

# **Topic II**

# **Chemistry of Transition Metals**

## **Part 1. General Considerations**

## **Some general properties of TM elements**

- 1. Metals**
- 2. Almost all: HARD, STRONG, High m.p., b.p.**
- 3. Conduct heat & electricity (Cu and Al wire)**
- 4. Form Alloys**
- 5. Show variable oxidation states**
- 6. At least one of the ions & compounds colored.**
- 7. Form paramagnetic species because of partially filled shells**
- 8. Form coordination compounds (complexes) and organometallic compounds.**

# Variable oxidation states

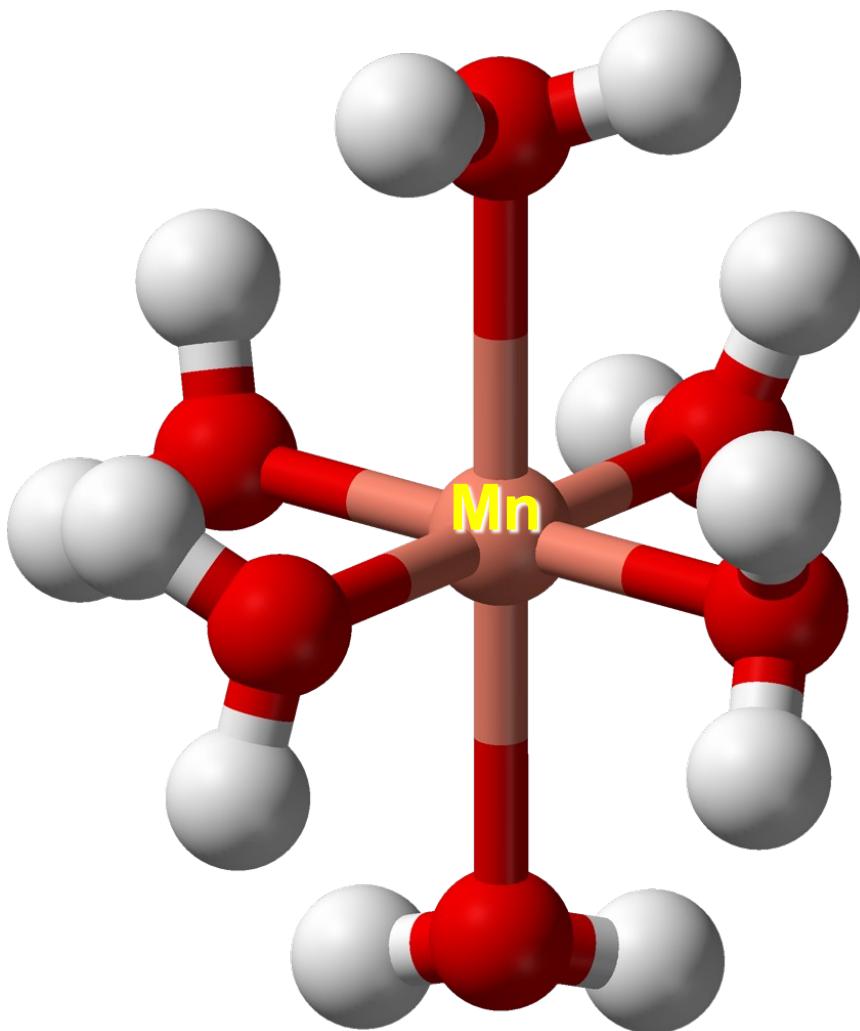
Sc		+3					
Ti	+1	+2	+3	+4			
V	+1	+2	+3	+4	+5		
Cr	+1	+2	+3	+4	+5	+6	
Mn	+1	+2	+3	+4	+5	+6	+7
Fe	+1	+2	+3	+4	+5	+6	
Co	+1	+2	+3	+4	+5		
Ni	+1	+2	+3	+4			
Cu	+1	+2	+3				
Zn		+2					

1. Increase in the number of oxidation states from Sc to Mn. All are possible only in case of Mn.
2. Decrease in the number of oxidation states from Mn to Zn, due to the pairing of d-e's after Mn.
3. Stability of higher oxidation states decreases along Sc to Zn. Mn(VII) and Fe(VI) are powerful oxidizers.
4. Down the group, the stability of high oxidation states increases (easier availability of both d and s electrons for ionization).

# How to stabilize higher and lower oxidation states?

- Low oxidation state using  $\pi$ -acceptor ligands such as CN<sup>-</sup>  
example: [Cr(CO)<sub>6</sub>]
- Intermediate oxidation state complexes often have ligands such as chloride, ammonia or water  
example: [Cr(Cl)<sub>3</sub>(H<sub>2</sub>O)<sub>3</sub>]
- High oxidation state complexes usually have oxide or fluoride ligands.  
example: K<sub>2</sub>[Cr<sub>2</sub>O<sub>7</sub>]

# An example of a metal complex



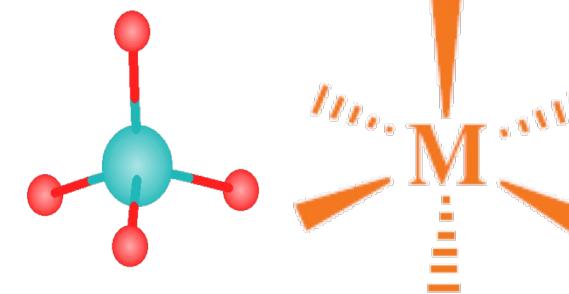
**Metal ion:** Central & is a Lewis acid

**Ligand:** Is bound to the metal ion & is a Lewis base

**Coordination number:** The number of ligands surrounded by a metal ion.

# Coordination Number & Geometry

- TM ions generally form complexes with well defined number of ligands.
- Common coordination geometry



## Factors controlling geometry

### Metal & Ligand

#### Low Coord. Number

- Soft ligand with
- Low M oxidation state
- Counter ion with low basicity
- Steric ligand

Size

type

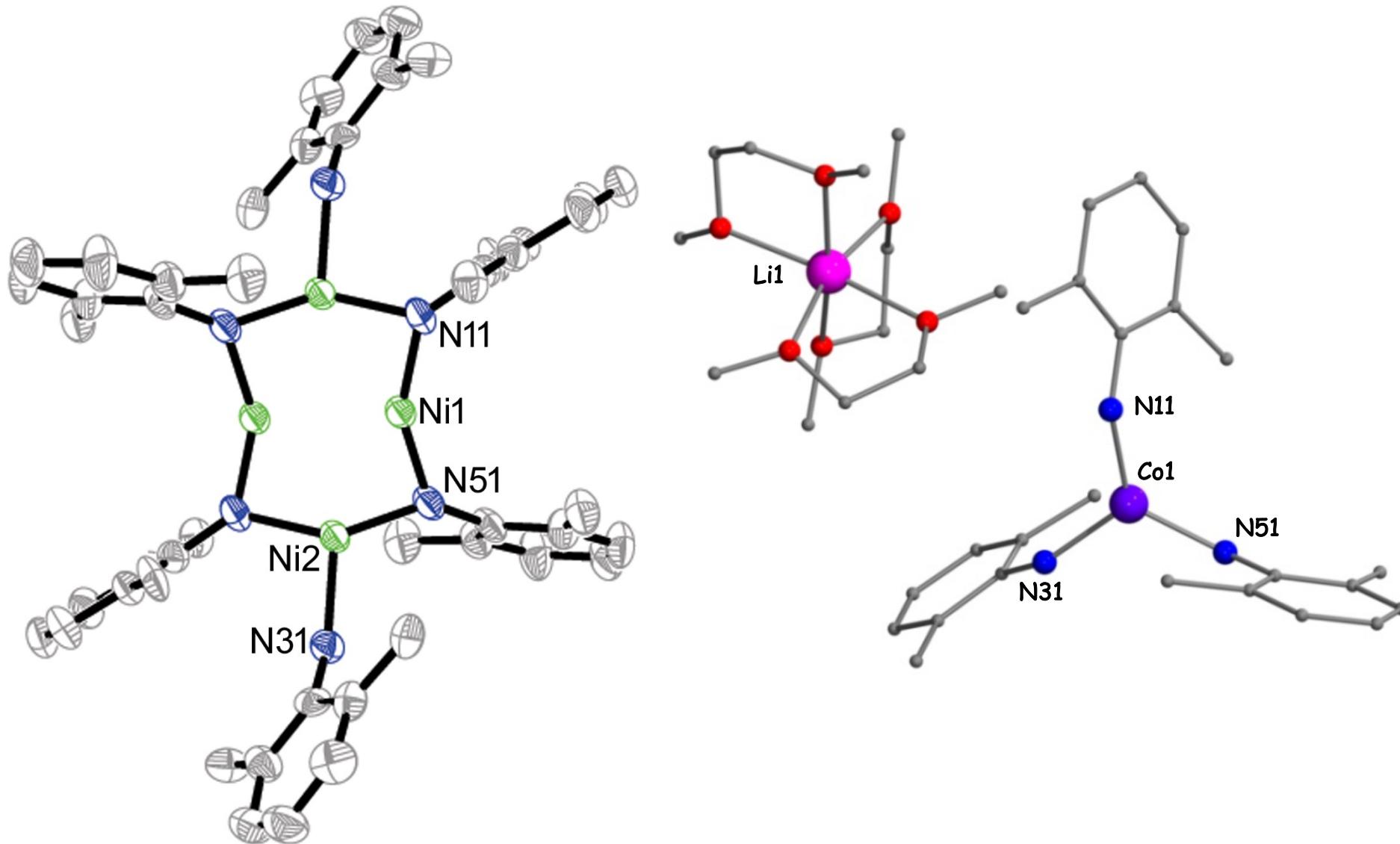
Charge

Electronic factors

#### High Coord. Number

- hard ligand with
- high M oxidation state
- Large non acidic cation
- small steric

# Influence of sterically bulky ligand on geometry



# **Open questions in coordination chemistry**

- (i) Why the complexes are colored?**
- (ii) Why same stoichiometric species ( $\text{CoCl}_3 \cdot 4\text{NH}_3$ ) yield different colour?**
- (iii) Why some compounds are high-spin while others are low-spin?**
- (iv) Some coordination compounds the metal-ligand bond lengths are different?**
- (v) Can the structure of spinel's be rationalized?**

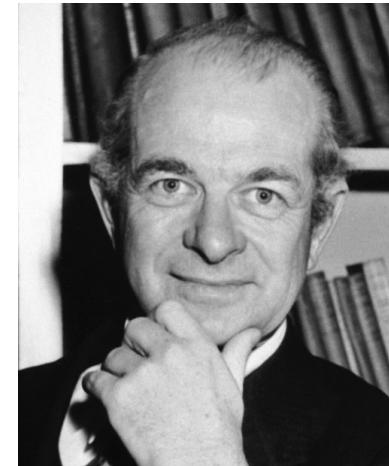
# Theoretical foundations of coordination complexes

- (i) Werner's coordination theory
- (ii) Valence bond theory (VBT; Linus Pauling)
- (iii) (self-reading Ref: Concise Inorganic Chemistry by J. D. Lee)

(iii) Crystal field theory  
(Hans Bethe and J. H. Van Vleck)

(iv) Ligand field theory  
(Molecular orbital approach; J. H. Van Vleck,  
John Stanley Griffith and Leslie Orgel)

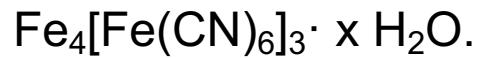
Ref: Inorganic Chemistry by Shriver & Atkins')



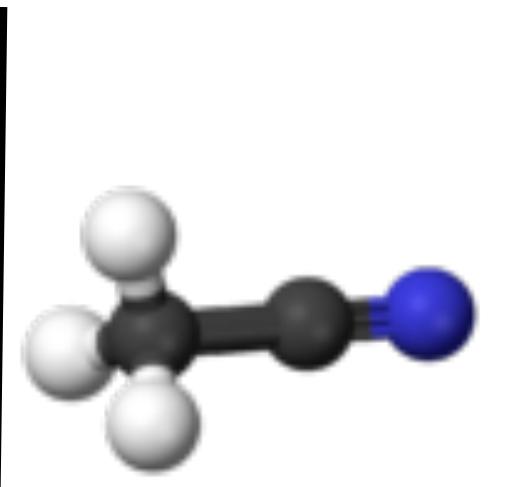
# How strong is the co-ordinate bond?



Prussian blue



Prussian blue is used for certain heavy metal poisons.



Modest toxicity.  
Can be metabolised to produce HCN, which is very toxic



KCN is a poison by itself....

