

# **Topic III**

# **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

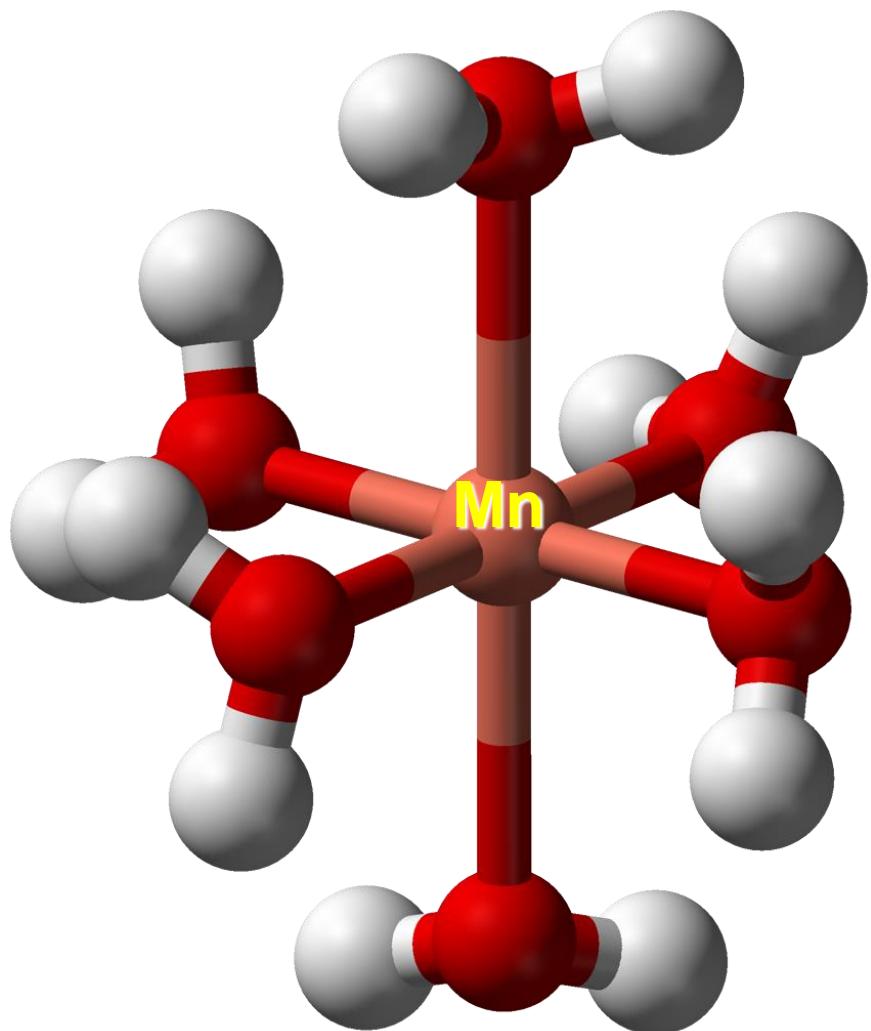
Sc		+3					
Ti	+1	+2	+3	+4			
V	+1	+2	+3	+4	+5		
Cr	+1	+2	+3	+4	+5	+6	
Mn	+1	+2	+3	+4	+5	+6	+7
Fe	+1	+2	+3	+4	+5	+6	
Co	+1	+2	+3	+4	+5		
Ni	+1	+2	+3	+4			
Cu	+1	+2	+3				
Zn		+2					

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-  
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



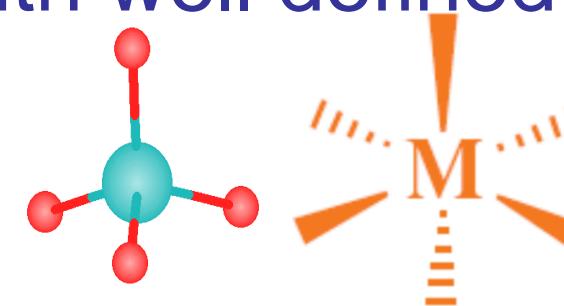
**Metal ion:** Central & is a Lewis acid

**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

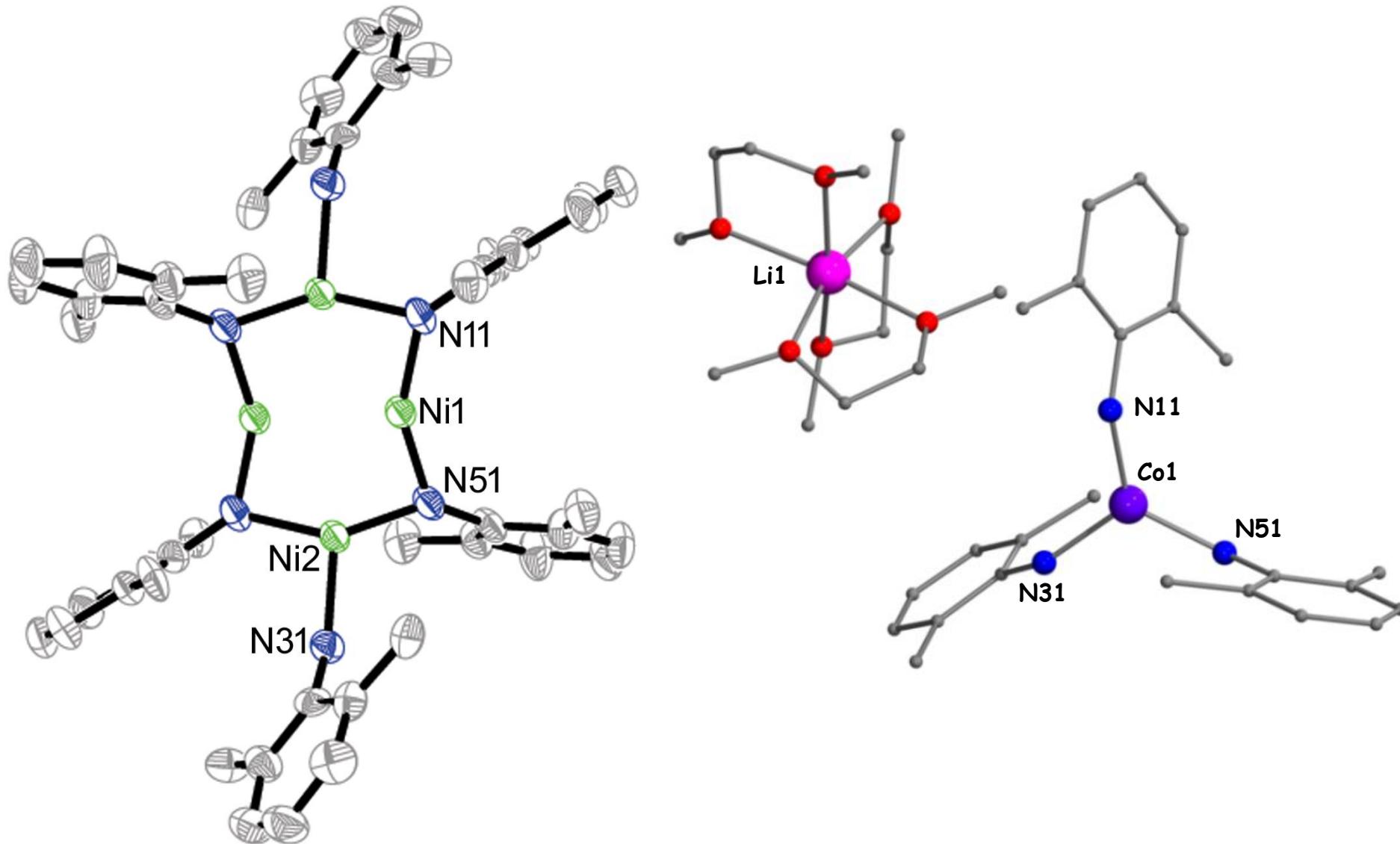
Charge

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?**

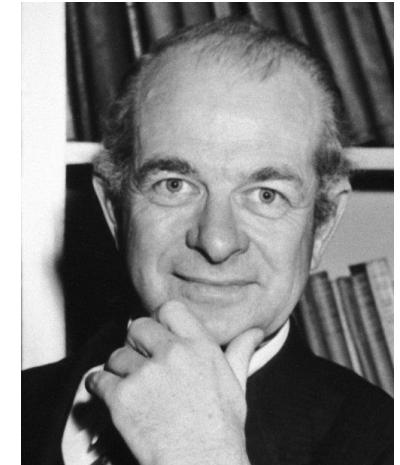
# Theoretical foundations of coordination complexes

- (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)

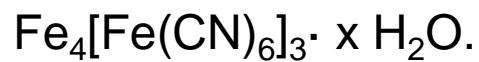
Ref: Inorganic Chemistry by Shriver & Atkins')



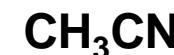
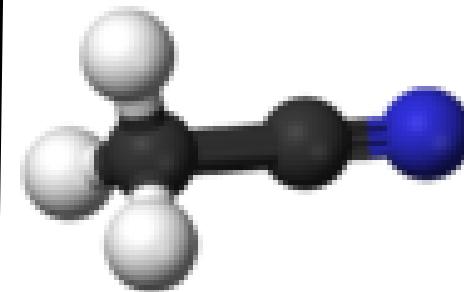
# How strong is the co-ordinate bond?



