

Bonding in coordination compounds

- Pioneering work of

Alfred Werner – 1893

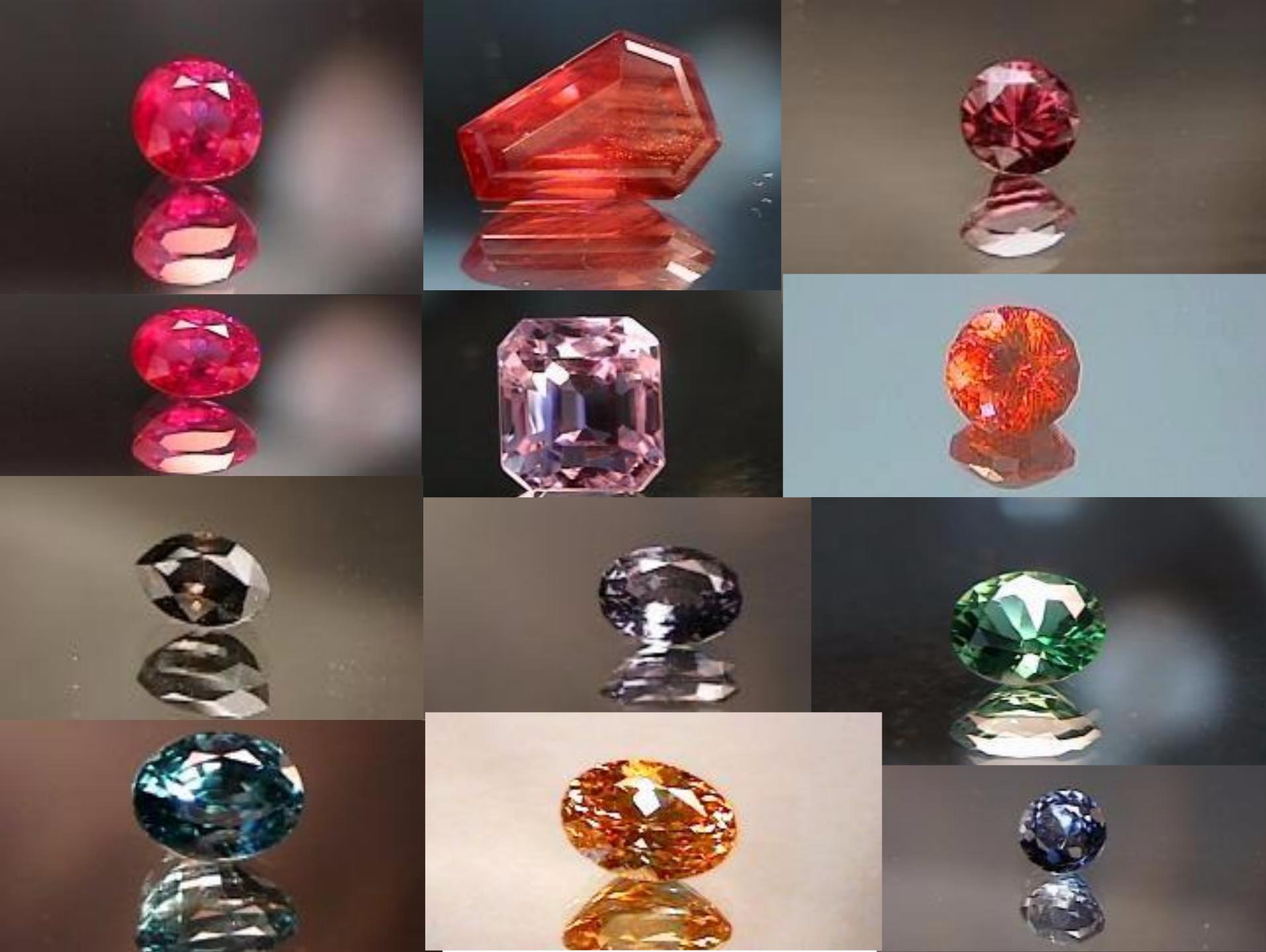
Numbers and properties of
isomers – the correct
geometric structure and M-L
bonds are fixed in space.

- VBT
- Crystal Field Theory (CFT)
- Modified CFT, known as
Ligand Field Theory
- MOT

Nobel prize 1913







Gemstone owe their color from trace transition-metal ions

- Corundum mineral, Al_2O_3 : Colorless
 - $\text{Cr} \rightarrow \text{Al}$: Ruby
 - $\text{Mn} \rightarrow \text{Al}$: Amethyst
 - $\text{Fe} \rightarrow \text{Al}$: Topaz
 - $\text{Ti} \& \text{Co} \rightarrow \text{Al}$: Sapphire
- Beryl mineral, $\text{Be}_3\text{Al}_2\text{Si}_6\text{O}_{18}$: Colorless
 - $\text{Cr} \rightarrow \text{Al}$: Emerald
 - $\text{Fe} \rightarrow \text{Al}$: Aquamarine

Periodic table of the elements

period	group	1*	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	1	H																	
1	2		Be																
2	3	Li																	
2	4		Mg																
3	11			3	4	5	6	7	8	9	10	11	12						
3	12																		
3	Na																		
4	19	K		Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	
4	20																		
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4	34																		
4	35																		
5	37	Rb		Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	
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6	55	Cs		Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	
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6	72																		
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6	85																		
6	86																		
7	87	Fr		Ra	Ac	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn	Nh	Fl	Mc	Lv	
7	88																		
7	89																		
7	104																		
7	105																		
7	106																		
7	107																		
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7	112																		
7	113																		
7	114																		
7	115																		
7	116																		
7	117																		
7	118																		
lanthanoid series		58	59	60	61	62	63	64	65	66	67	68	69	70	71				
		Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu				
actinoid series		90	91	92	93	94	95	96	97	98	99	100	101	102	103				
		Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr				

*Numbering system adopted by the International Union of Pure and Applied Chemistry (IUPAC).

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The d block metal and transition metal are not the same – different

- ‘transition metal’ derived from the fact that their chemical properties were transitional between those of the s and p blocks.
- The IUPAC defines - a transition element is an element that has an incomplete d subshell in either the neutral atom or its ions.
- Zn and Cd are members of the d block but are not transition element as they do not have any compounds with an incomplete d subshell. Hg is a transition element as it has Hg(IV) d⁸ compound.

TM classified as 3d, 4d and 5d series;

Elements towards the left of the d blocks are called as *early* and those towards the right are as *late*.

Note that when d block elements form ions the s electrons are lost first.

TM complex: Variable valence

Sc			+3				
Ti	+1	+2	+3	+4			
V	+1	+2	+3	+4	+5		
Cr	+1	+2	+3	+4	+5	+6	
Mn	+1	+2	+3	+4	+5	+6	+7
Fe	+1	+2	+3	+4	+5	+6	
Co	+1	+2	+3	+4	+5		
Ni	+1	+2	+3	+4			
Cu	+1	+2	+3				
Zn			+2				

Complexes: Have metal ion (can be zero oxidation state) bonded to number of ligands.

Complex contains central metal ion bonded to one or more molecules or anions

Lewis acid = metal = center of coordination

Transition metals can act as Lewis acid

Lewis base = ligand = molecules/ions covalently bonded to metal in complex

The term ligand (ligare [Latin], to bind) was first used by Alfred Stock in 1916 in relation to silicon chemistry. The first use of the term in a British journal was by H. Irving and R.J.P. Williams in *Nature*, 1948, 162, 746.

For a fascinating review on 'ligand' in chemistry - *Polyhedron*, 2, 1983, 1-7.

Ligand: Lewis base – contains electrons to bond to a metal electrons



Lewis acid

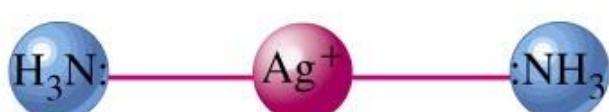
Lewis base

Complex ion

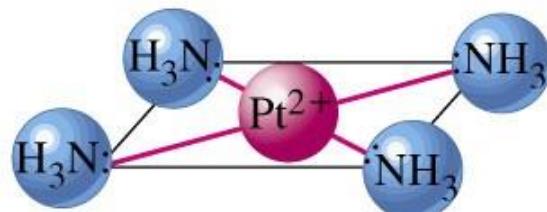
◆ Coordination compound

- * $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$; $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$; $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$
- * $[\text{Cu}(\text{NH}_3)_4][\text{PtCl}_4]$
- * $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$

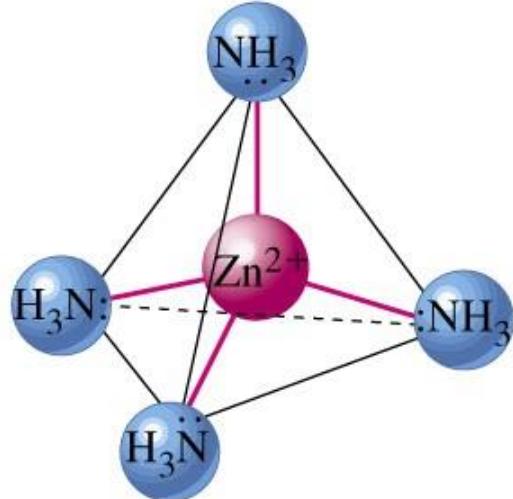
How & Why?



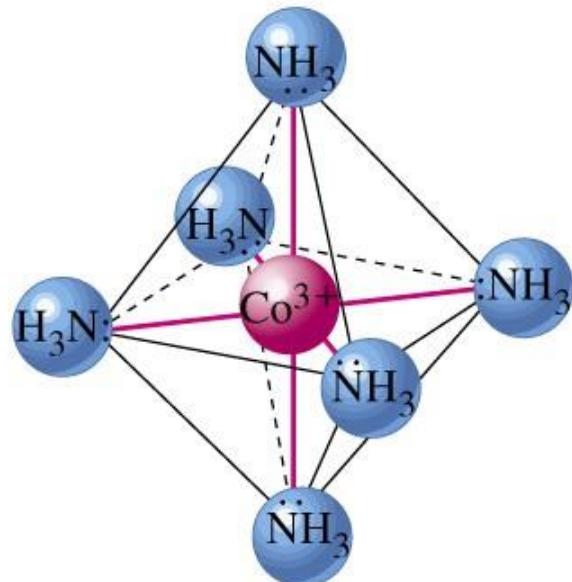
Linear



Square planar



Tetrahedral

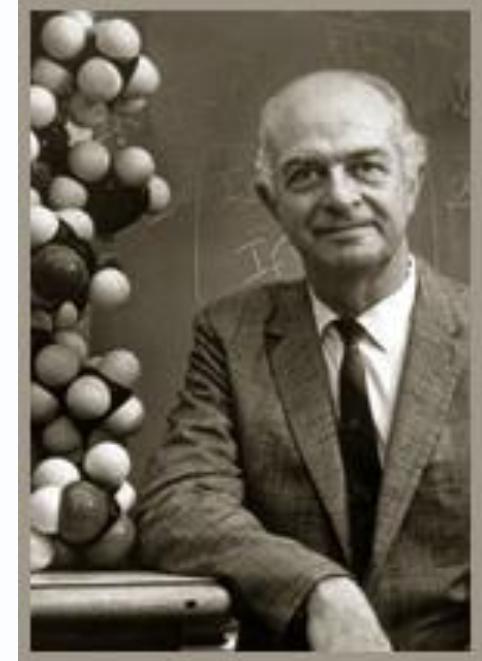


Octahedral

Valence Bond Theory

Basic Principle

A covalent bond forms when the orbitals of two atoms overlap and are occupied by a pair of electrons that have the highest probability of being located between the nuclei.



Linus Carl Pauling
(1901-1994)
Nobel prizes: 1954, 1962

Valence Bond Model

Ligand = Lewis base

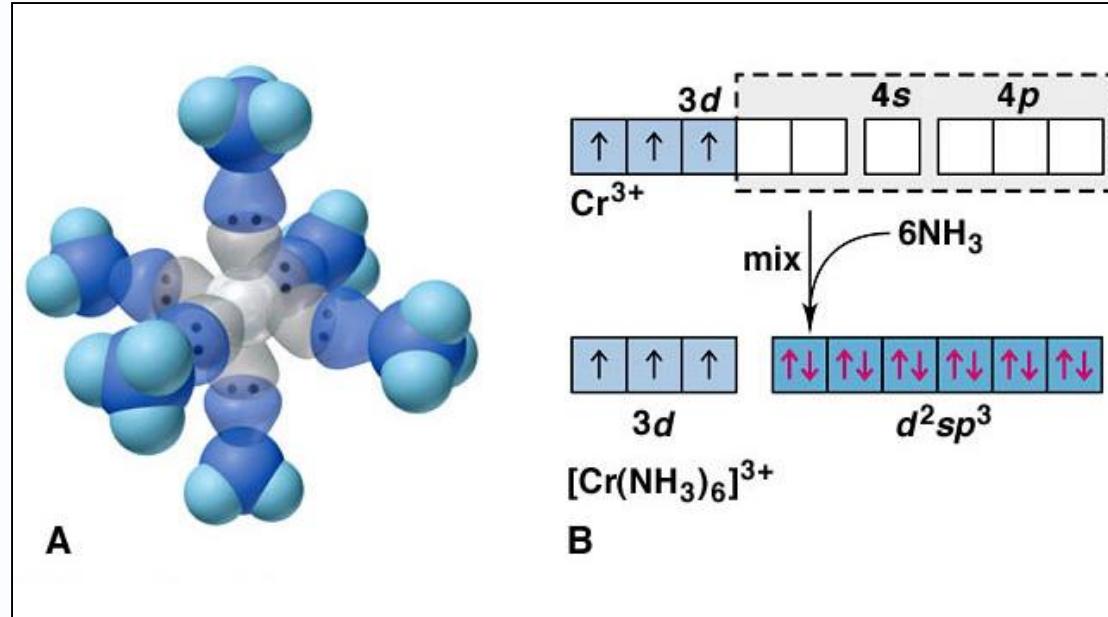
Metal = Lewis acid

s, p and d orbitals give hybrid orbitals with specific geometries

Number and type of M-L hybrid orbitals determines geometry of the complex

Octahedral Complex

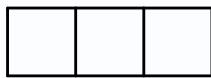
e.g. $[\text{Cr}(\text{NH}_3)_6]^{3+}$



$$d_x^2, d_y^2, d_z^2$$

 d^2sp^3 

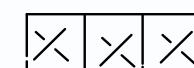
4s



4p



4s



4p



4d



4s



4p

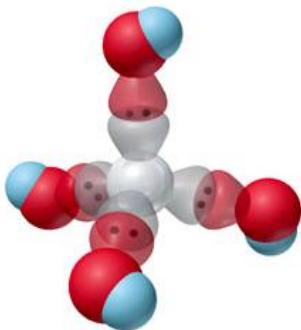
sp^3d^2 outer orbital hybridization
(4d)

Co-F ionic; high spin complex

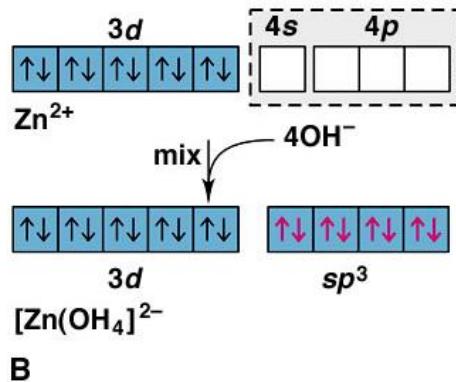
d^2sp^3 inner orbital hybridization
(3d)

Co-NH₃ covalent; low spin complex

Tetrahedral e.g. $[\text{Zn}(\text{OH})_4]^{2-}$



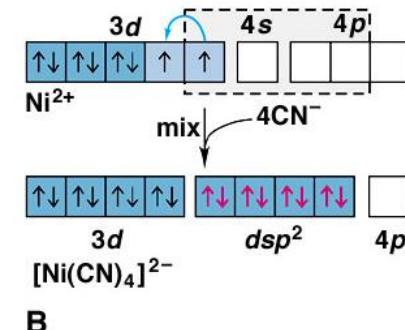
A



Square Planar e.g. $[\text{Ni}(\text{CN})_4]^{2-}$



A



NiCl_4^{2-} , sp^3 , tetrahedral, has free metal ion configuration -paramagnetic for two unpaired electrons.

‘The magnetic criterion of bond type’ – if magnetic property is known, geometry of four coordinate d8 complex can be predicted.

Diamagnetic – square planar

Paramagnetic - tetrahedral

Limitations of VB theory

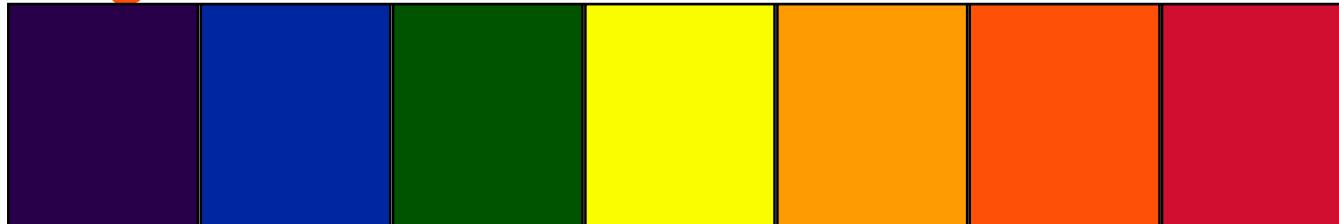
Cannot account for colour of complexes

May predict magnetism wrongly

Cannot account for spectrochemical series

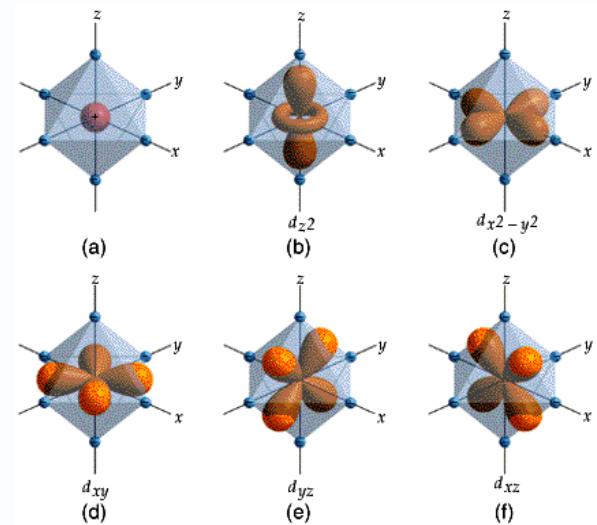
No antibonding concept

Crystal Field Theory



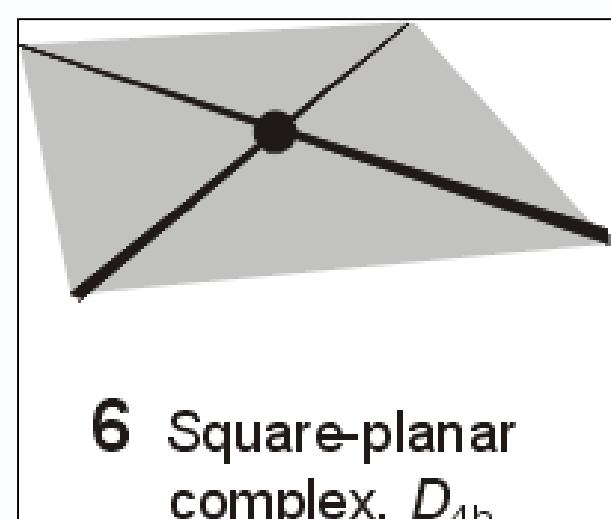
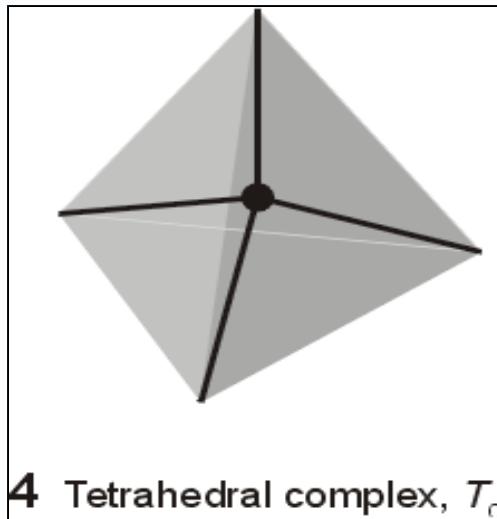
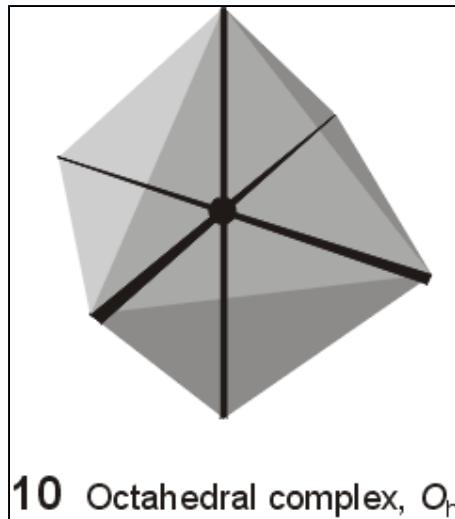
400 500 600 800