## **Limitation of VBT**

### **❖ VBT could not explain**

- The origin of color in transition metal complexes
- Thermodynamic stability

## **Crystal Field Theory (CFT)**

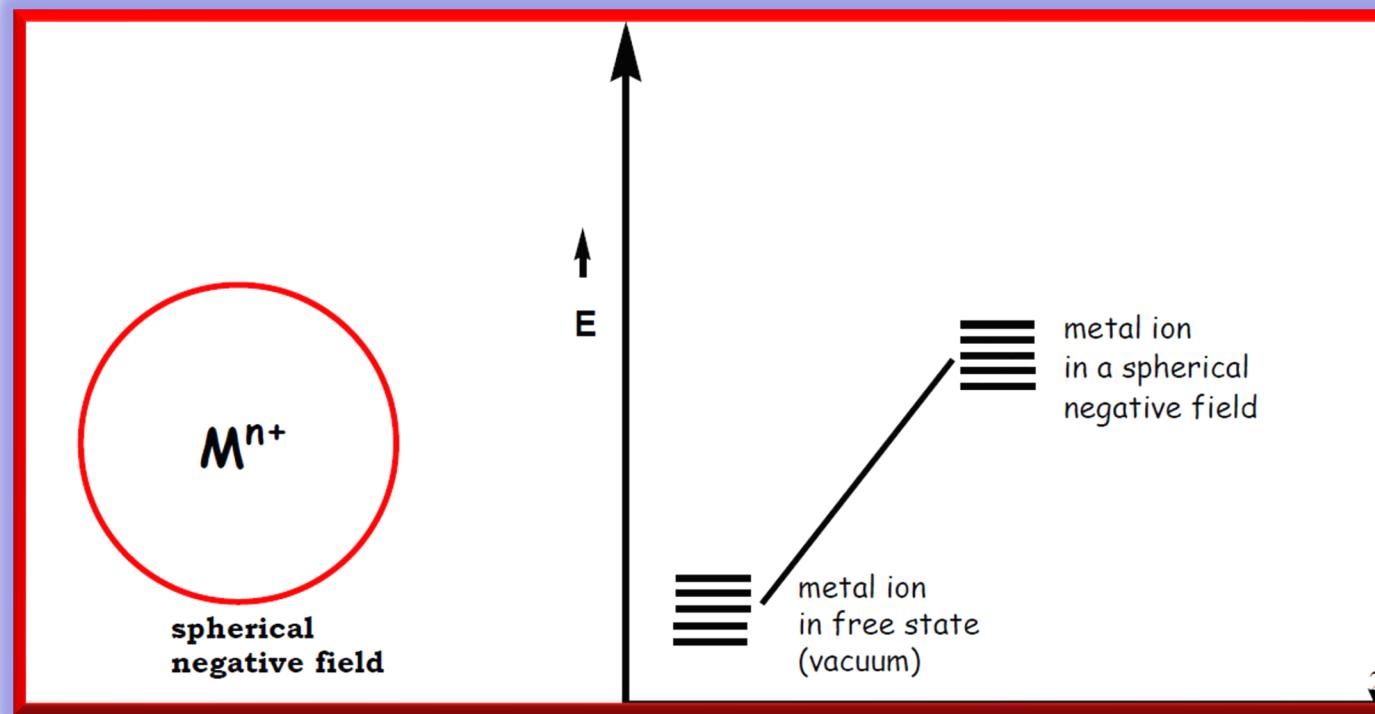
### **❖ CFT could explain**

- The stability and origin of colour
- Optical spectrum (UV-Vis) of 3d complex
- Magnetic properties of metal complex
- Predict the structure of spinel or inverse spinel

## CFT - Assumptions

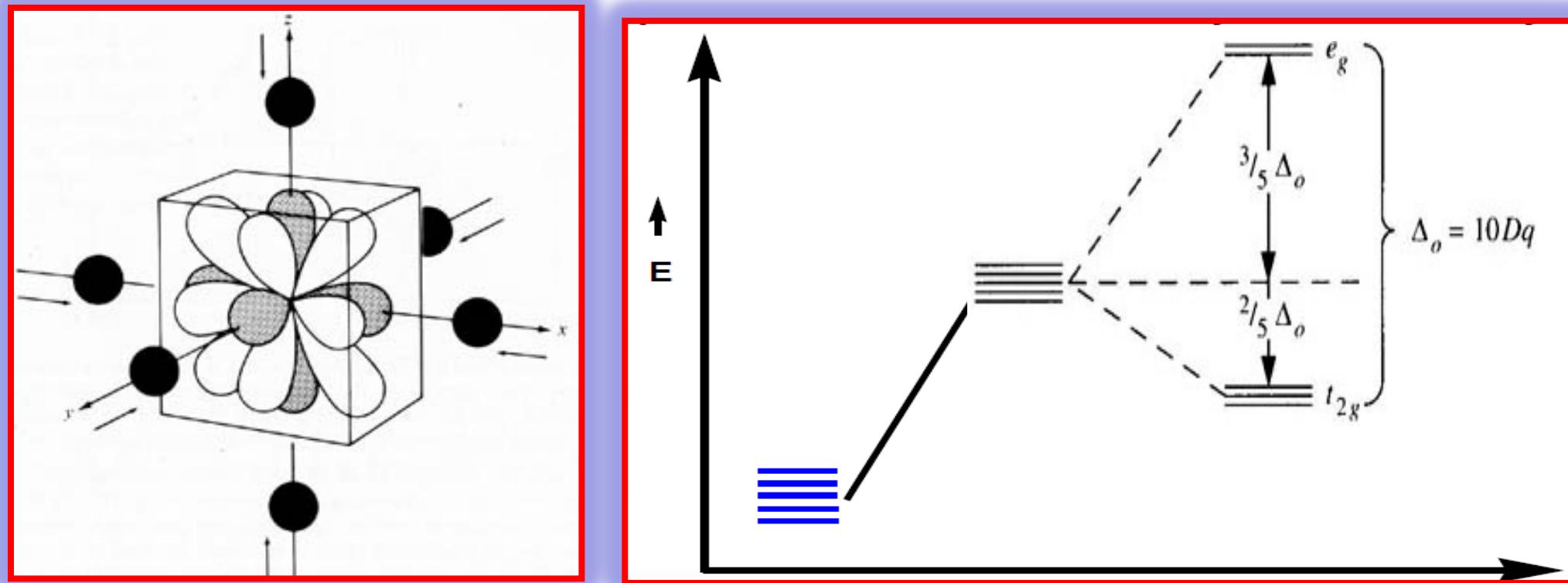
- (i) Interactions between the metal ion and ligands are purely electrostatic (ionic in nature).
- (ii) Ligands are considered as point charge
  - (a) For anionic ligand - ion- ion
  - (b) For neutral ligand - ion-dipole
- (iii) Electrons on the metals are under repulsive force from the ligands.
- (iv) Electrons on the metal occupy those d-orbitals which face least repulsion from the ligands.

# Influence of symmetric ligand field on the d-orbitals

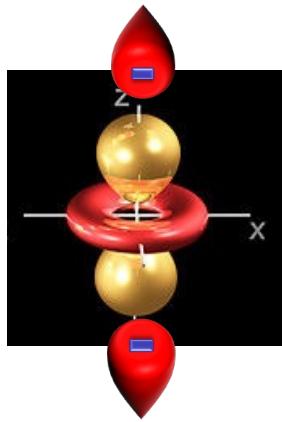
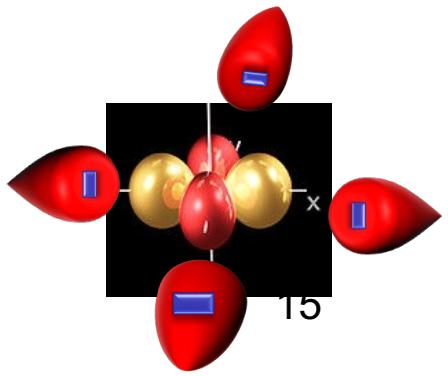


- The  $5 \times d$  orbitals in an isolated gaseous metal are degenerate
- If a spherically symmetric field of negative charges is placed around the metal, these orbitals remain degenerate, but all of them are raised in energy as a result of the repulsion between the negative charges on the ligands and electrons present in the d orbitals.

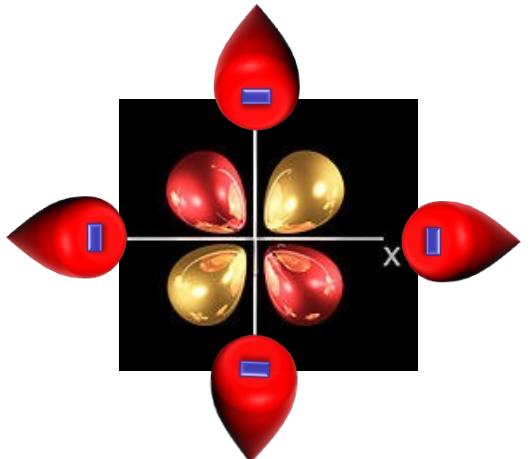
# Octahedral Field



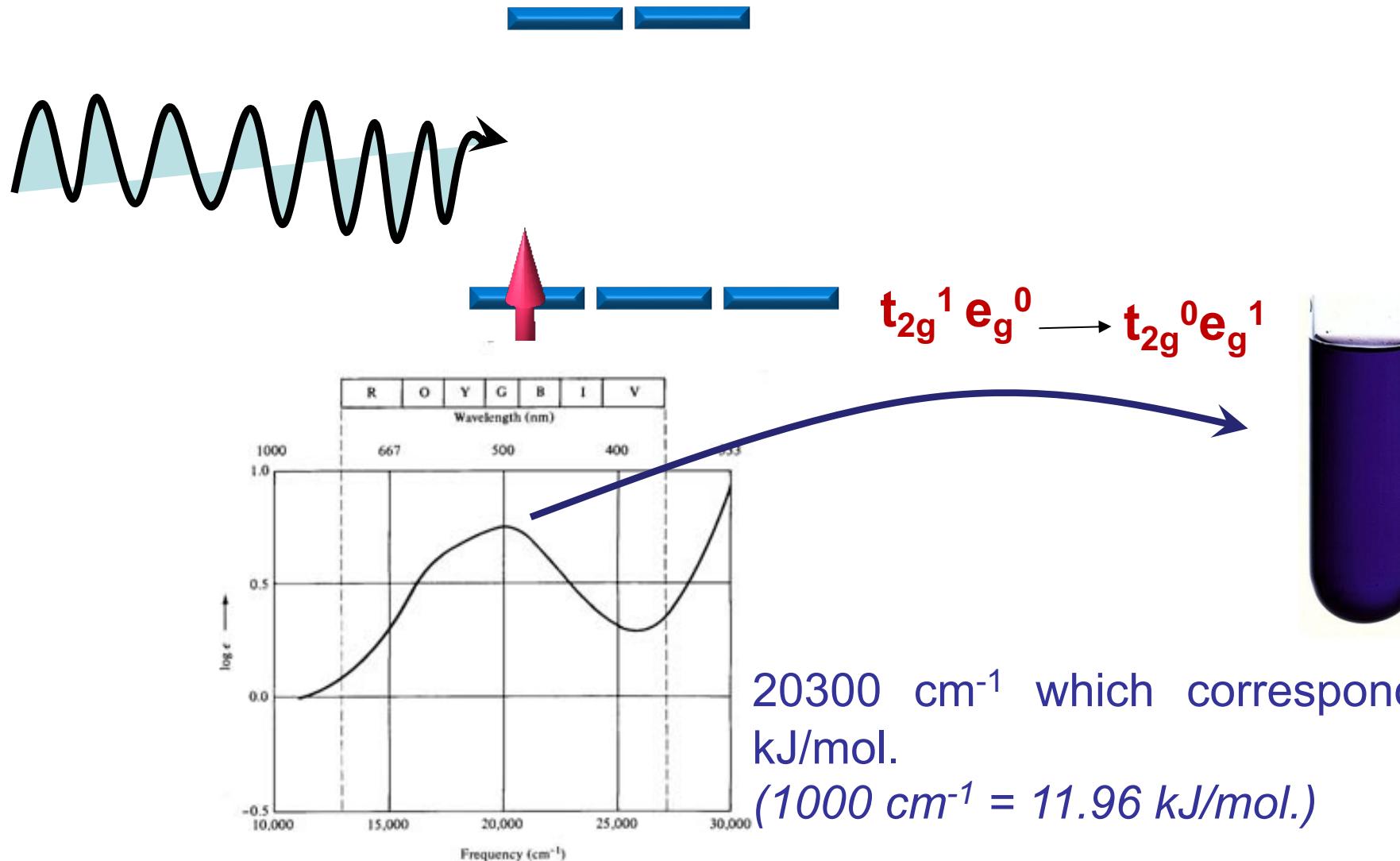
- ✓ Not all d- orbitals will interact to the same extent with the six point charges located on the +x, -x, +y, -y, +z and -z axes respectively.
- ✓ The orbitals which lie along these axes (i.e.  $x^2-y^2$ ,  $z^2$ ) will be destabilized more than the orbitals which lie in-between the axes (i.e.  $xy$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



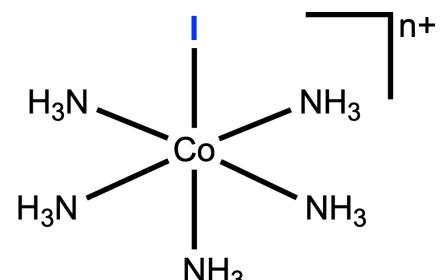
$d_z^2$      $d_{x^2-y^2}$      $d_{xy}$      $d_{xz}$      $d_{yz}$



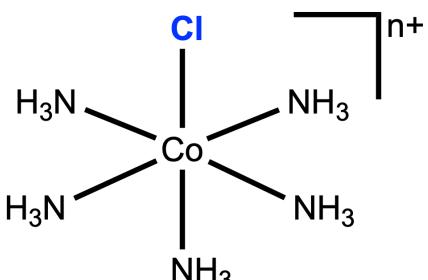
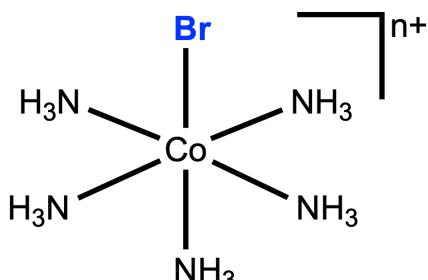
# Rationale for the observation of UV-Vis spectrum



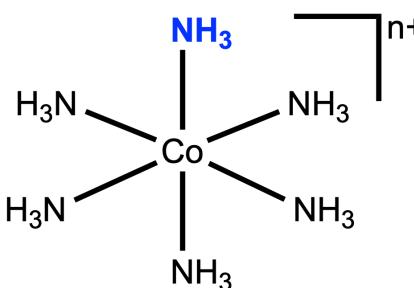
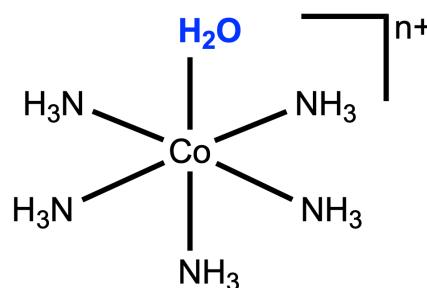
# Why color of the complexes change when changing a ligand?



