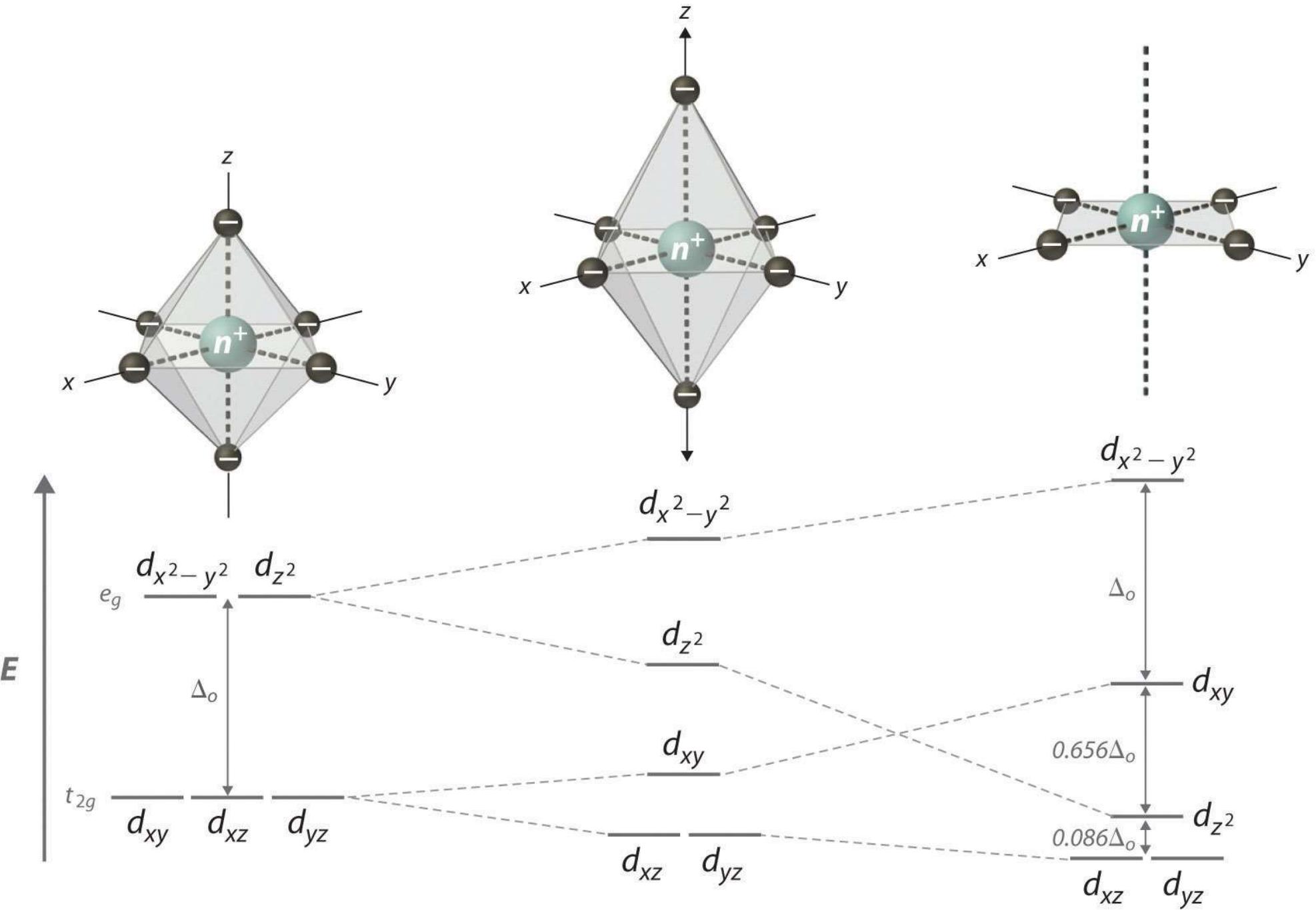


$$\Delta_t < \Delta_o$$

$$\Delta_t = 0.45 \Delta_o$$

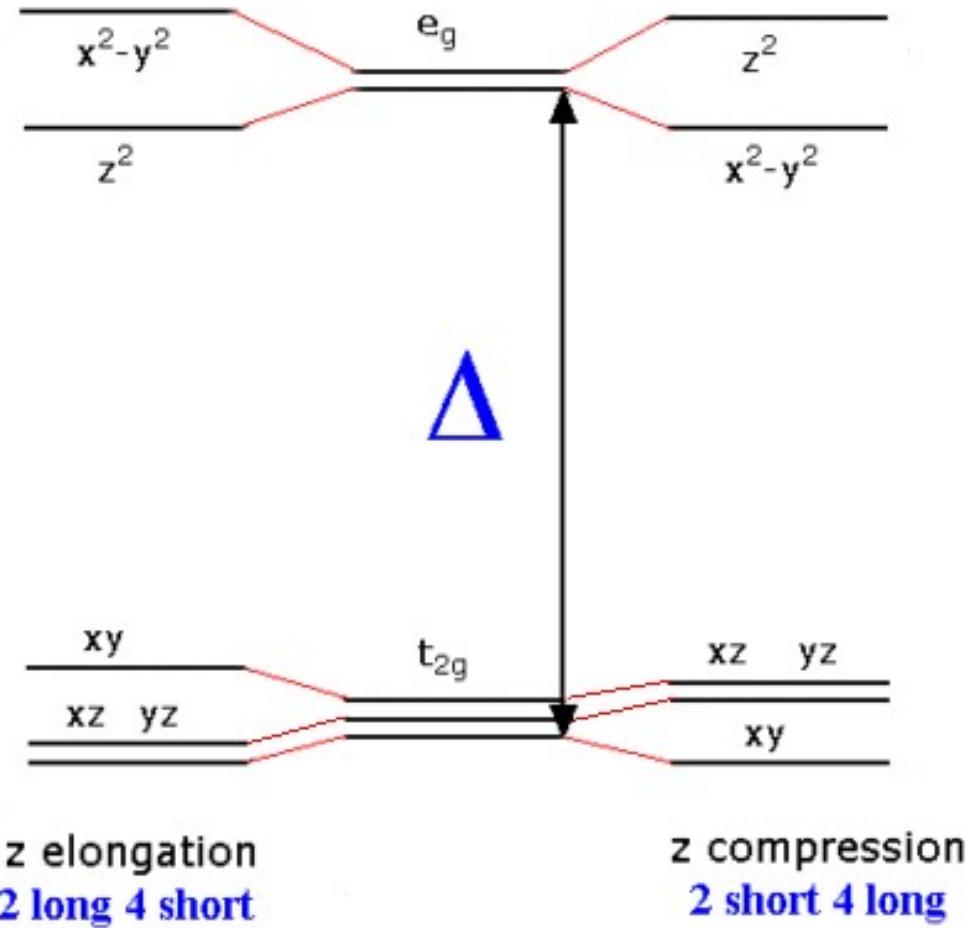
For the same metal and ligands and the same internuclear distances