- The relationship between colors and complex metal ions

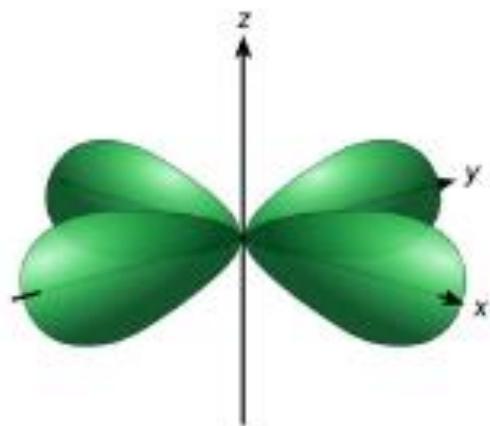


Crystal Field Theory

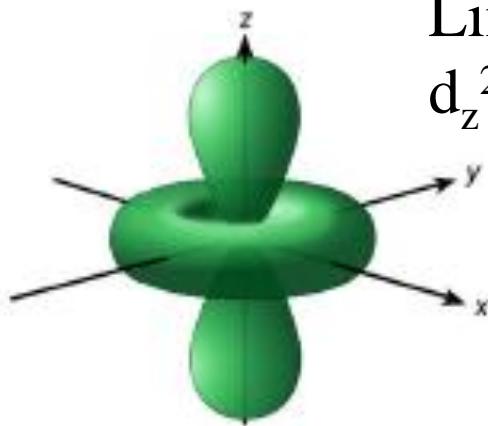
- A purely *ionic* model for transition metal complexes.
- Ligands are considered as negatively charged points.
- Predicts the pattern of splitting of d-orbitals.
- Used to rationalize spectroscopic and magnetic properties.



d-orbitals: look attentively along the axis



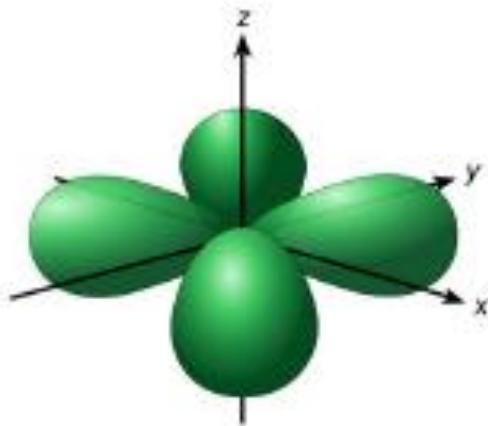
$d_{x^2-y^2}$



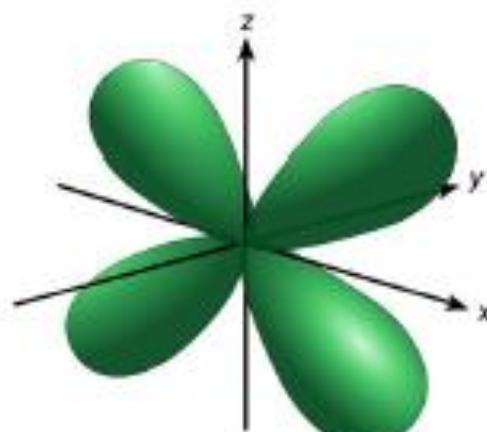
d_{z^2}

Linear combination of
 $d_z^2 - d_x^2$ and $d_z^2 - d_y^2$

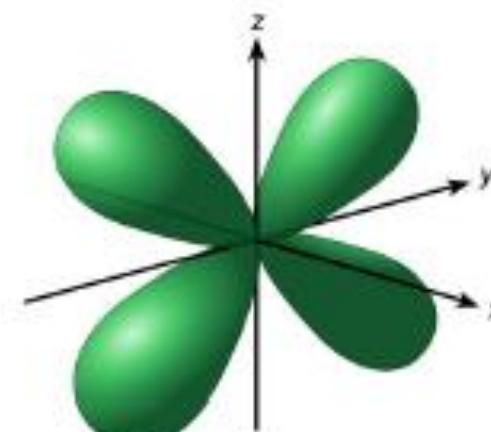
$$d_{2z}^2 - d_x^2 - d_y^2$$



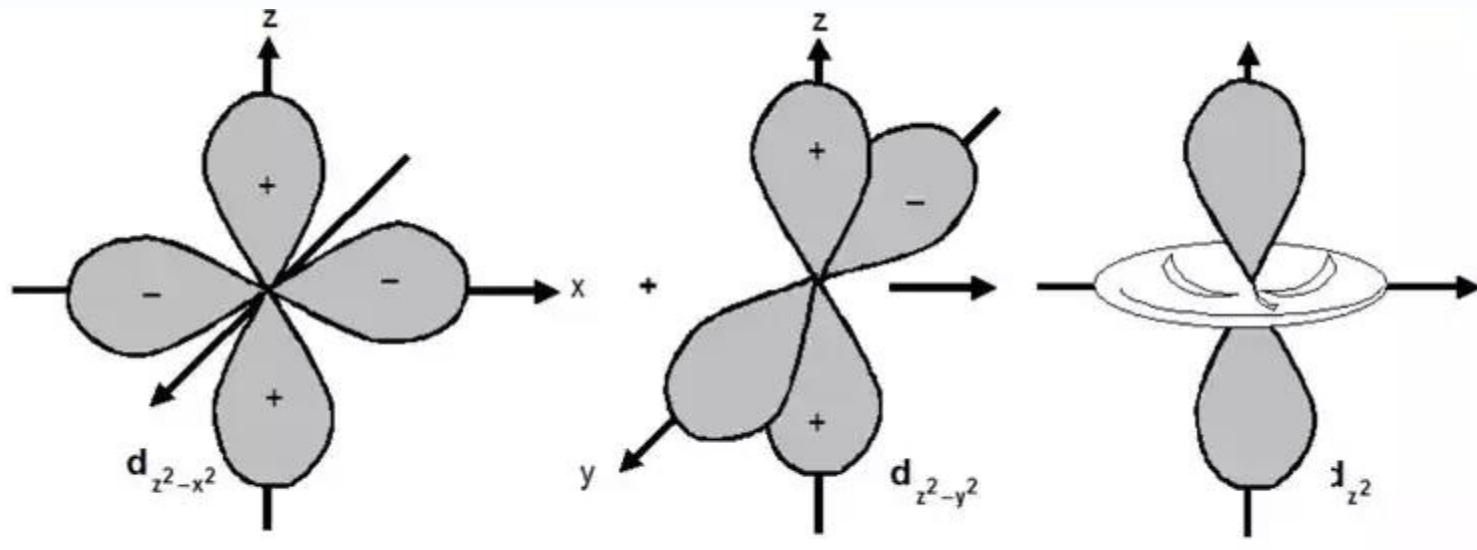
d_{xy}



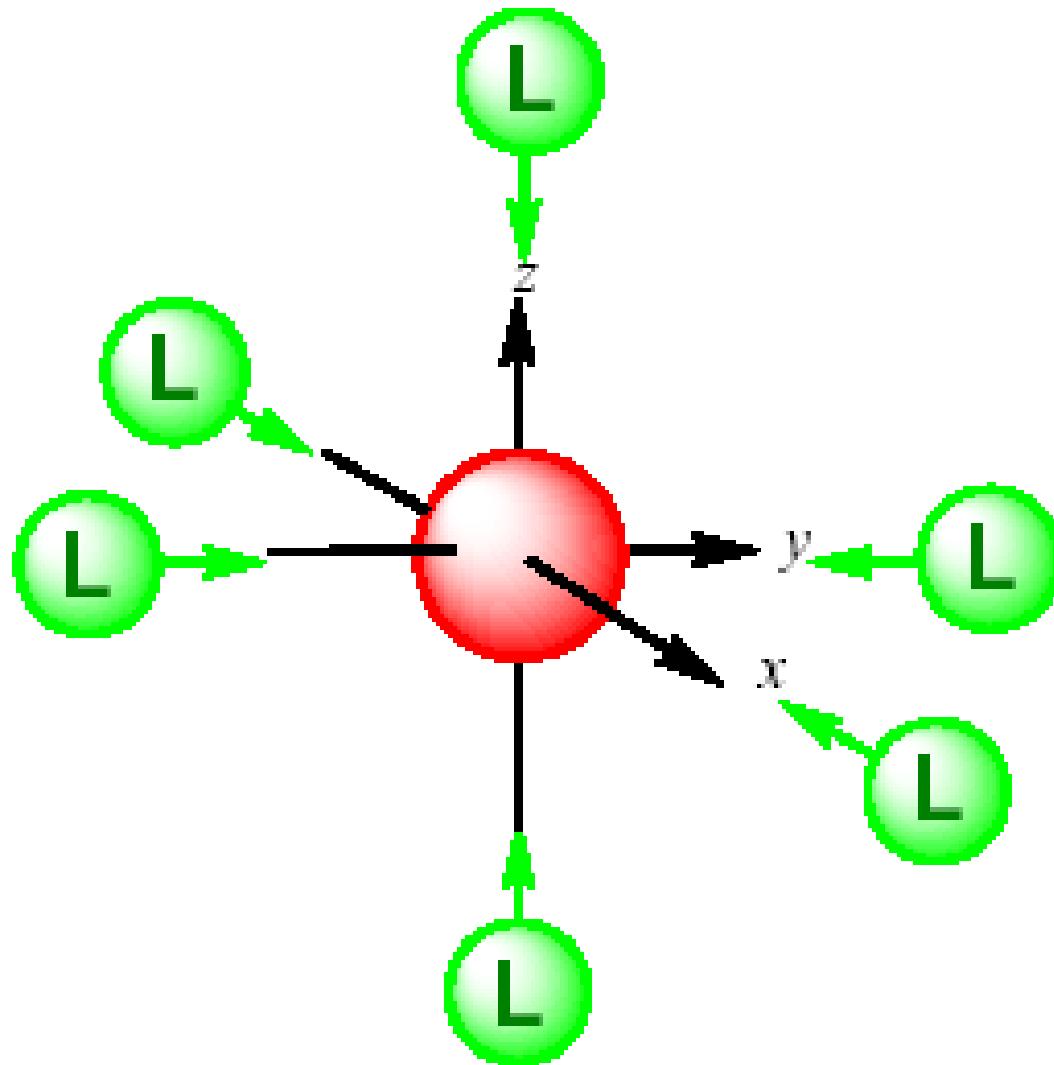
d_{xz}



d_{yz}

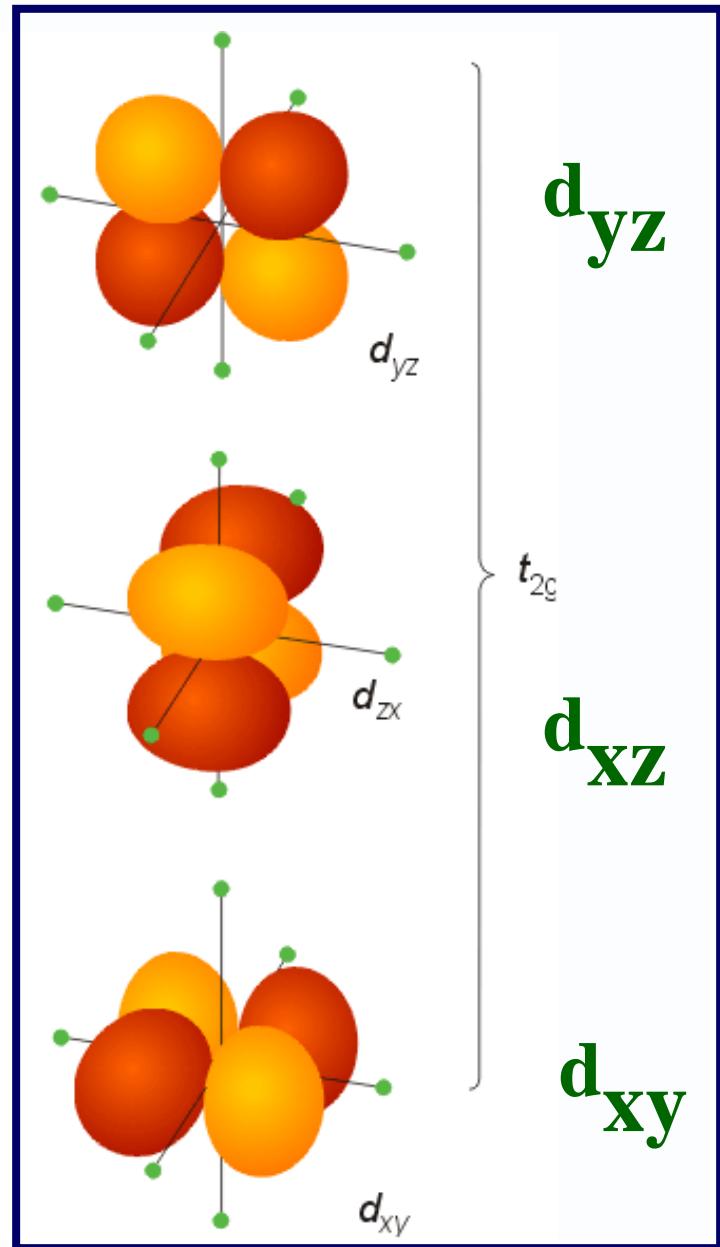
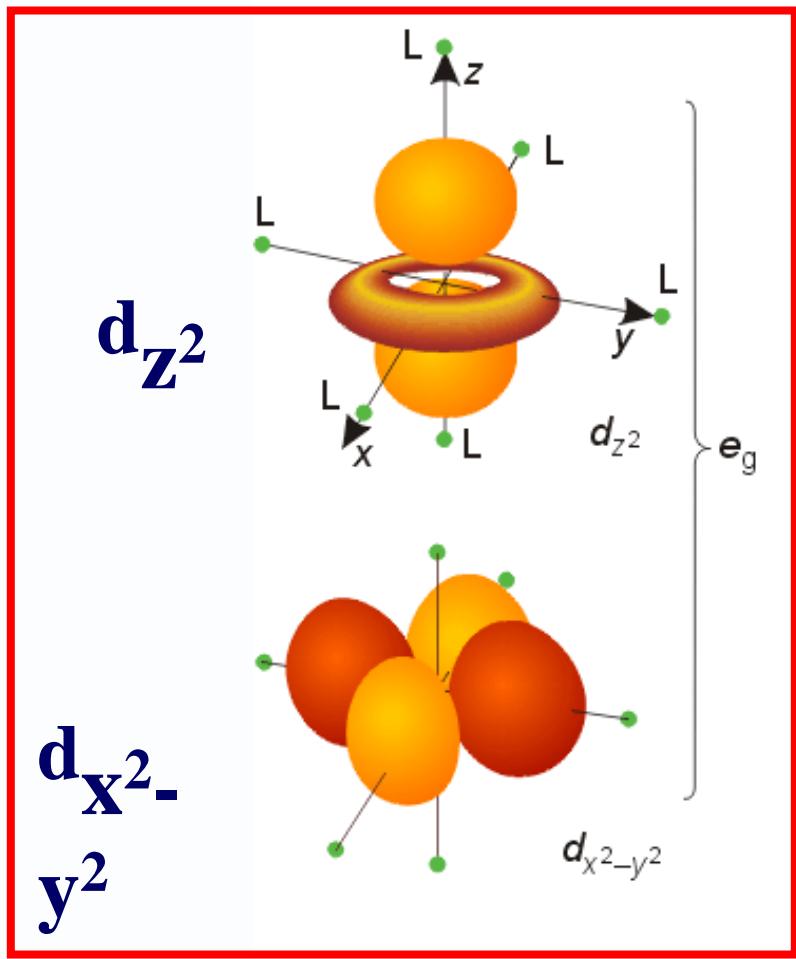


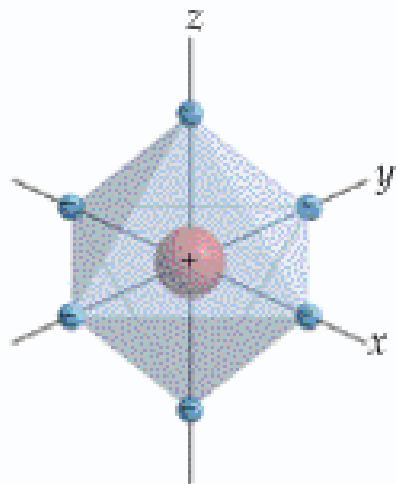
Octahedral Field



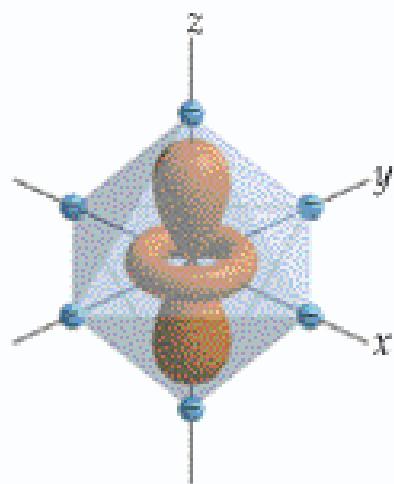
M has d¹ -

In Octahedral Field

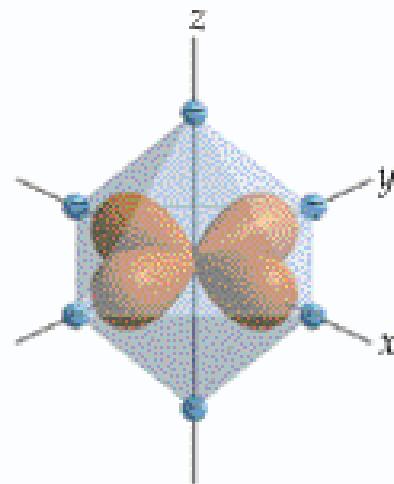




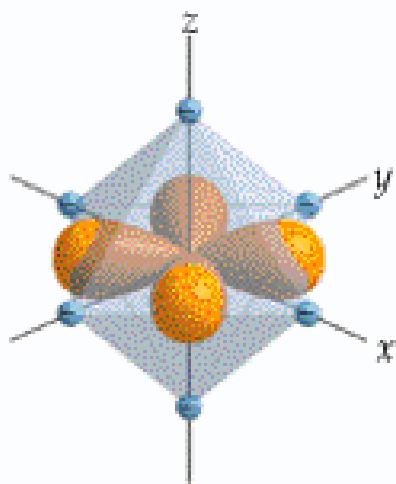
(a)