Purple

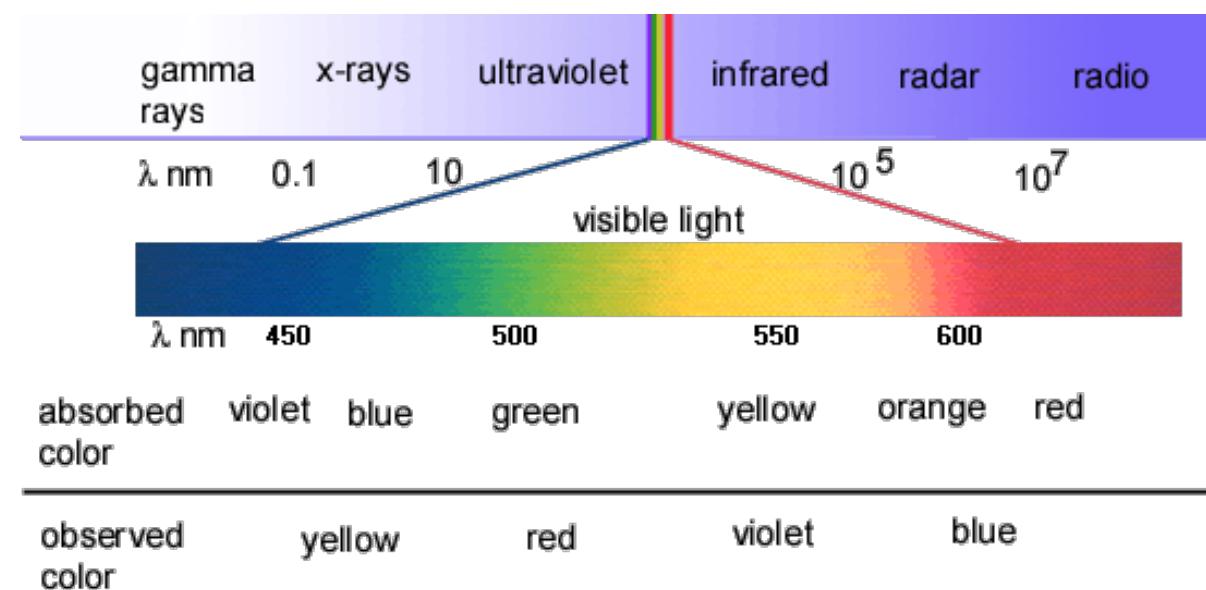


Pink



Yellow

$\Delta_o$  follows the order of  
 $\text{I} < \text{Br} < \text{Cl} < \text{H}_2\text{O} < \text{NH}_3$

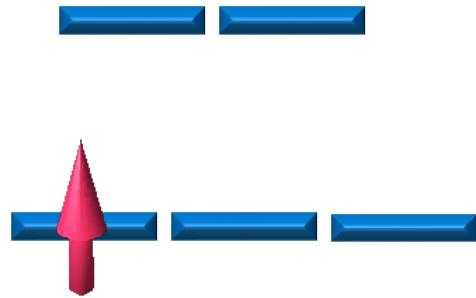


## Spectrochemical series

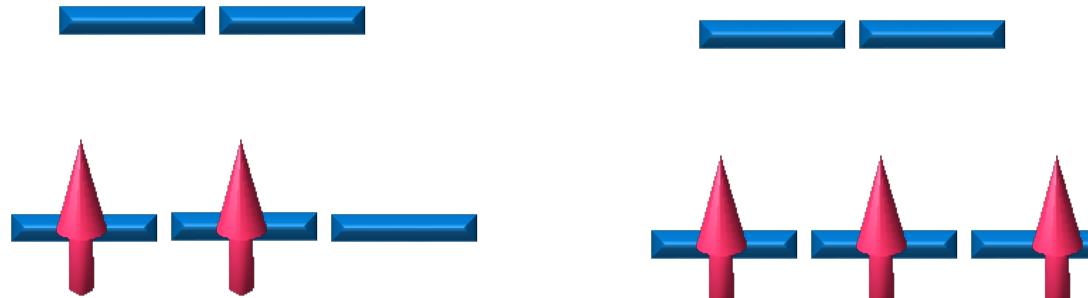
$\text{I}^- < \text{Br}^- < \text{S}^{2-} < \text{SCN}^- < \text{Cl}^- < \text{N}_3^-$ ,  $\text{F}^- < \text{urea}$ ,  $\text{OH}^- < \text{ox}$ ,  $\text{O}^{2-} < \text{H}_2\text{O} < \text{NCS}^- < \text{py}$ ,  $\text{NH}_3 < \text{en} < \text{bpy}$ ,  $\text{phen} < \text{NO}_2^- < \text{CH}_3^-$ ,  $\text{C}_6\text{H}_5^- < \text{CN}^- < \text{CO}$ .

What happens for more than 1 electron in d orbitals? / Magnetic property of paramagnetic systems

For  $d^1$ - $d^3$  system



Electron-electron repulsion; Hund's rule

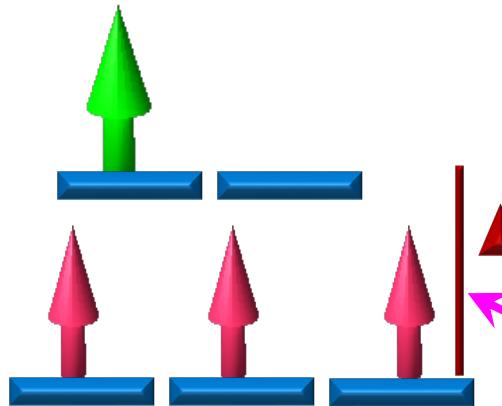


Due to the  $e^-e^-$  repulsion, calculating  $\Delta_o$  is not straight forward for system with more than one unpaired electrons.

# High spin and Low spin complexes

For d<sup>4</sup>-d<sup>7</sup> systems

d<sup>4</sup>: High spin



So which one?

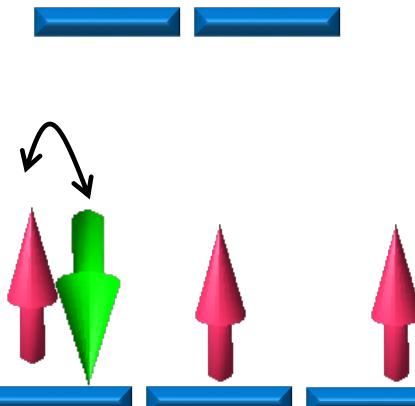
Decided by

- (i)  $\Delta_0$
- (ii) Pairing E.

$$\Delta_0 < P$$

$$\Delta_0 > P$$

d<sup>4</sup>: Low spin



## $\Delta_0$ vs. Pairing Energy (repulsive energy)

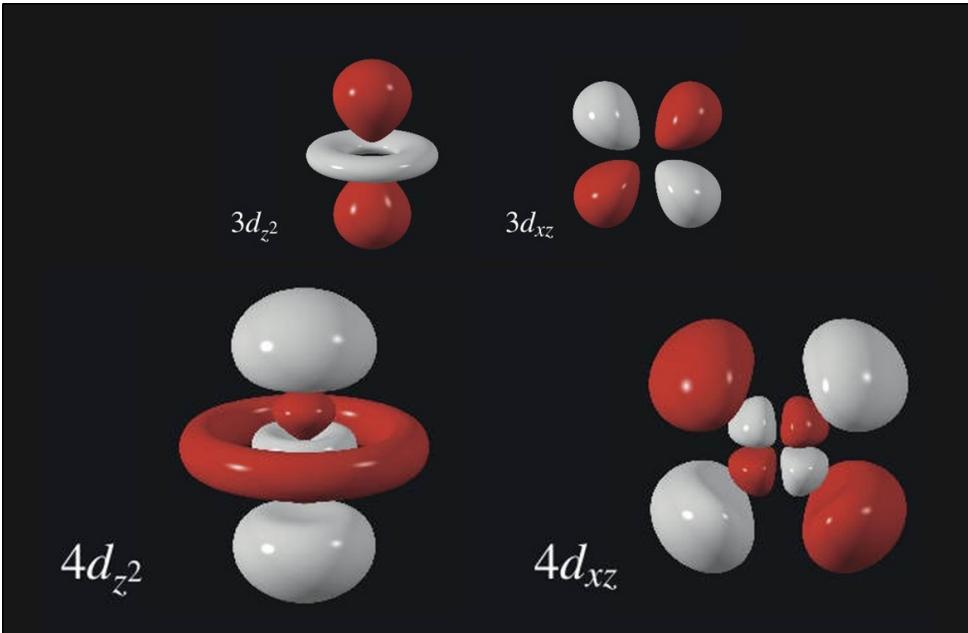
Complex	Config.	$\Delta_0$ , cm <sup>-1</sup>	P, cm <sup>-1</sup>	spin-state
[Fe(OH <sub>2</sub> ) <sub>6</sub> ] <sup>2+</sup>	d <sup>6</sup>	10,400	17,600	high-spin
[Fe(CN) <sub>6</sub> ] <sup>4-</sup>	d <sup>6</sup>	32,850	17,600	low-spin
[CoF <sub>6</sub> ] <sup>3-</sup>	d <sup>7</sup>	13,000	21,000	high-spin
[Co(NH <sub>3</sub> ) <sub>6</sub> ] <sup>3-</sup>	d <sup>7</sup>	23,000	21,000	low-spin

## Factors affecting $\Delta_o$

### (i) The charge on the metal ion



### (ii) Nature of orbital (3d, 4d, or 5d)



$[Co(NH_3)_6]^{3+}$	$24800 \text{ cm}^{-1}$	$297 \text{ kJ/mol}$
$[Rh(NH_3)_6]^{3+}$	$34000$	$407$
$[Ir(NH_3)_6]^{3+}$	$41000$	$490$