Distortions of Octahedral Complexes

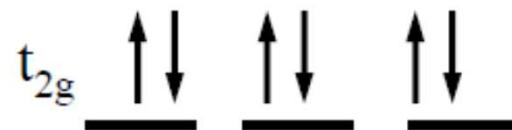
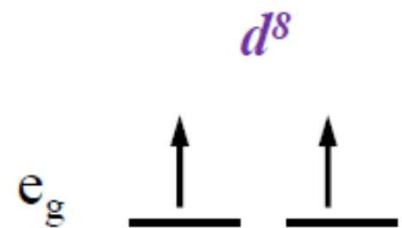


Distortions of Octahedral Complexes: Jahn-Teller effect

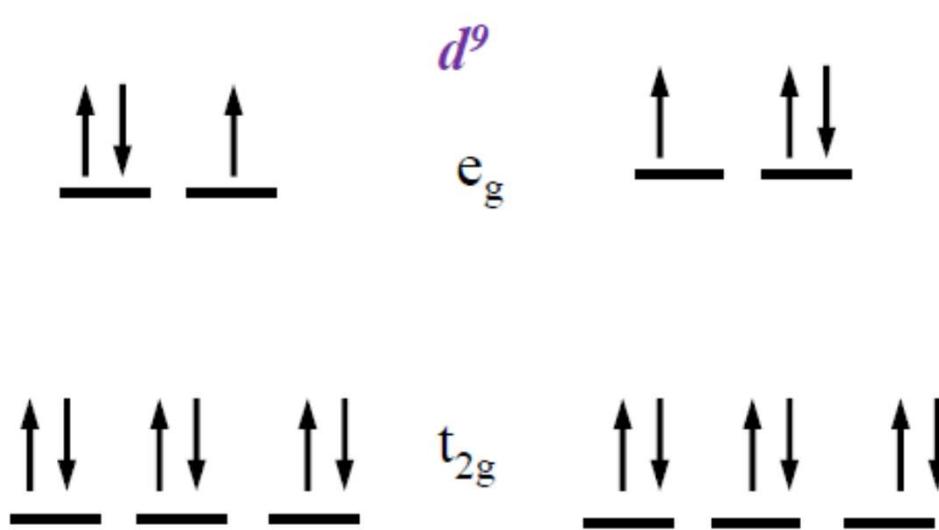
'Any non-linear molecule having an orbitally degenerate electronic configuration is unstable, and the system undergo distortion to remove the degeneracy.'



Distortions of Octahedral Complexes

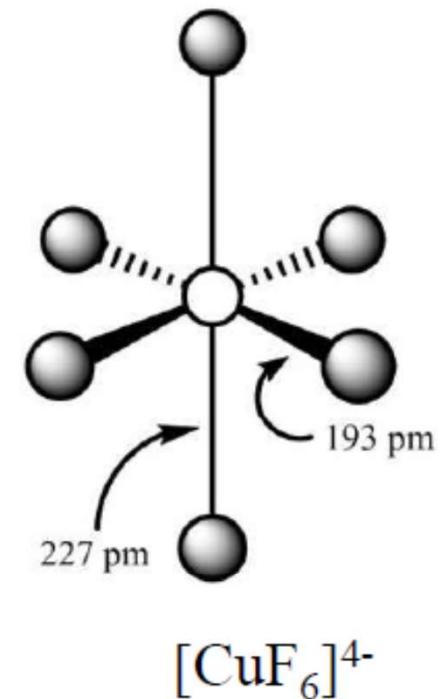
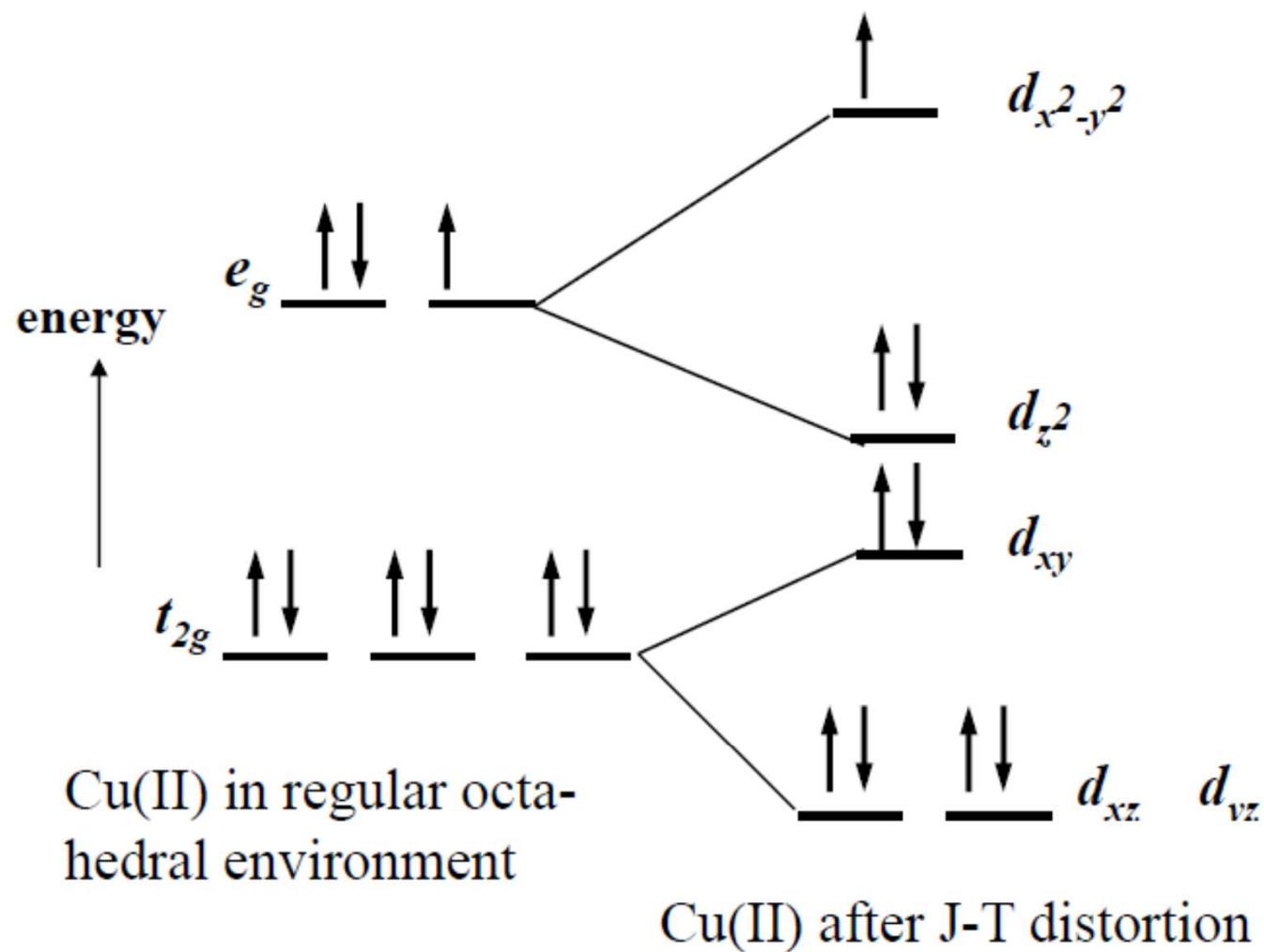


