

CHEMISTRY -THEORY

(CYI 101)

Inorganic Chemistry

Instructor: Dr. R P John

Department of Chemistry & Chemical Biology

Evaluation and Study Material

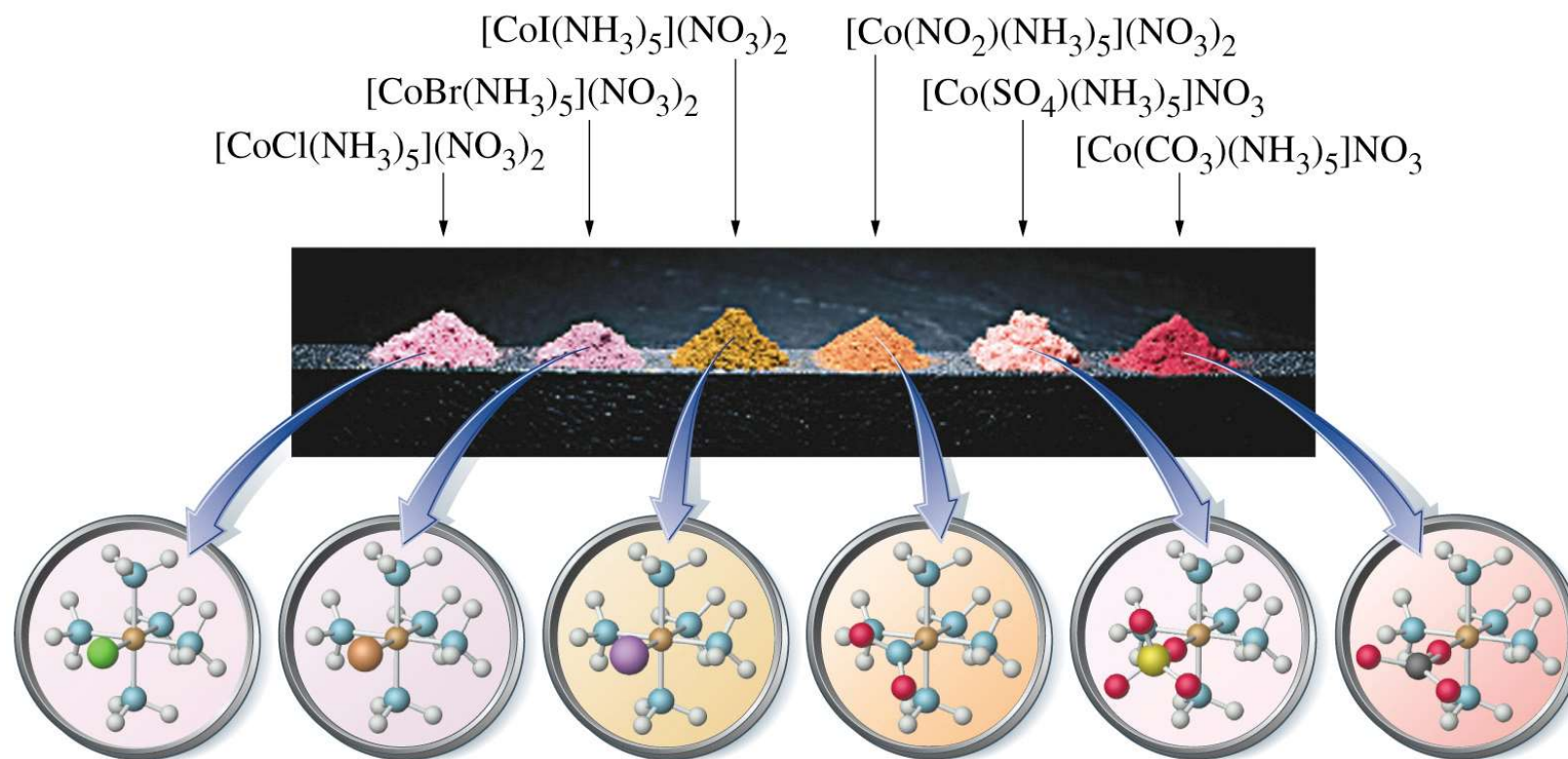
Examination/Class tests/others

- See Academic Calendar
- Will be informed time to time

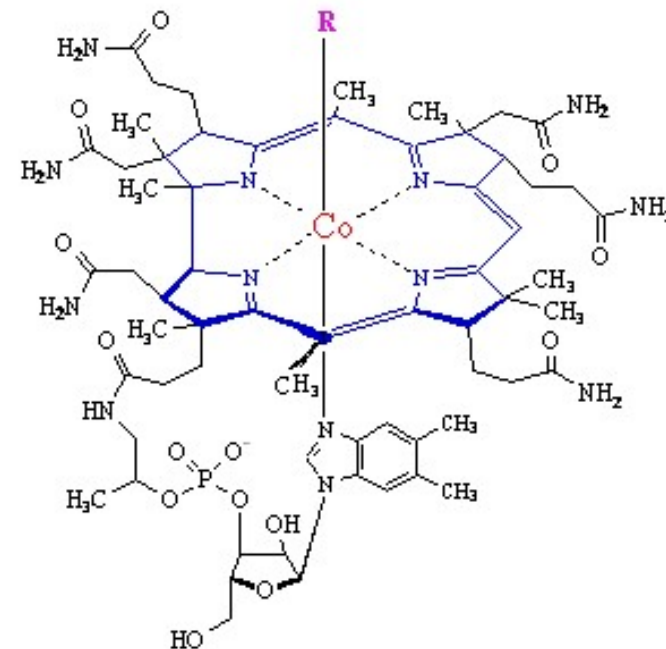
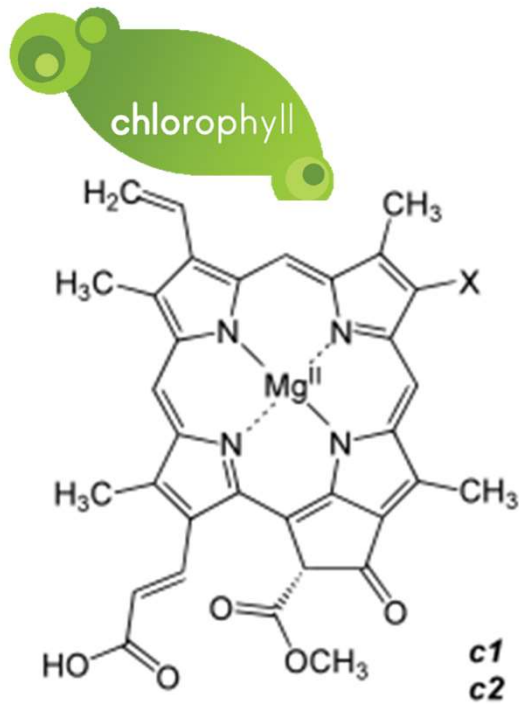
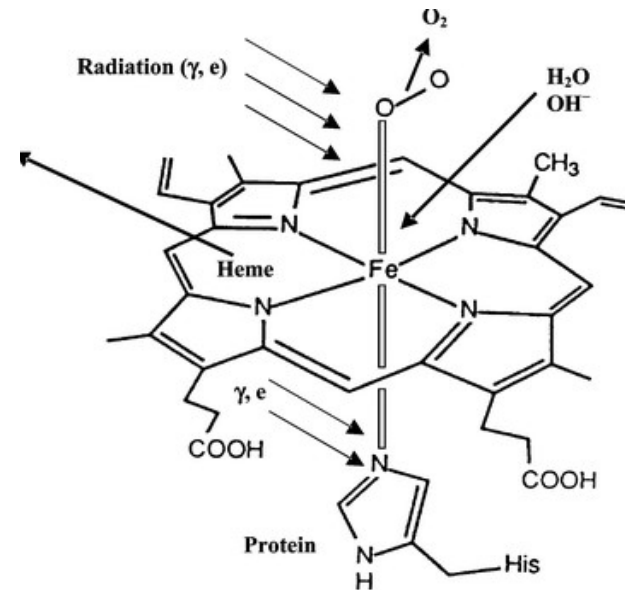
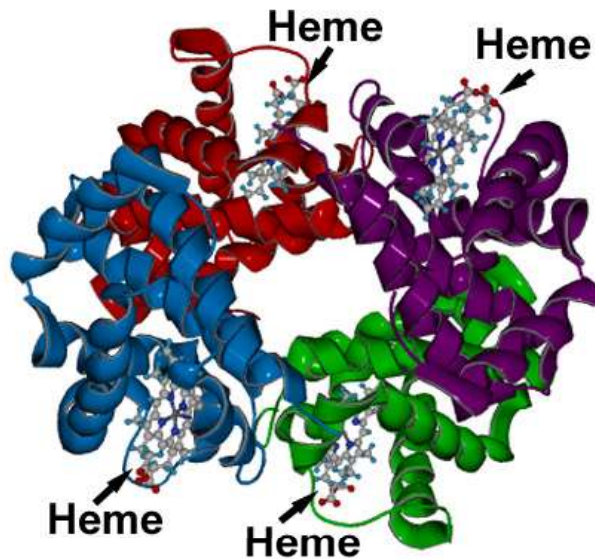
Course Material