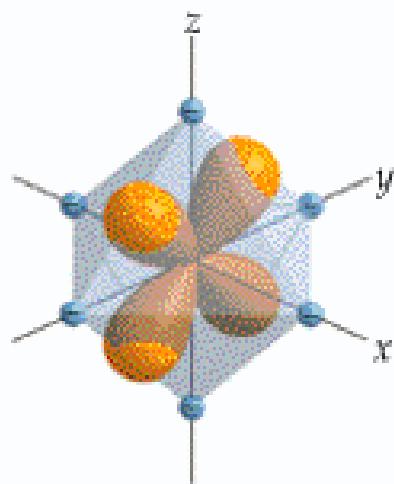
(b)



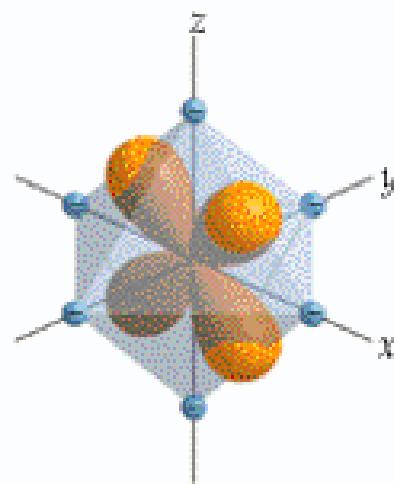
(c)



(d)



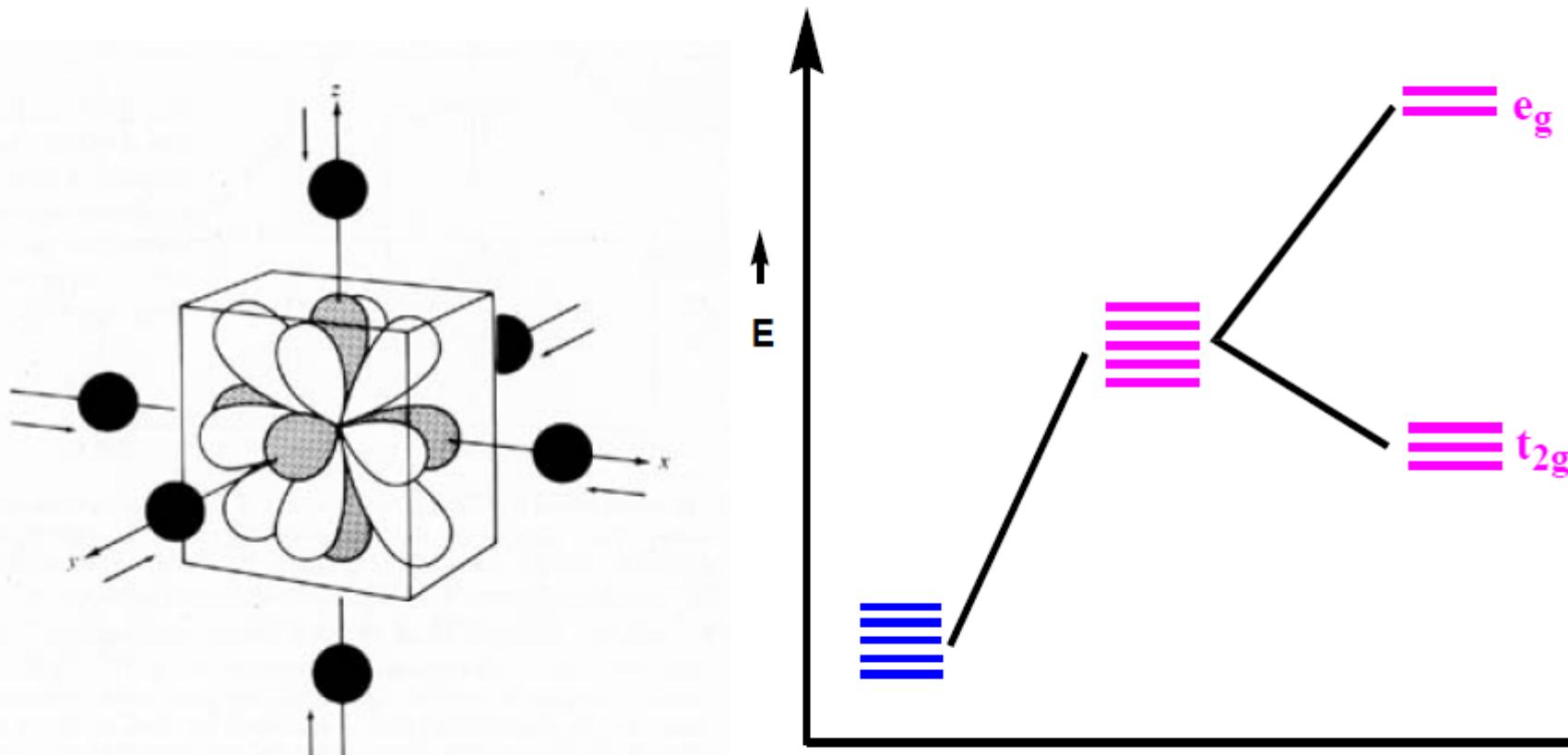
(e)



(f)

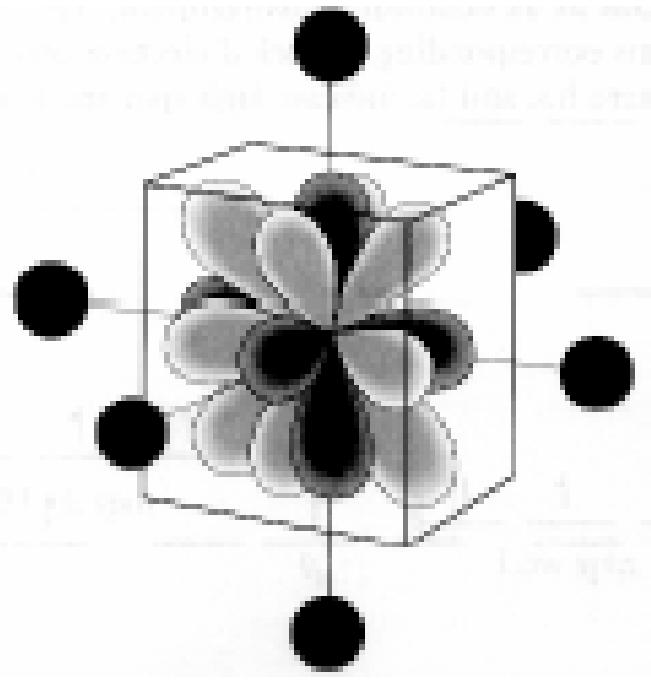
Octahedral Field

- If rather than a spherical field, discrete point charges (ligands) are allowed to interact with the metal, the degeneracy of the d orbitals is removed (or, better said, lifted). The splitting of d orbital energies and its consequences are at the heart of crystal field theory.

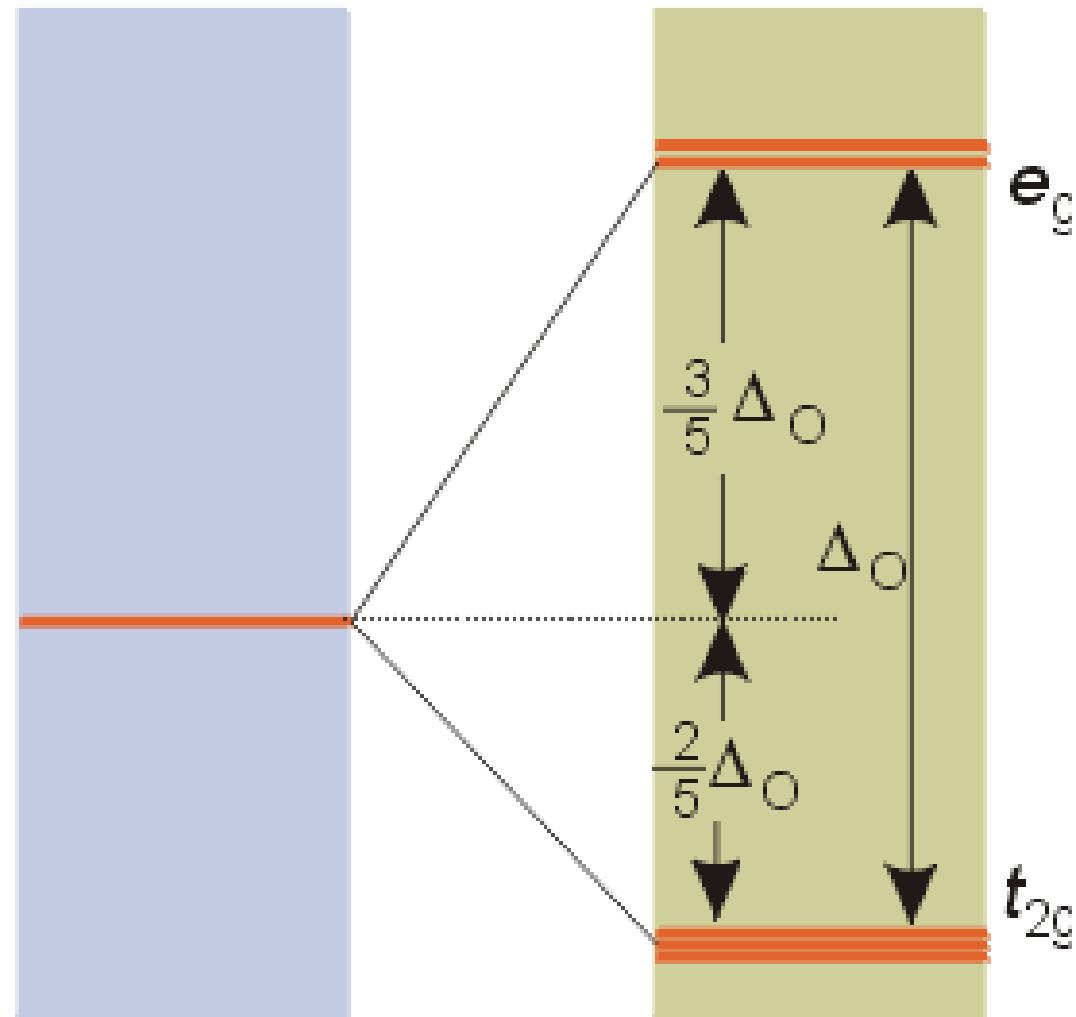


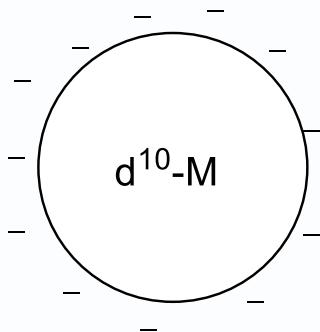
- Not all d orbitals will interact to the same extent with the six point charges located on the +x, -x, +y, -y, +z and -z axes respectively.
- The orbitals which lie along these axes (i.e. x^2-y^2 , z^2) will be destabilized more than the orbitals which lie in between the axes (i.e. xy , xz , yz).