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)**

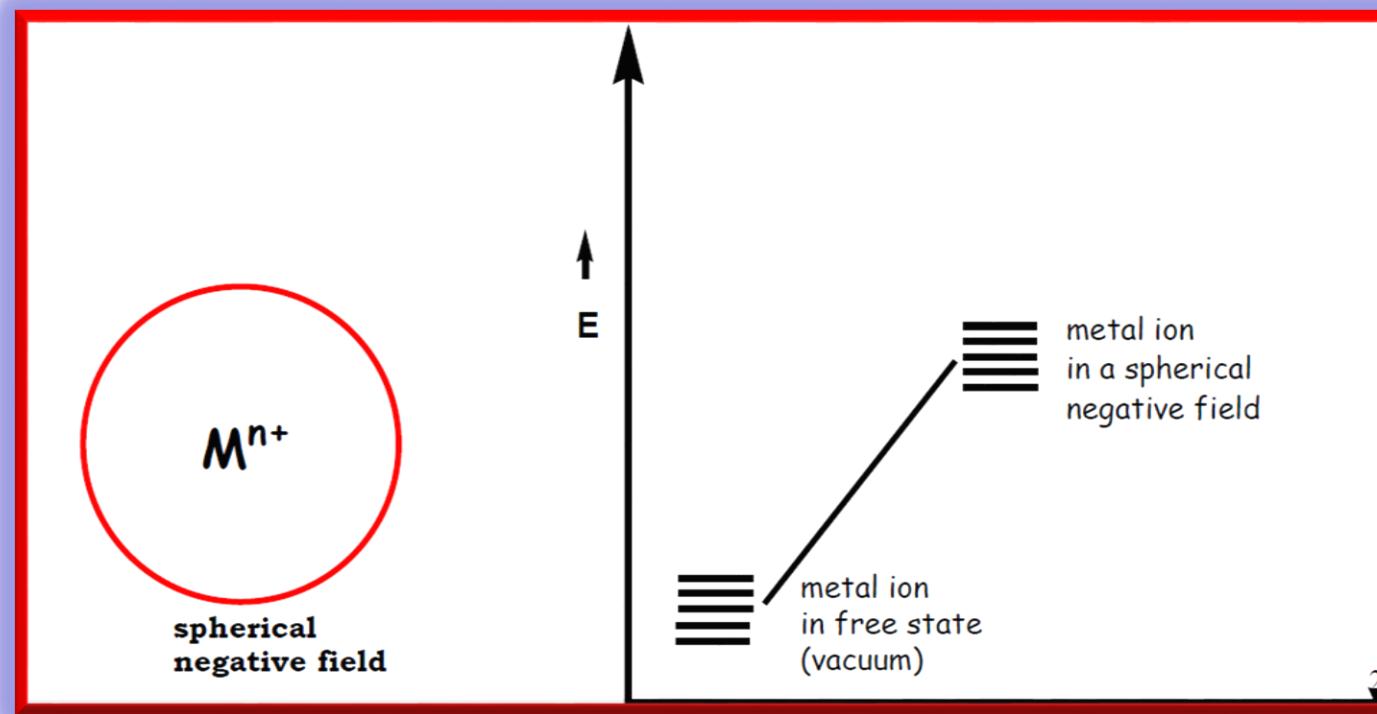
- ❖ **CFT could explain**

- 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

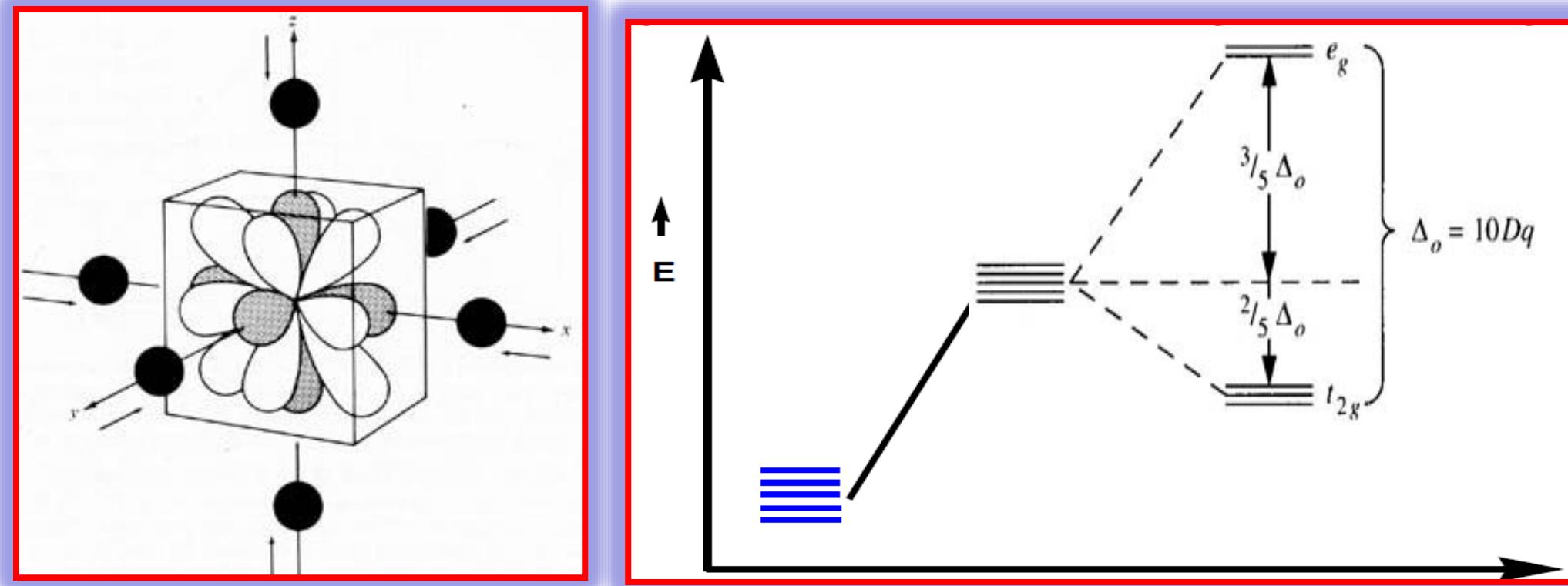
- (i) Interactions between the metal ion and ligands are purely electrostatic (ionic in nature).
- (ii) Ligands are considered as point charge
  - (a) For anionic ligand - ion- ion
  - (b) For neutral ligand - ion-dipole
- (iii) Electrons on the metals are under repulsive force from the ligands.
- (iv)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

# Influence of symmetric ligand field on the d-orbitals

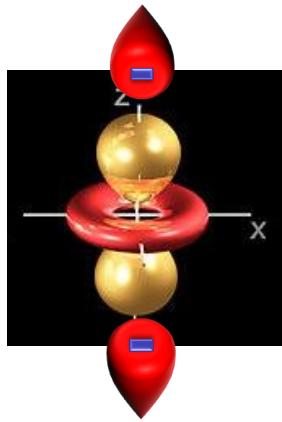
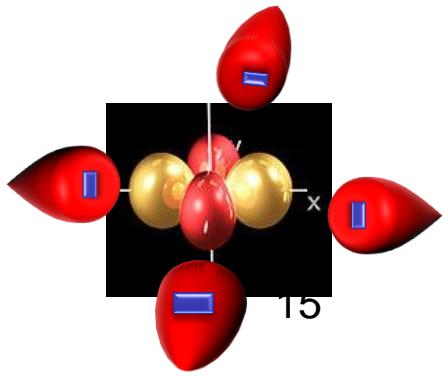


- The  $5 \times d$  orbitals in an isolated gaseous metal are degenerate
- If a spherically symmetric field of negative charges is placed around the metal, these orbitals remain degenerate, but all of them are raised in energy as a result of the repulsion between the negative charges on the ligands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