$3d < 4d < 5d$

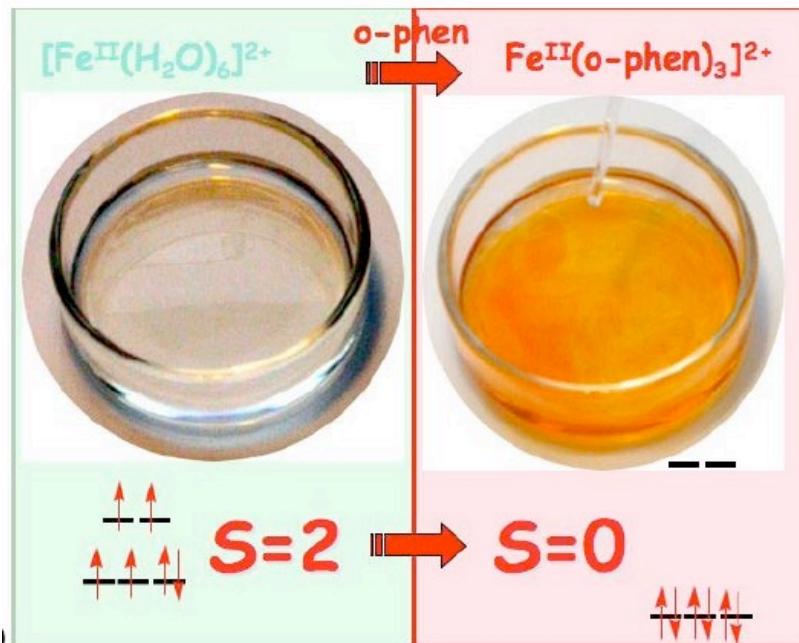
## Factors affecting $\Delta_o$

### (iii) Nature of ligand

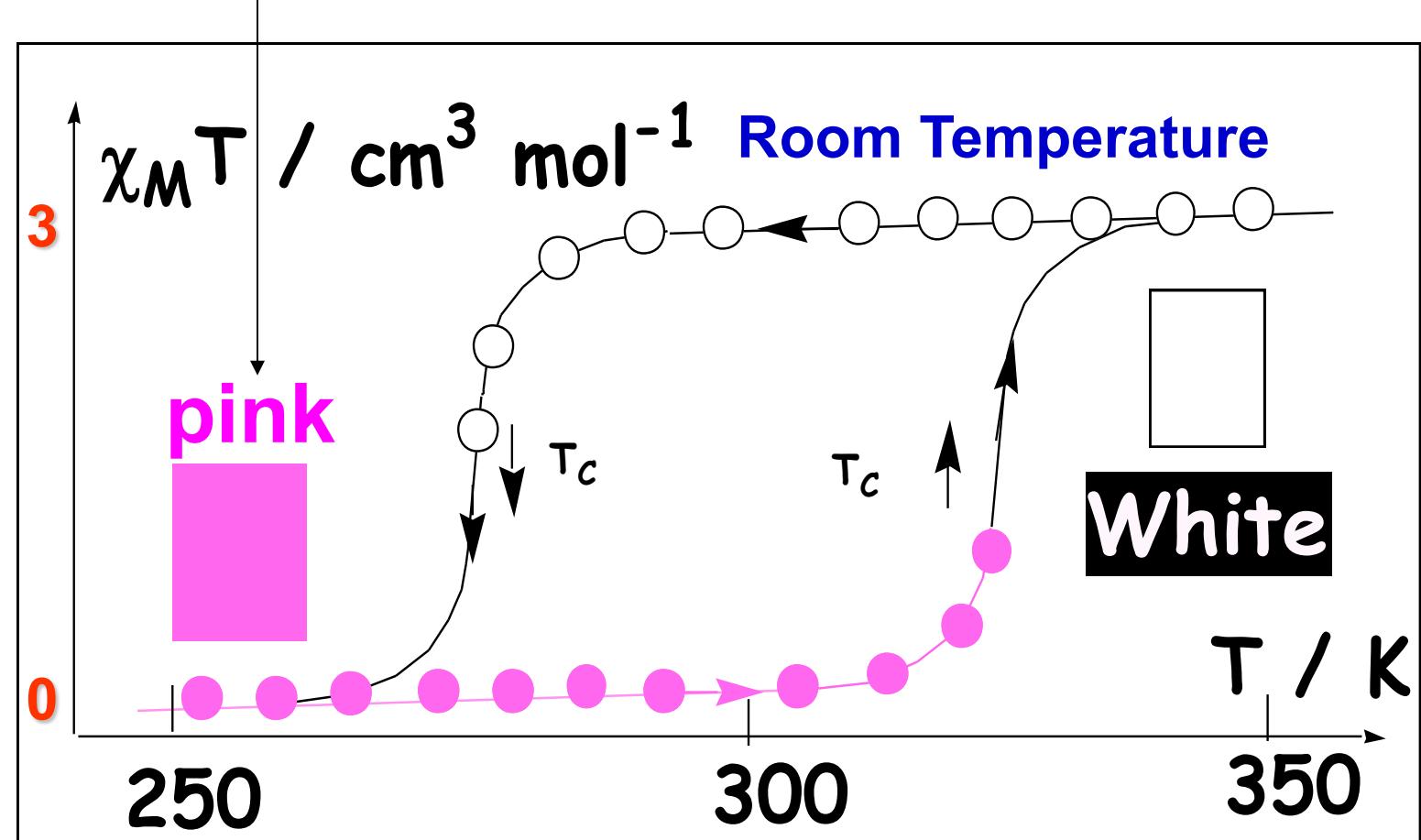
Ligands which cause a small splitting are *Weak field ligands* ( $\Delta_o$  in the range  $7000 - 30000 \text{ cm}^{-1}$ ) and those cause a large splitting are *Strong field ligands* ( $\text{CFSE typically} > 30000 \text{ cm}^{-1}$ )

$[\text{CrCl}_6]^{3-}$	$13640 \text{ cm}^{-1}$	$163 \text{ kJ/mol}$
$[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$	$17830$	$213$
$[\text{Cr}(\text{NH}_3)_6]^{3+}$	$21680$	$259$
$[\text{Cr}(\text{CN})_6]^{3-}$	$26280$	$314$

# From basic science to real time applications: Story on HS-LS complexes

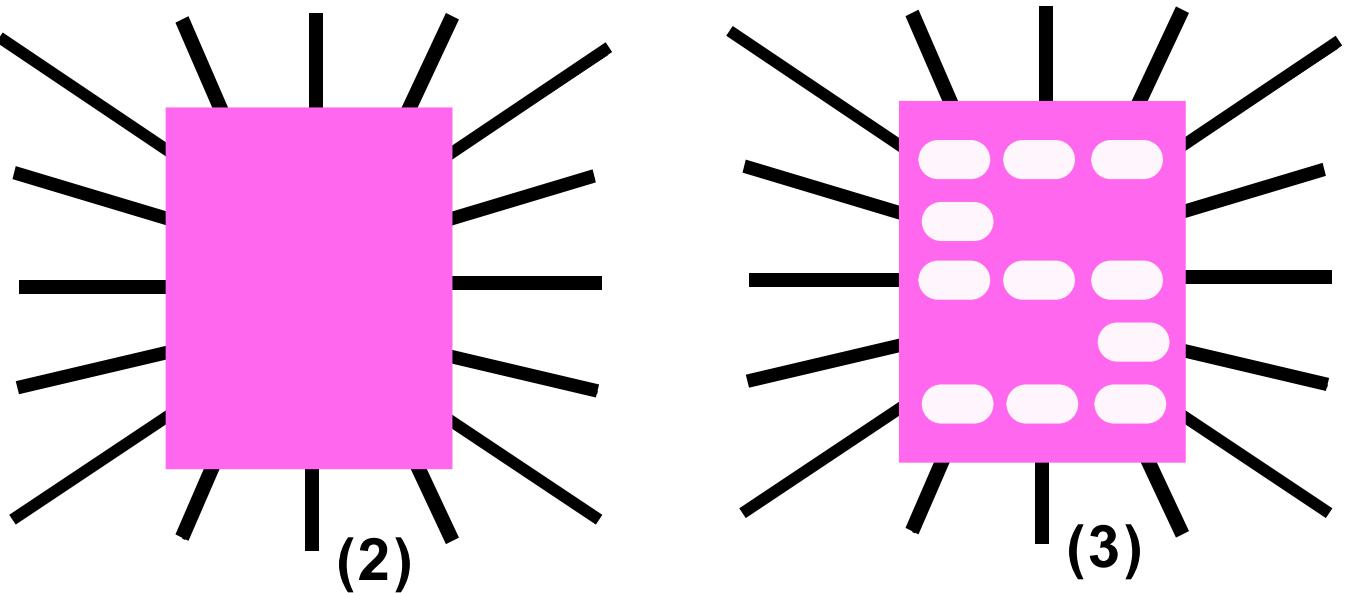


A Fe(II) HS-LS compound: Colour change



# Application of Spin-Crossover complexes

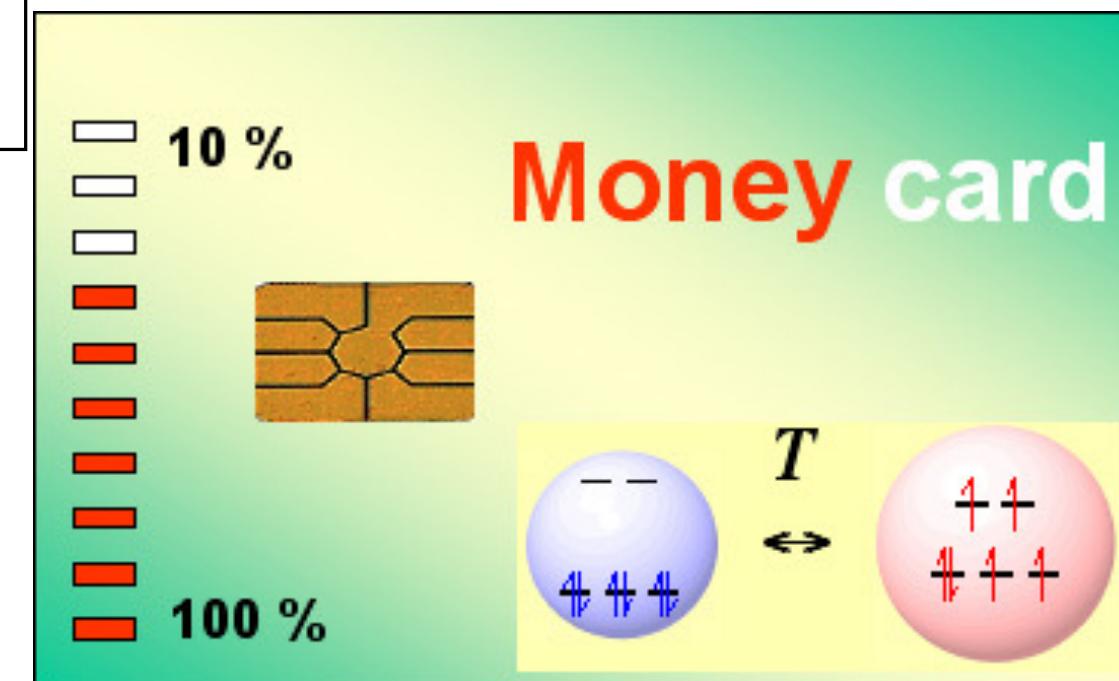
## Display device



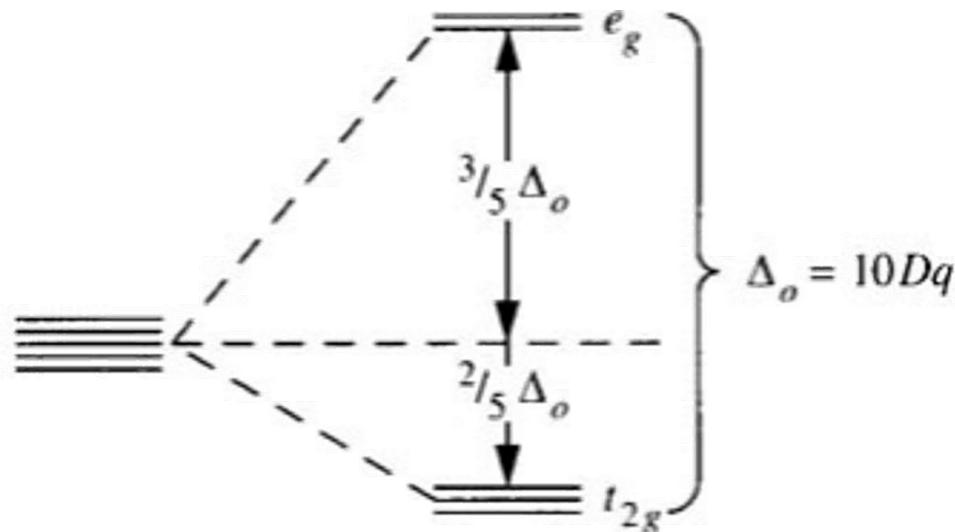
Compound in  
Low spin state  
(Thin Layer)

Display

LS-HS transition (Spin crossover) tuneable with light (or Temperature or Pressure): Applications



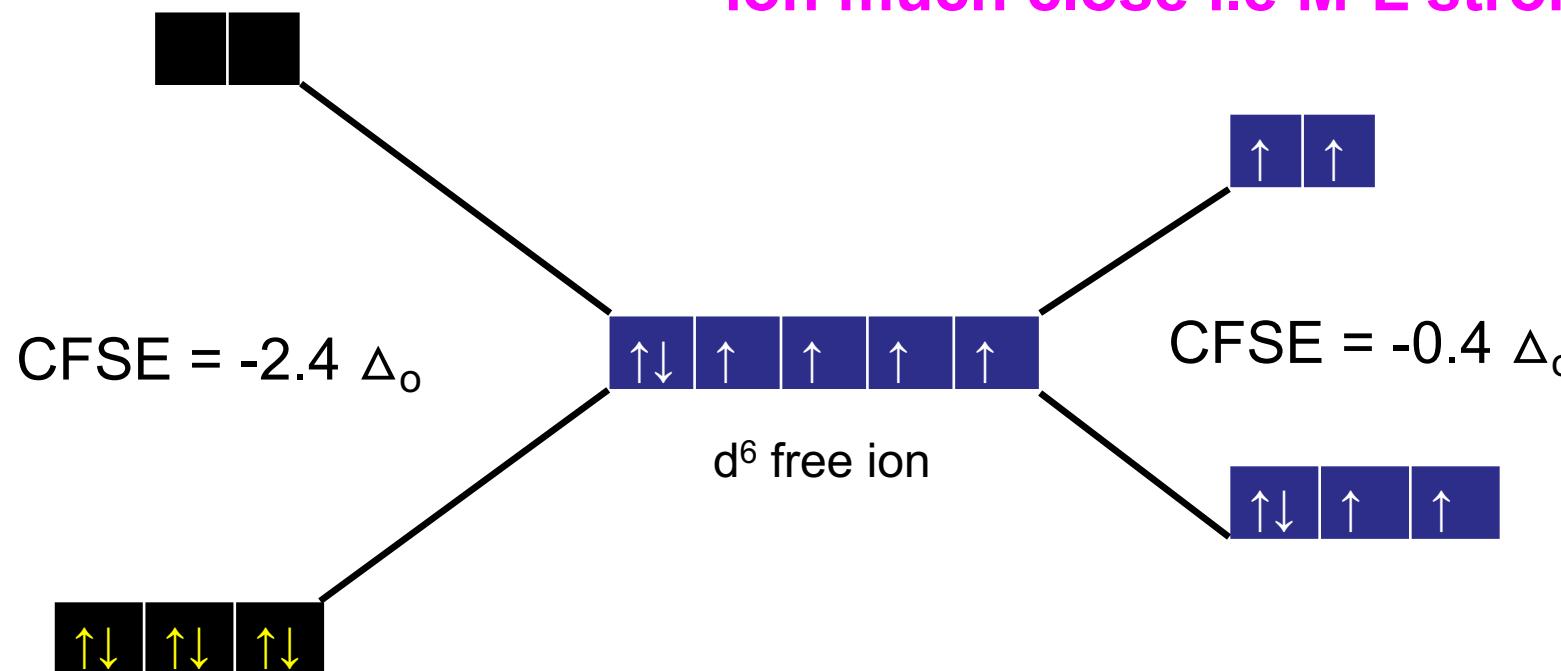
# Application of CFT / Thermodynamic stability of complexes (CFSE)