Spherical environment

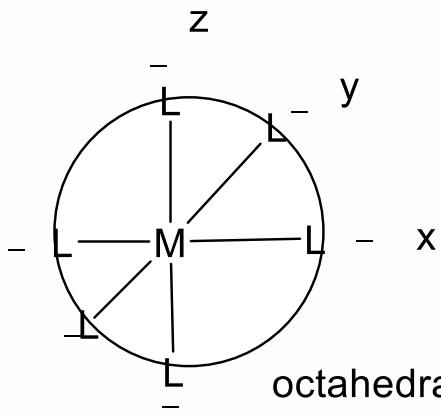


In octahedral crystal field

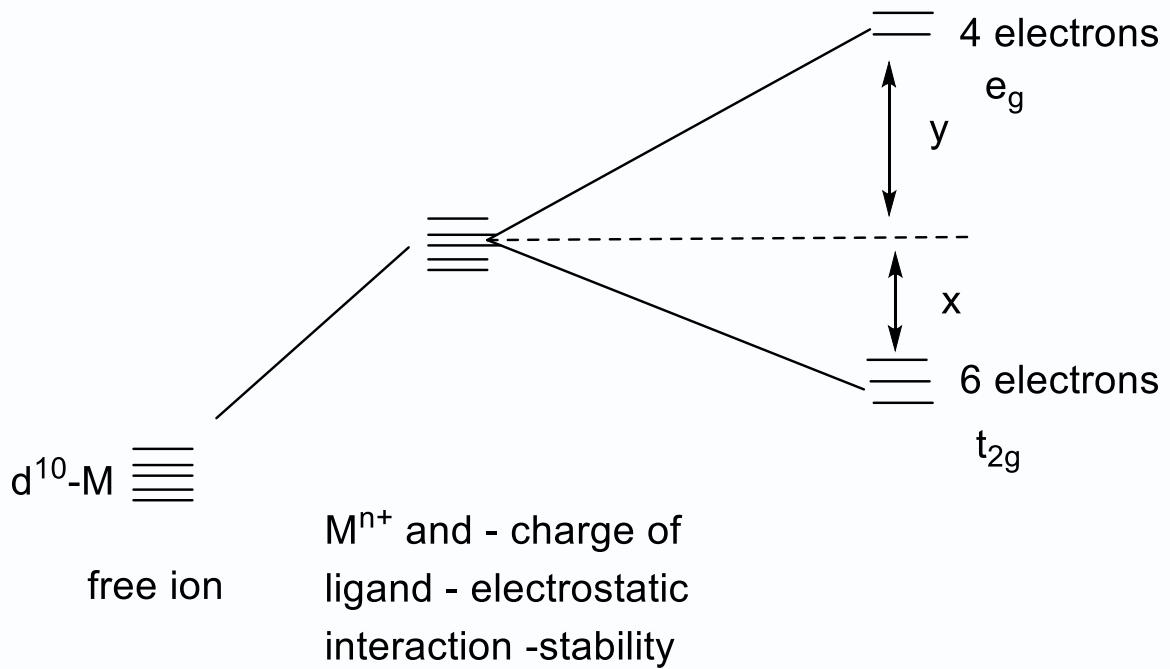




spherical field

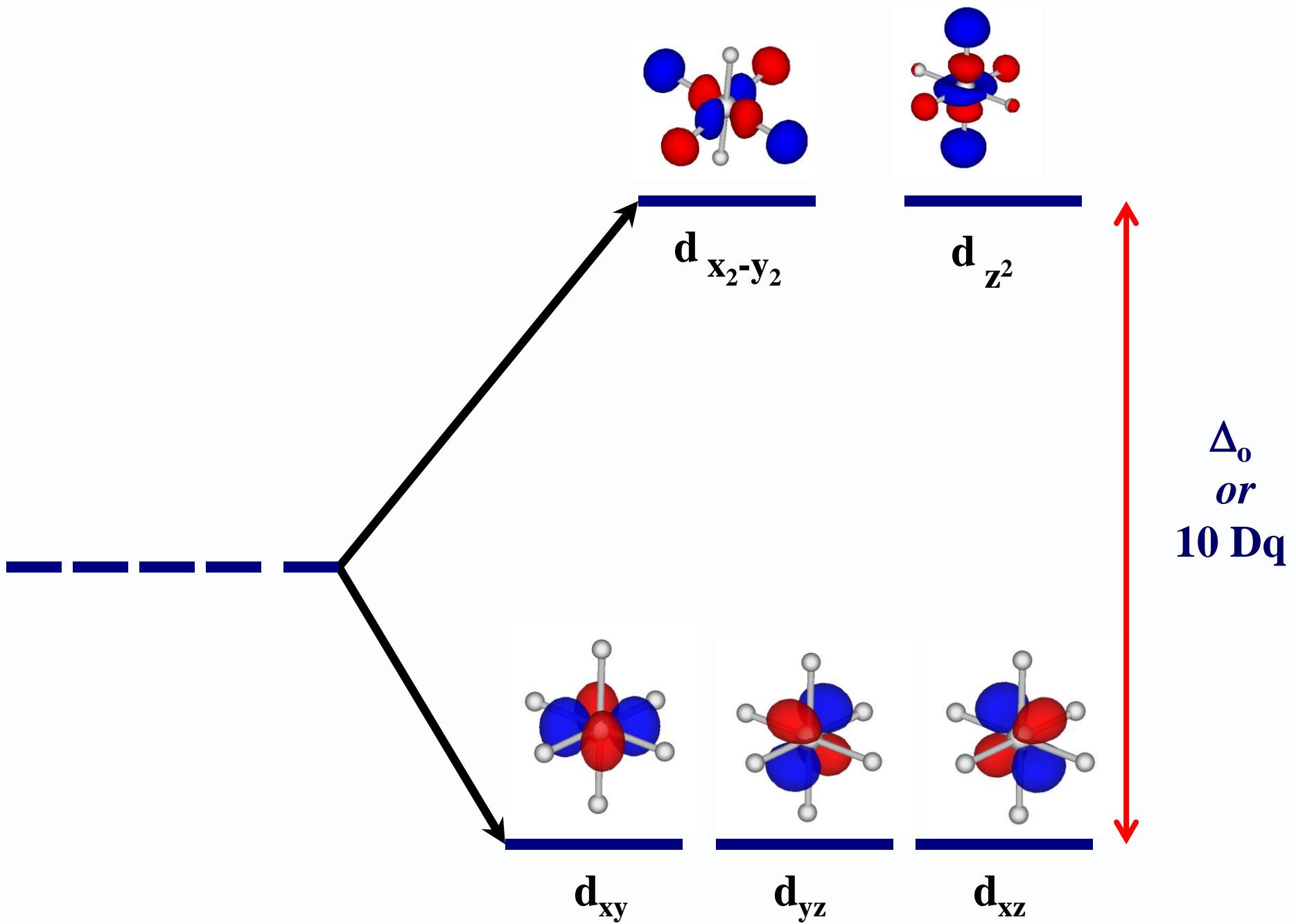


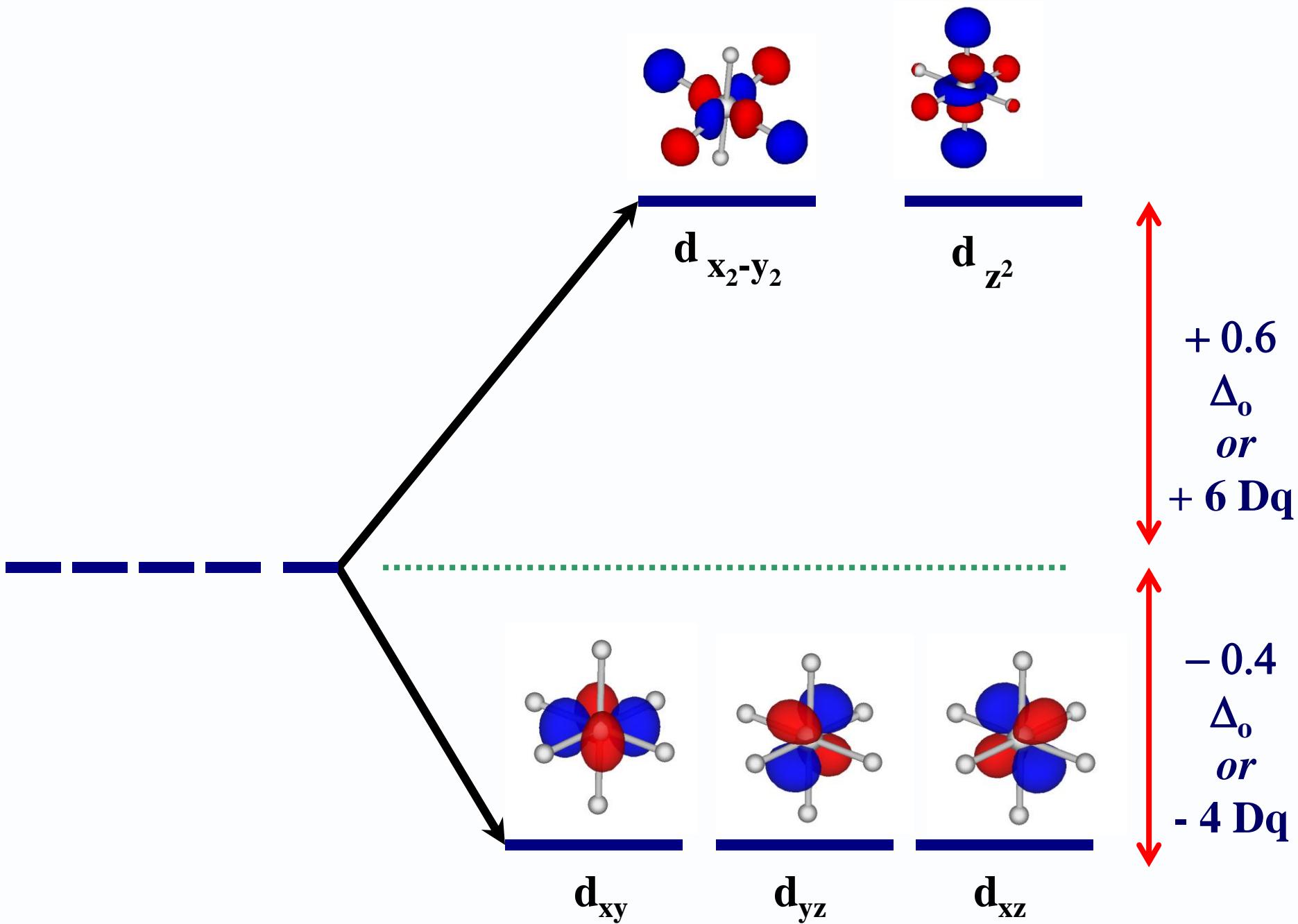
octahedral geometry

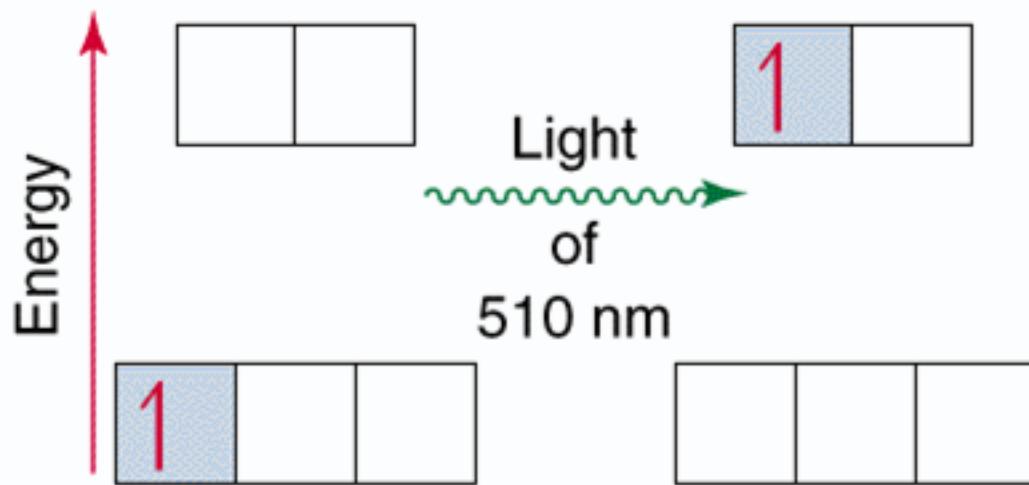
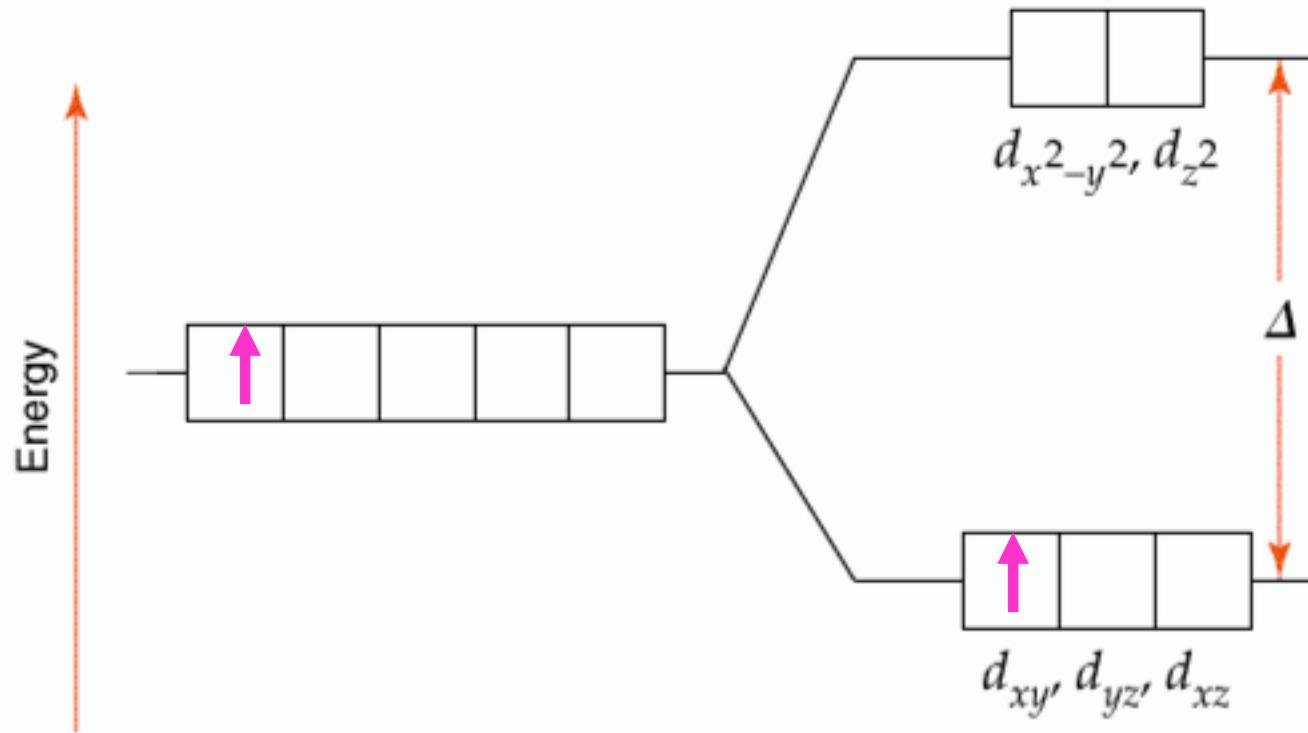


Say $x + y = 1$; Since $y = 1.5 x$
 $x + 1.5 x = 1$; $2.5x = 1$,
 $x = 1/2.5 = 0.4$, then, $y = 0.6$
 This is equal to 3/5:2/5 ratio

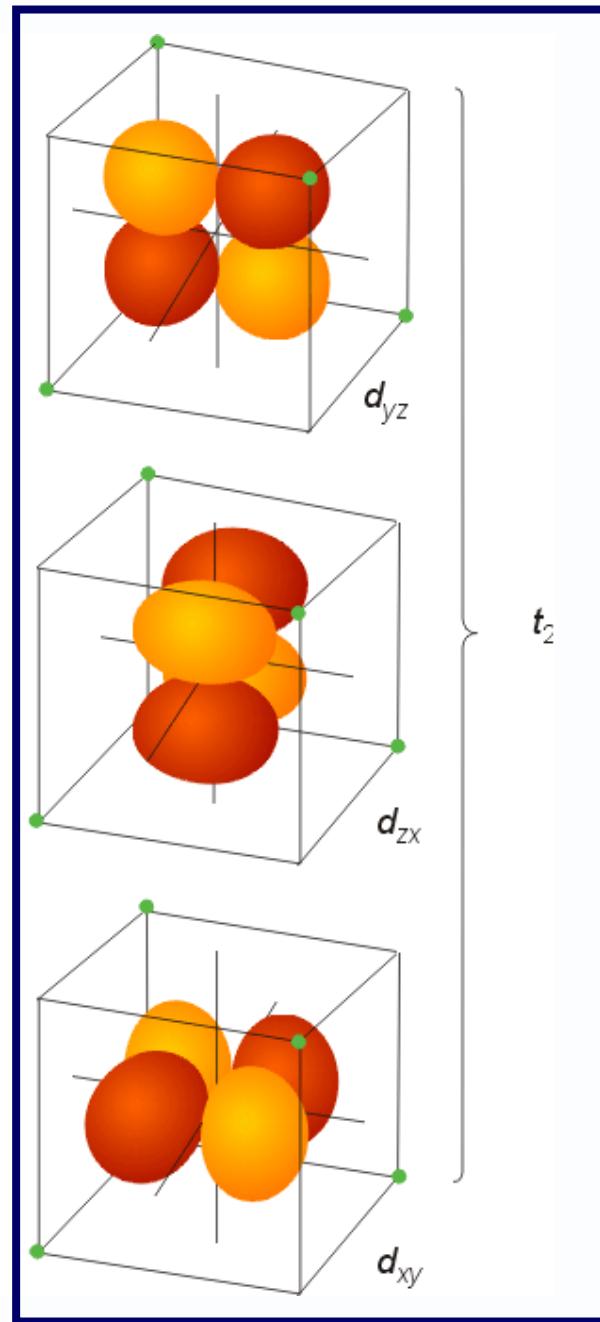
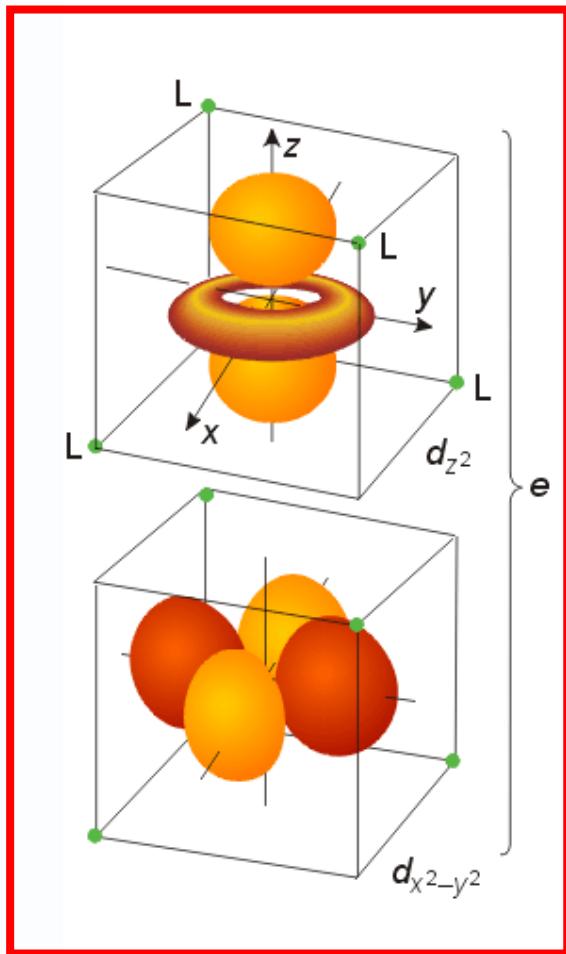
The rise in the energy of the e_g orbitals is 6/4 times the drop in energy of the t_{2g} orbitals, equivalent to the 3/5:2/5 ratio.