- 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

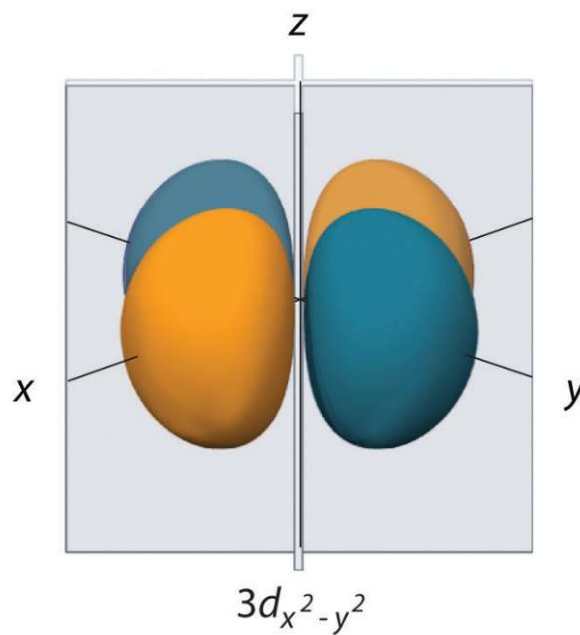
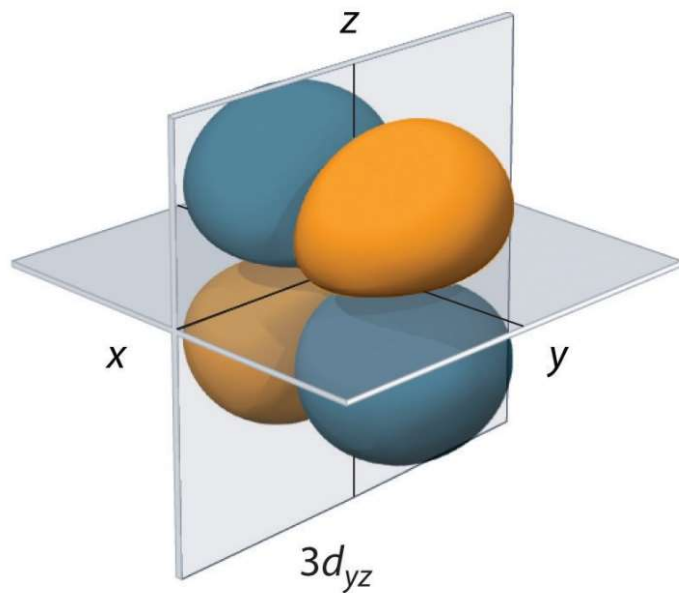
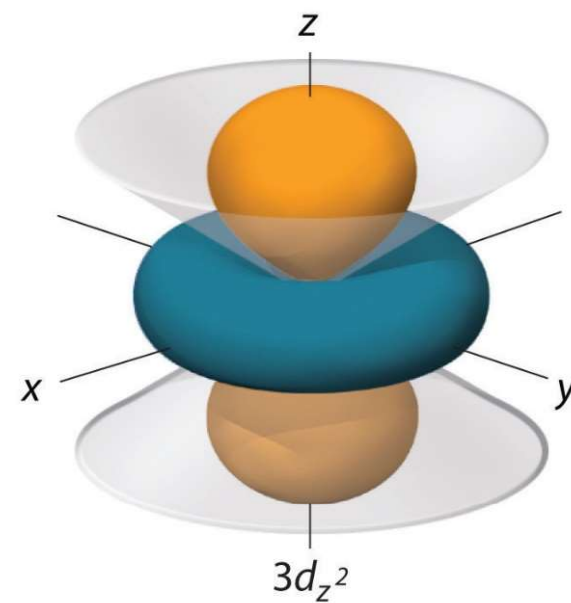
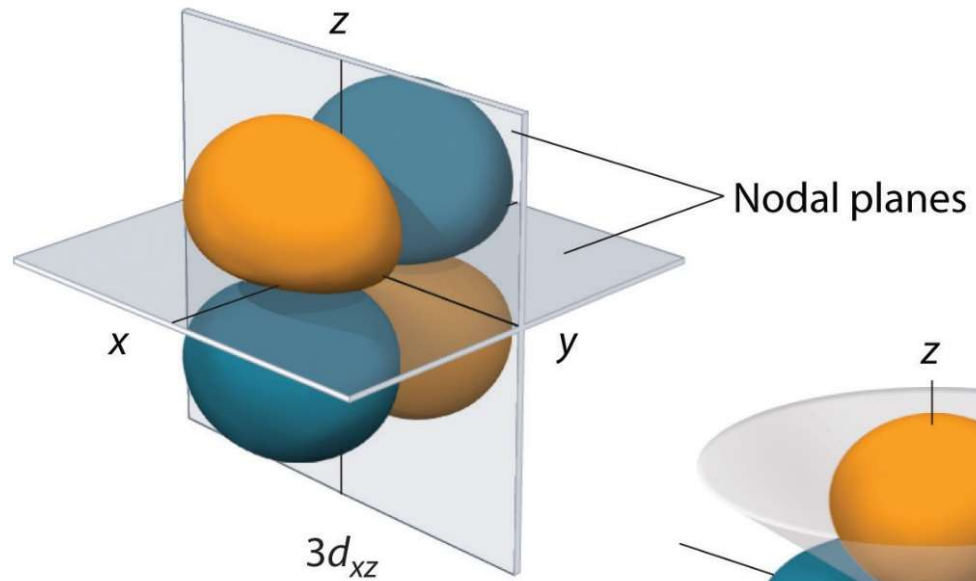
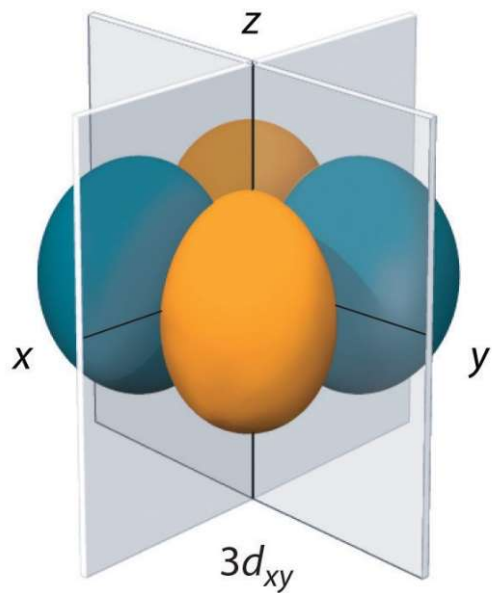
Color of transition metal complexes