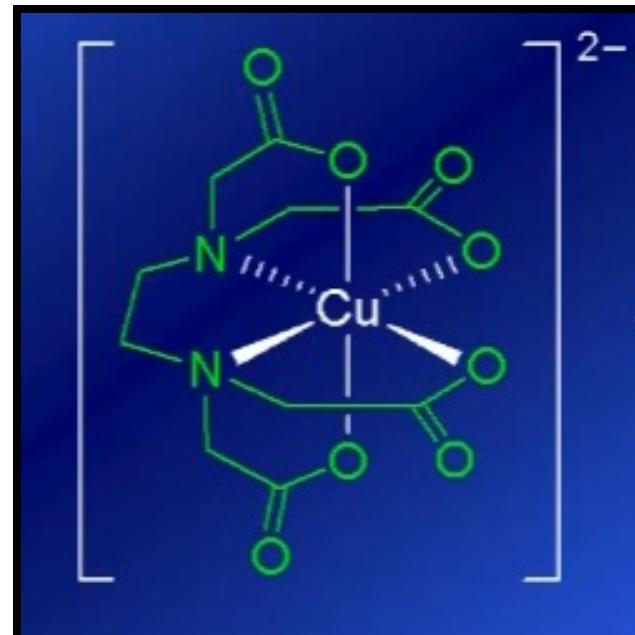
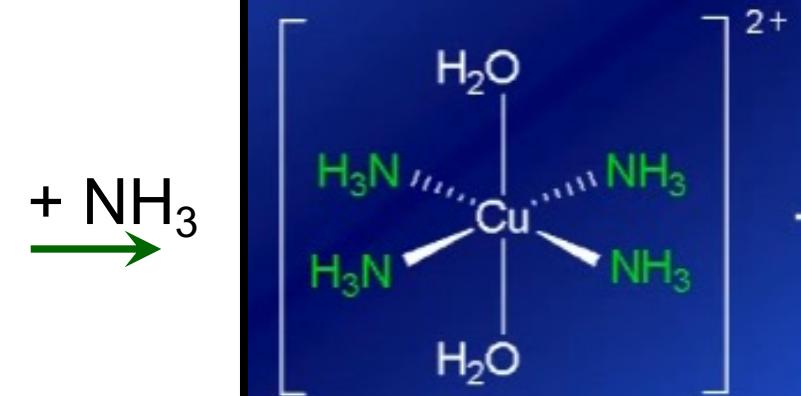
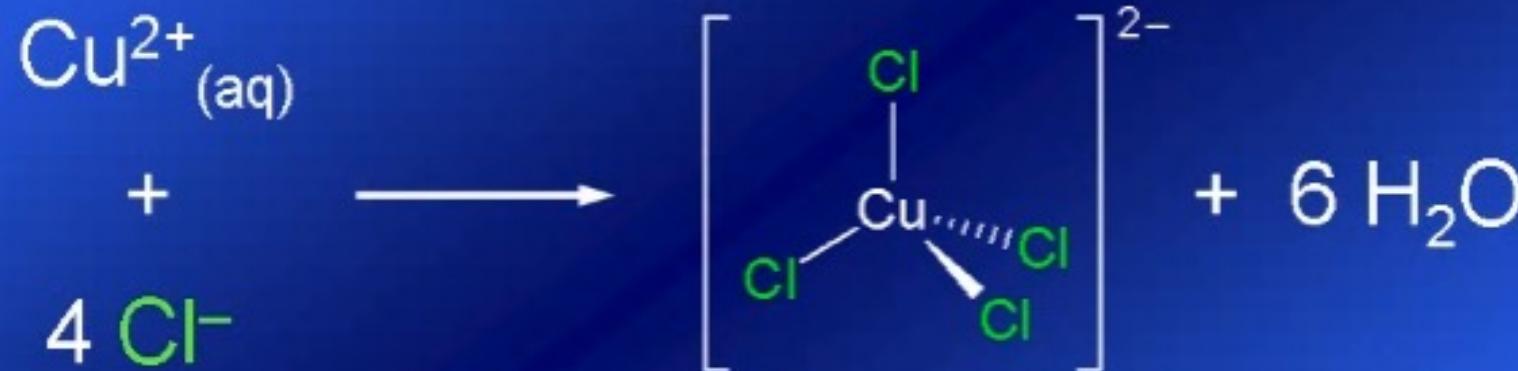
$$= -0.4 \times n(t_{2g}) + 0.6 \times n(e_g) \Delta_o$$

Where  $n(t_{2g})$  and  $n(e_g)$  are the number of electrons occupying the respective levels.

Since there are no electrons in the e<sub>g</sub> orbitals (low spin), ligands can approach the metal ion much close i.e M-L strong (than in HS)



## Stability of complex due to chelation effect

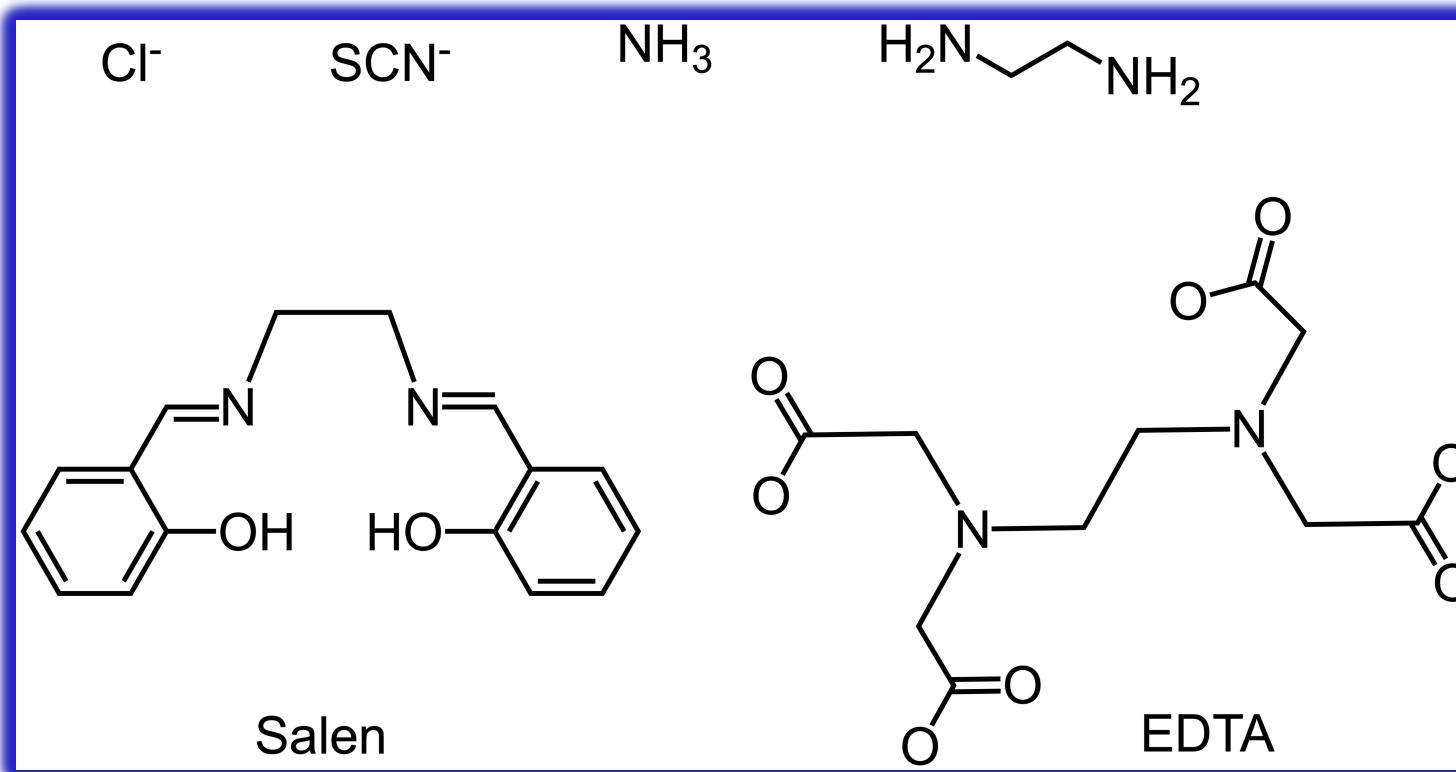


+ EDTA

# Demonstration

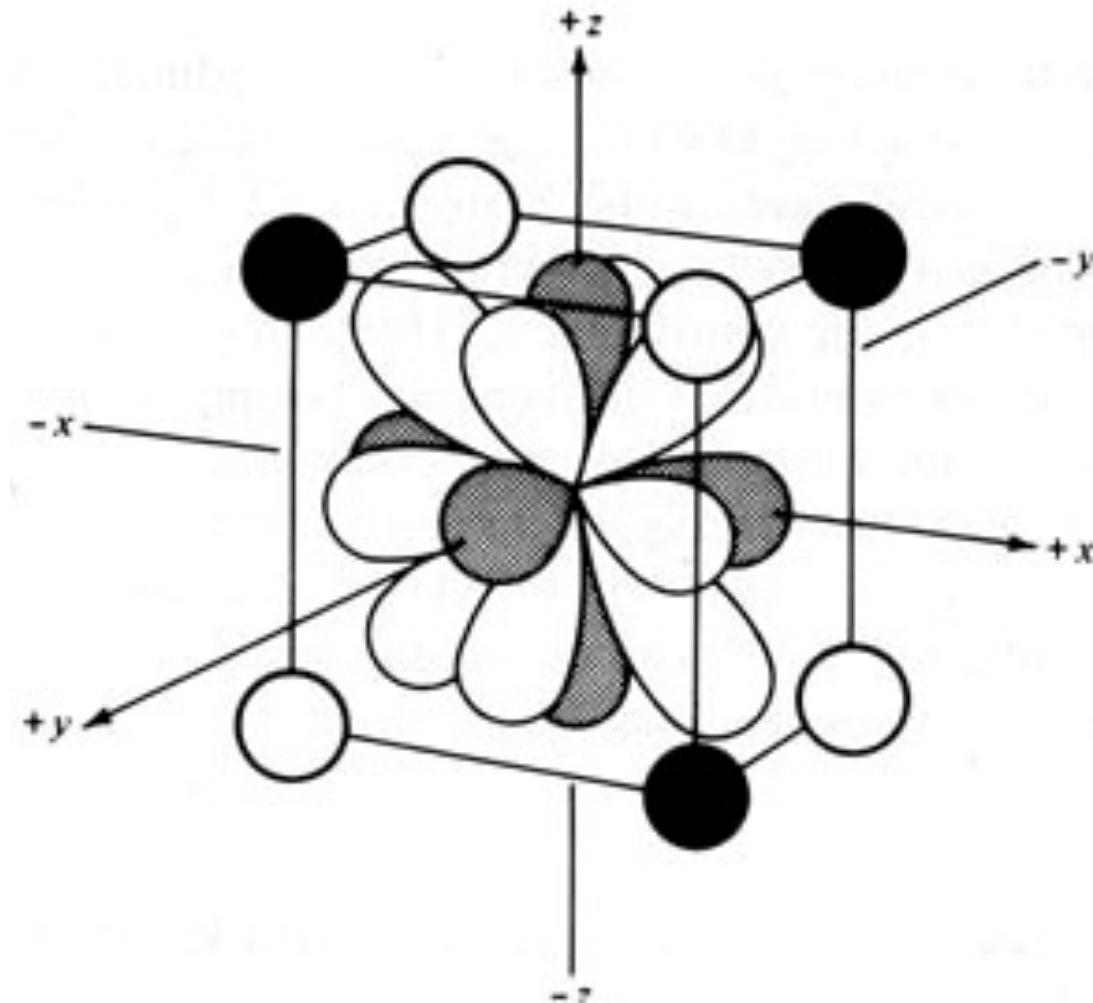
## Spectrochemical Series/Chelate effect

$\text{I}^- < \text{Br}^- < \text{S}^{2-} < \text{SCN}^- < \text{Cl}^- < \text{N}_3^-$ ,  $\text{F}^- < \text{urea}$ ,  $\text{OH}^- < \text{ox}$ ,  $\text{O}^{2-} < \text{H}_2\text{O} < \text{NCS}^- < \text{py}$ ,  $\text{NH}_3 < \text{en} < \text{bpy}$ ,  $\text{phen} < \text{NO}_2^- < \text{CH}_3^-$ ,  $\text{C}_6\text{H}_5^- < \text{CN}^- < \text{CO}$ .