Ni^{2+} : Only one way of filling the orbitals; not degenerate and no Jahn-Teller Distortion

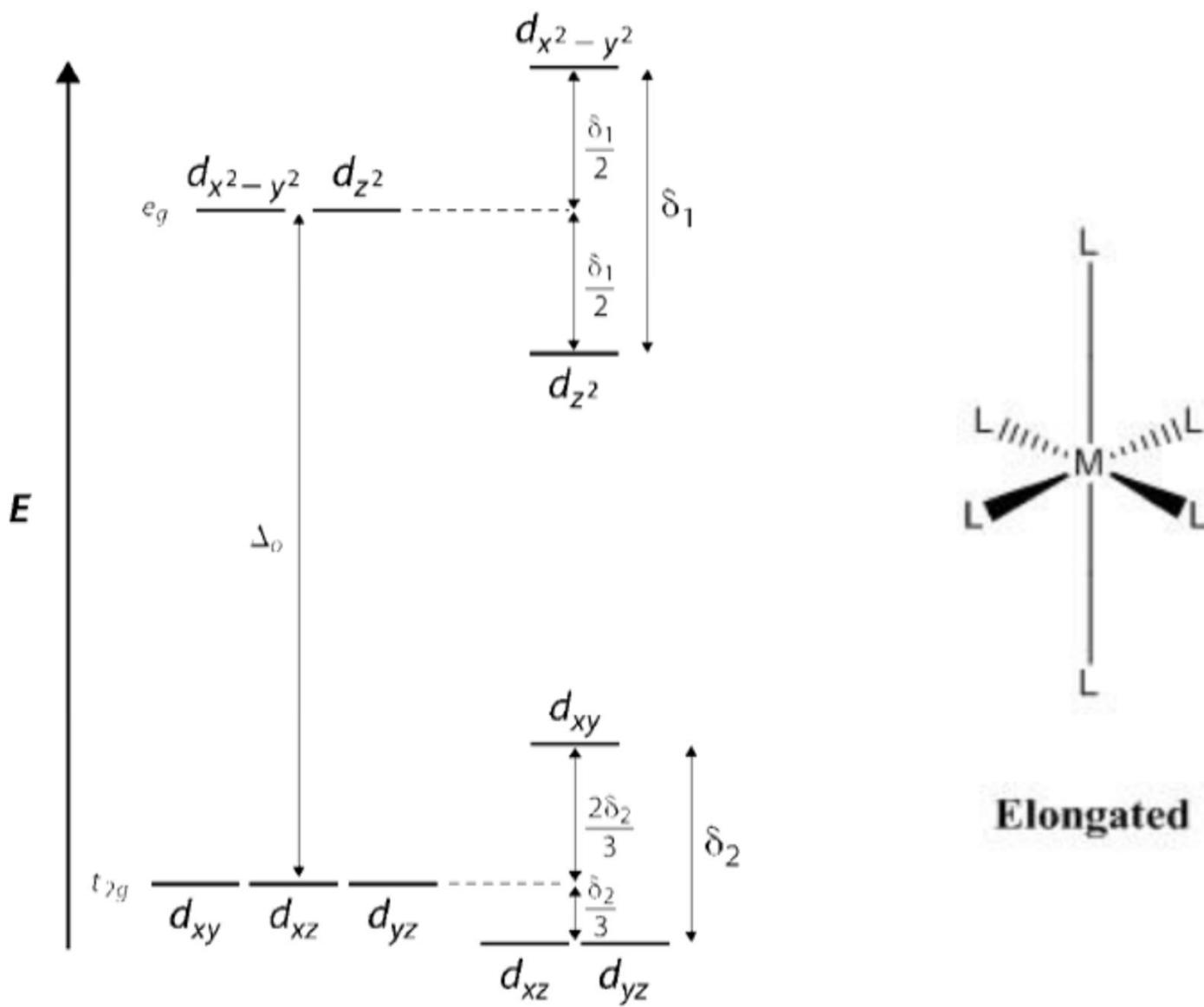


Cu^{2+} : Two ways of filling the e_g orbitals; there is degeneracy and Jahn-Teller Distortion is observed