Naturally Occurring Coordination Compounds

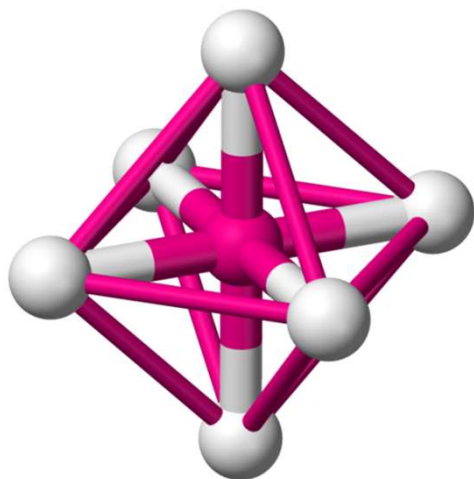


d-orbitals

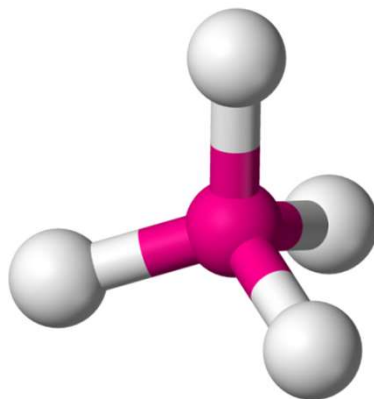


Crystal Field Theory

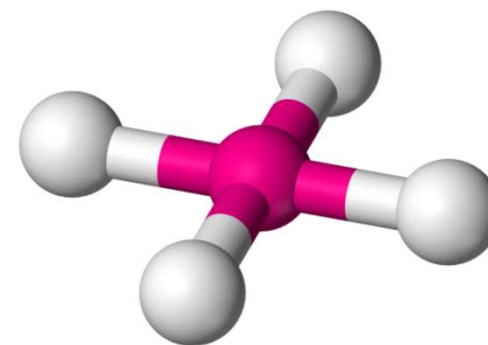
1. This is an electrostatic model for transition metal complexes.
2. Ligands are considered as point charge.
3. The CFT does not provide for electrons to enter the metal orbitals, i.e. it does not consider any orbital overlap.
4. Predicts the pattern of splitting of d-orbitals.
5. Used to rationalize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



Octahedral complex (O_h)

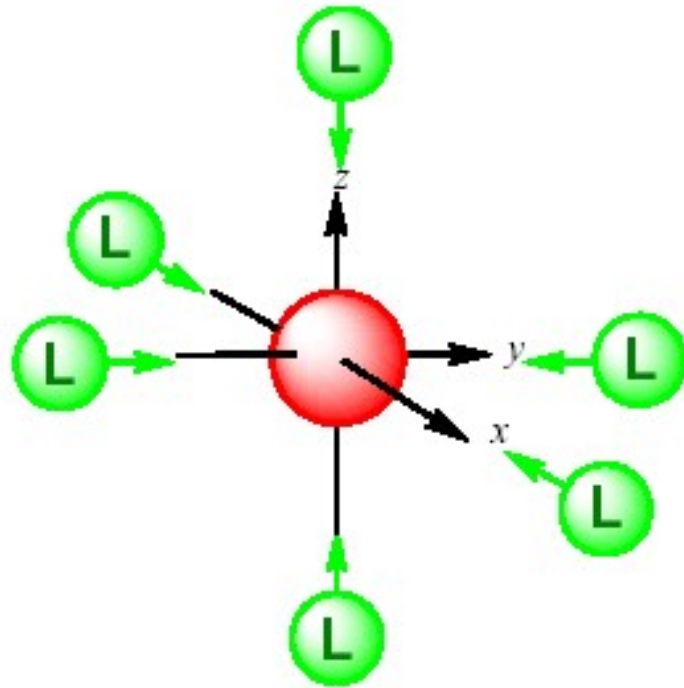


Tetrahedral complex (T_d)



Square planer complex (Sp)

Octahedral Field



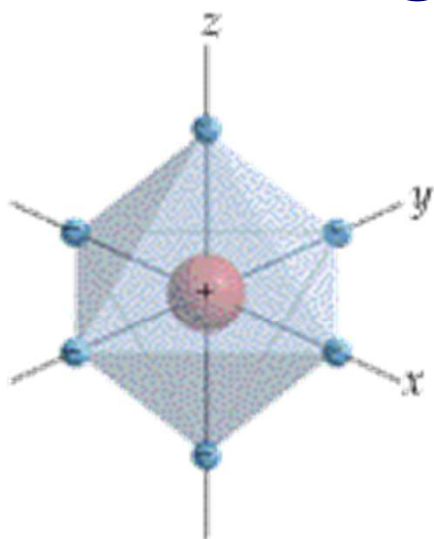
- Six point negative charges (Ligands) representing the ligands are placed in an octahedral array around the central metal ion.
- The ligand and orbitals lie on the same axes.
- These charges interact strongly with the central metal ion.

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

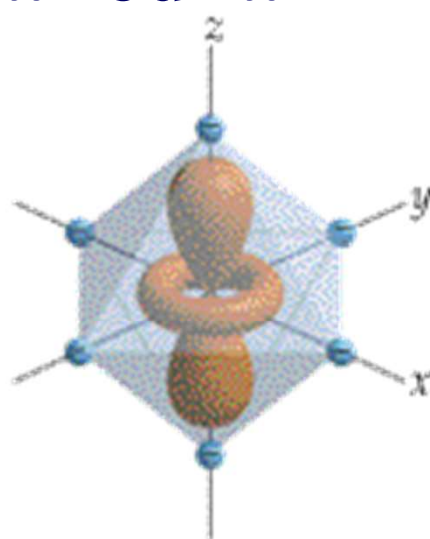
2. There is a much smaller but very important secondary effect arising from the fact that electrons in different d orbitals interact with the ligands to different extents.

❖ 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.