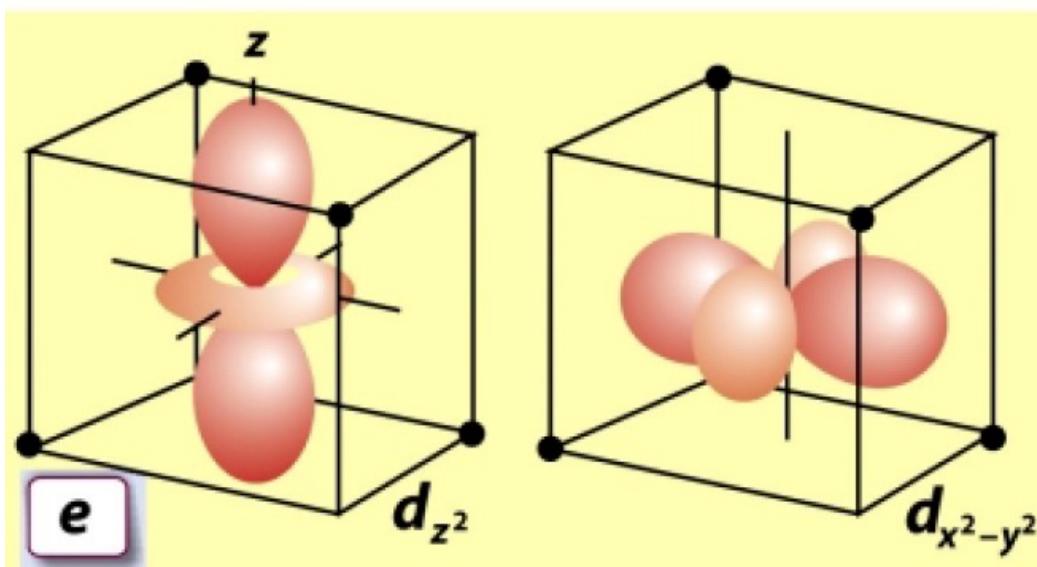
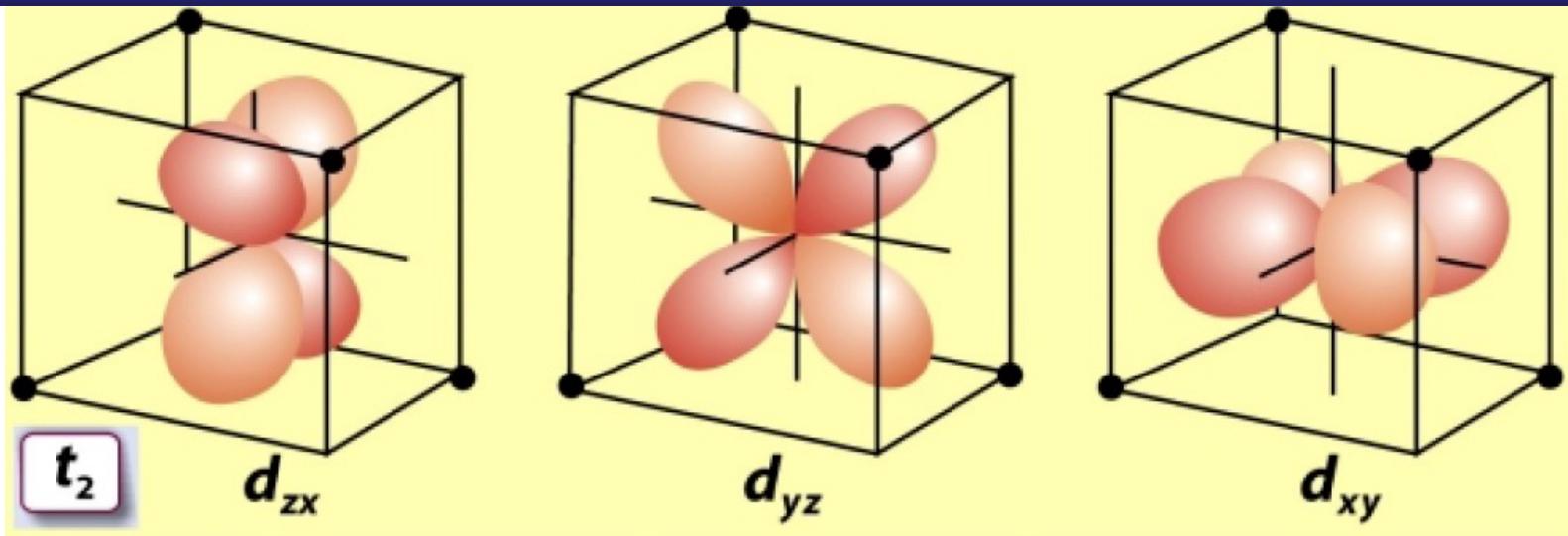


## Tetrahedral Field- Considerations

- Imagine a tetrahedral molecule inside a cube with metal ions at the center of the cube. The ligands occupy the four alternate corners of the cube leaving the rest four corners empty.
- The two 'e' orbitals point to the center of the face of the cube while the three 't<sub>2</sub>' orbitals point to the center of the edges of the cube.



# Tetrahedral complexes



The three ' $t_2$ ' orbitals  
point to the center of the  
edges of the cube  
 $109^\circ 28' / 3 = 35^\circ 16'$ .

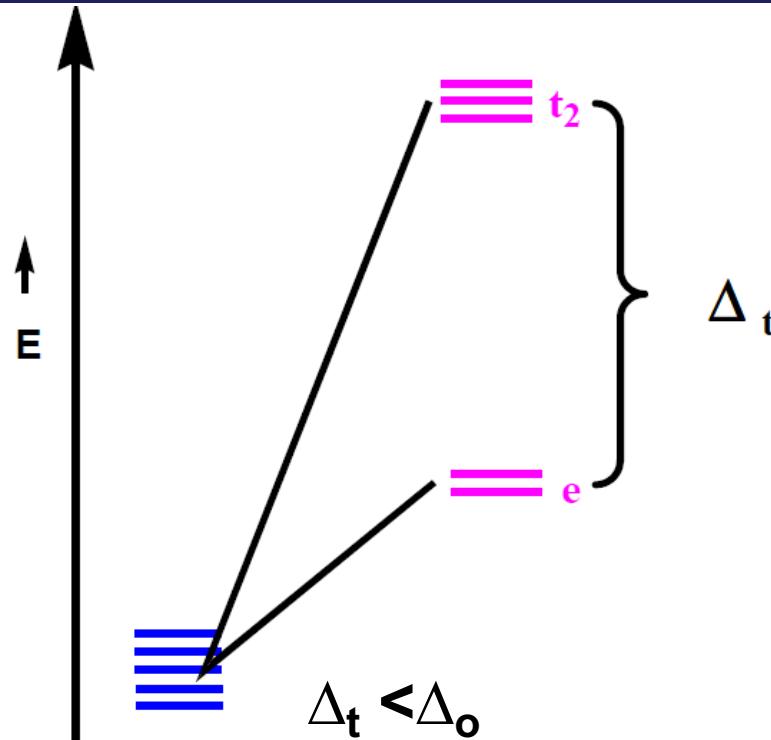
The two 'e' orbitals  
point to the center of  
the face of the cube  
 $109^\circ 28' / 2 = 54^\circ 44'$ .

figure 19-8

Shriver & Atkins Inorganic Chemistry, Fourth Edition

2006 by D. F. Shriver, P. W. Atkins, T. L. Overton, J. P. Rourke, M. T. Weller, and F. A. Armstrong

# Tetrahedral complexes



Thus the  $t_2$  orbitals are nearer to the direction of approach of the ligands than the  $e$  orbitals. Hence,  $t_2$  orbitals have higher energy compared to  $e$ -orbitals

In Td four ligands  $\sim 2/3$  of O<sub>h</sub> field

In Td the ligands do not coincide with d-orbitals  $\sim 2/3$   
Hence,

$$\Delta_t \approx 4/9 \Delta_o$$

Due to this, tetrahedral complexes are high-spin, in general.

Complex	$\Delta_T/\text{cm}^{-1}$
VCl <sub>4</sub>	9010
[CoCl <sub>4</sub> ] <sup>2-</sup>	3300
[CoBr <sub>4</sub> ] <sup>2-</sup>	2900

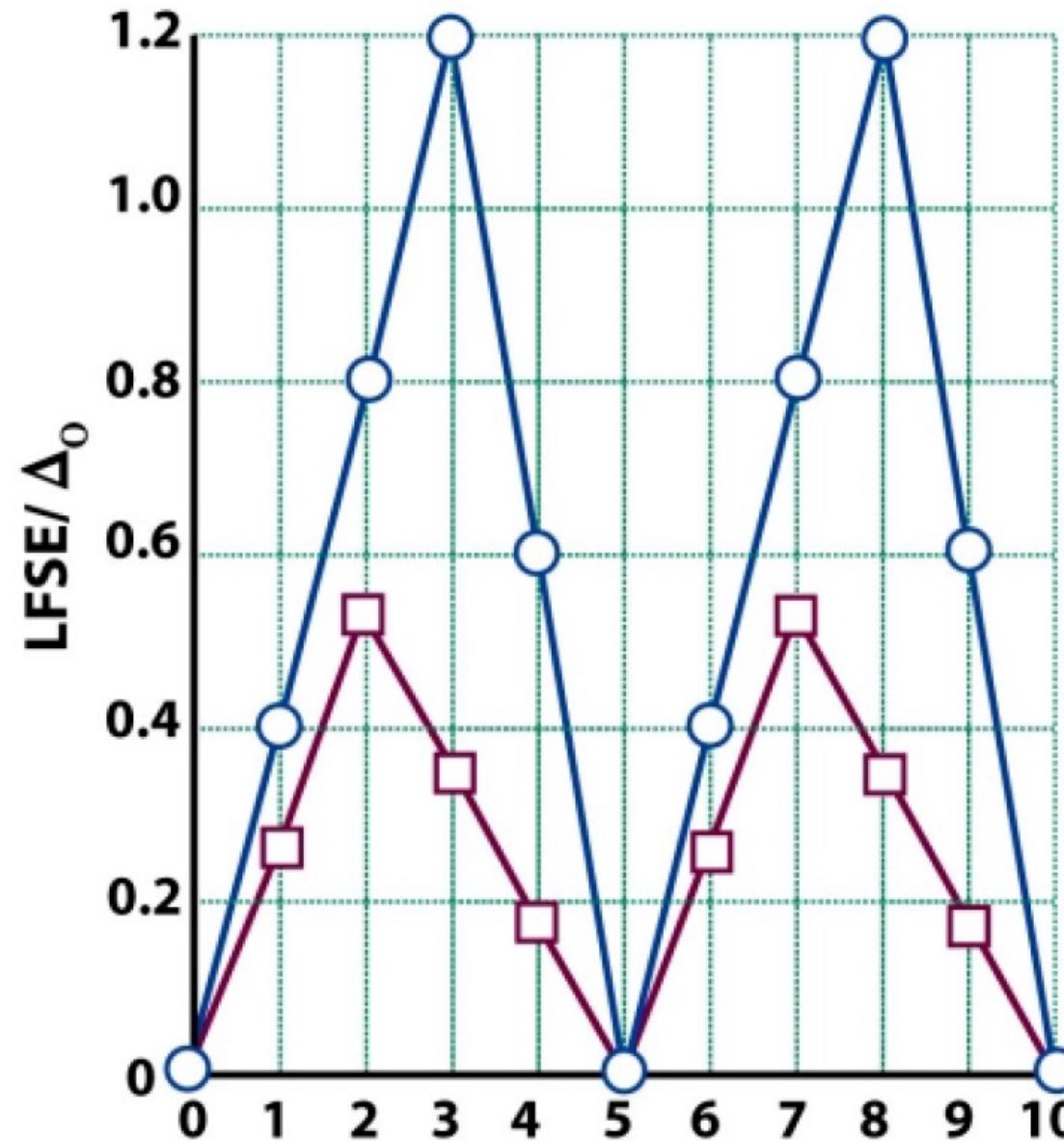
[CoI <sub>4</sub> ] <sup>2-</sup>	2700
[Co(NCS) <sub>4</sub> ] <sup>2-</sup>	4700

**Table 19.2** Ligand-field stabilization energies\*

$d^n$	Example	Octahedral			Tetrahedral			
		$N$	LFSE		$N$	LFSE		
$d^0$		0	0		0	0		
$d^1$	Ti <sup>3+</sup>	1	0.4		1	0.6		
$d^2$	V <sup>3+</sup>	2	0.8		2	1.2		
$d^3$	Cr <sup>3+</sup> , V <sup>2+</sup>	3	1.2		3	0.8		
		Strong-field		Weak-field				
$d^4$	Cr <sup>2+</sup> , Mn <sup>3+</sup>	2	1.6		4	0.6	4	0.4
$d^5$	Mn <sup>2+</sup> , Fe <sup>3+</sup>	1	2.0		5	0	5	0
$d^6$	Fe <sup>2+</sup> , Co <sup>3+</sup>	0	2.4		4	0.4	4	0.6
$d^7$	Co <sup>2+</sup>	1	1.8		3	0.8	3	1.2
$d^8$	Ni <sup>2+</sup>		2	1.2			2	0.8
$d^9$	Cu <sup>2+</sup>		1	0.6			1	0.4
$d^{10}$	Cu <sup>+</sup> , Zn <sup>2+</sup>	0	0		0	0		

\*  $N$  is the number of unpaired electrons; LFSE is in units of  $\Delta_0$  for octahedra or  $\Delta_T$  for tetrahedra; the calculated relation is  $\Delta_T \approx 0.45\Delta_0$ .

# $O_h$ vs. $T_d$ CFSE



## Application of CFSE: Determination of Spinels Structures

**Spinel** is the name given to the mineral  $\text{MgAl}_2\text{O}_4$ .

It has a common structural arrangement shared by many oxides of the transition metals with formula  $\text{AB}_2\text{O}_4$ .

In the **normal spinel**

The oxygens form a cubic close packed array

The Mg(II) (A-type) sit in tetrahedral sites

The Al(III) (B-type) sit in octahedral sites



An **inverse spinel** is an alternative arrangement where half of the trivalent ions swap with the divalent ions so that the Mg(II) now occupy octahedral sites ie  $\text{B}(\text{AB})\text{O}_4$ .



## Spinels- Use of CFSE

There are several transition metal oxides which have the formula  $AB_2O_4$  and crystallize in spinel or inverse spinel structure. E.g.  $FeCr_2O_4$ ,  $ZnAl_2O_4$ ,  $Co_3O_4$ ,  $Mn_3O_4$ ,  $Fe_3O_4$ ,  $NiFe_2O_4$  etc.