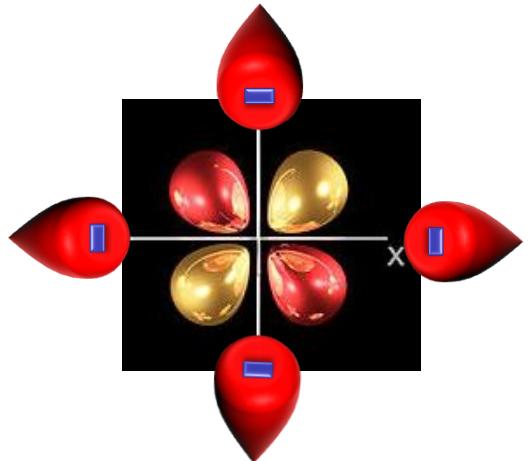
# Octahedral Field



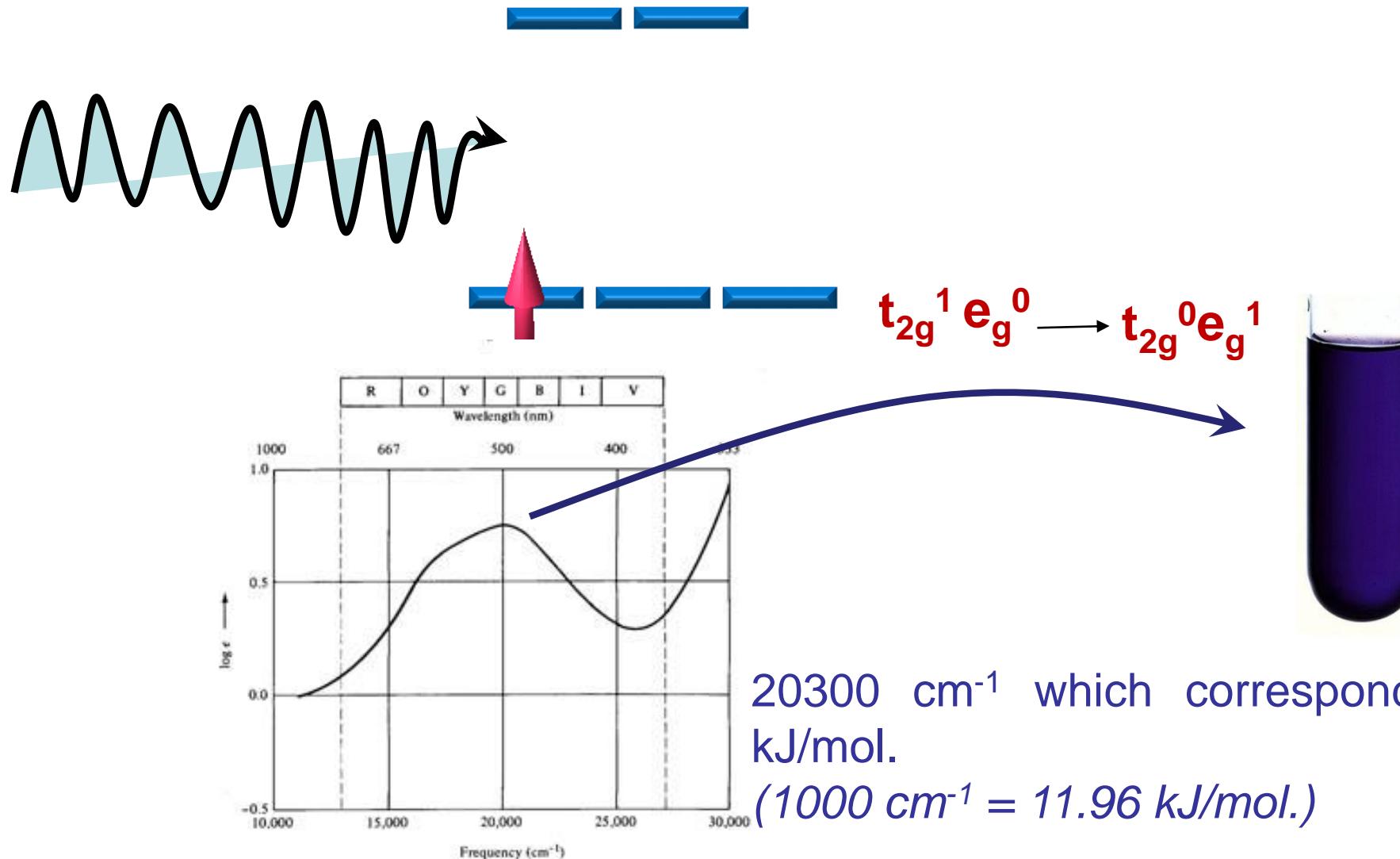
- ✓ Not all d- orbitals will interact to the same extent with the six point charges located on the +x, -x, +y, -y, +z and -z axes respectively.
- ✓ The orbitals which lie along these axes (i.e.  $x^2-y^2$ ,  $z^2$ ) will be destabilized more than the orbitals which lie in-between the axes (i.e. xy, xz,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



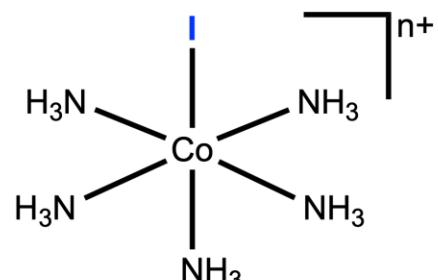
$d_z^2$      $d_{x^2-y^2}$      $d_{xy}$      $d_{xz}$      $d_{yz}$



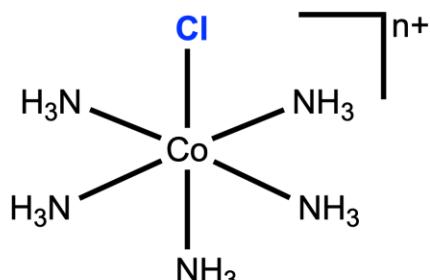
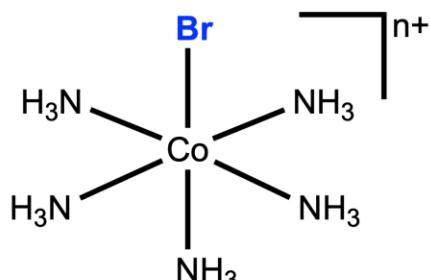
# Rationale for the observation of UV-Vis spectrum



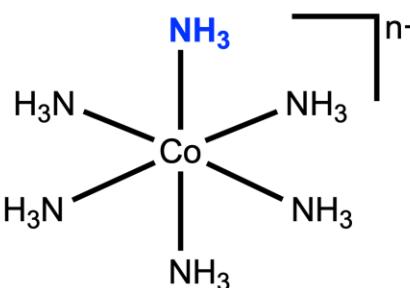
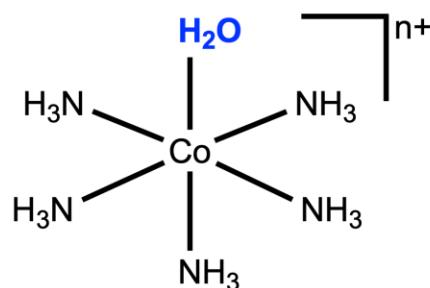
# Why color of the complexes change when changing a ligand?



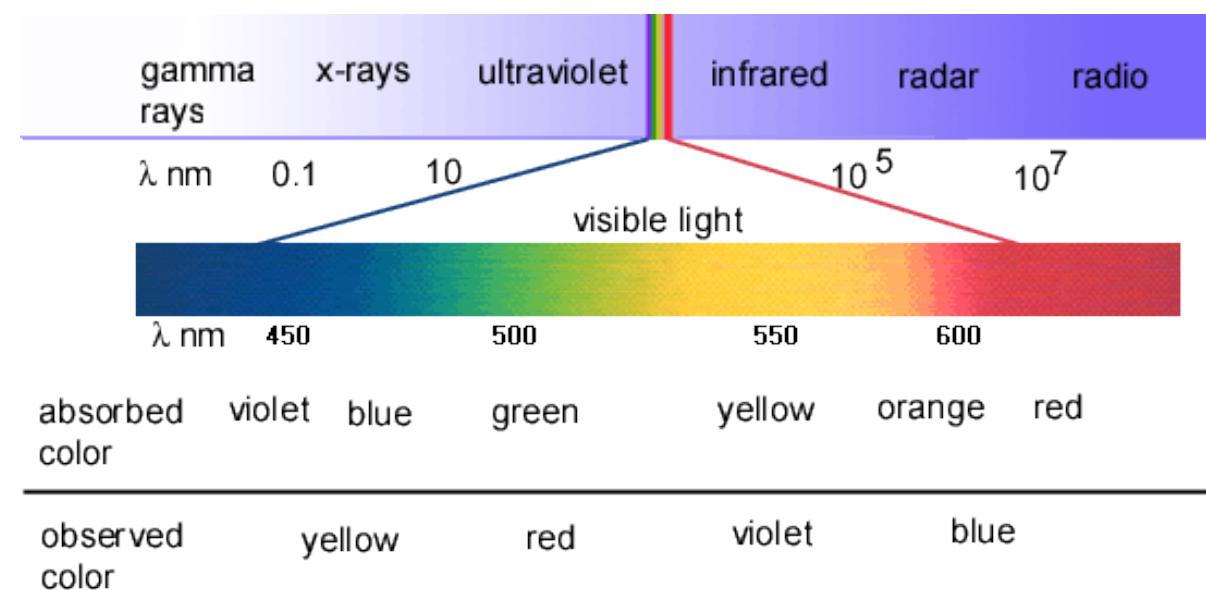
Purple



Pink



Yellow



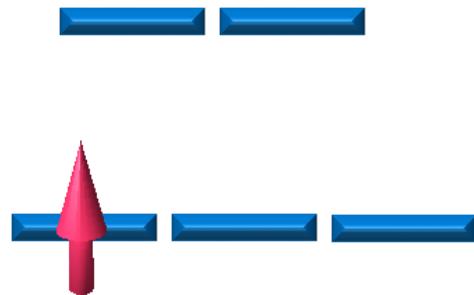
$\Delta_o$  follows the order of  
I < Br < Cl < H<sub>2</sub>O < NH<sub>3</sub>

## Spectrochemical series

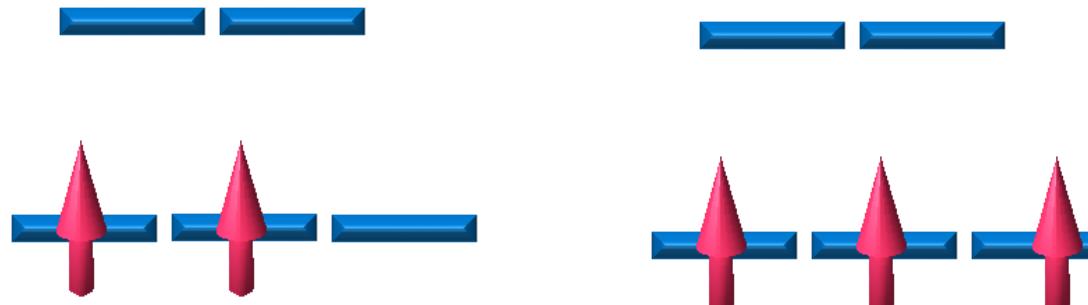
$\text{I}^- < \text{Br}^- < \text{S}^{2-} < \text{SCN}^- < \text{Cl}^- < \text{N}_3^-$ ,  $\text{F}^- < \text{urea}$ ,  $\text{OH}^- < \text{ox}$ ,  $\text{O}^{2-} < \text{H}_2\text{O} < \text{NCS}^- < \text{py}$ ,  $\text{NH}_3 < \text{en} < \text{bpy}$ ,  $\text{phen} < \text{NO}_2^- < \text{CH}_3^-$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

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

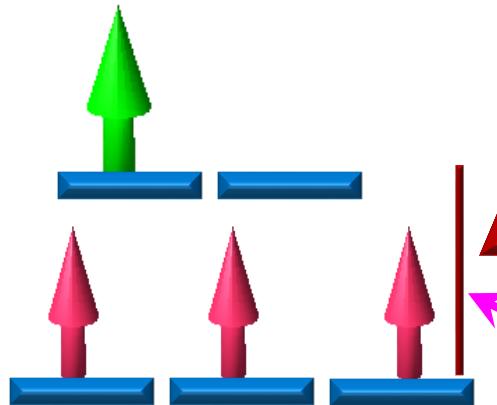


Due to the  $e^-e^-$  repulsion, calculating  $\Delta_o$  is not straight forward for system with more than one unpaired electrons.