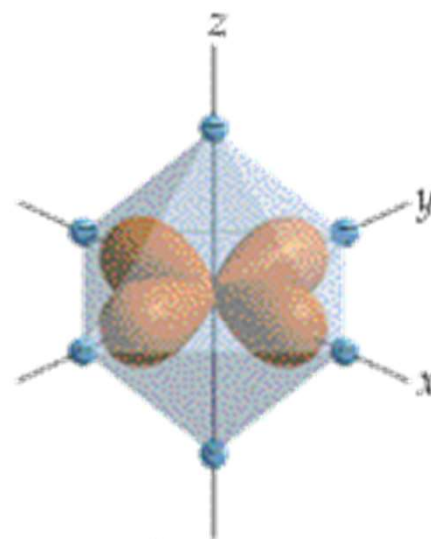
Octahedral Field



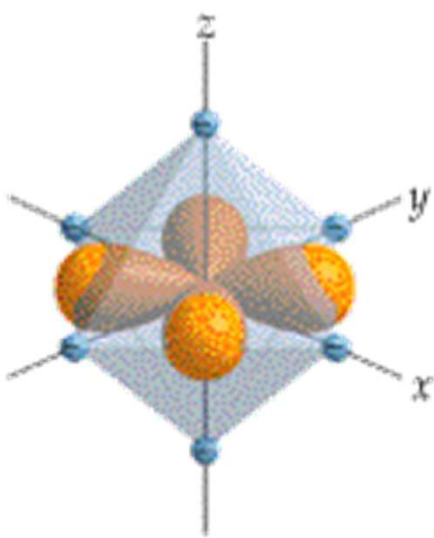
(a)



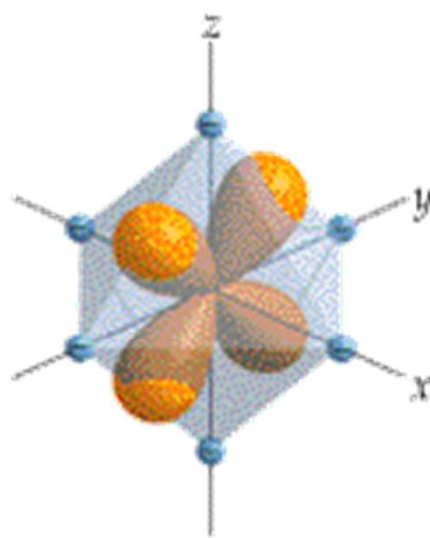
d_{z^2}
(b)



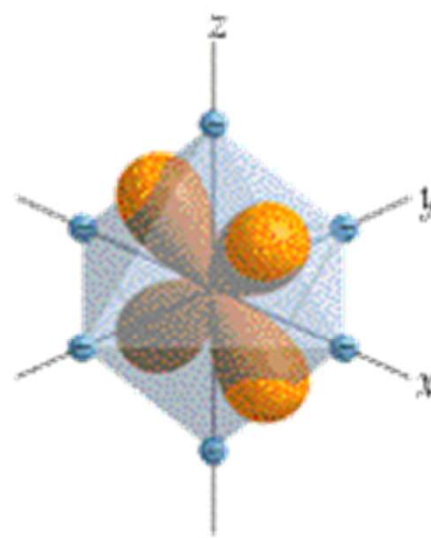
$d_{x^2 - y^2}$
(c)



d_{xy}
(d)

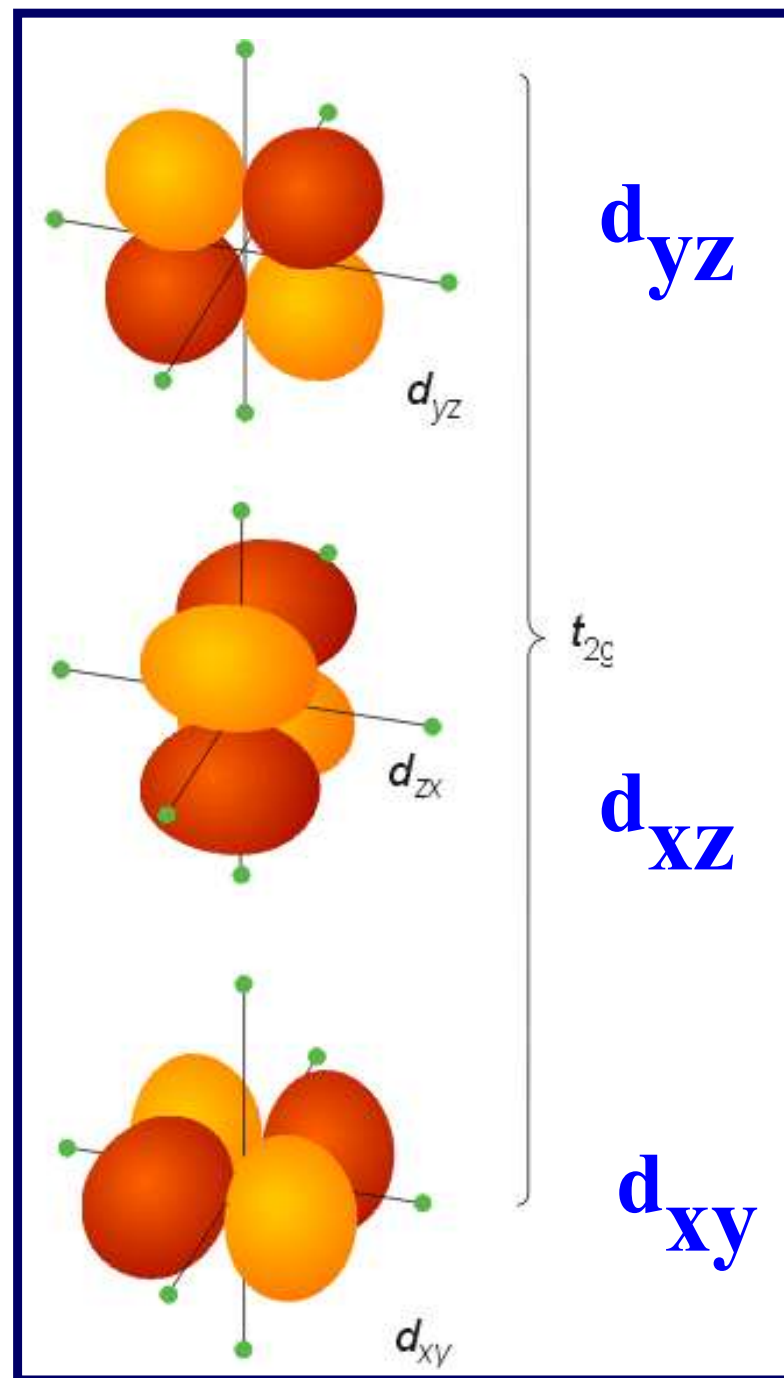
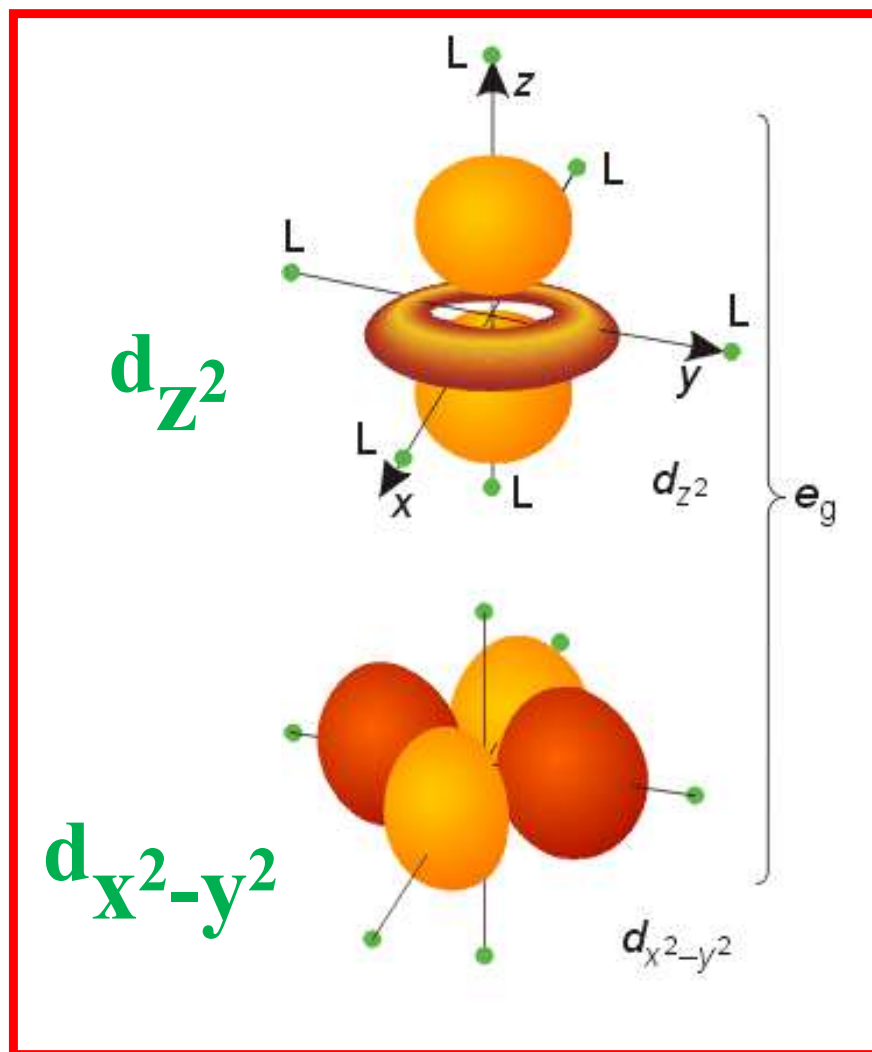