CFSE is highly useful to determine whether a structure would be normal or inverse

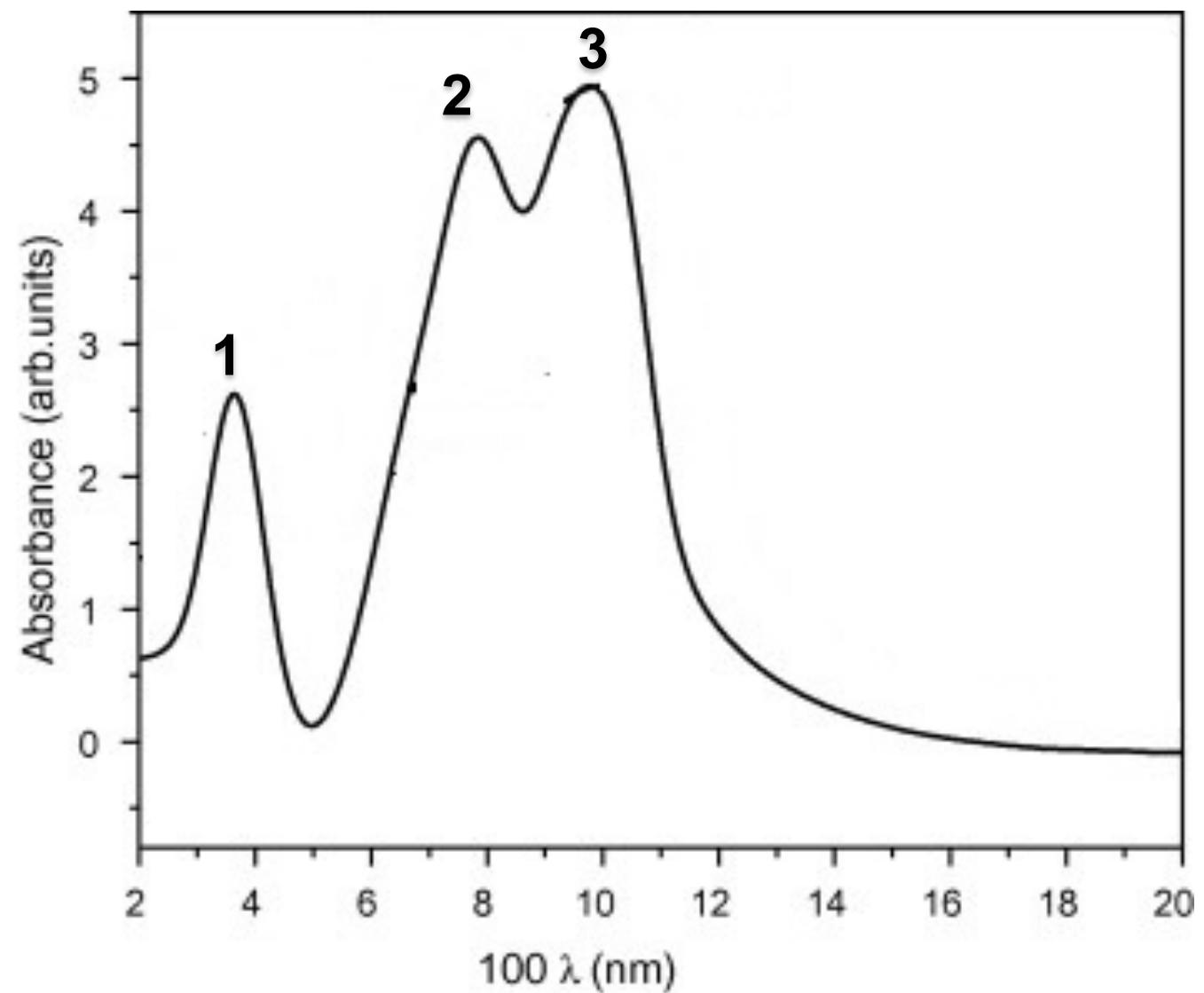
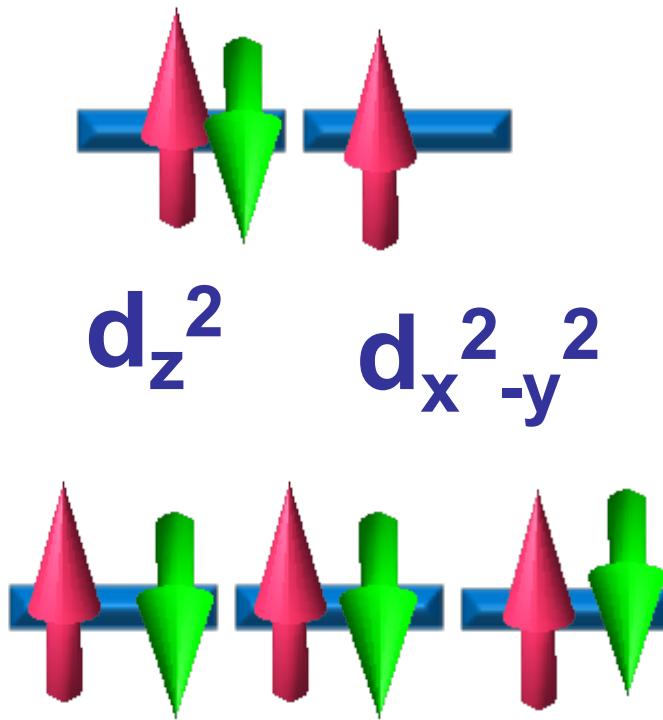
If  $M^{3+}$  ion has a higher CFSE in an octahedral field compared to  $M^{2+}$  ion, **normal spinel** will result.

If  $M^{2+}$  ion has a higher CFSE in an octahedral field compared to  $M^{3+}$  ion, **inverse spinel** will result.

**normal**  $[M^{II}]_{\text{tet}}[M^{III}M^{III}]_{\text{oh}}O_4$ ; **inverse**  $[M^{III}]_{\text{tet}}[M^{II}M^{III}]_{\text{oh}}O_4$

# Absorption spectra of d<sup>9</sup> octahedral complexes

Can we explain this?

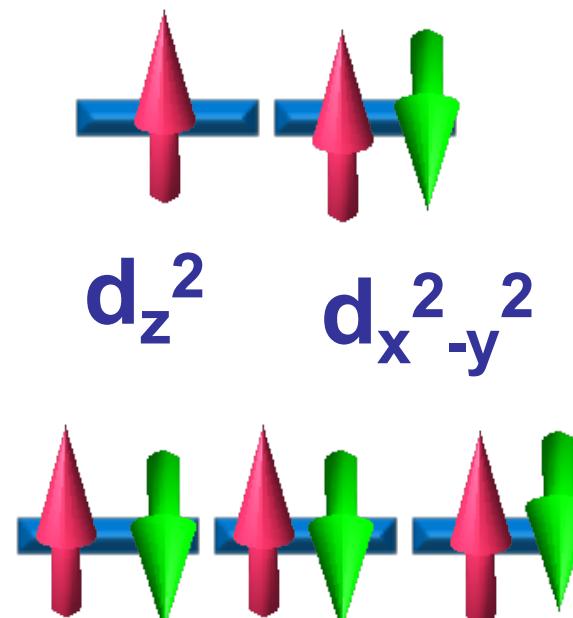
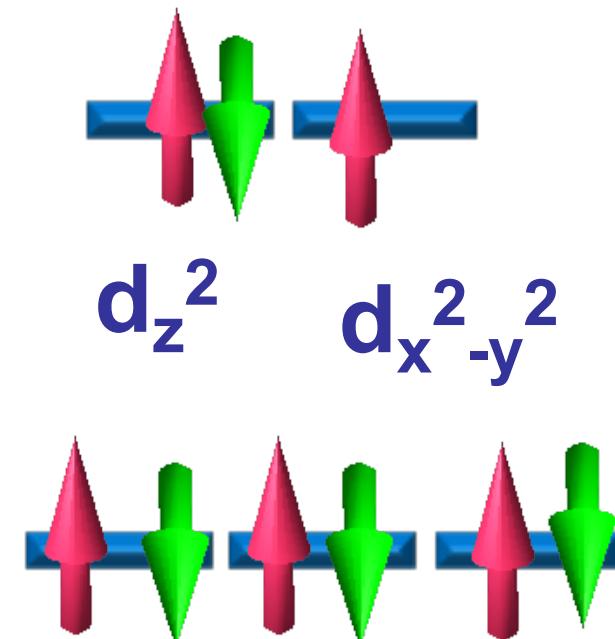


## Case of degeneracy: Jahn-Teller distortion

### Jahn-Teller Distortion:

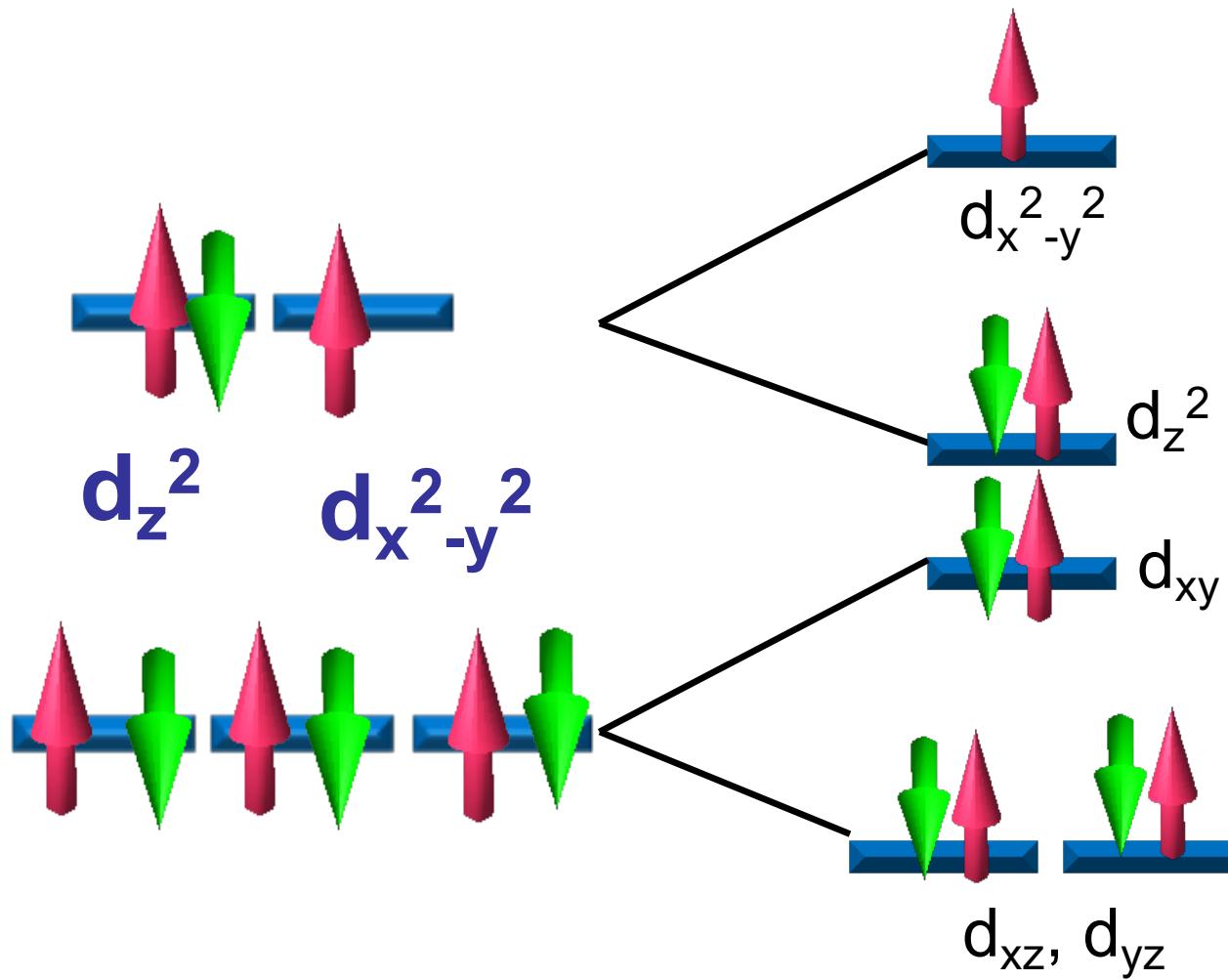
Any non-linear molecular system in a degenerate electronic state will be unstable and will undergo distortion to form a system of lower symmetry and lower energy thereby removing the degeneracy.