# 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?

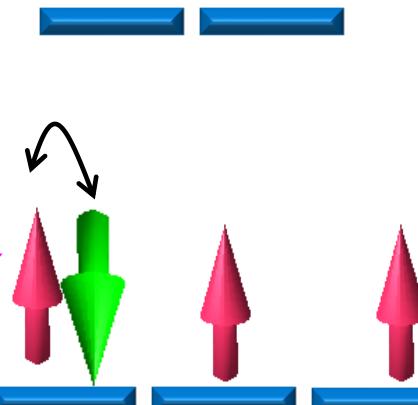
Decided by

- (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)

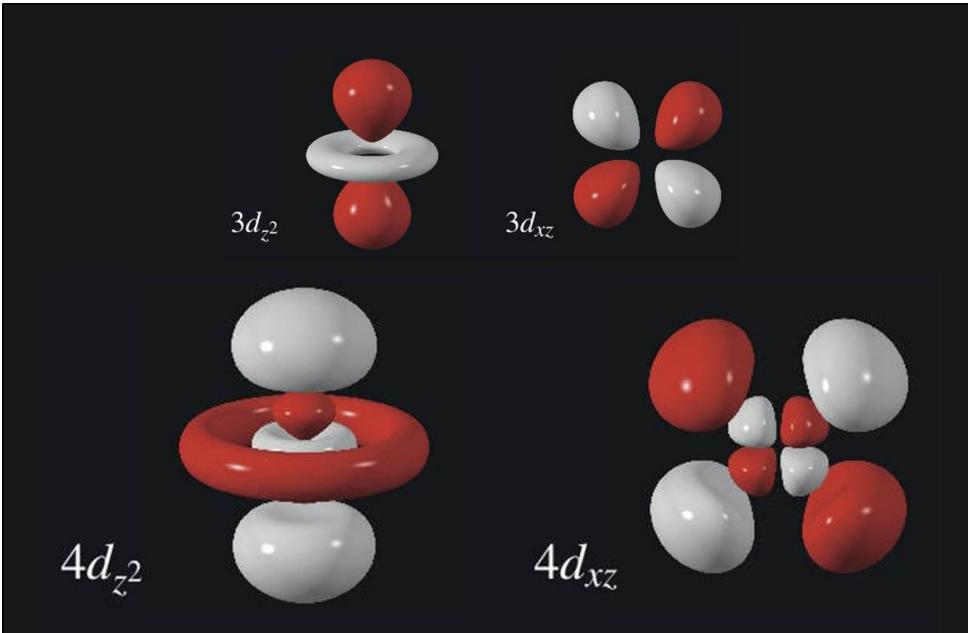
Complex	Config.	$\Delta_0$ , cm <sup>-1</sup>	P, cm <sup>-1</sup>	spin-state
[Fe(OH <sub>2</sub> ) <sub>6</sub> ] <sup>2+</sup>	d <sup>6</sup>	10,400	17,600	high-spin
[Fe(CN) <sub>6</sub> ] <sup>4-</sup>	d <sup>6</sup>	32,850	17,600	low-spin
[CoF <sub>6</sub> ] <sup>3-</sup>	d <sup>7</sup>	13,000	21,000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



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

$3d < 4d < 5d$

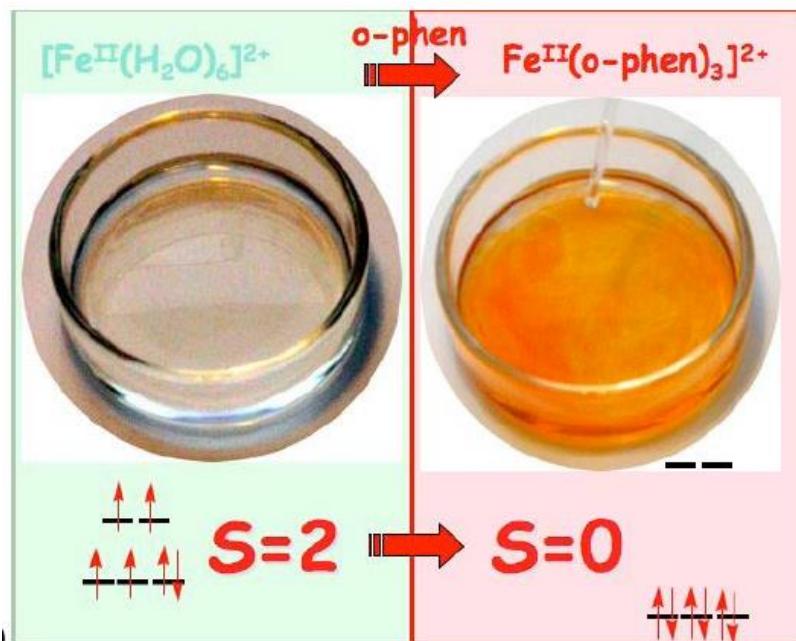
## Factors affecting $\Delta_o$

### (iii) Nature of ligand

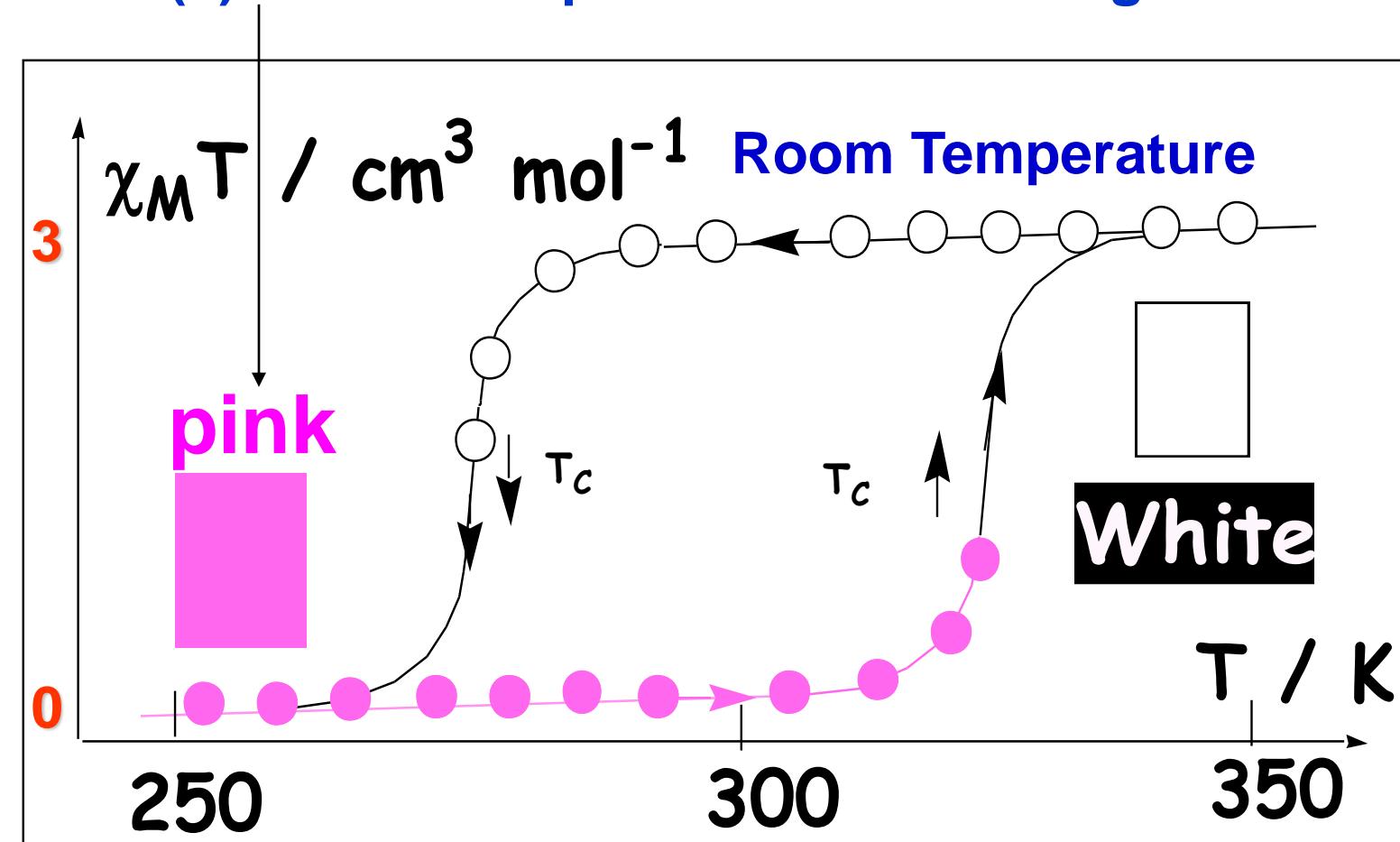
Ligands which cause a small splitting are *Weak field ligands* ( $\Delta_o$  in the range  $7000 - 30000 \text{ cm}^{-1}$ ) and those cause a large splitting are *Strong field ligands* ( $\text{CFSE}$  typically  $> 30000 \text{ cm}^{-1}$ )