d_{yz}
(e)

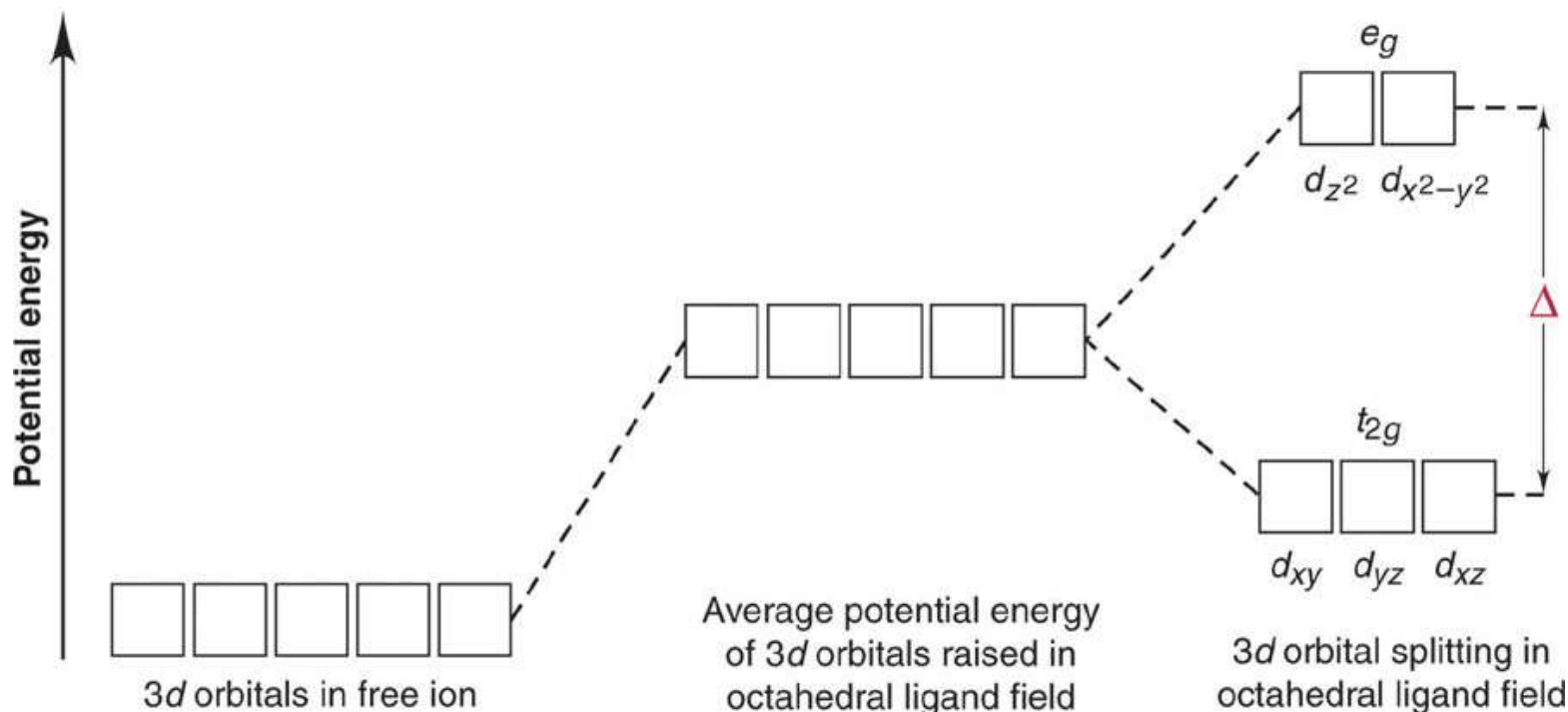


d_{xz}
(f)

Octahedral Field

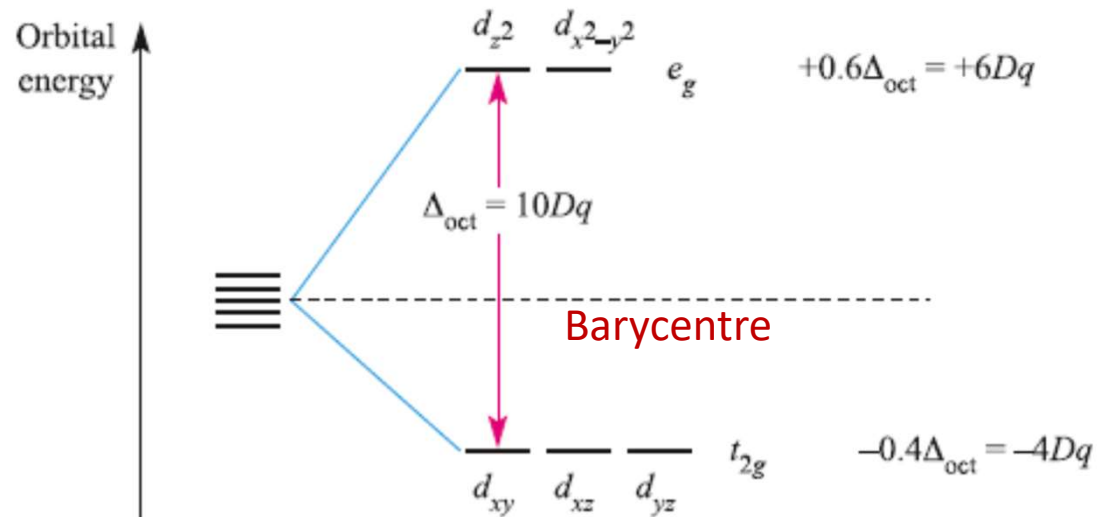
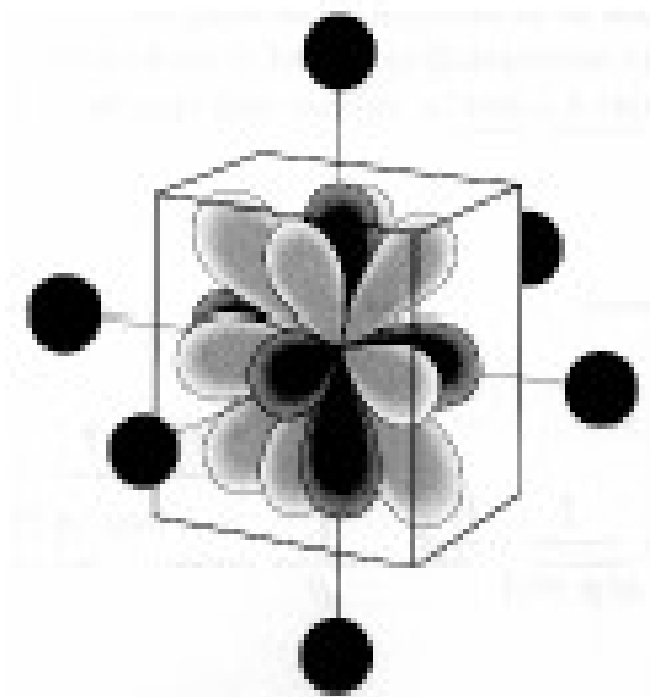