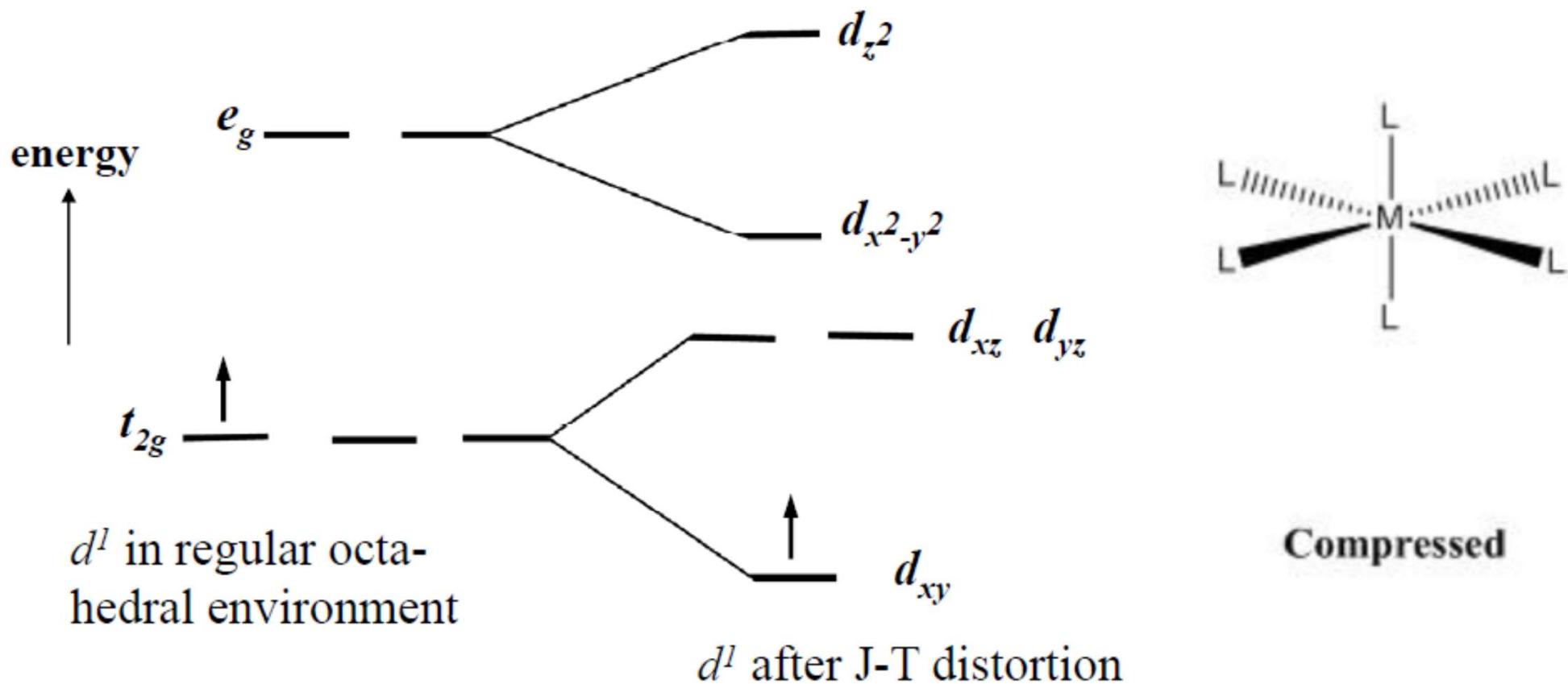
Distortions of Octahedral Complexes



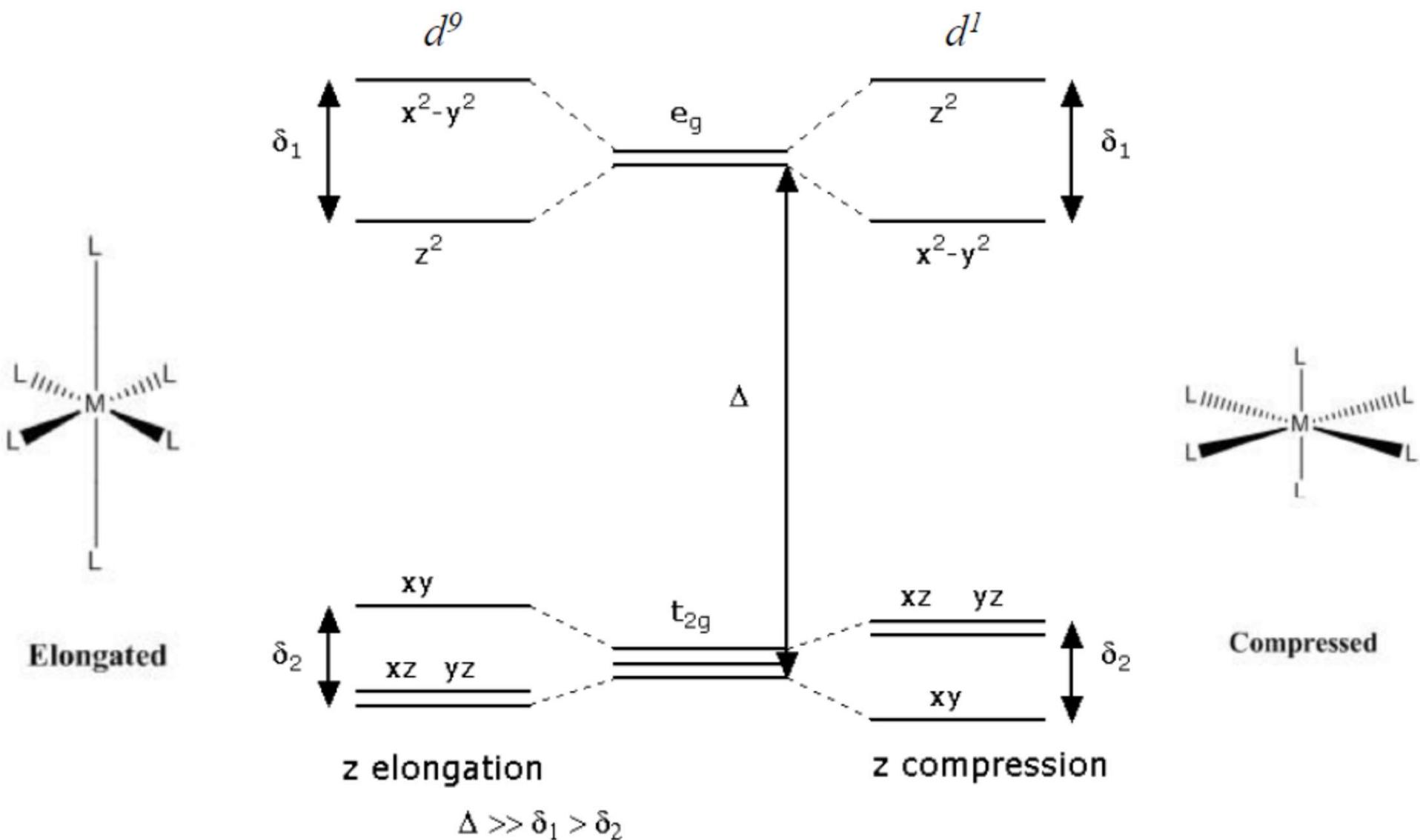
Jahn-Teller Distortion in d^9 Complexes



Jahn-Teller Distortion in d^1 Complexes

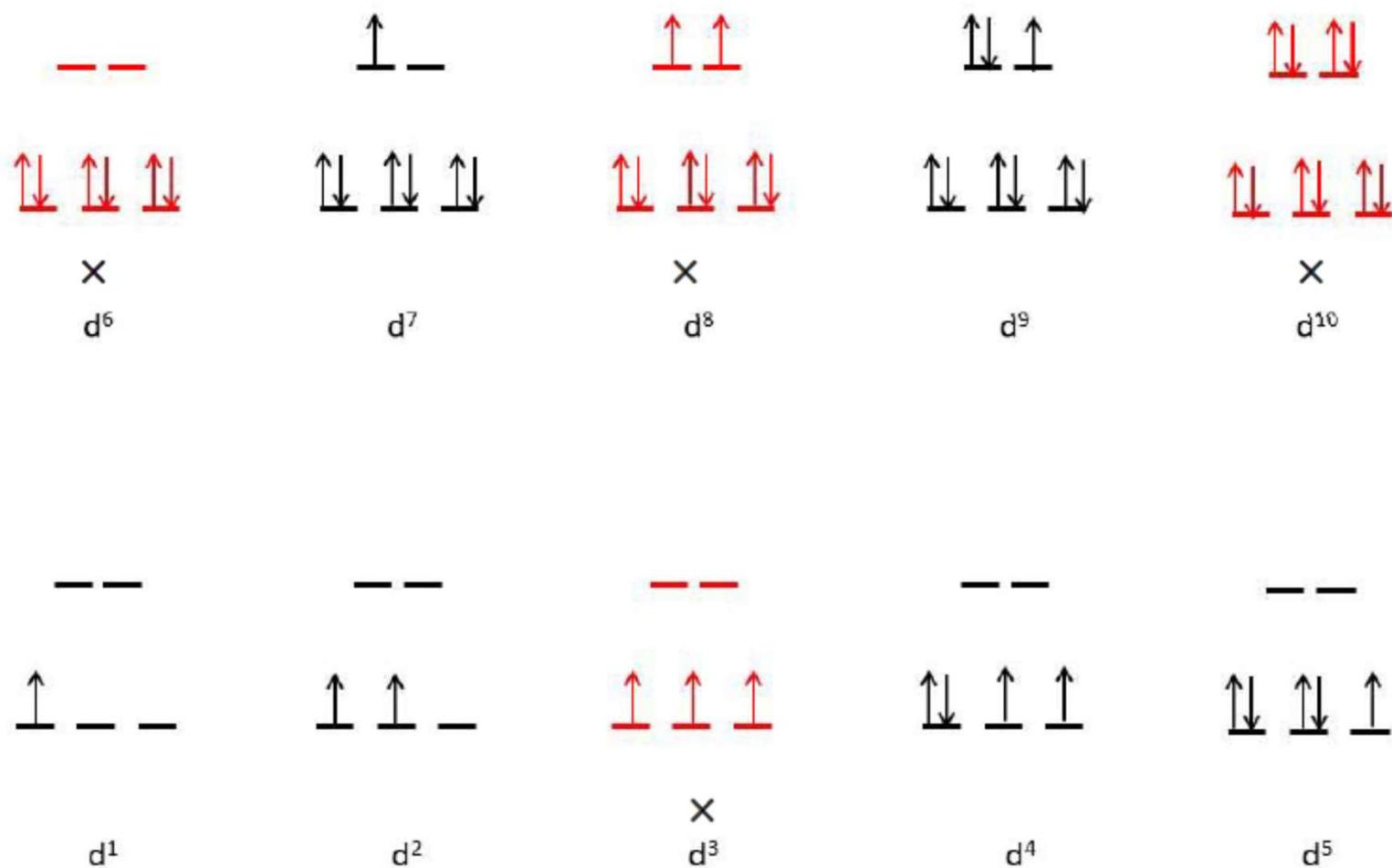


d^l Vs d^9



Distortions are more pronounced if the degeneracy occurs in an e_g orbital

Distortions in Low-Spin Complexes



Distortions in High-Spin Complexes

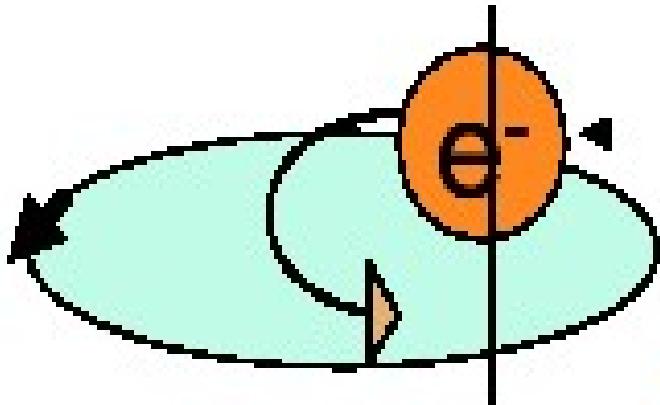
$\uparrow\uparrow$	$\uparrow\uparrow$	$\uparrow\uparrow$	$\uparrow\downarrow$	$\uparrow\downarrow$
$\downarrow\downarrow \uparrow \uparrow$	$\downarrow\downarrow \uparrow \uparrow$	$\downarrow\downarrow \uparrow \downarrow \uparrow$	$\downarrow\downarrow \uparrow \uparrow \uparrow$	$\downarrow\downarrow \uparrow \downarrow \uparrow$