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

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

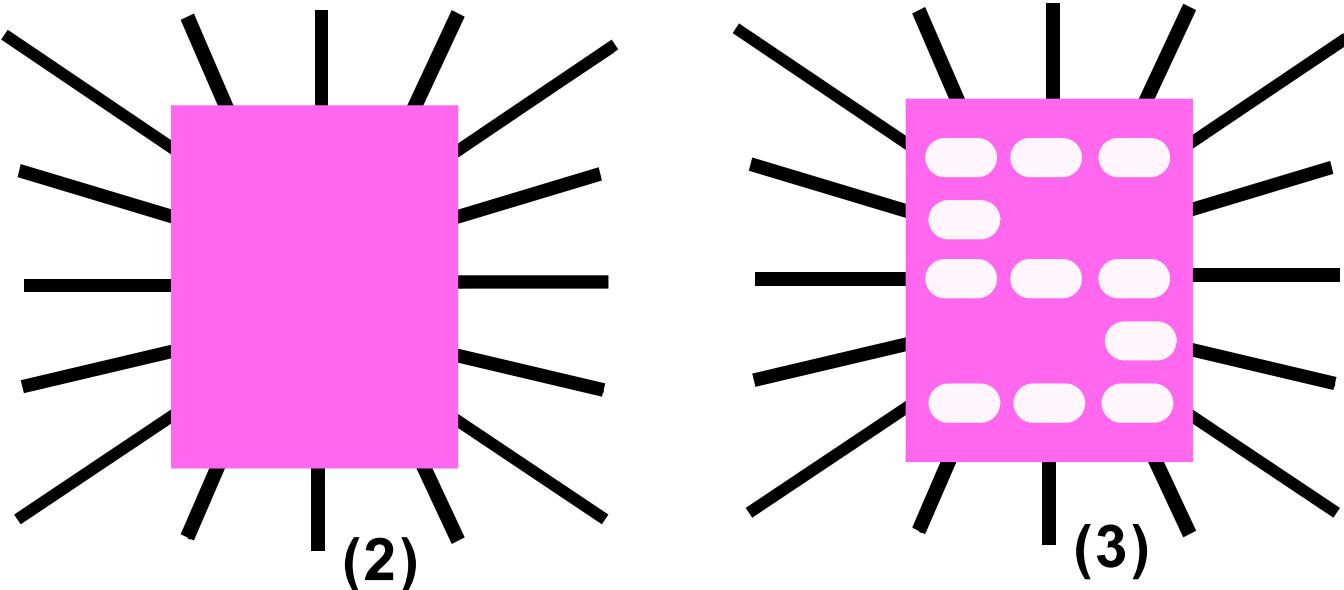


A  $\text{Fe}(\text{II})$  HS-LS compound: Colour change



# Application of Spin-Crossover complexes

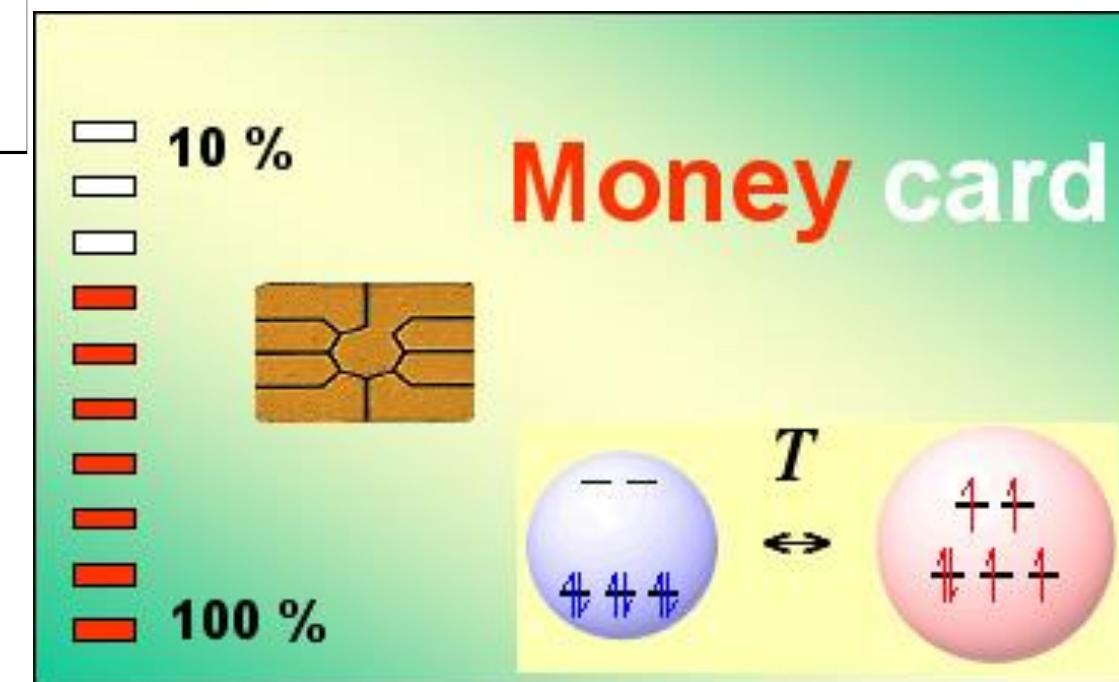
## Display device



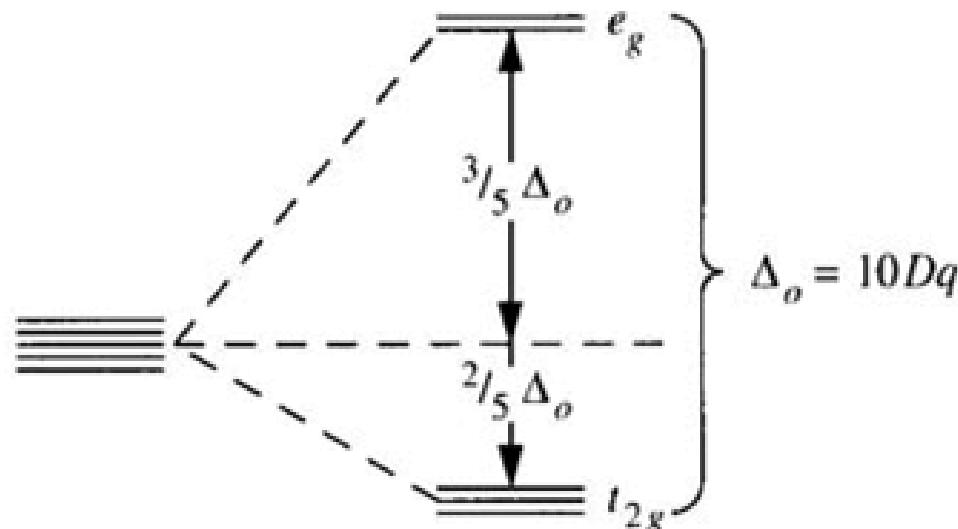
Compound in  
Low spin state  
(Thin Layer)

Display

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



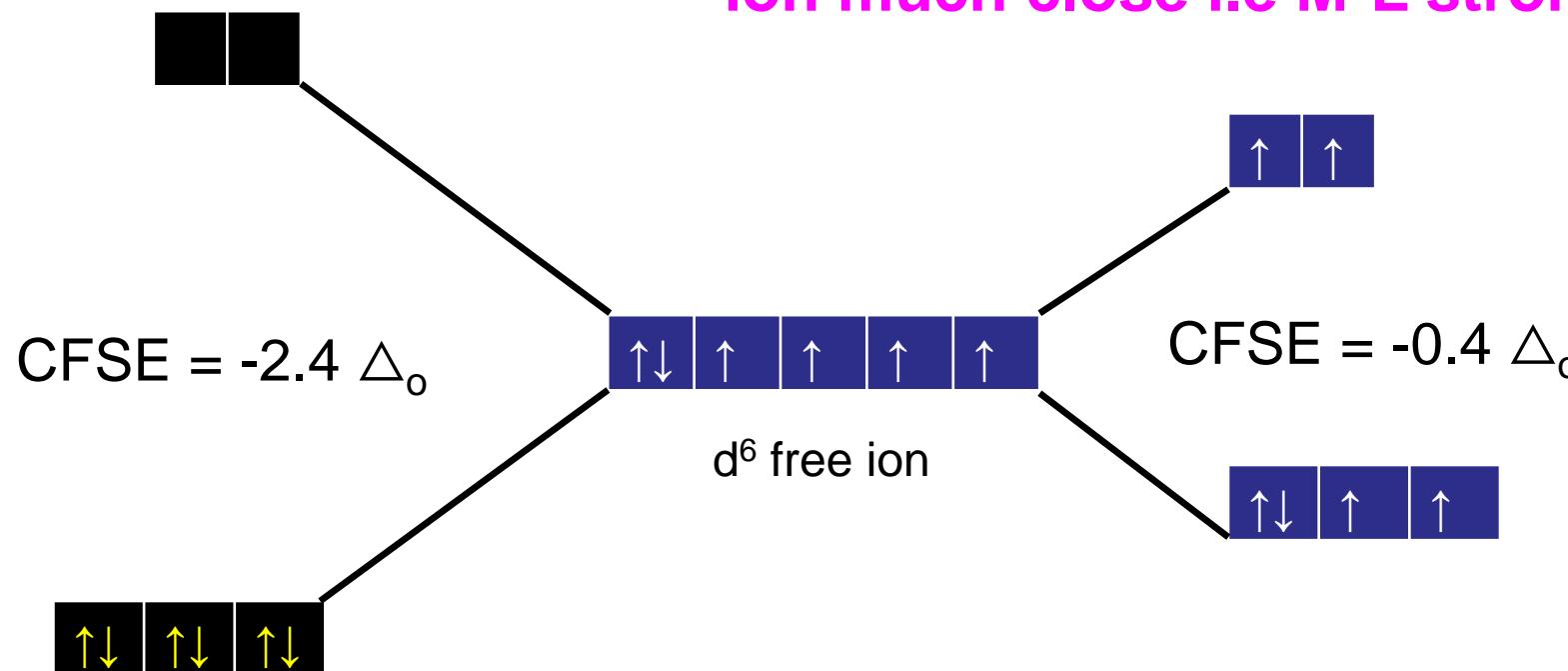
# Application of CFT / Thermodynamic stability of complexes (CFSE)