Splitting of d -orbital energies in an octahedral field of ligands.



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 by about same amount again from $4d^n$ to $5d^n$. The increase down a group reflects the larger size of the 4d and 5d orbitals compared with the compact 3d orbitals and the consequent stronger interactions with the ligands.

Strong and weak ligands: Spectrochemical Series

Weak Field

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

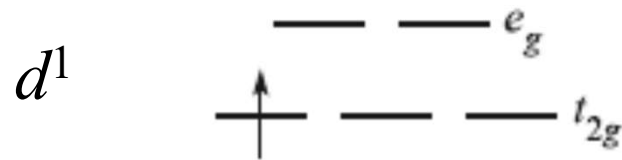
Strong Field

Crystal Field Stabilization Energy (CFSE)

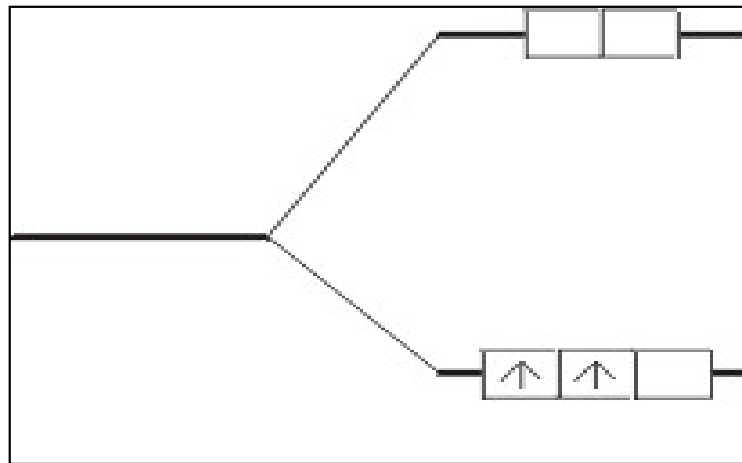
- In Octahedral field, **configuration is: $t_{2g}^x e_g^y$**
- Net energy of the configuration relative to the average energy of the orbitals is:

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

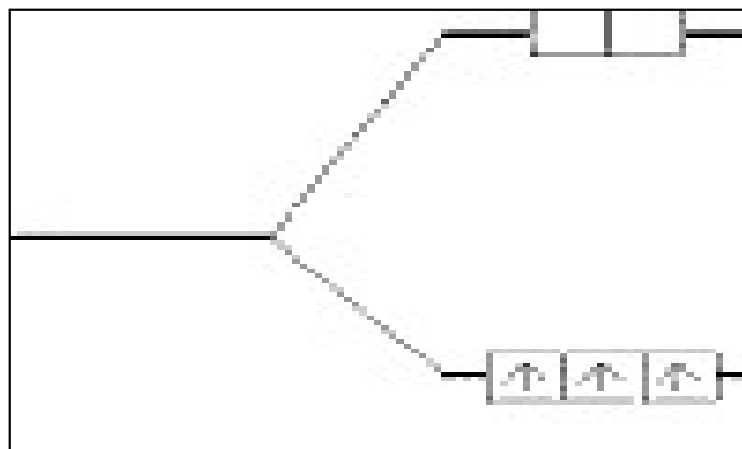
$$\Delta_o = 10 \text{ Dq}$$



Crystal Field Stabilization Energy (CFSE)