d^6	d^7	d^8	d^9	d^{10}
$--$	$--$	$--$	$\uparrow -$	$\uparrow\uparrow$
$\uparrow - -$	$\uparrow \uparrow -$	$\uparrow \uparrow \uparrow$	$\uparrow \uparrow \uparrow$	$\uparrow \uparrow \uparrow$
d^1	d^2	d^3	d^4	d^5

Magnetism

Each electron has a magnetic moment owing to its:

spin angular momentum

orbital angular momentum



Orbital motion of e generates current and magnetic field

Spin motion of e about its own Axis also generates a magnetic field

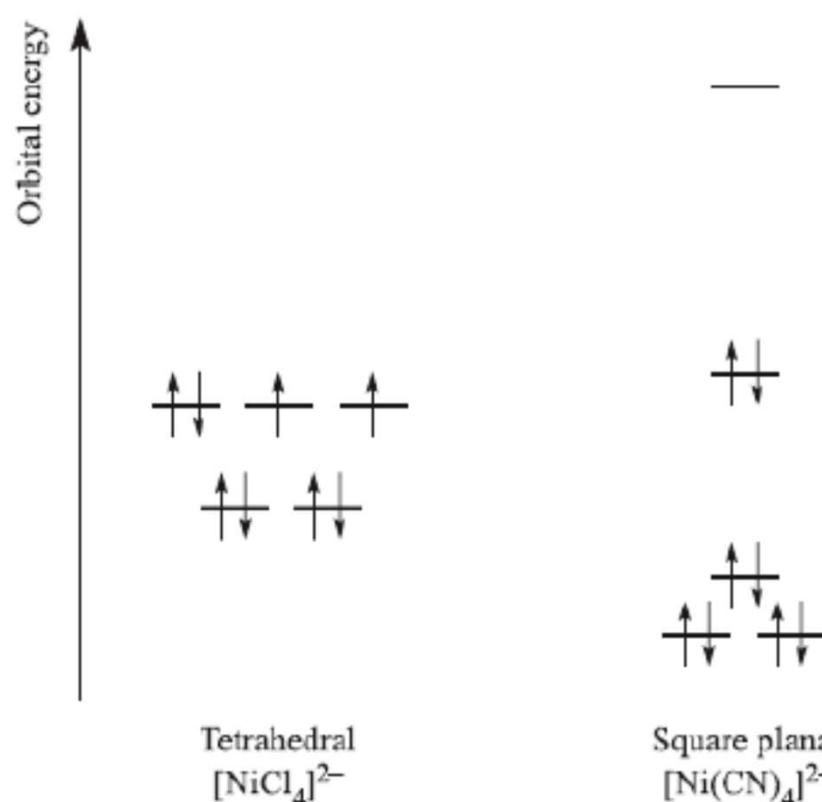
n = no. of unpaired electrons

$$\mu = \{n(n+2)\}^{1/2} \mu_B$$

Ion	n	S	μ/μ_B Calculated	Experimental
Ti ³⁺	1	1/2	1.73	1.7 – 1.8
V ³⁺	2	1	2.83	2.7 – 2.9
Cr ³⁺	3	3/2	3.87	3.8
Mn ³⁺	4	2	4.90	4.8 – 4.9
Mn ²⁺	5	5/2	5.92	5.9 - 6.3