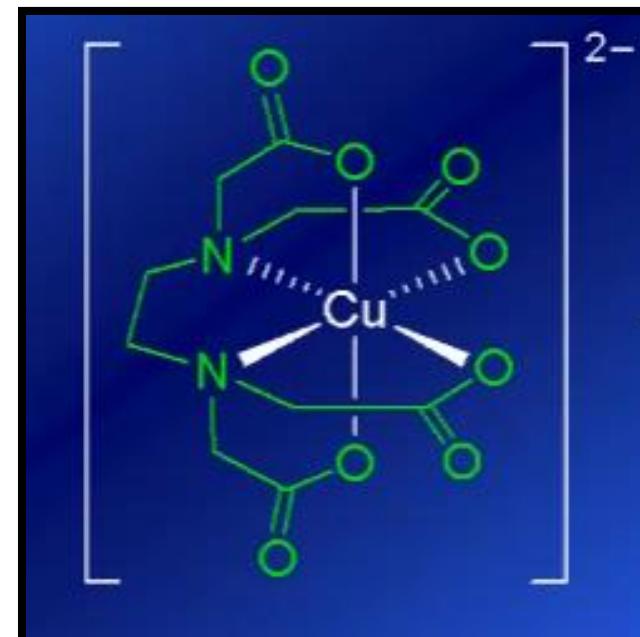
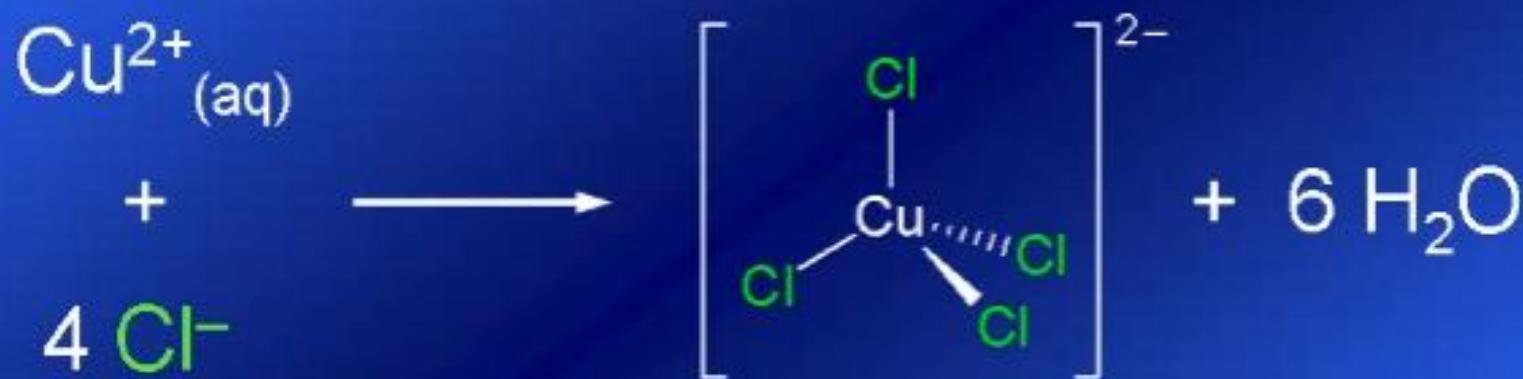
$$= -0.4 \times n(t_{2g}) + 0.6 \times n(e_g) \Delta_o$$

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

Since there are no electrons in the  $e_g$  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**