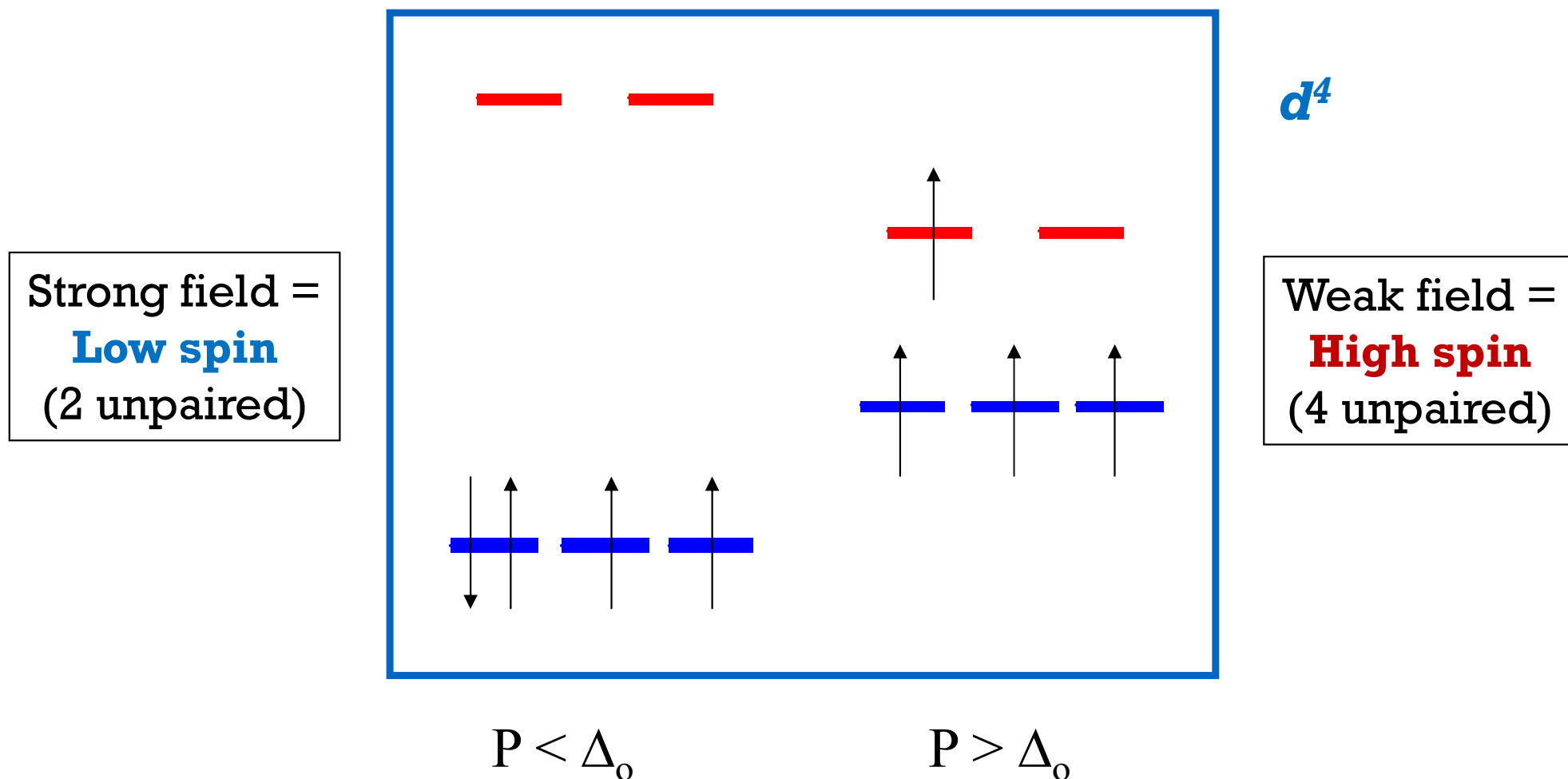


d^2 $\text{Ti}^{2+}, \text{V}^{3+}$

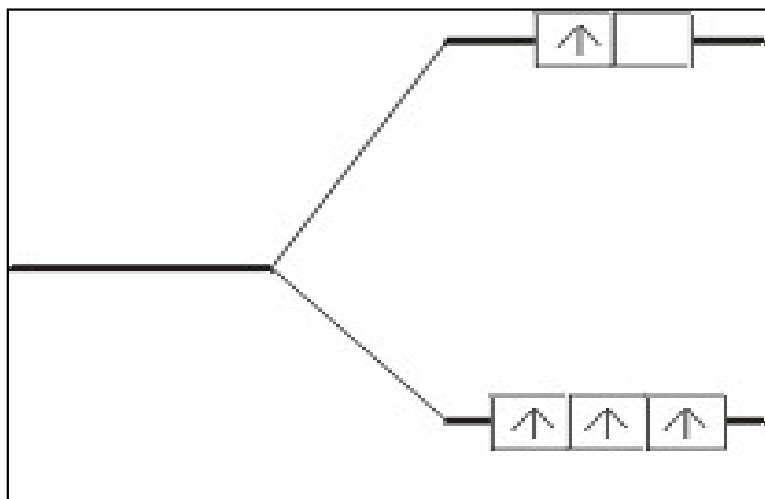


d^3 $\text{Cr}^{3+}, \text{Mn}^{4+}, \text{V}^{2+}$

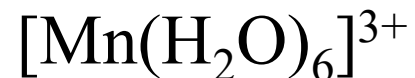
When the **4th electron** is assigned it will either go into **the higher energy e_g orbital** at an energy cost of Δ_o or be **paired** at an energy cost of **P**, the pairing energy.



Crystal Field Stabilization Energy (CFSE)