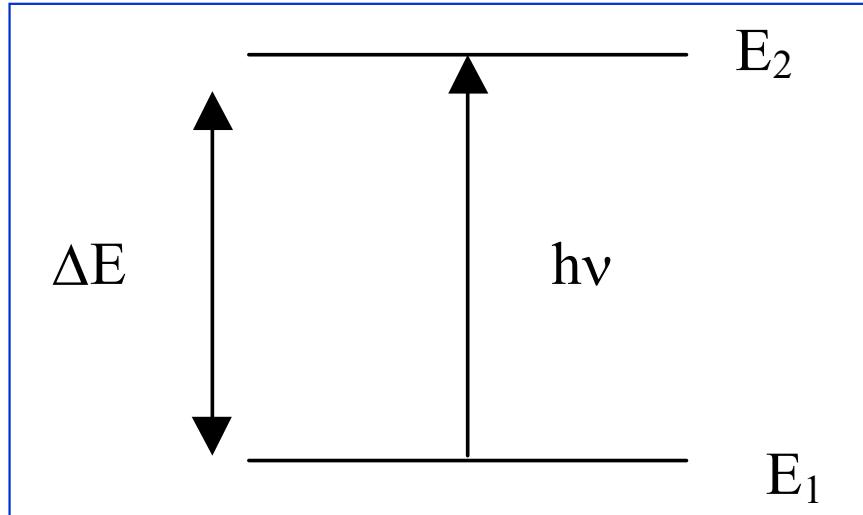
**Similar Calculation can be done
for Low-spin Complex**

The d^8 complexes $[\text{Ni}(\text{CN})_4]^{2-}$ and $[\text{NiCl}_4]^{2-}$ are square planar and tetrahedral respectively. Will these complexes be paramagnetic or diamagnetic?



Thus, $[\text{NiCl}_4]^{2-}$ is paramagnetic while $[\text{Ni}(\text{CN})_4]^{2-}$ is diamagnetic.

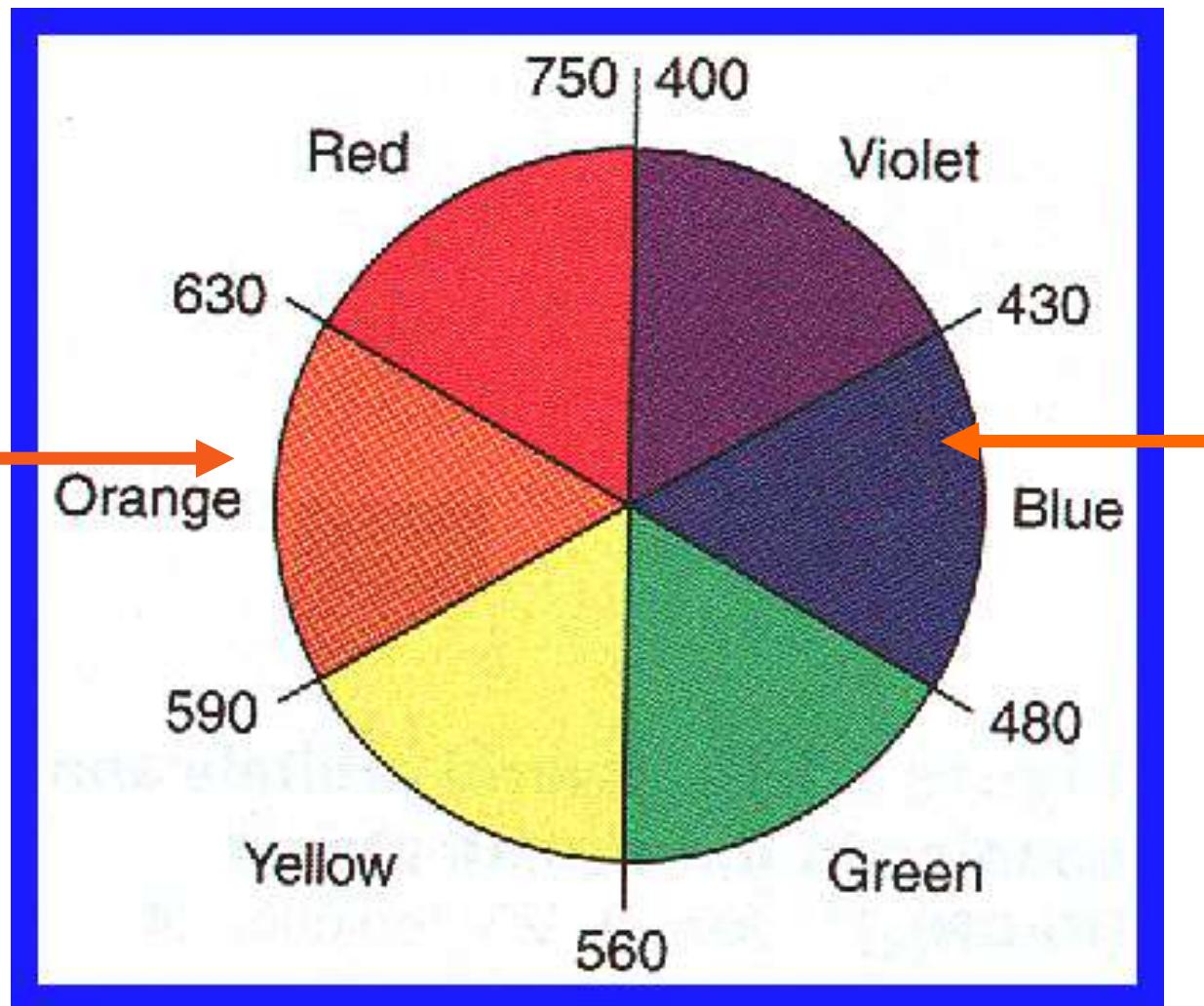
The origin of the color of the transition metal compounds