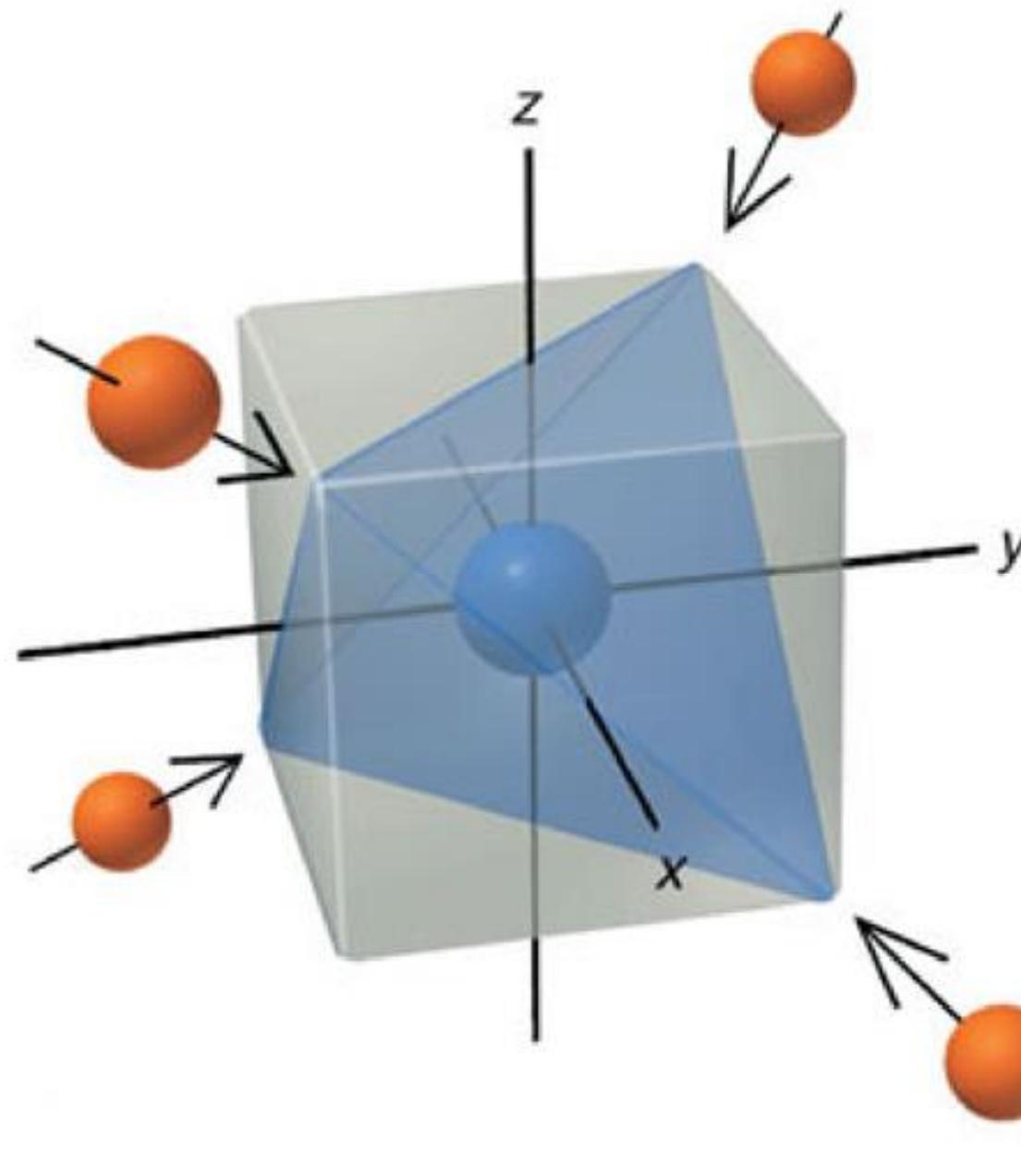




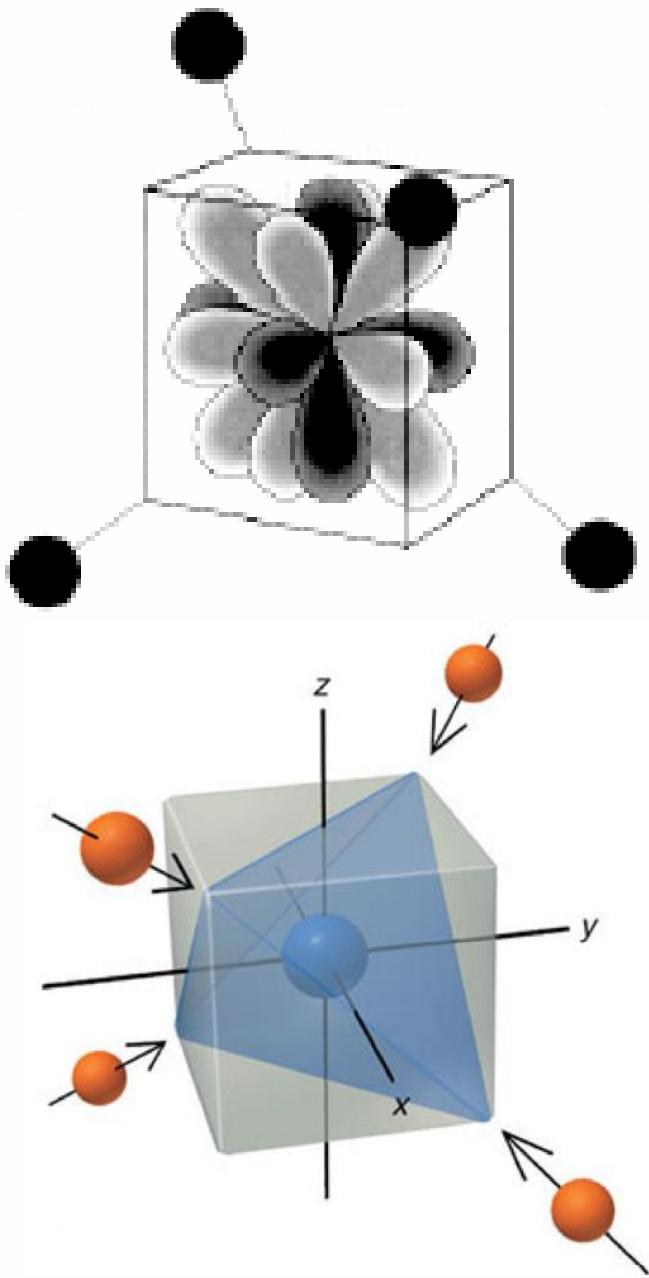


In Tetrahedral Field

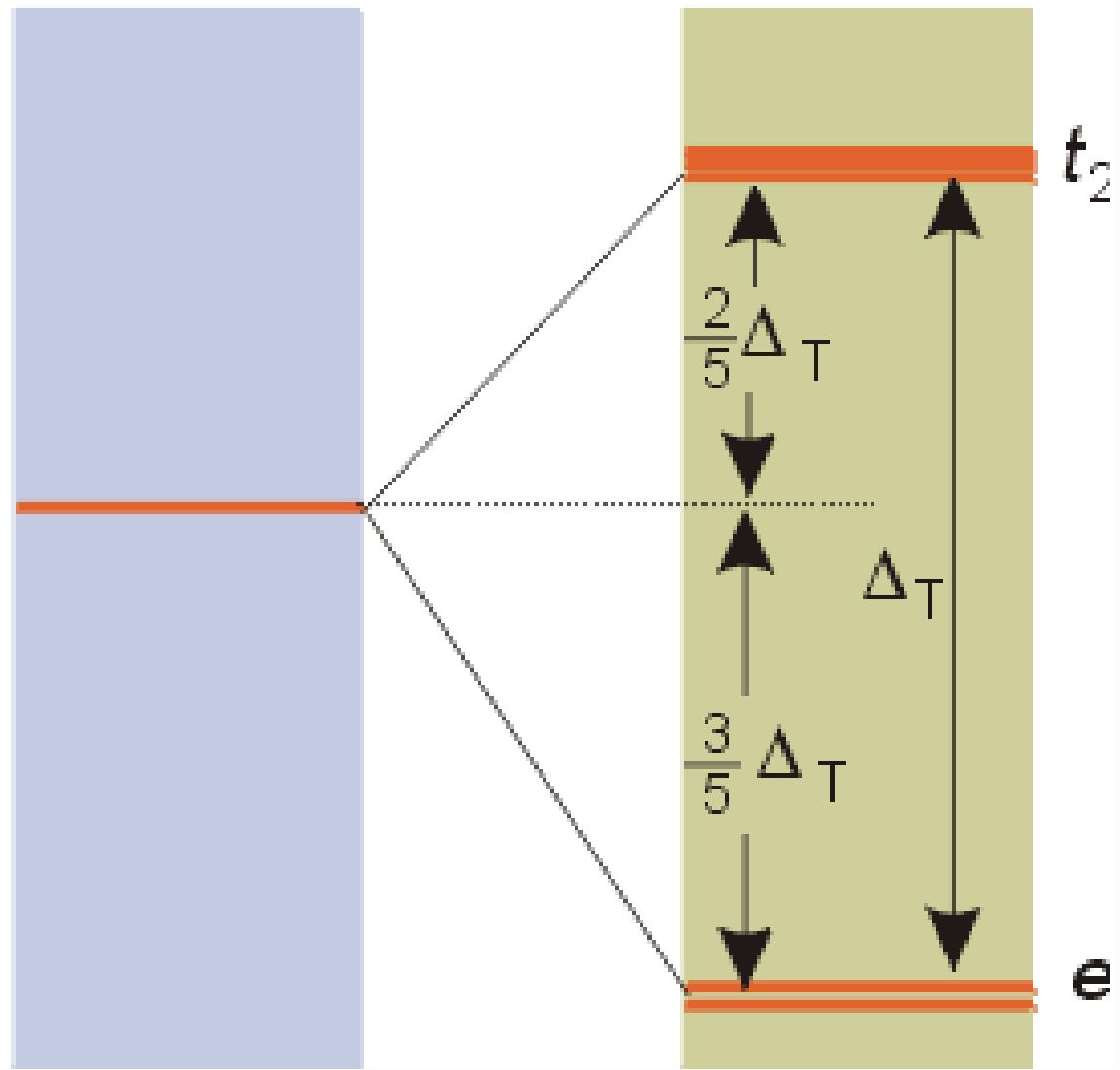




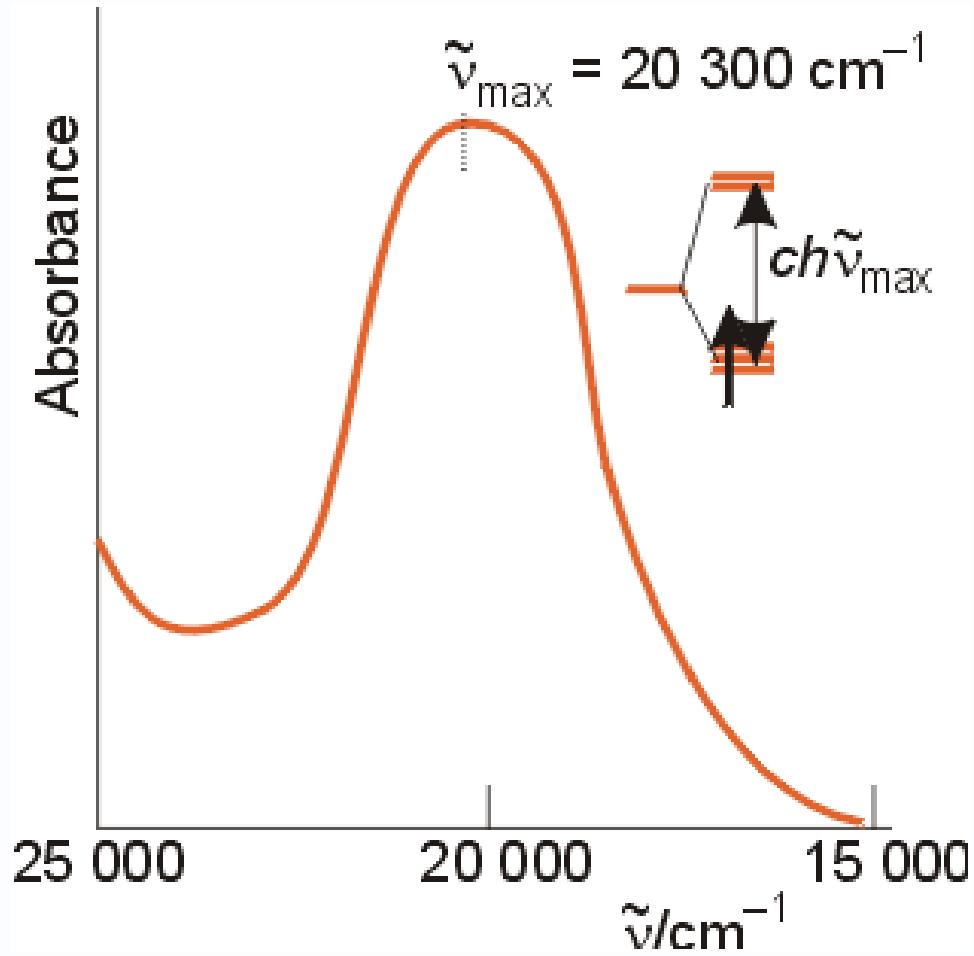
Spherical environment



In tetrahedral crystal field



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



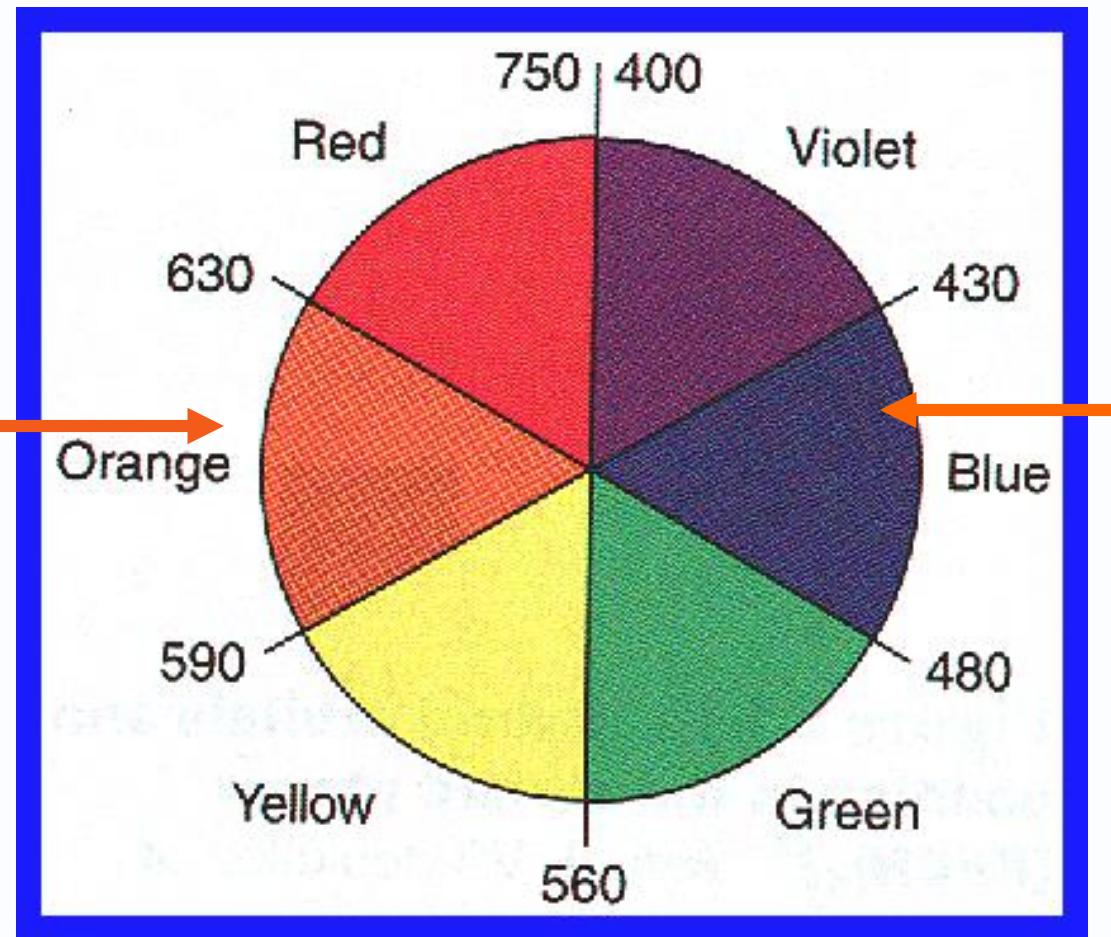
Assigned transition:
This corresponds to

the energy gap

$$\Delta_0 = 243 \text{ kJ mol}^{-1}$$

490 nm

**absorbed
color**



**observed
color**

Factors affecting the magnitude of Δ_o

Oxidation state of the metal ion



Nature of the metal ion: 3d < 4d < 5d

From Cr to Mo or Co to Rh, the value of Δ_o increases by about 50%

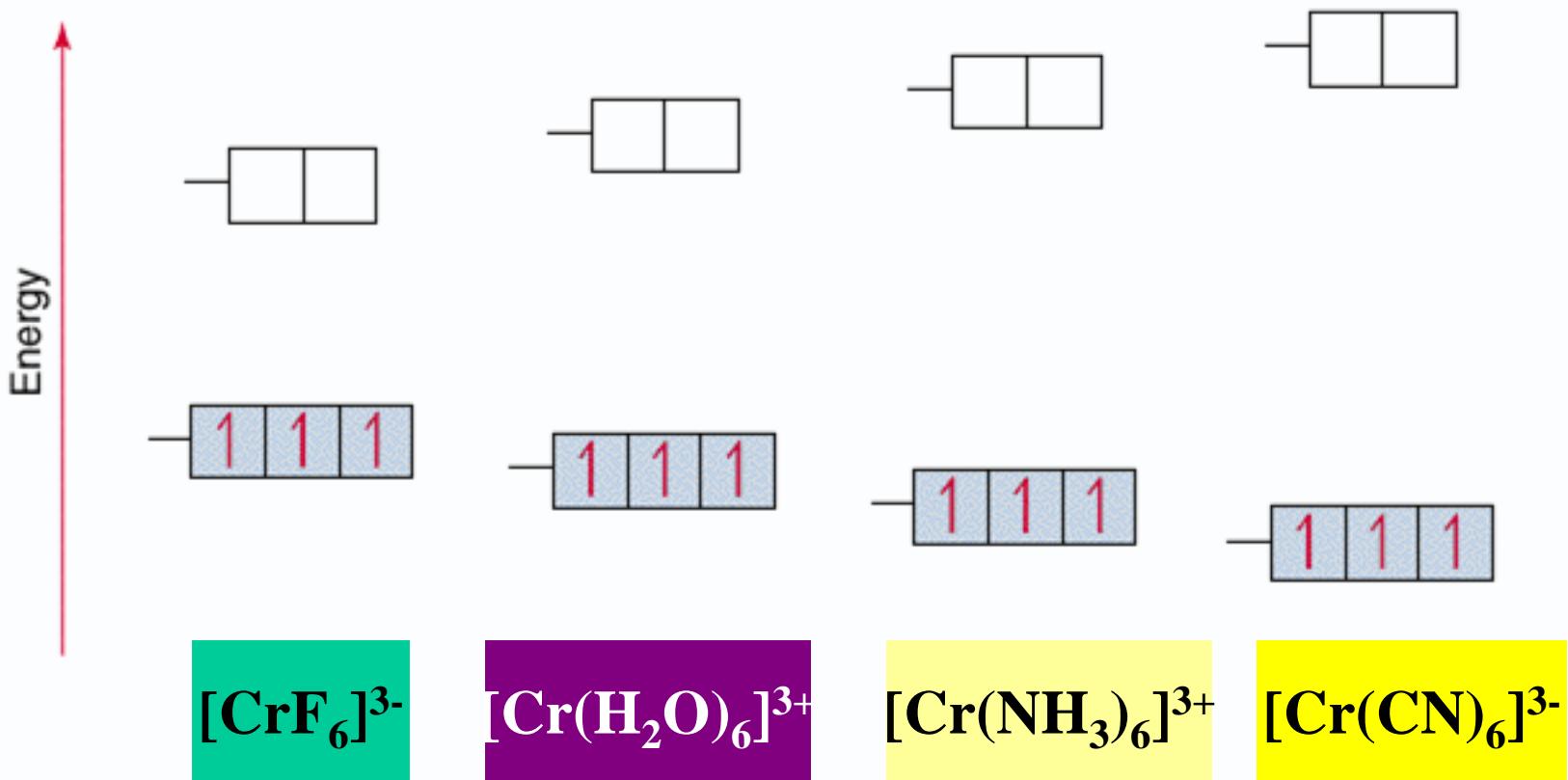
Number of ligands and geometry

$$\Delta_t < \Delta_o$$

$$\Delta_t = 4/9 \Delta_o$$

Nature of the ligand





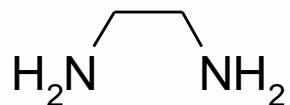
As Cr³⁺ goes from being attached to a weak field ligand to a strong field ligand, Δ increases and the color of the complex changes from green to yellow.

- Spectrochemical Series: An order of ligand field strength based on experiment:

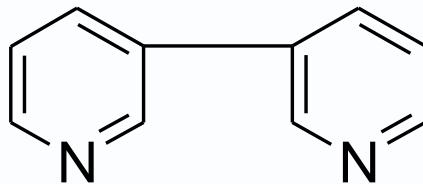
Weak Field

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

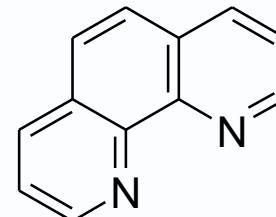
Strong Field



Ethylenediamine (en)



2,2'-bipyridine (bipy)



1,10 - phenanthroline (phen)

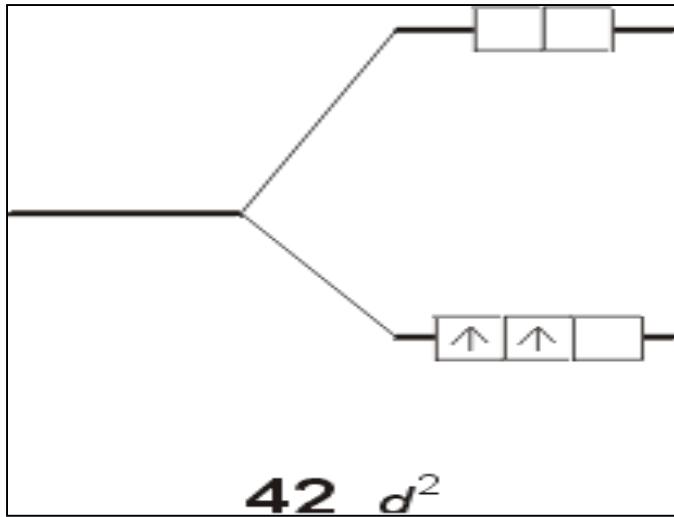
Crystal Field Splitting Energy (CFSE)

- In Octahedral field, configuration is: $t_{2g}^x e_g^y$

$$\text{CFSE} = (\text{no. of electrons in } t_{2g} \times 0.4 \Delta_o) - (\text{no. of electrons in } e_g \times 0.6 \Delta_o) = X \Delta_o$$

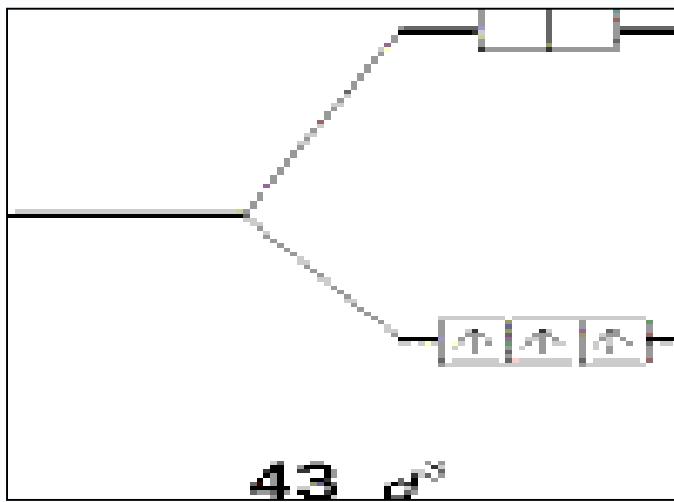
$$\Delta_O = 10 \text{ Dq}$$

Ground-state Electronic Configuration, Magnetic Properties and Colour



t_{2g}^2

$$\begin{aligned} \text{CFSE} &= (2 \times 0.4 \Delta_0) - (0 \times 0.6 \Delta_0) \\ &= 0.8 \Delta_0 \end{aligned}$$

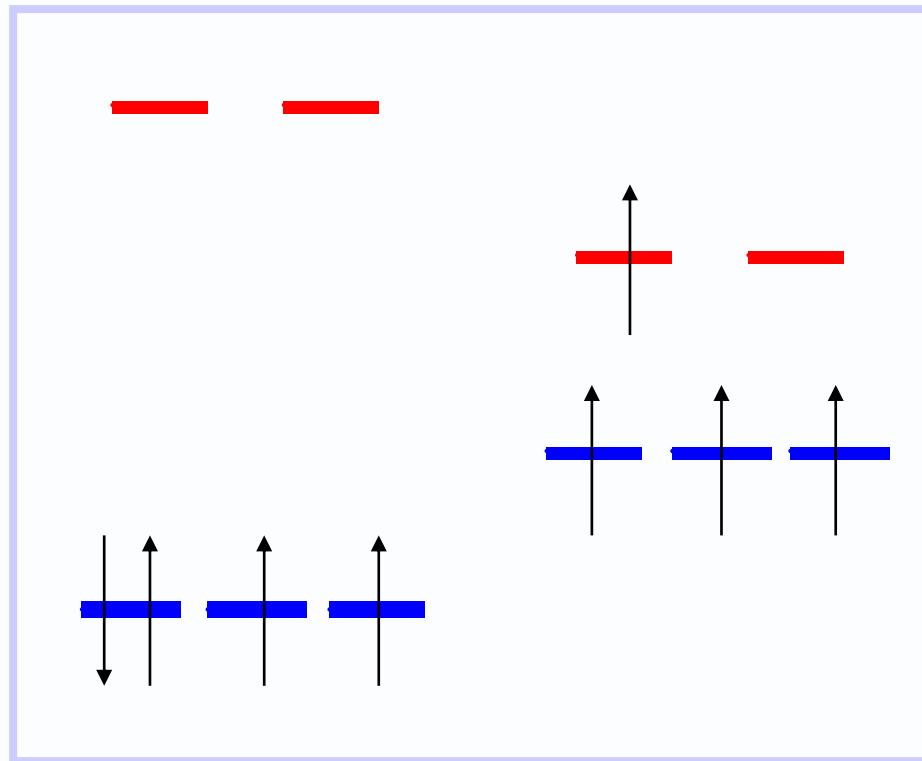


t_{2g}^3

$$\begin{aligned} \text{CFSE} &= (3 \times 0.4 \Delta_0) - (0 \times 0.6 \Delta_0) \\ &= 1.2 \Delta_0 \end{aligned}$$