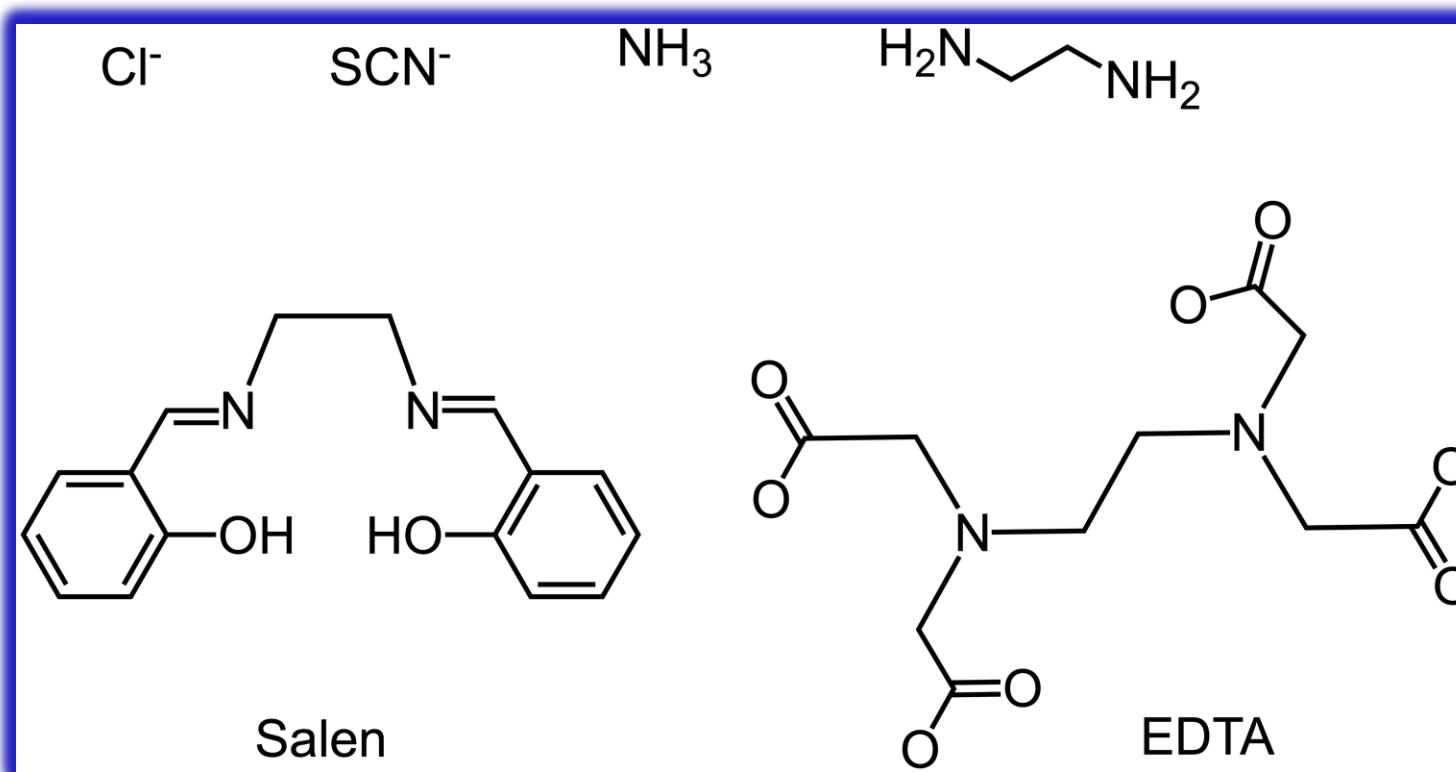


+ EDTA

# Demonstration

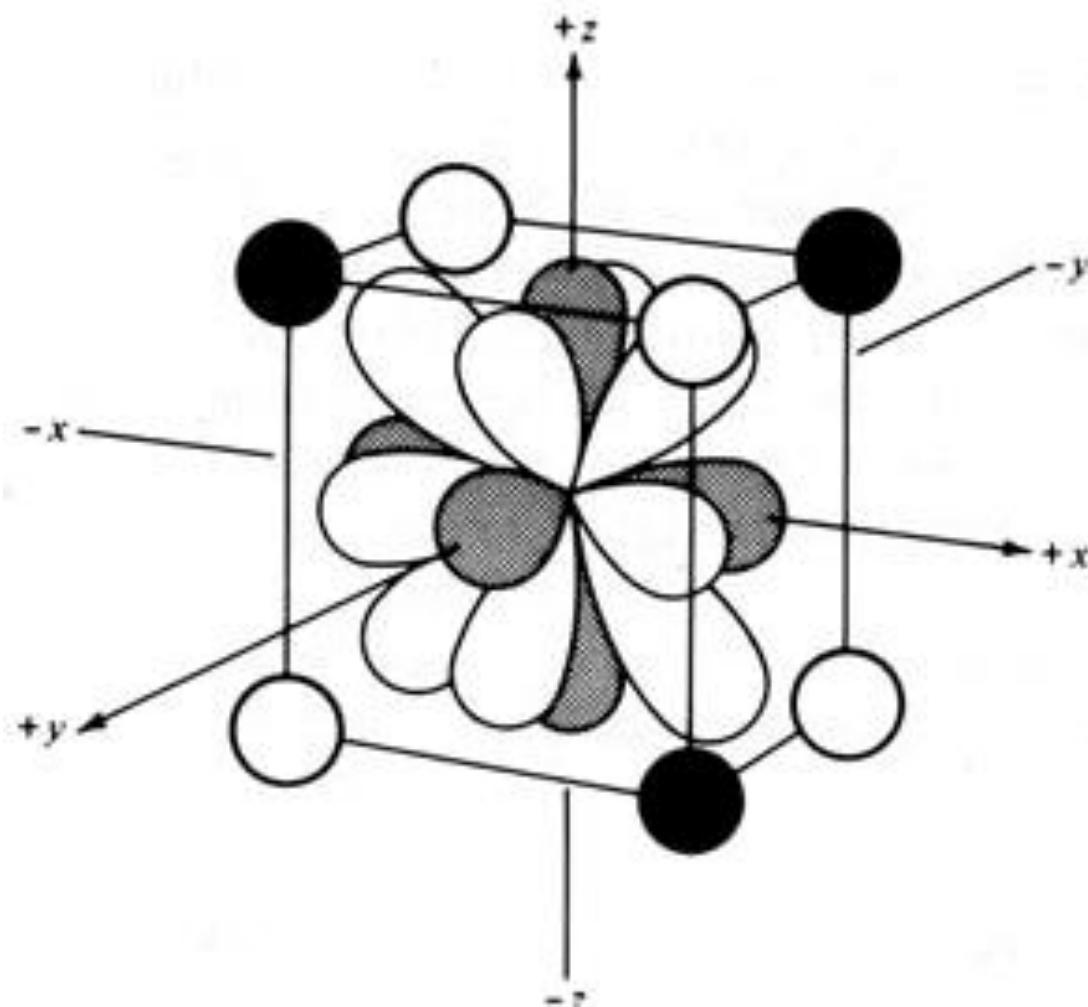
## Spectrochemical Series/Chelate effect

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

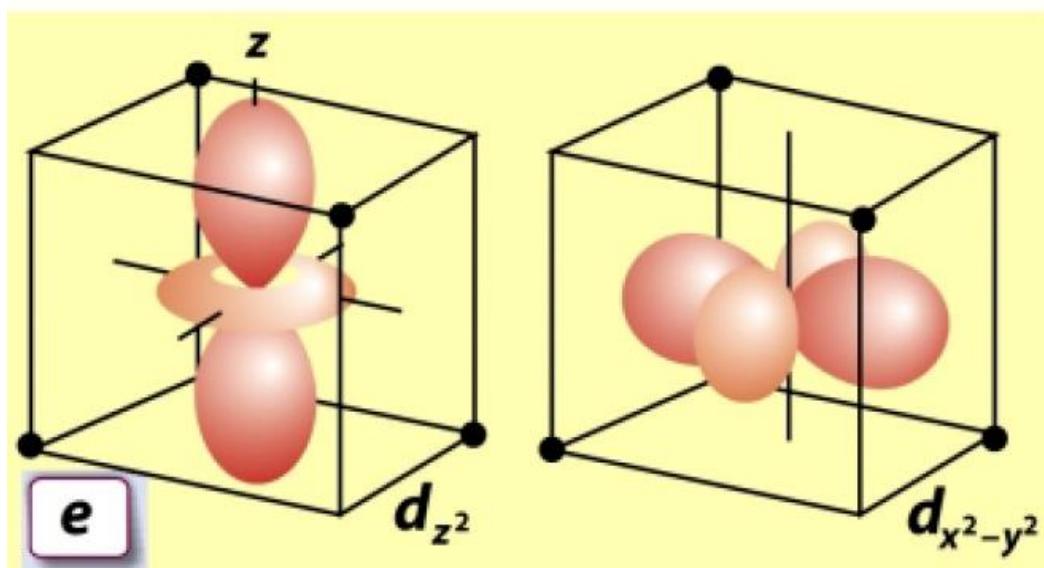
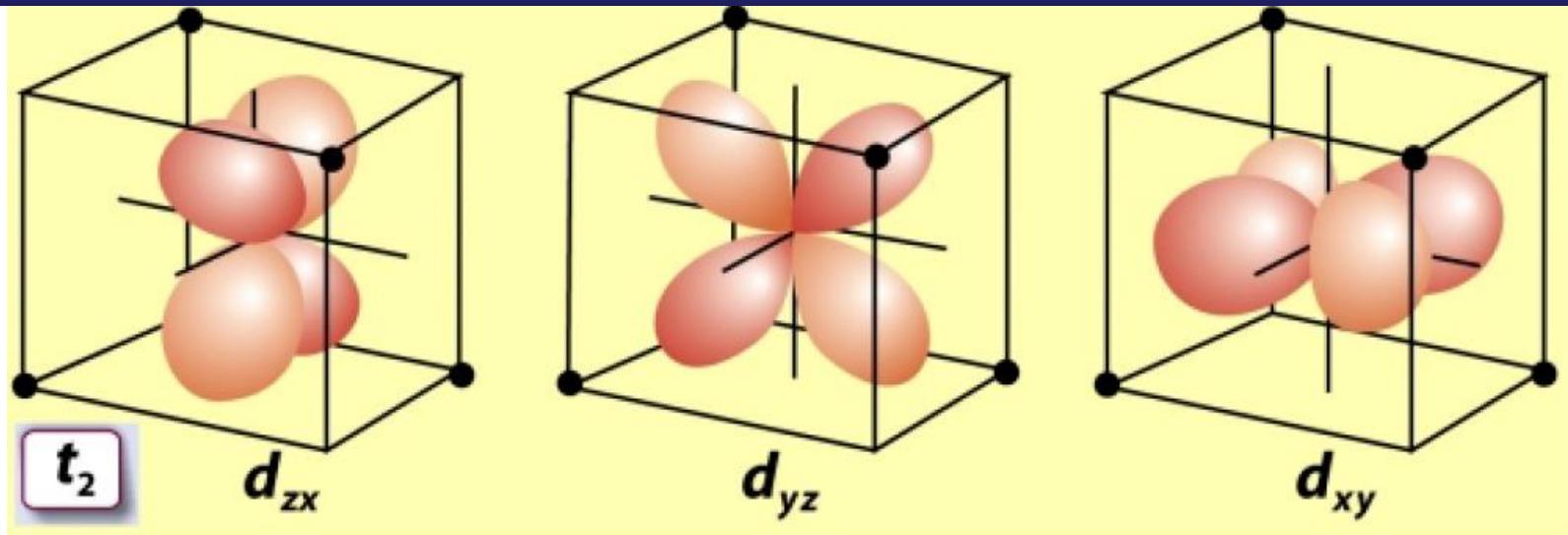


## Tetrahedral Field- Considerations

- 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  
 $109^\circ 28' / 3 = 35^\circ 16'$ .

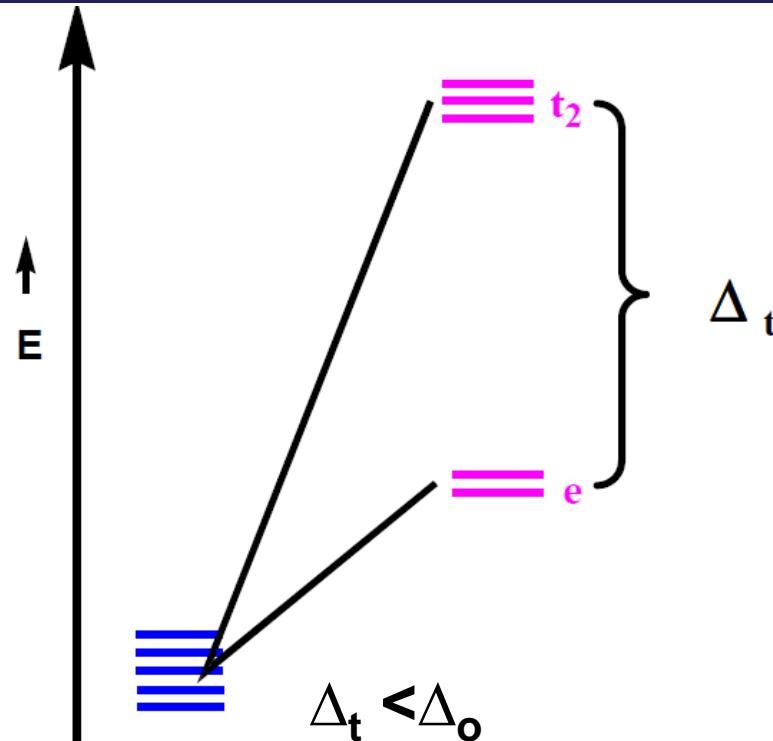
The two 'e' orbitals point to the center of the face of the cube  
 $109^\circ 28' / 2 = 54^\circ 44'$ .

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 Oh 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.