Example: Cu(II) Oh complex – d<sup>9</sup> configuration



Degenerate electronic state: Complex undergoes distortion

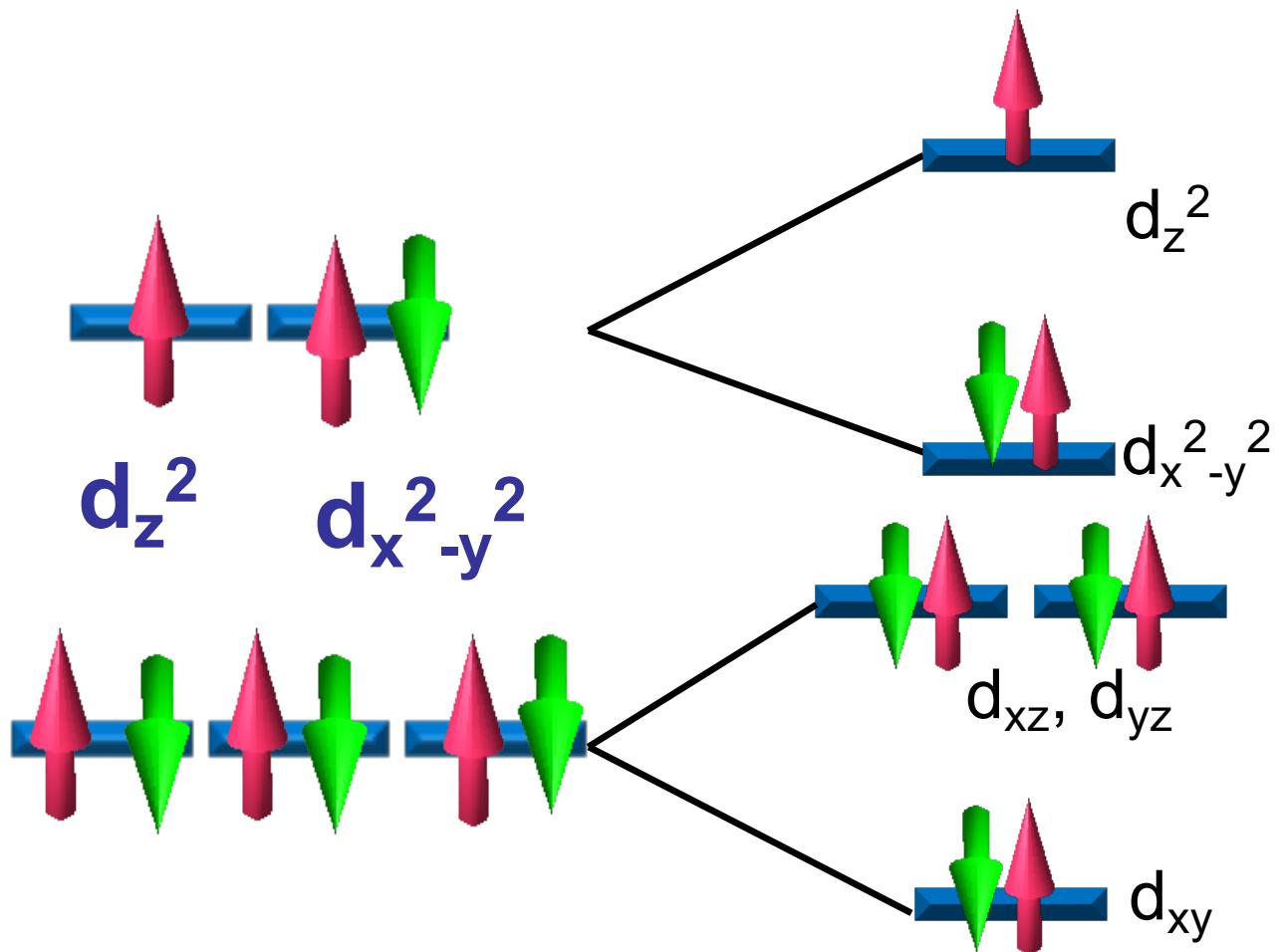
# Axial elongation: Jahn-Teller distortion



**As ligands approached along the axis in  $O_h$**

- ❖ The ligands can not approach Cu(II) ion closely along z-axis because  $d_z^2$  orbital contains two electron (i.e. due to the ligand  $e^-$  and metal  $e^-$  repulsion), hence stabilized
- ❖ While along xy plane ligands can approach towards Cu(II) ion much more closer than the z-axis, since  $d_{x^2-y^2}^2$  orbital consists of only one unpaired electron. Therefore, destabilized.
- ❖ Distortion felt even in  $t_{2g}$  orbitals, where all the z-component of the orbitals ( $d_{xz}$  and  $d_{yz}$ ) stabilized since ligands along z-axis do not come closer to the Cu(II) ion.
- ❖ Consequently Cu(II)-L bond lengths along z-axis is longer than Cu(II)-L bond lengths along xy-plane (i.e. axially elongated or tetragonal elongation geometry around Cu(II) ion).

# Axial compression: Jahn-Teller distortion

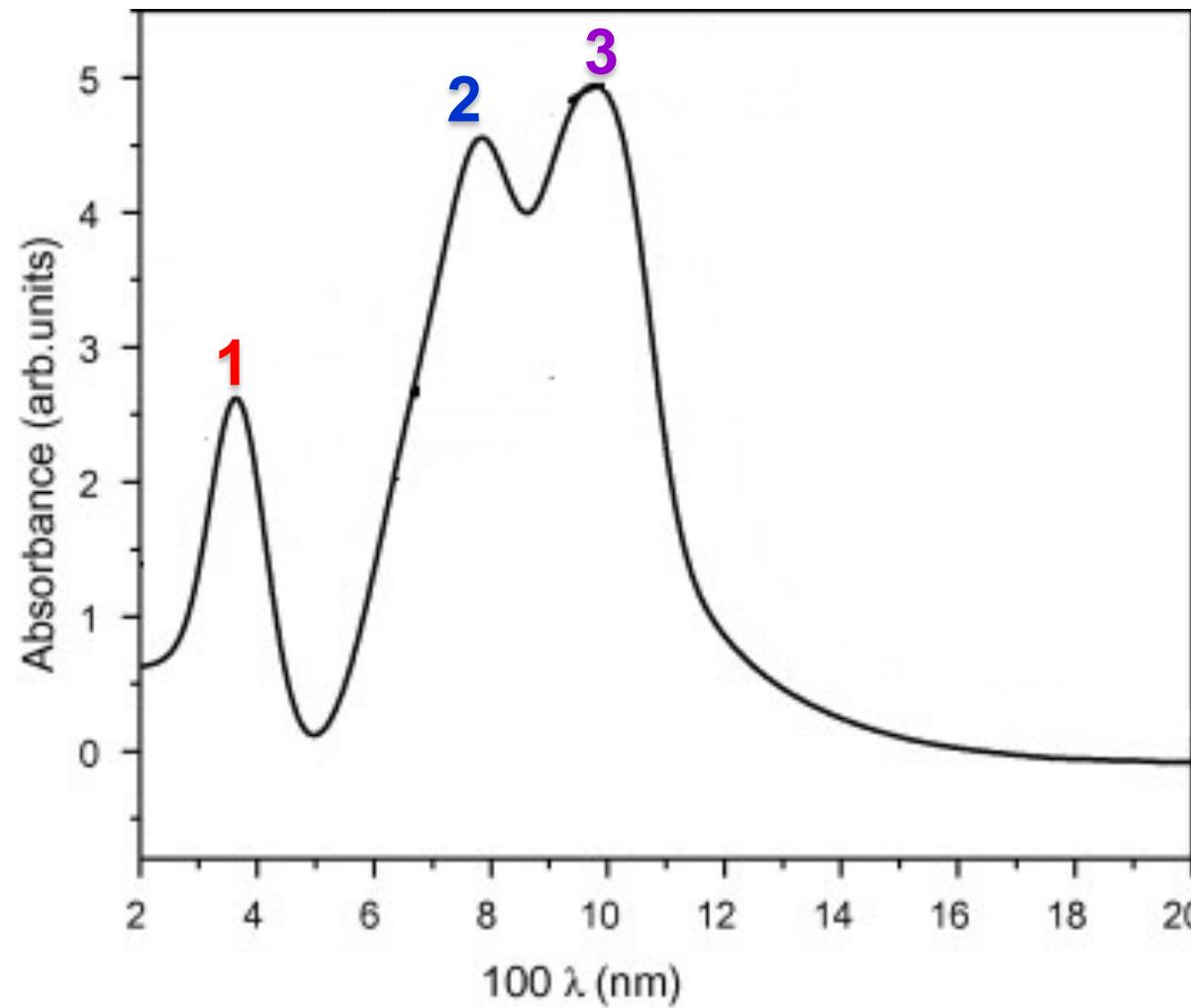
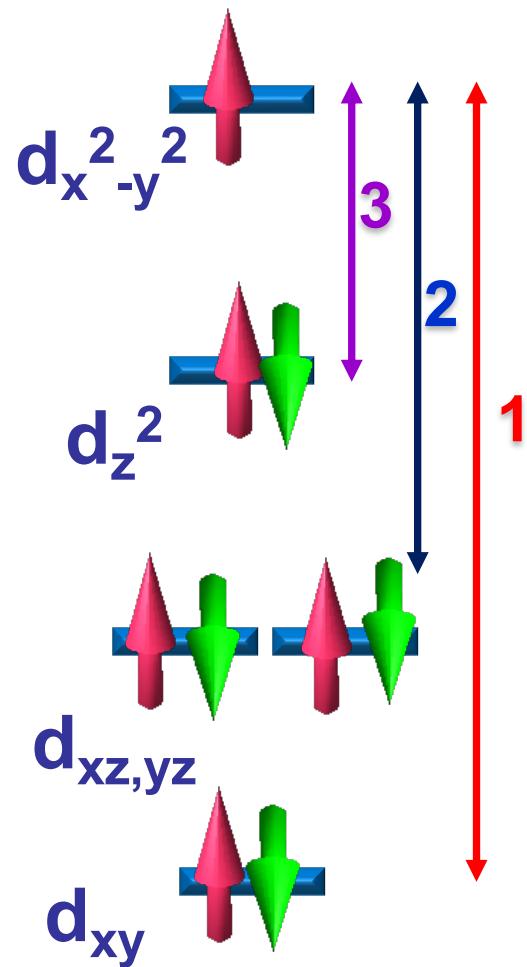


**As ligands approached along the axis in  $\text{O}_\text{h}$**

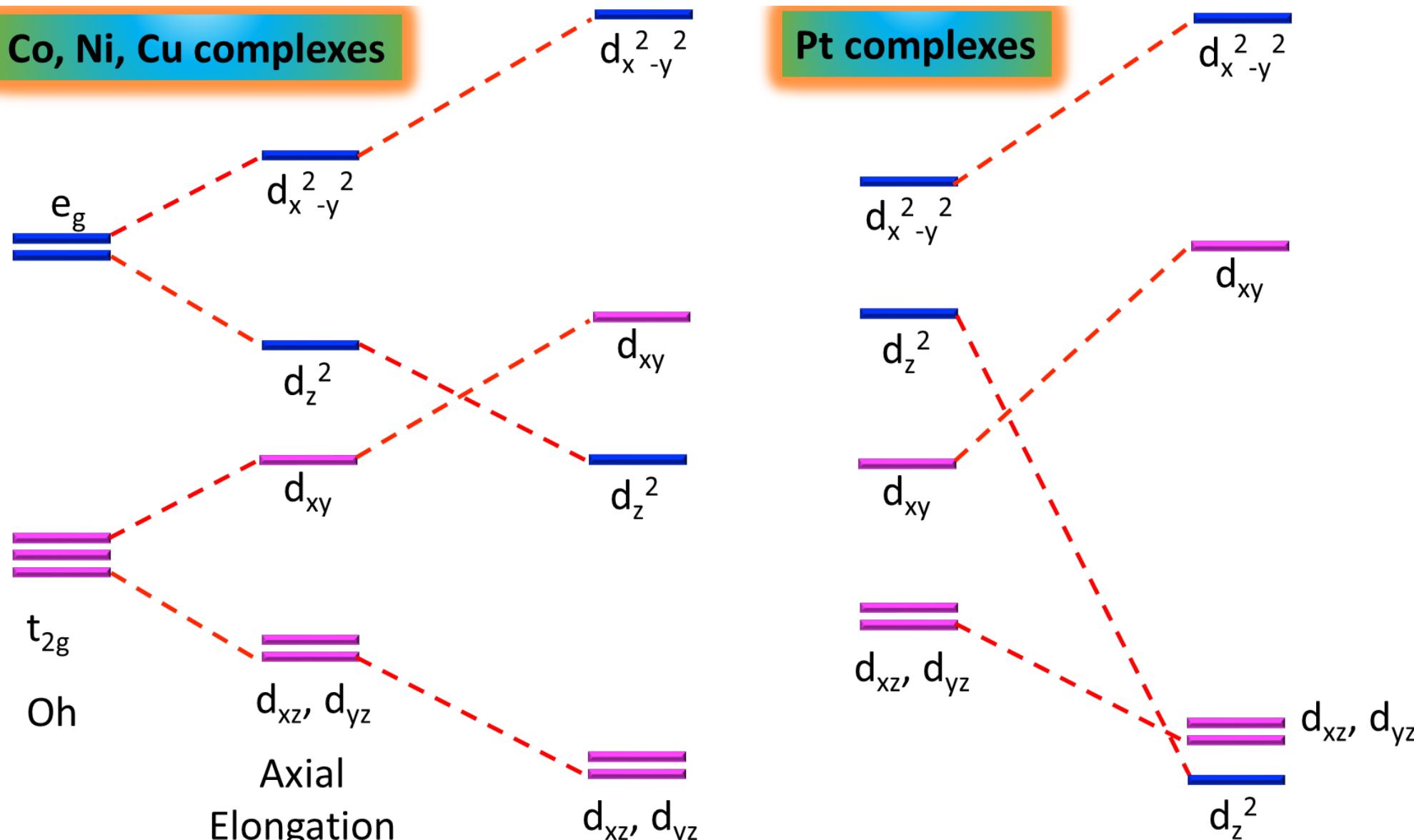
- ❖ The ligands can not approach  $\text{Cu}(\text{II})$  ion closely along  $xy$ -plane because  $d_{x^2-y^2}$  orbital contains two electron (i.e. due to the ligand  $e^-$  and metal  $e^-$  repulsion)
- ❖ While along  $d_{z^2}$  axis ligands can approach toward  $\text{Cu}(\text{II})$  ion much more closer than the  $xy$ -plane, since  $d_{z^2}$  orbital consists of only one unpaired electron.
- ❖ Distortion felt in  $t_{2g}$  orbitals as well, where all z-component of the orbitals ( $d_{xz}$  and  $d_{yz}$ ) destabilized since ligands along z-axis come closer to metal ion.
- ❖ Consequently  $\text{Cu}(\text{II})$ -L bond lengths along z-axis is shorter than  $\text{Cu}(\text{II})$ -L bond lengths along  $xy$ -plane (i.e. axially compressed or tetragonal compression geometry around  $\text{Cu}(\text{II})$  ion).

# Absorption spectra of d<sup>9</sup> octahedral complexes

## Rationale for 3 transitions!



# Crystal field splitting for square planar complexes



Examples:

$\text{Ni}^{2+}$ ,  $\text{Pd}^{2+}$ ,  $\text{Pt}^{2+}$ ,  $\text{Cu}^{3+}$ ,  $\text{Ag}^{3+}$ ,  $\text{Au}^{3+}$

# Crystal field splitting for other geometries