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

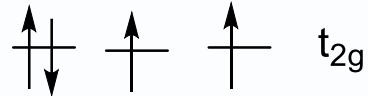
Weak field =
High spin
(4 unpaired)

$$P < \Delta_o$$

$$P > \Delta_o$$

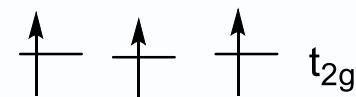
Coulombic repulsion energy and exchange energy

A



Strong field or low spin

B



Weak field or high spin

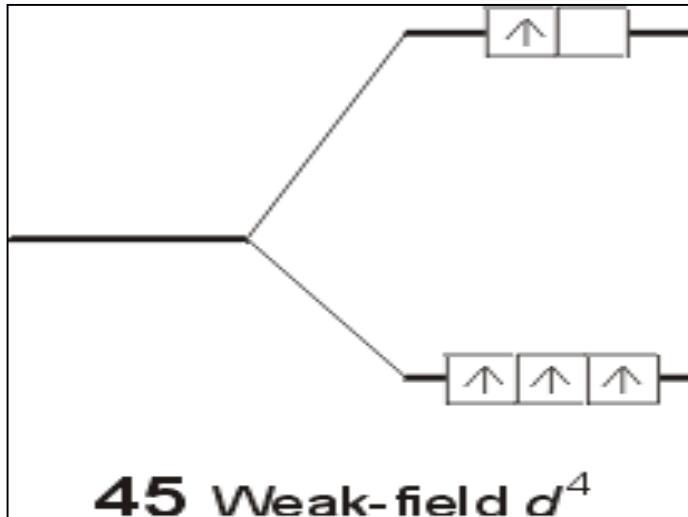
For A:

$$\text{CFSE} = (4 \times 0.4 \Delta_o) - (0 \times 0.6 \Delta_o) = 1.6 \Delta_o + P$$

For B:

$$\text{CFSE} = (3 \times 0.4 \Delta_o) - (1 \times 0.6 \Delta_o) = 0.6 \Delta_o$$

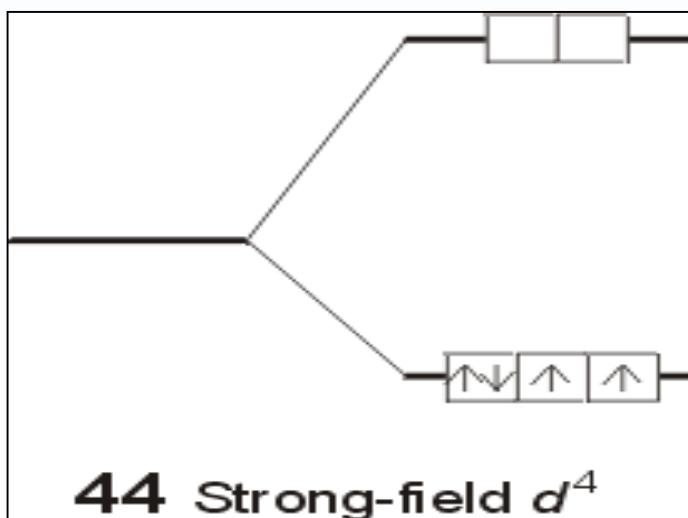
Ground-state Electronic Configuration, Magnetic Properties and Colour



Weak Field Complex

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

High Spin Complex



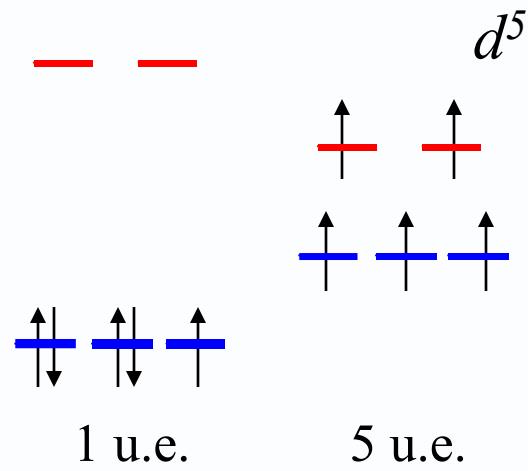
Strong field Complex

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

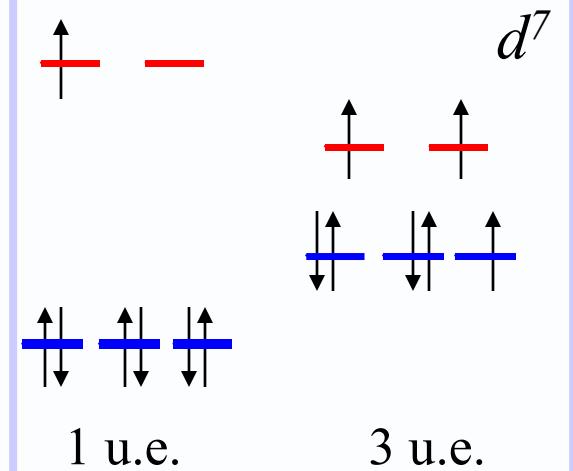
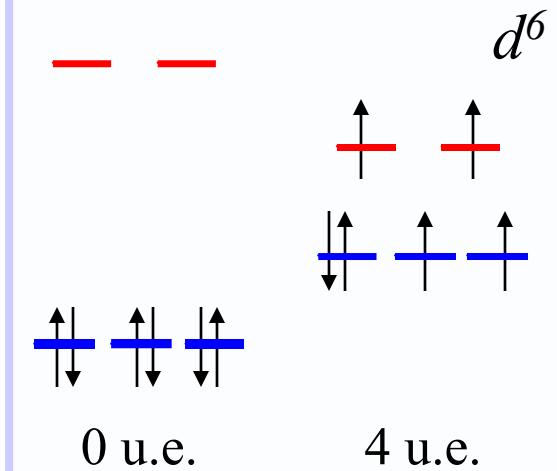
Low Spin Complex

Placing electrons in d orbitals

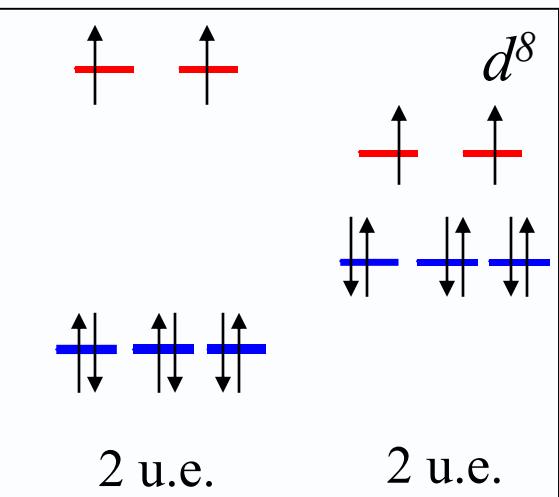
$$\text{CFSE} = 2.0 \Delta_o + 2\mathbf{P}$$



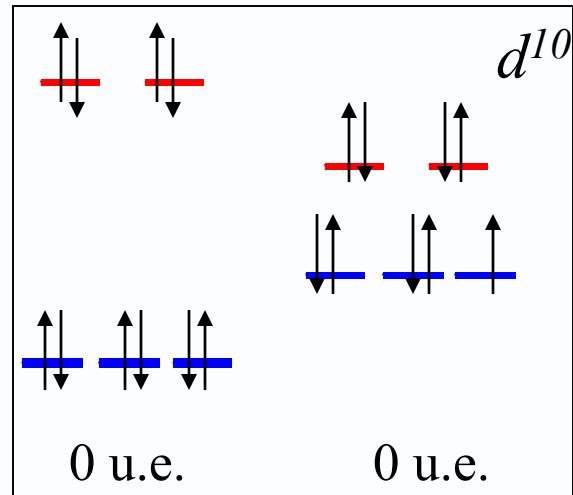
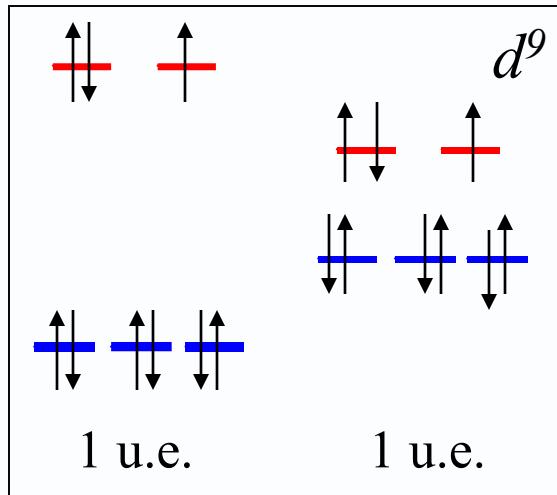
$$\text{CFSE} = 2.4 \Delta_o + 3\mathbf{P}$$



$$\text{CFSE} = 0.0 \Delta_o \text{ (for WF)}$$



$$\text{CFSE} = 0.4 \Delta_o + \mathbf{P} \text{ (for WF)}$$



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

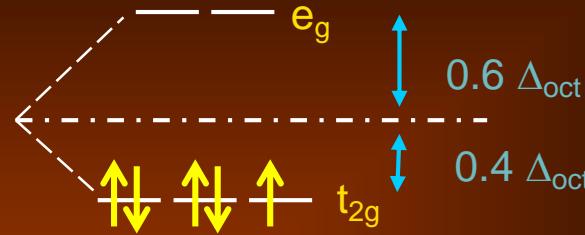
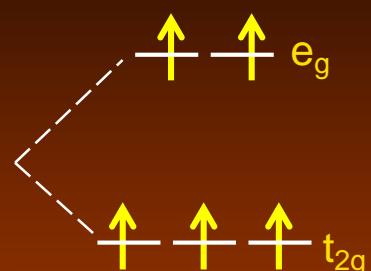
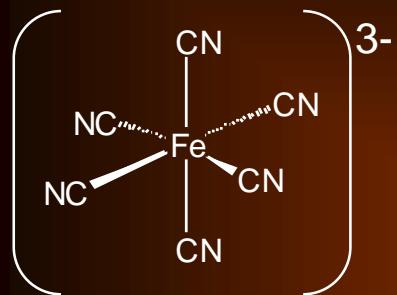
C.N. = 6 ∴ O_h

$\text{Fe(III)} \therefore \text{d}^5$

h.s.

I.s.

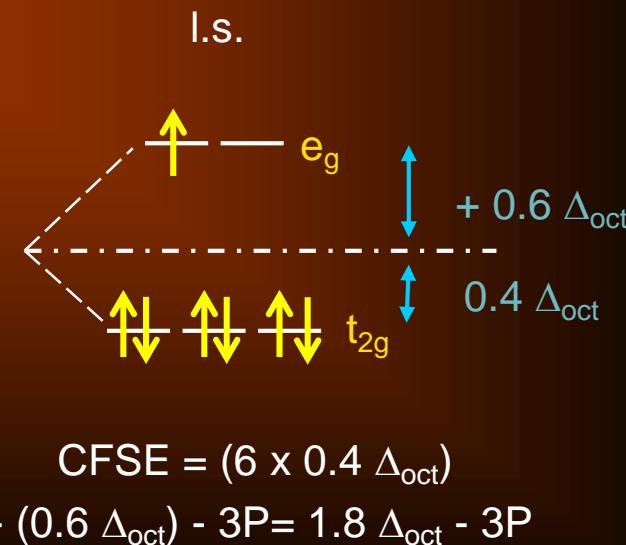
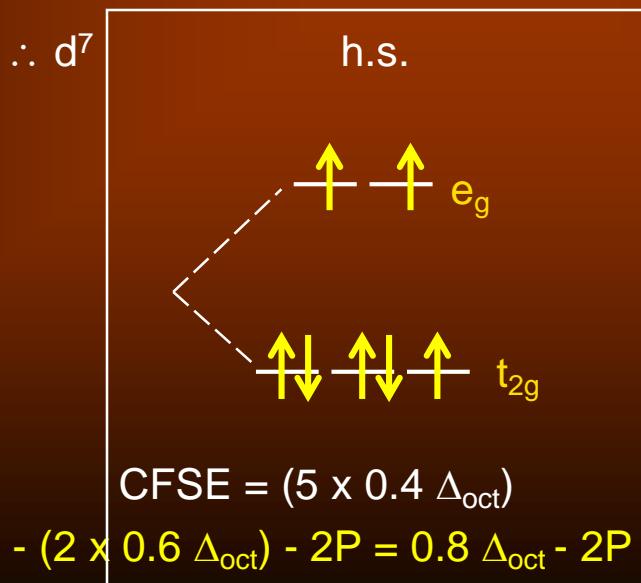
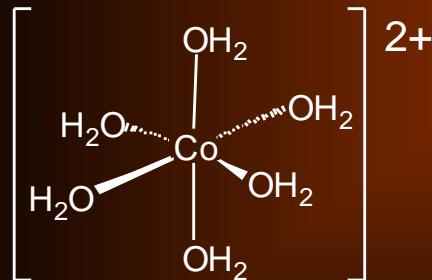
$\text{CN}^- = \text{s.f.l.}$



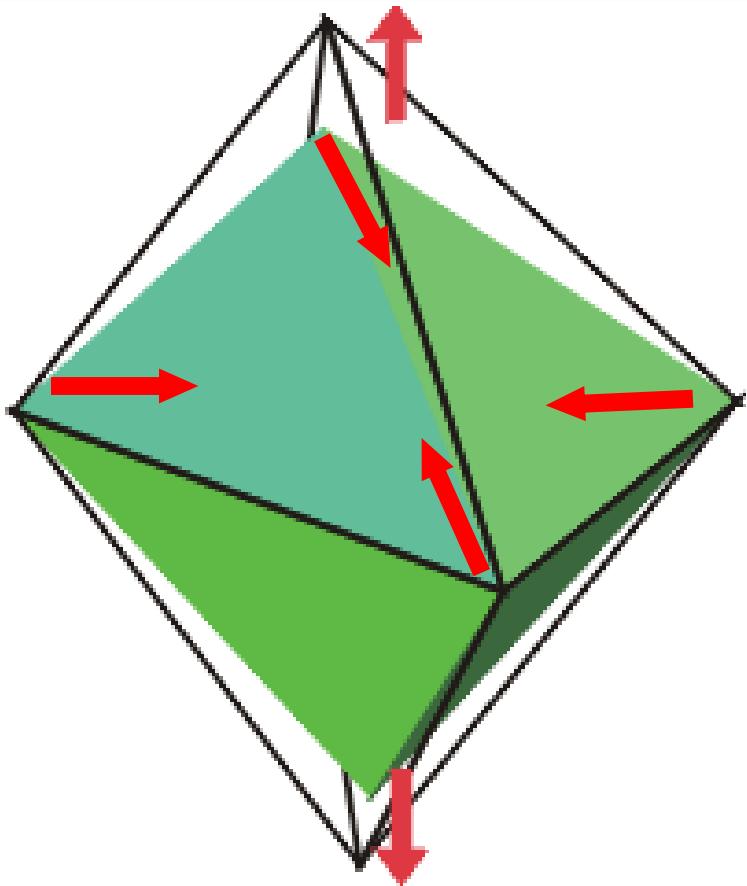
$$\text{CFSE} = 5 \times 0.4 \Delta_{\text{oct}} - 2P = 2.0 \Delta_{\text{oct}} - 2P$$

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

C.N. = 6 ∴ O_h $\text{Co(II)} \therefore \text{d}^7$



Tetragonal Distortion

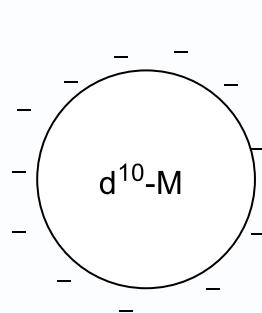


The elongation along the z axis causes the d orbitals with density along the axis to drop in energy. As a result, the d_{xz} and d_{yz} orbitals lower in energy.

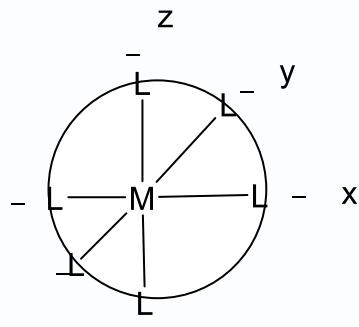
The Jahn-Teller Theorem

The theorem states that for a nonlinear molecule in an electronically degenerate state, distortion must occur to lower the symmetry, remove the degeneracy, and lower the energy. Such a distortion is called Jahn-Teller distortion

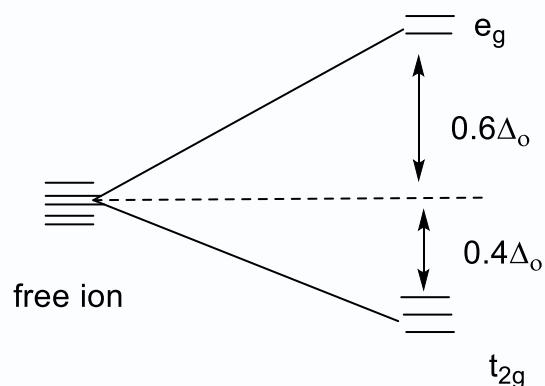
Free ion in a spherical field has a degenerate d orbitals.
 When Oh applied, two levels resulted. So by lowering symmetry, distortion can be effected. Lowering symmetry can be done by several ways.