$$\Delta E = E_2 - E_1 = h\nu$$

Ligands influence Δ_0 , therefore the colour

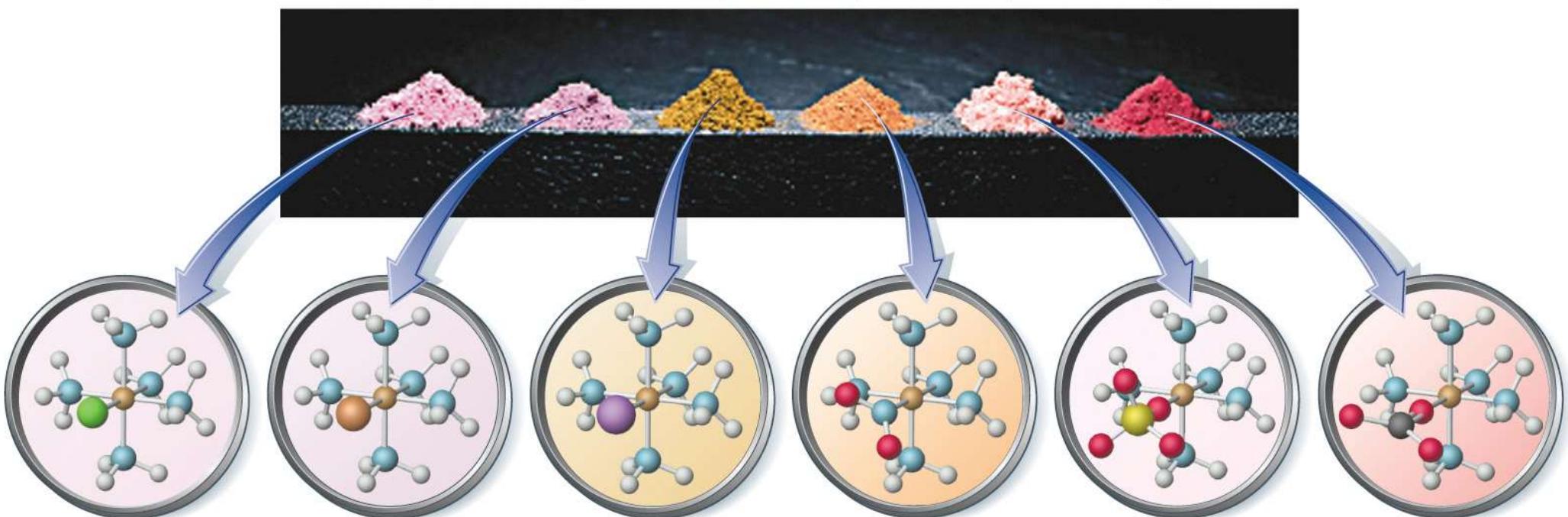
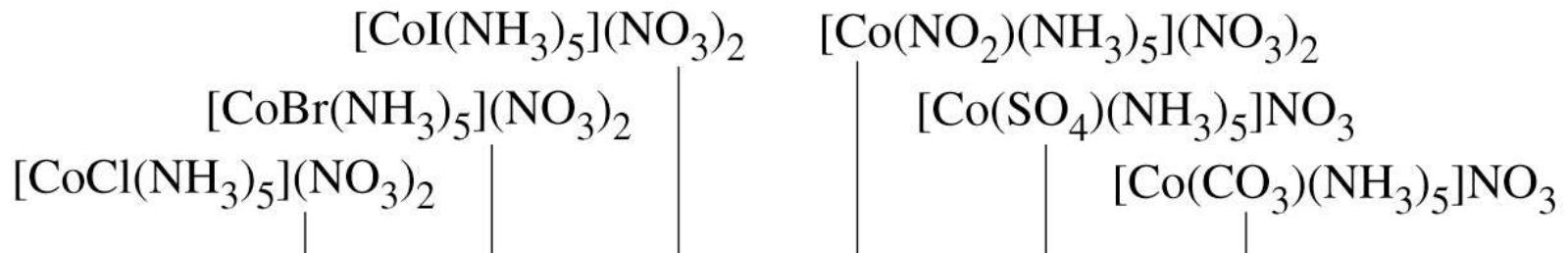
**absorbed
color**