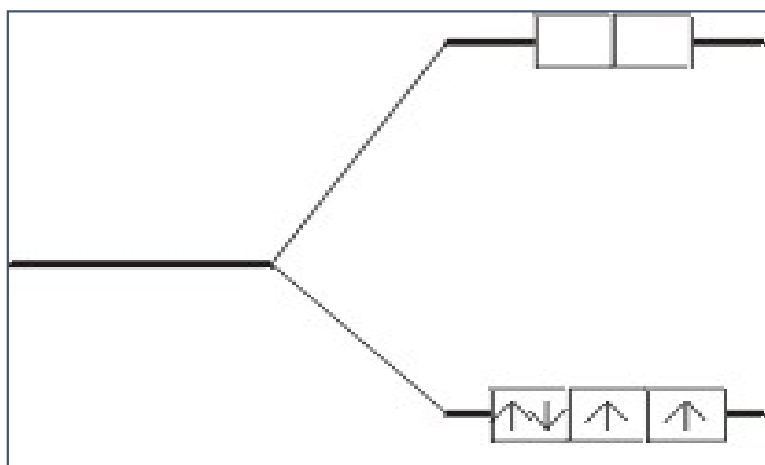
Weak field d^4



Weak Field Complex

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

High Spin Complex



Strong field d^4

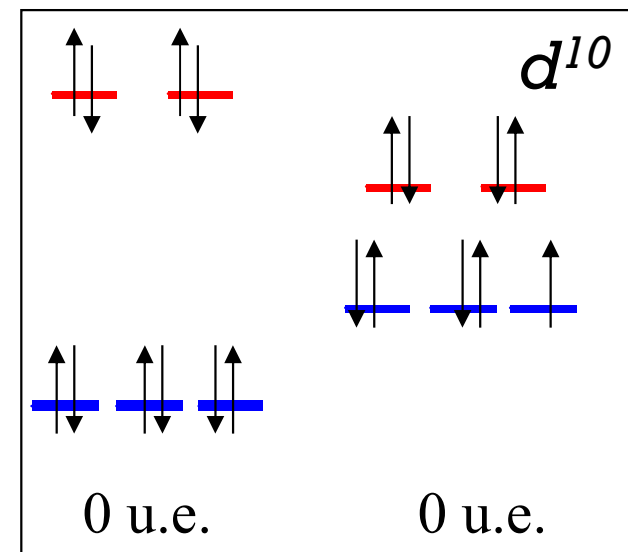
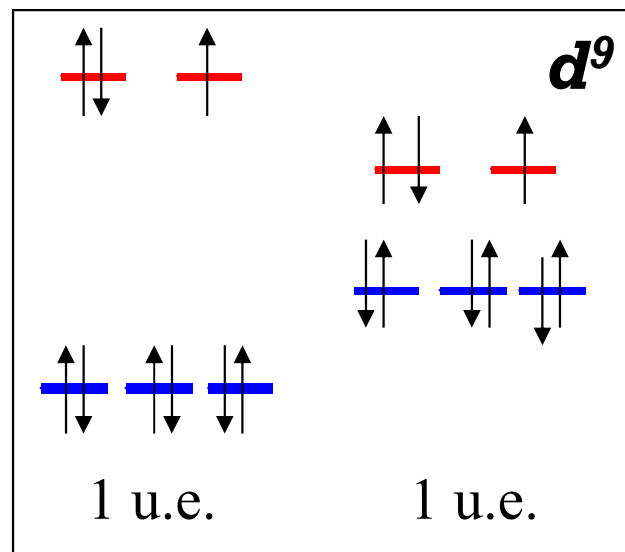
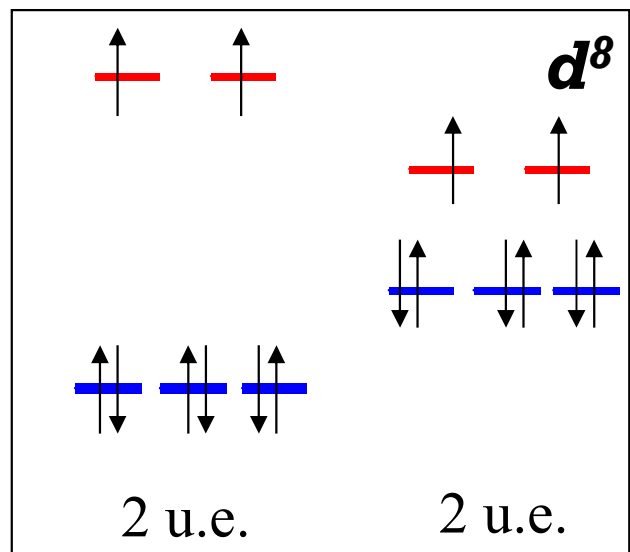
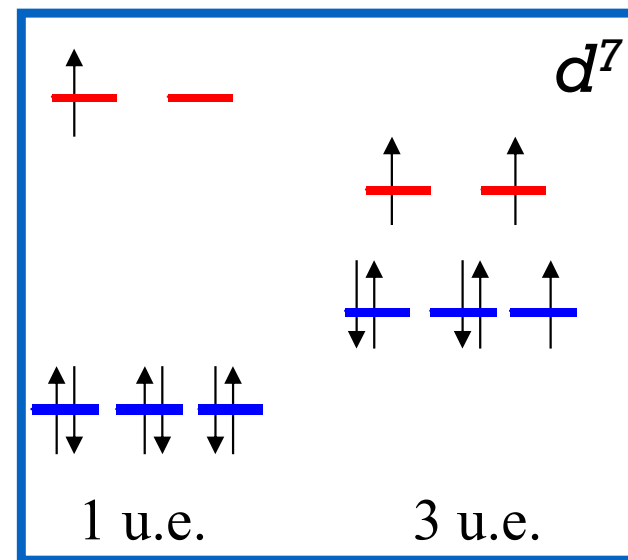
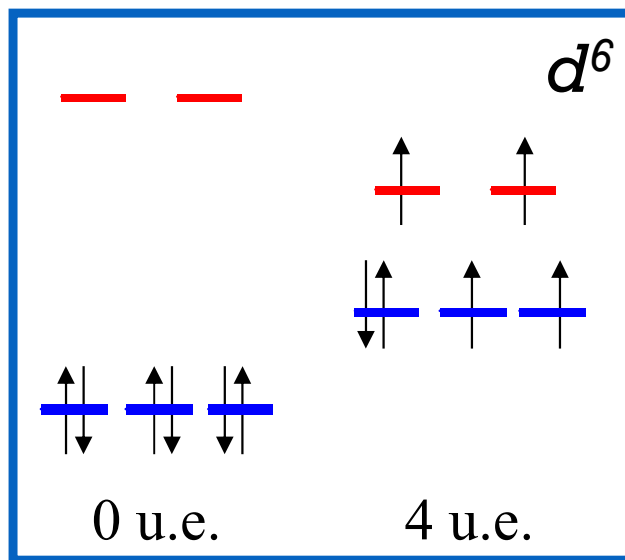
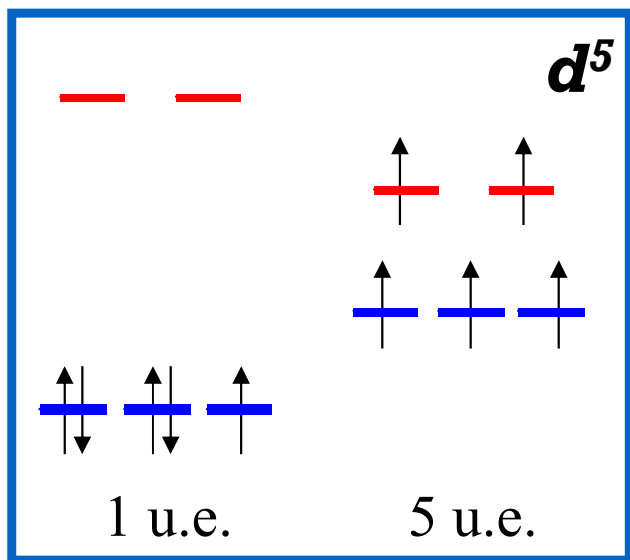


Strong field Complex

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

Low Spin Complex

Placing electrons in d orbitals

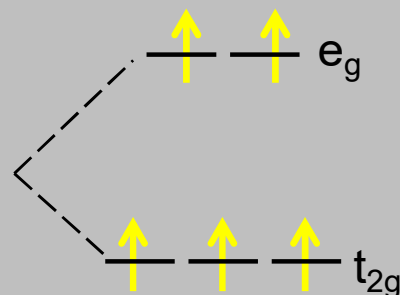
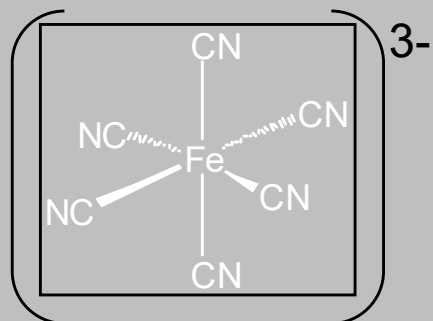


What is the CFSE of $[\text{Fe}(\text{CN})_6]^{3-}$?

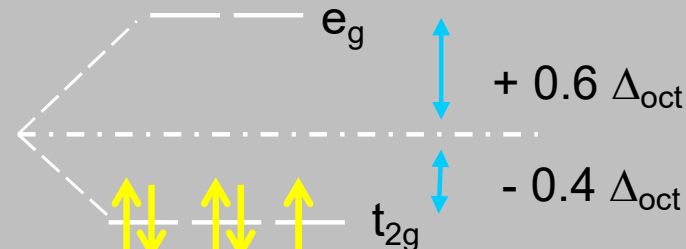
C.N. = 6 $\therefore O_h$

Fe(III) $\therefore d^5$

H.S.



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

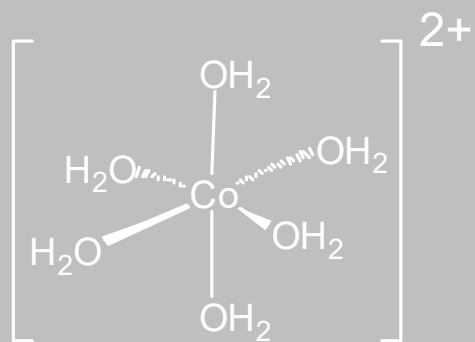


$$\text{CFSE} = 5 \times -0.4 \Delta_{\text{oct}} + 2P = -2.0 \Delta_{\text{oct}} + 2P$$

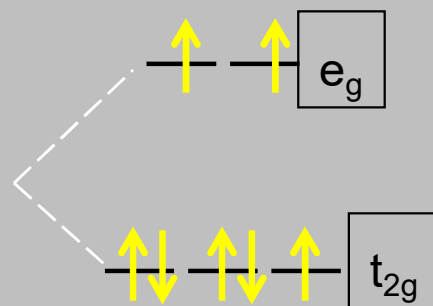
If the CFSE of $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ is $-0.8 \Delta_o$, what spin state is it in?

C.N. = 6 $\therefore O_h$

Co(II) $\therefore d^7$

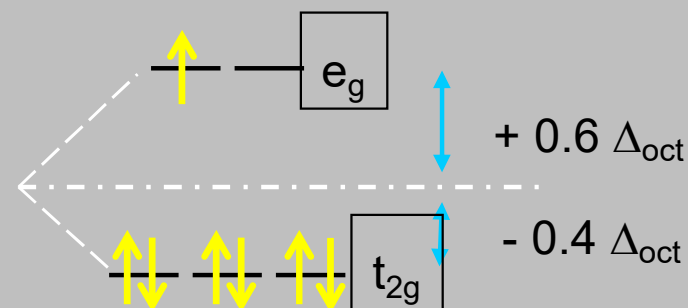


H.S.



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

L.S.



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

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		