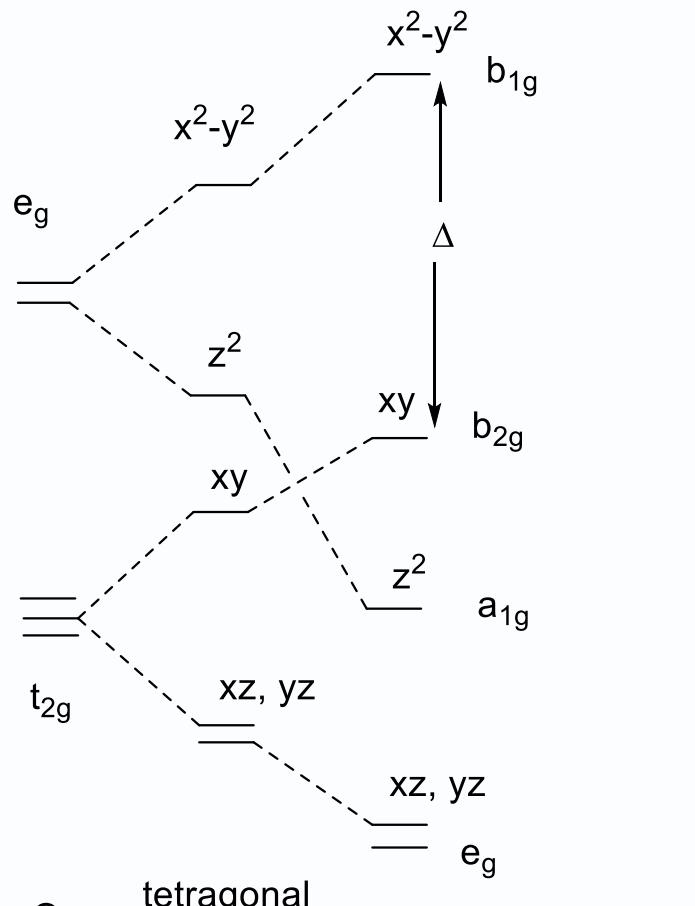
spherical field



octahedral geometry



Square planar geometry



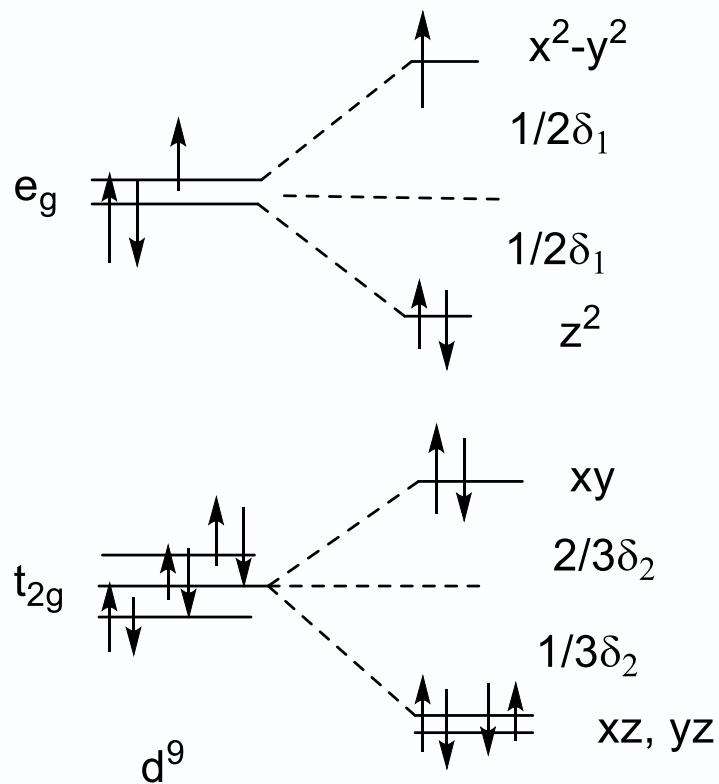
O_h
tetragonal
distortion

square planar (D_{4h})

(removal of
z ligands)

d^9 in O_h and z -out tetragonal D_{4h} fileds

No nonlinear molecule can be stable in a degenerate electronic state. The molecule must become distorted in a such a way as to break the degeneracy.



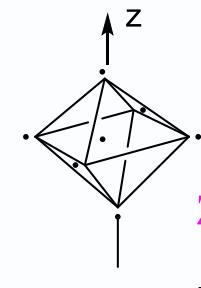
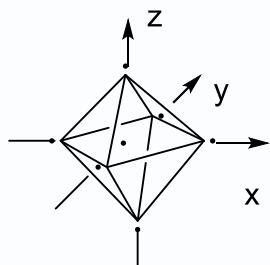
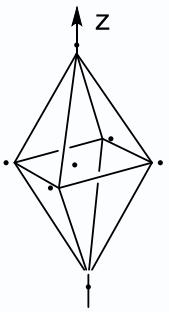
$$2 \times 1/2 \delta_1 - 1 \times 1/2 \delta_1 = 1/2 \delta_1$$

(net stabilization energy
deriving the distortion)

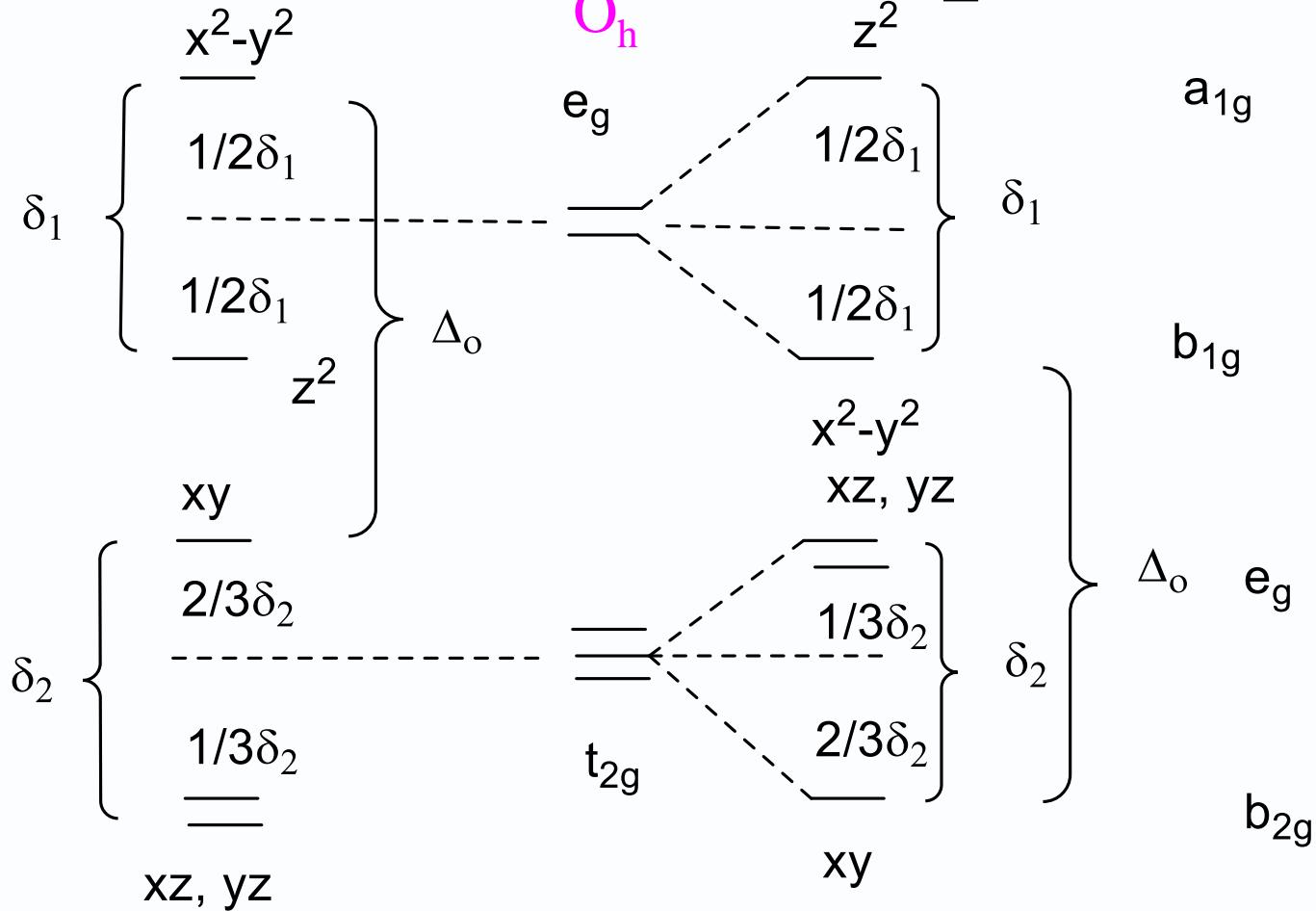
$$4 \times 1/3 \delta_2 - 2 \times 2/3 \delta_2 = 0$$

Distortions

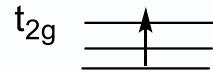
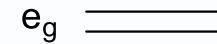
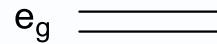
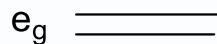
z ligands out



z ligands in



Asymmetric electron occupation of either the e_g or t_{2g} orbitals are susceptible for JT distortion.



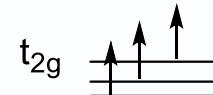
d^1

JT is YES
and weak



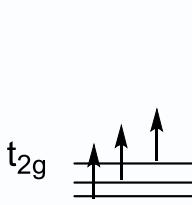
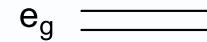
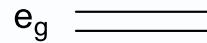
d^2

JT is YES
and weak



d^3

JT is NO



d^4

High spin
JT is YES
and strong



d^4

Low spin
JT is YES
and weak



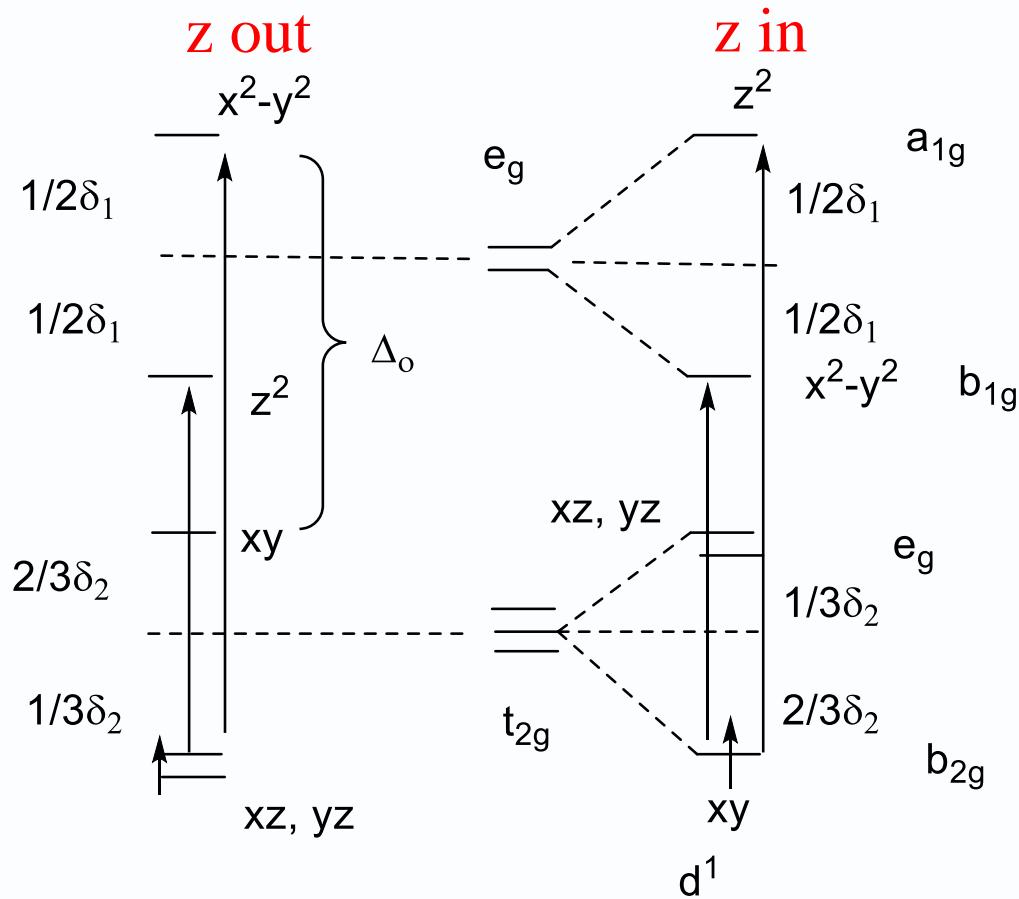
d^5

High spin
JT is NO



d^5

Low spin
JT is YES
and weak



For d^1 , **z-in or z-out?**

$$\text{If z in, } 1 \times 2/3 \delta_2 - 0 = 2/3 \delta_2$$

$$\text{If z out, } 1 \times 1/3 \delta_2 - 0 = 1/3 \delta_2$$

So **z-in** is favoured and observed as well.

For d^2 , **z-in or z-out?**

Assume $\delta_2 < P$

$$\text{If z in, } 1 \times 2/3 \delta_2 - 1 \times 1/3 \delta_2 = 1/3 \delta_2$$

$$\text{If z out, } 2 \times 1/3 \delta_2 - 0 = 2/3 \delta_2$$

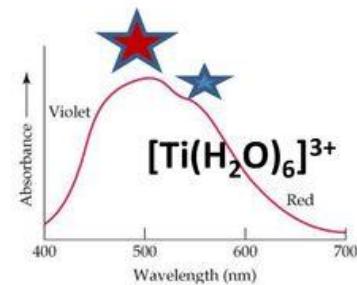
So **z-out (elongation)** is favoured.

Degeneracy in the t_{2g} orbital

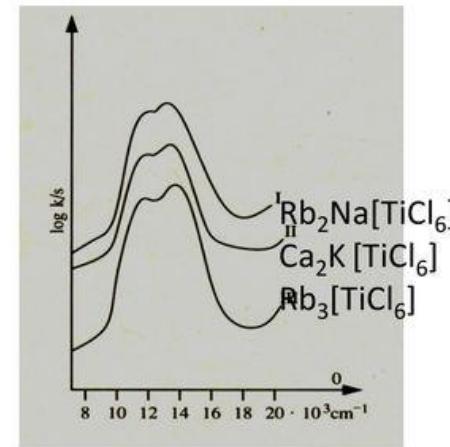
Not so significant Jahn Teller distortion



Distortion manifested as the
Splitting of UV Vis peaks

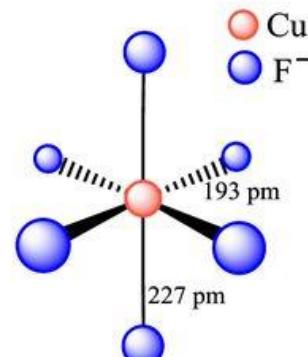
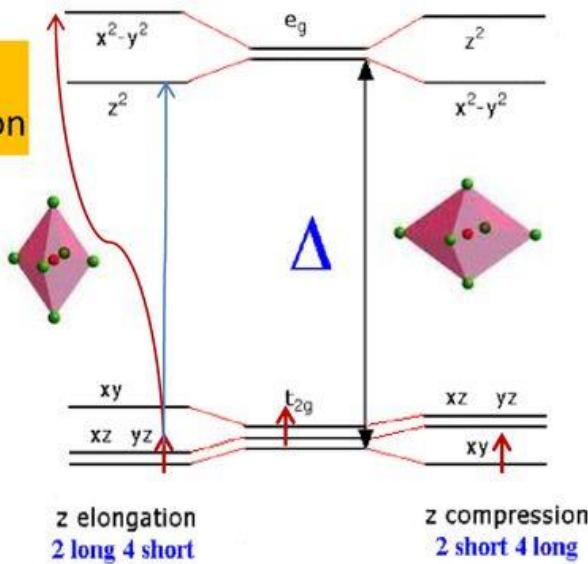


No Measurable differences in
bond lengths



Degeneracy in the e_g orbital

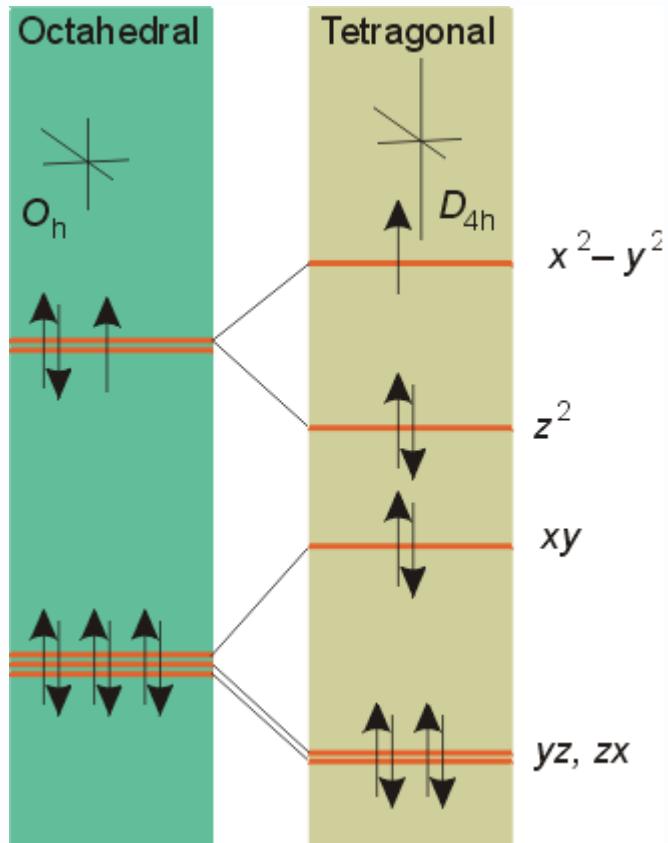
Significant Jahn Teller distortion



Measurable differences
in bond lengths

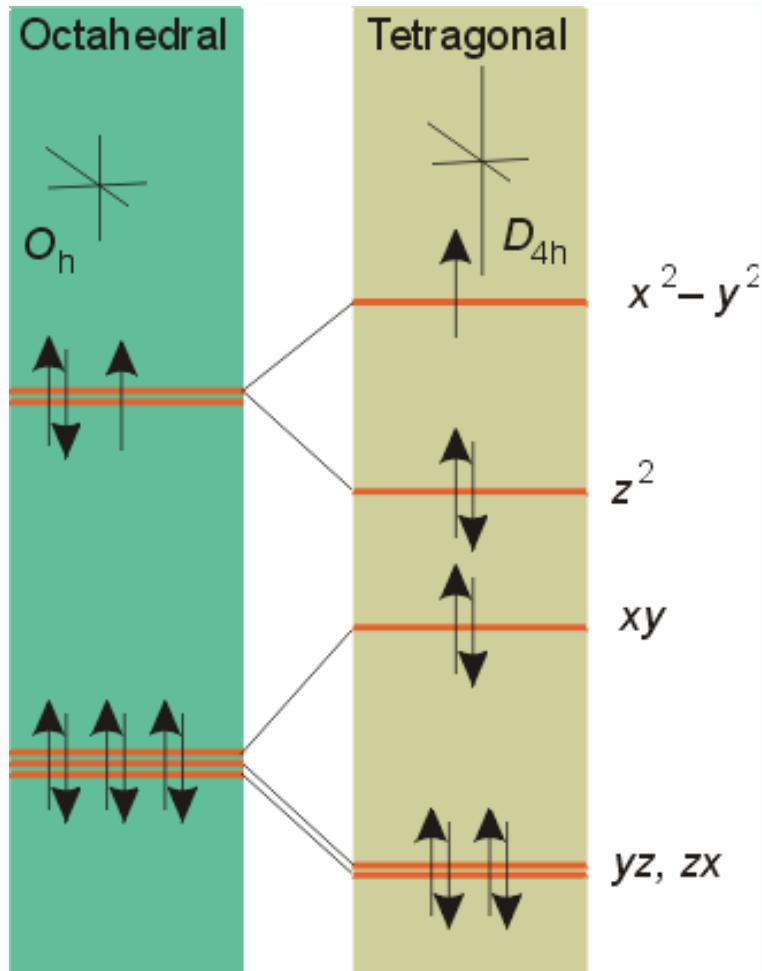
The Jahn-Teller effect predicts which structures will distort. It does not predict the nature or extent of the distortion. The effect is most often seen when the orbital degeneracy is in the orbitals that point directly towards the ligands.