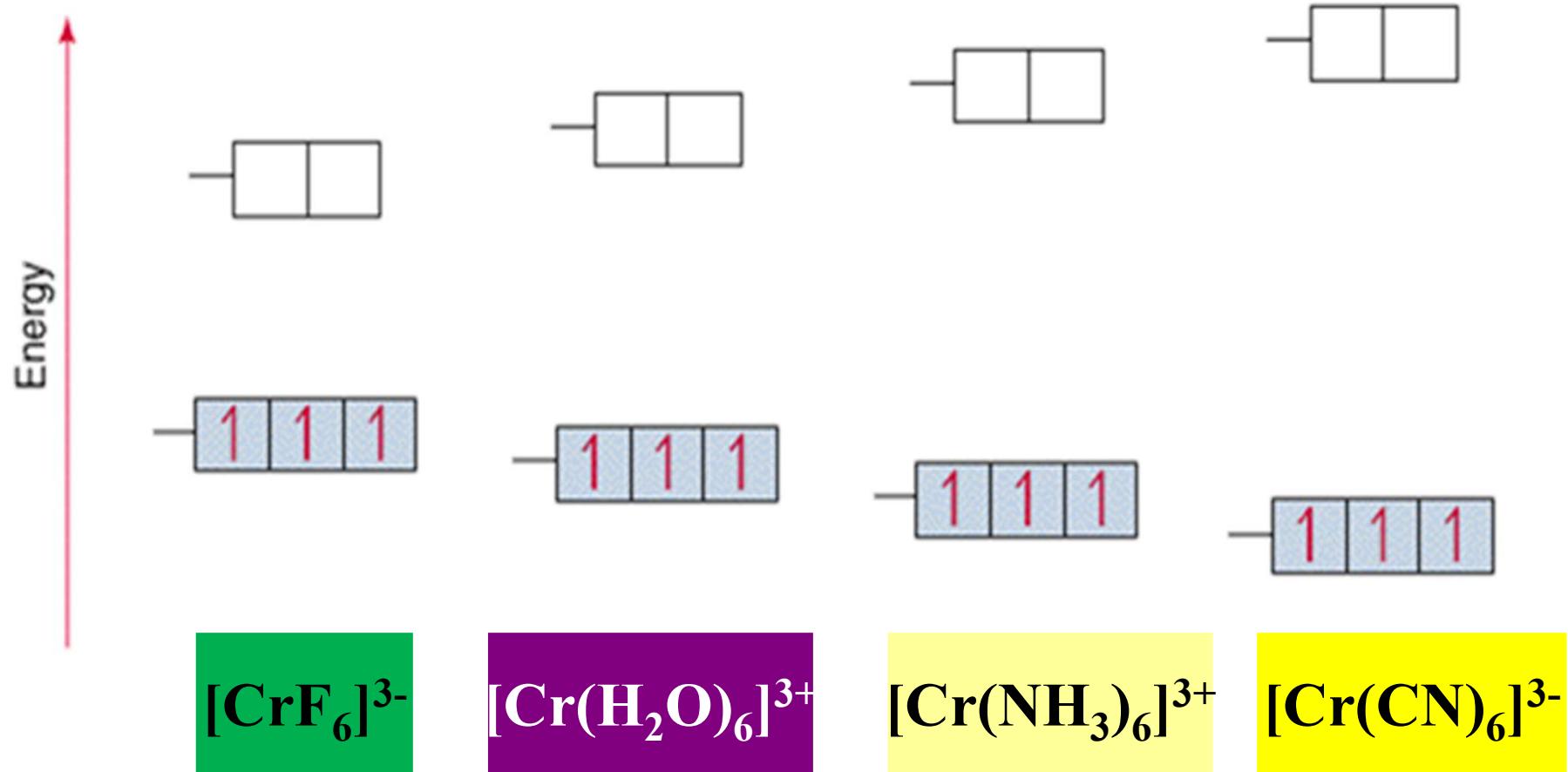


**observed
color**

The colour can change depending on a number of factors
e.g.

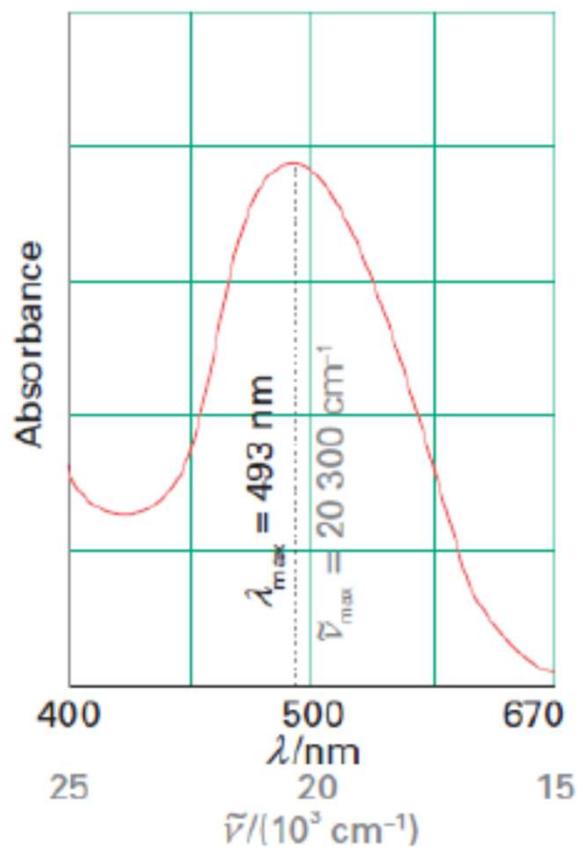
1. Metal charge
2. Ligand strength





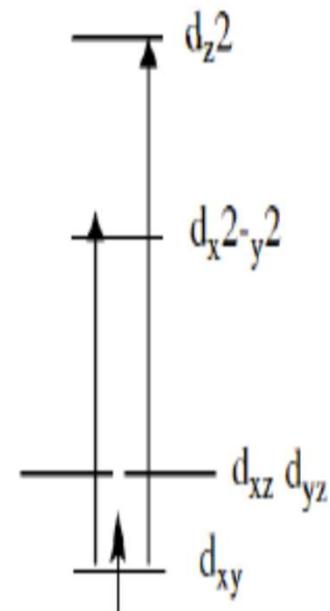
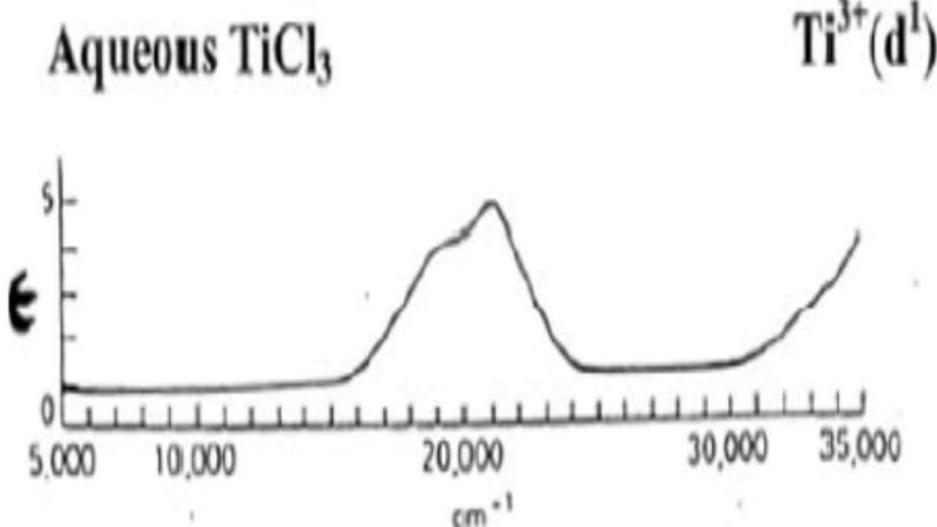
As Cr^{3+} goes from being attached to a **weak field ligand** to a **strong field ligand**, Δ **increases** and the **color of the complex changes from green to yellow**.

Calculate Δ_o for $[\text{Ti}(\text{OH}_2)_6]^{3+}$



The optical absorption spectrum of $[\text{Ti}(\text{OH}_2)_6]^{3+}$

A more resolved absorption spectrum of the complex has a shoulder



Limitations of CFT

Considers Ligand as Point charge/dipole only

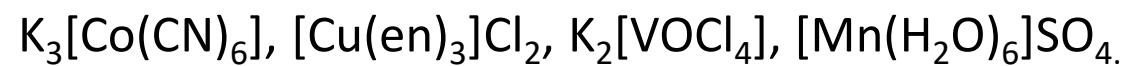
Does not take into account of the overlap of ligand and metal orbitals

Consequence

e.g. Fails to explain why CO is stronger ligand than CN⁻ in complexes having metal in low oxidation state

1. The crystal field splitting energy(Δ) for $[\text{CoCl}_6]^{4-}$ is 18000 cm^{-1} . What will be the Δ for $[\text{CoCl}_4]^{2-}$?
2. The magnetic moment of a certain octahedral Co(II) complex is $3.87 \mu_B$. What is its electron configuration?

3. Which of the following complexes show Jahn-Teller distortion and why?



4. Predict the spin only magnetic moment of the octahedral complexes formed by the reaction of Mn^{3+} with H_2O and CN^- . Given: the Pairing energy (P) for Mn^{3+} = $28,000\text{ cm}^{-1}$, $\Delta_o(H_2O) = 21000\text{ cm}^{-1}$, $\Delta_o(CN^-) = 38000\text{ cm}^{-1}$.