Tetragonal Complexes



For complexes with 1-3 electrons in the e_g set of orbitals, this type of tetragonal distortion may lower the energy of the complex.

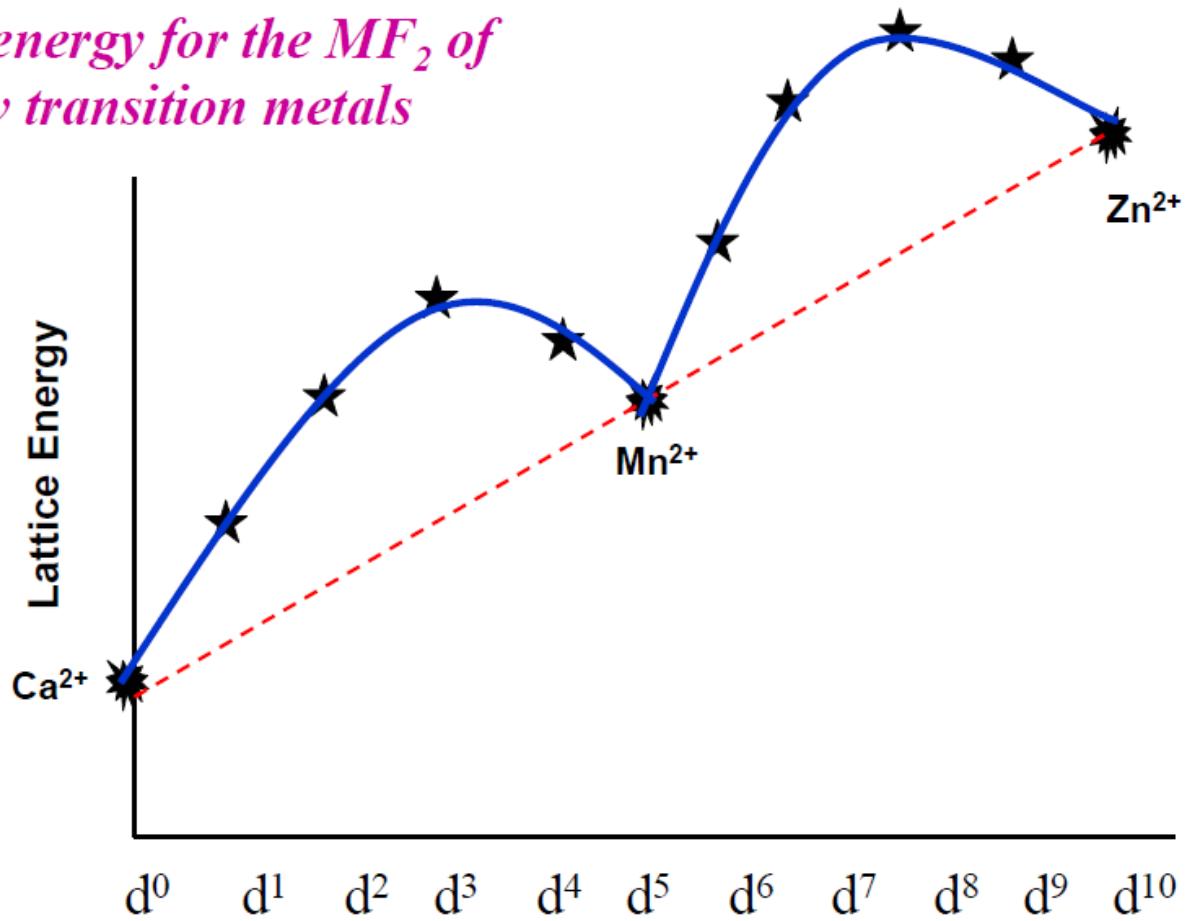
Square Planar Complexes



For complexes with 2 electrons in the e_g set of orbitals, a d⁸ configuration, a severe distortion may occur, resulting in a 4-coordinate square planar shape, with the ligands along the z axis no longer bonded to the metal.

Applications of CFT

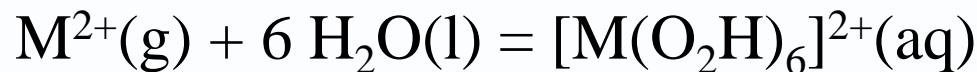
Lattice energy for the MF_2 of first row transition metals



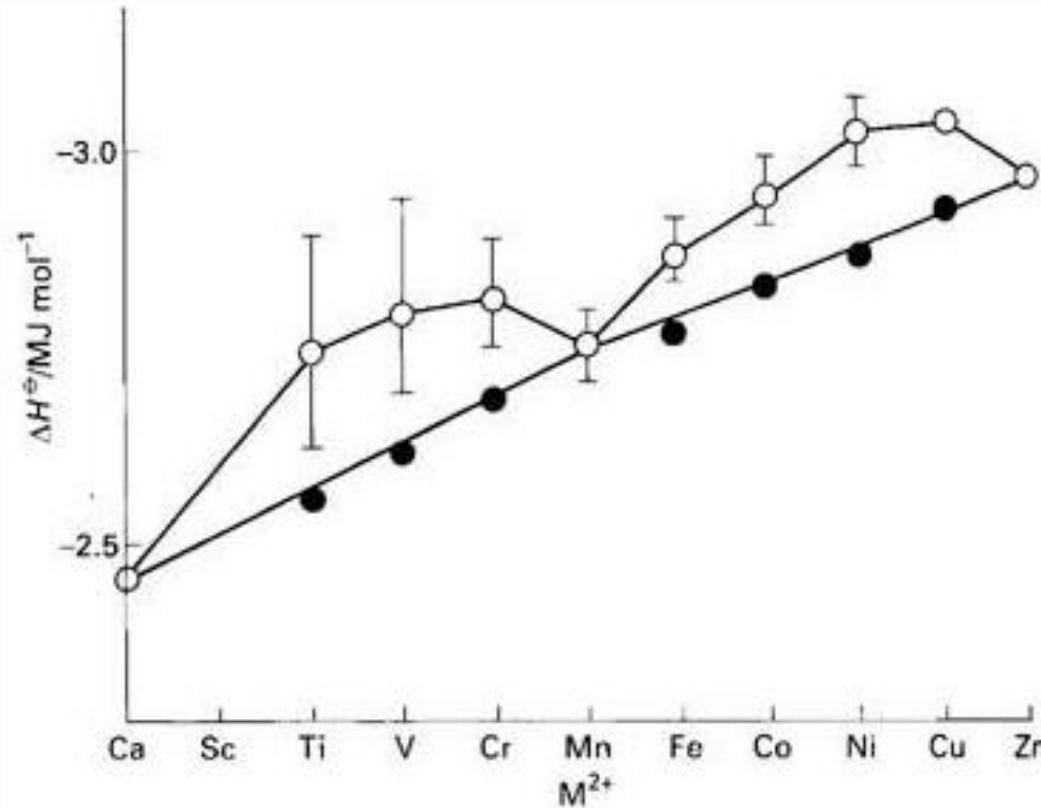
conf	CFSE, Δ_o
d^0	0
d^1	.4
d^2	0.8
d^3	1.2
d^4	0.6
d^5	0
d^6	0.4
d^7	0.8
d^8	1.2
d^9	0.6
d^{10}	0

F = weak field ligand

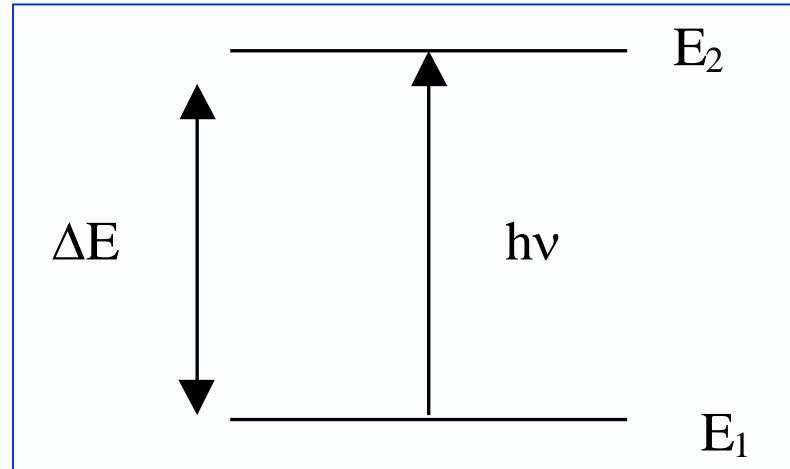
Hydration Enthalpy of M²⁺ ions (H₂O is weak field ligand, the complexes are high spin).



Plotting the enthalpy across the first transition series



The origin of the color of the transition metal compounds

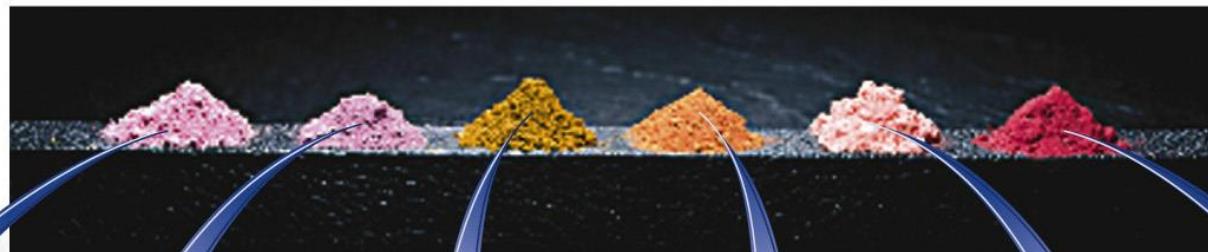
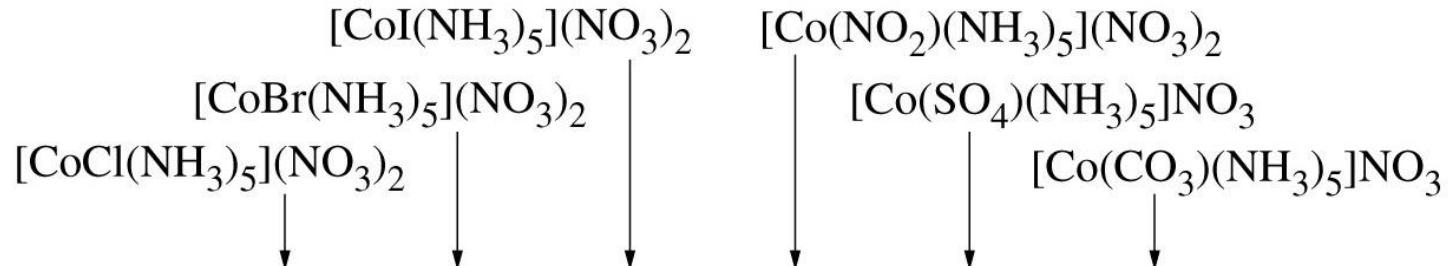


$$\Delta E = E_2 - E_1 = h\nu$$

Ligands influence Δ_O , therefore the colour

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

1. Metal charge
2. Ligand strength





Intensity of color? Selection rule

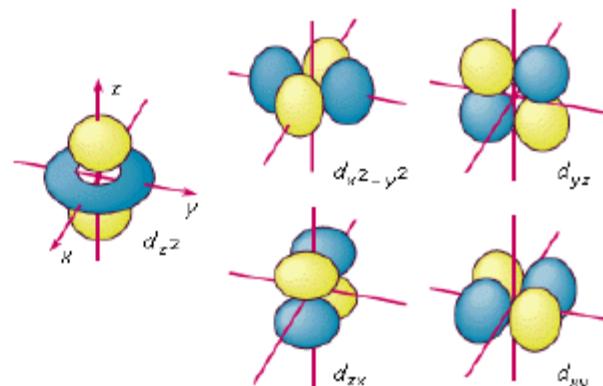
Spin selection rule: $\Delta S = 0$

-Transitions may occur from singlet to singlet, or from triplet to triplet states etc., but a change in spin multiplicity is *forbidden*.

Laporte selection rule: There must be a change in parity:

allowed transitions: $g \leftrightarrow u$

forbidden transitions: $g \leftrightarrow g$, $u \leftrightarrow u$

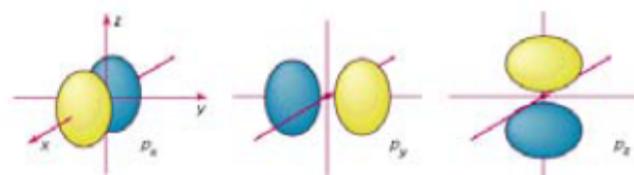


This leads to the selection rule:

$$\Delta l = \pm 1$$

allowed transitions are: $s \rightarrow p$, $p \rightarrow d$, $d \rightarrow f$,

forbidden transitions are: $s \rightarrow s$, $p \rightarrow p$, $d \rightarrow d$, $f \rightarrow f$, $s \rightarrow d$, $p \rightarrow f$,

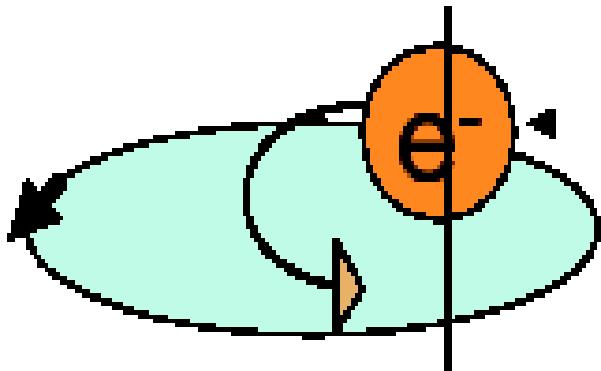


Magnetism

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

$\mu = 2[S(S+1)]^{1/2}$ after $S = n/2$

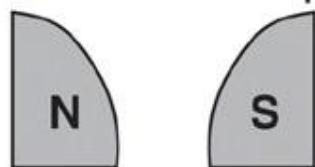
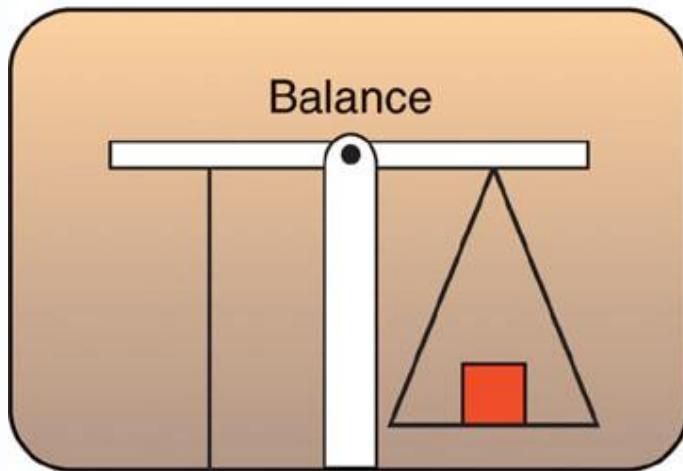
$\mu = [n(n+2)]^{1/2} \mu_B$ called spin-only moment
orbital angular moment L is zero

Ion	n	S	μ/μ_B Calculate d	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
Fe^{3+}	5	$5/2$	5.92	5.3

- μ_B is the Bohr magneton
- $\mu_B = eh/4\pi m_e = 9.274 \times 10^{-24} \text{ J T}^{-1}$
- Tetrahedral complexes - only high spin complexes result, for $\Delta_t \ll \Delta_0$.

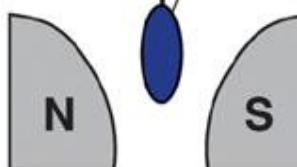
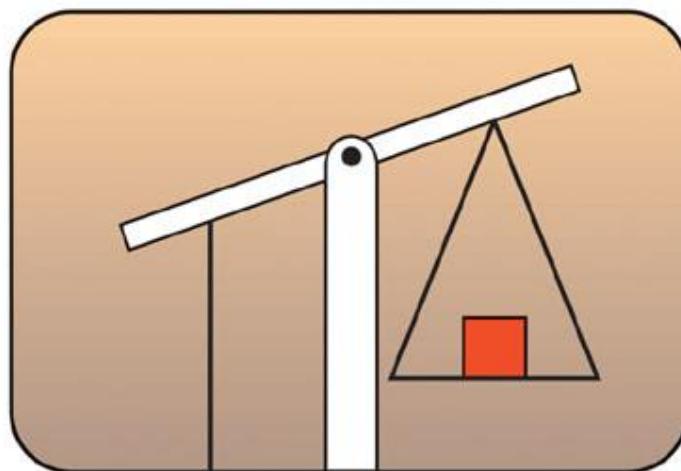
Determination Magnetic Properties

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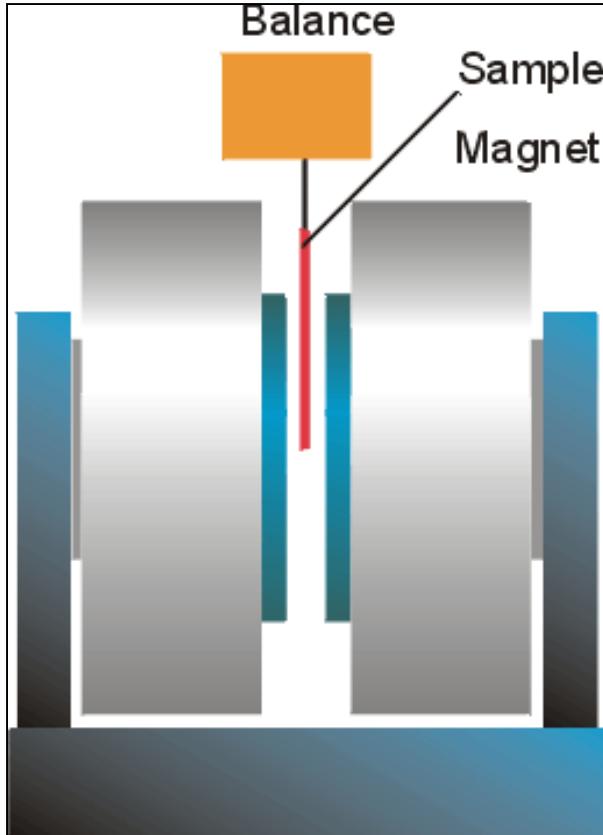
Electromagnet

A



Electromagnet

B



Gouy balance to measure the magnetic susceptibilities

- We can measure the magnetic properties of a sample by hanging a vial of material from a balance so that it sits partly in a magnetic field
 - The sample will be pulled down into the magnet if it contains unpaired electrons (said to be paramagnetic)
 - It will tend to be pushed out of the field if it contains no unpaired electrons (diamagnetic)
- The amount of material in the vial along with the extent to which the sample is pulled into the magnet allows us to calculate the magnetic susceptibility of the sample
 - Sample with a high magnetic susceptibility is strongly pulled into the magnetic field

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

Metals in Low Oxidation States

- In low oxidation states, the electron density on the metal ion is very high.
- To stabilize low oxidation states, we require ligands, which can simultaneously bind the metal center and also withdraw electron density from it.
- Very Interesting: We shall discuss about this in Organometallic/Catalysis topic

Note: You need to know CHELATE EFFECT

- to understand chemistry of transition metal complexes with multidentate ligands**
- to understand mode of action of transition metal complexes in biology/real life applications**

CHELATE EFFECT will be discussed in Tutorial Classes