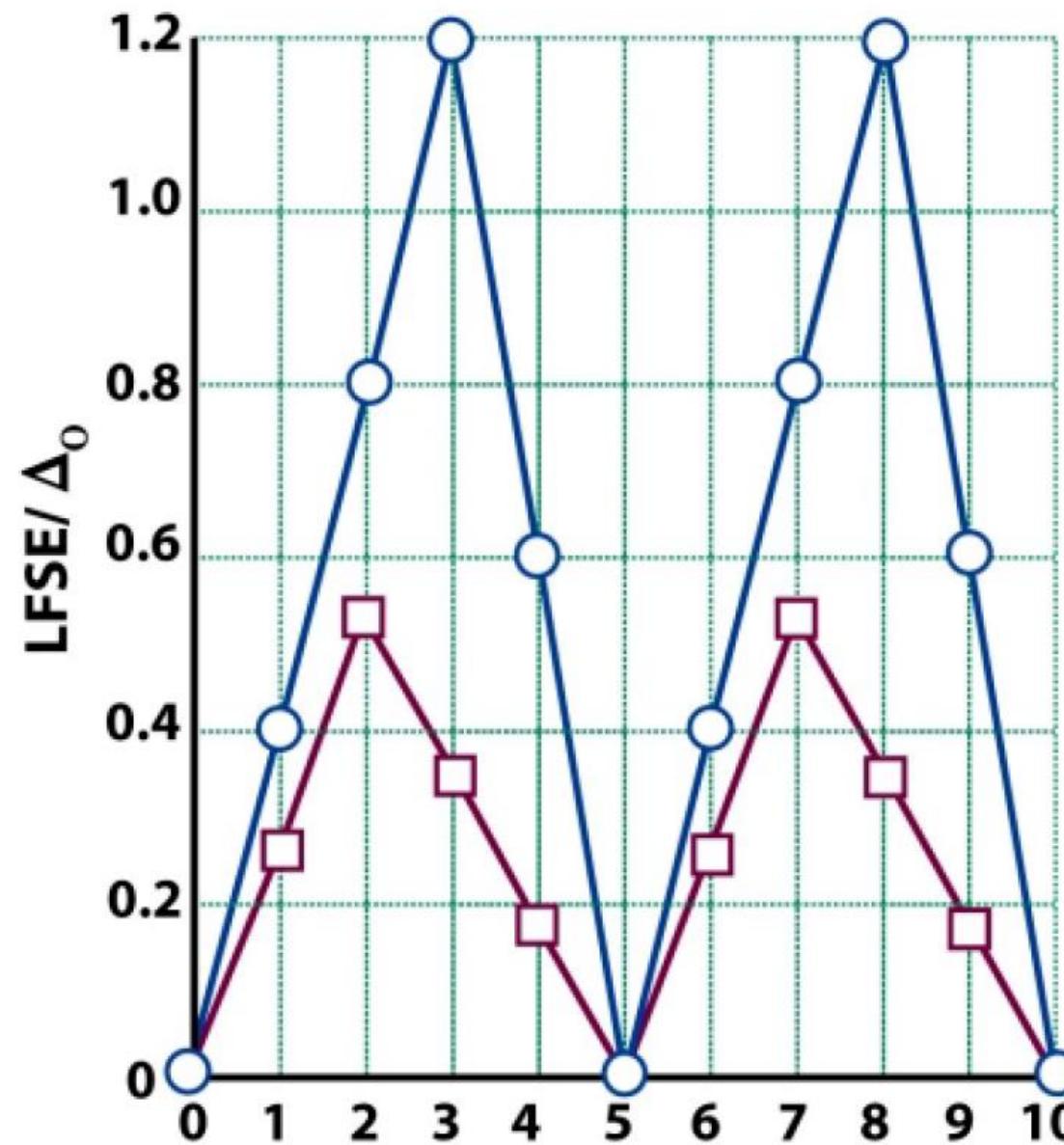
Complex	$\Delta_T/\text{cm}^{-1}$		
$\text{VCl}_4$	9010		
$[\text{CoCl}_4]^{2-}$	3300		
$[\text{CoBr}_4]^{2-}$	2900		
		$[\text{CoI}_4]^{2-}$	2700
		$[\text{Co(NCS)}_4]^{2-}$	4700

**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. Td 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

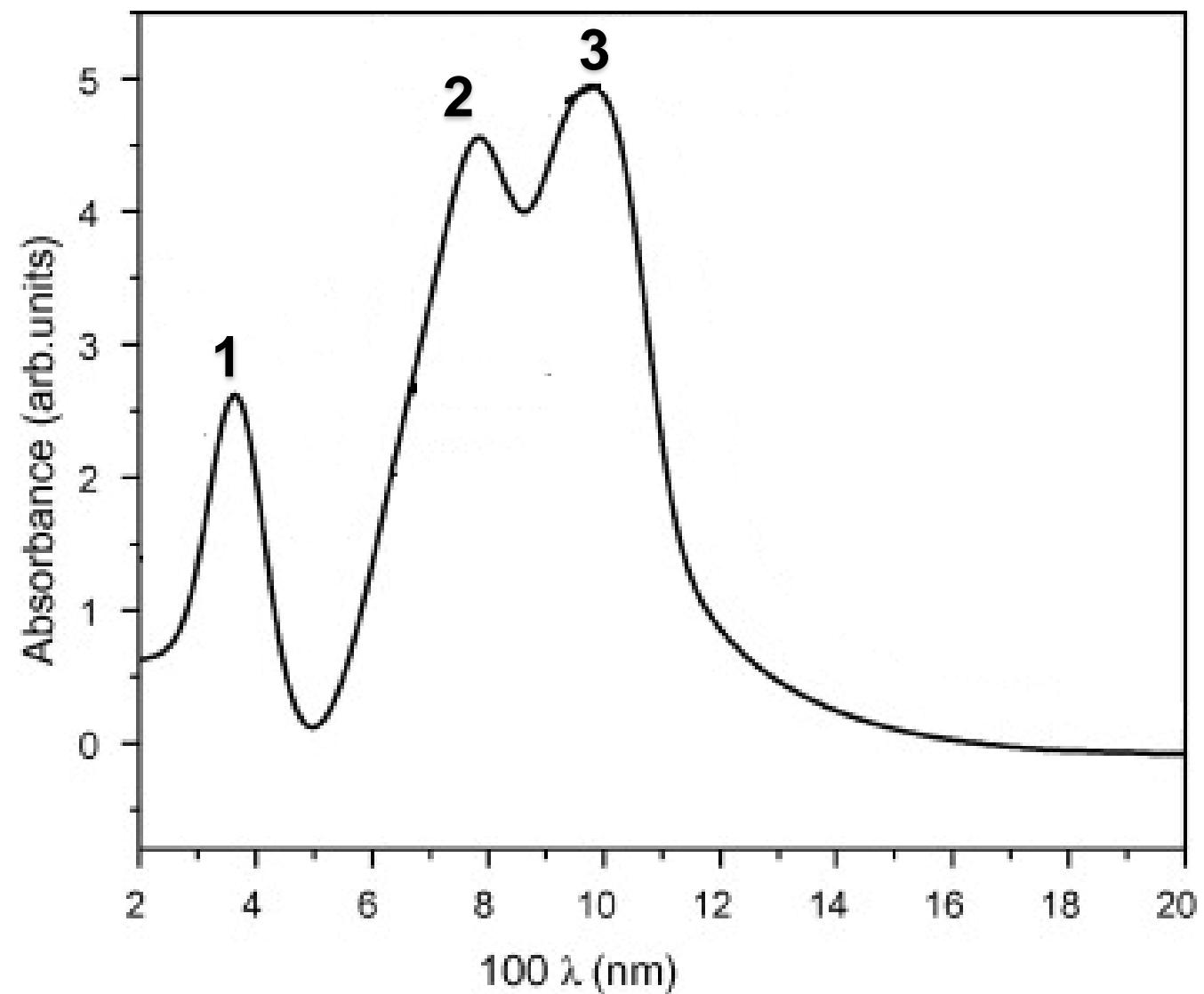
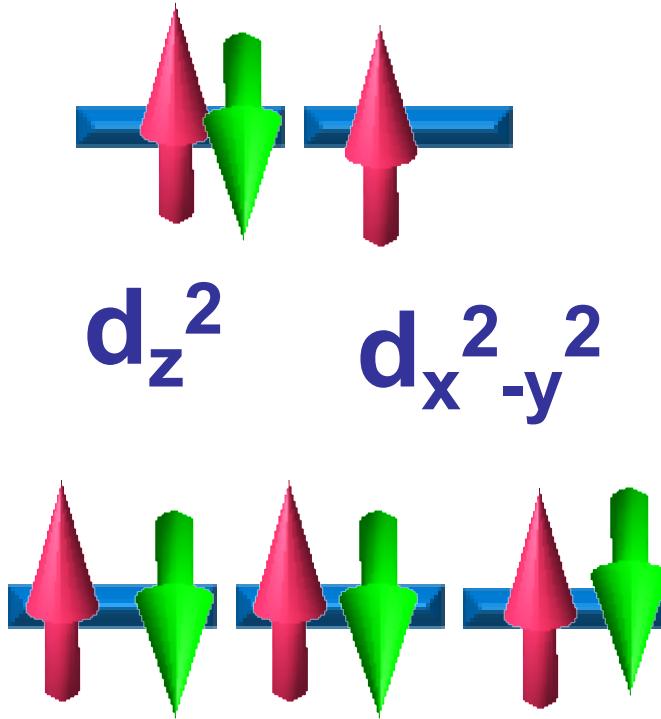
If  $M^{3+}$  ion has a higher CFSE in an octahedral field compared to  $M^{2+}$  ion, **normal spinel** will result.

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?

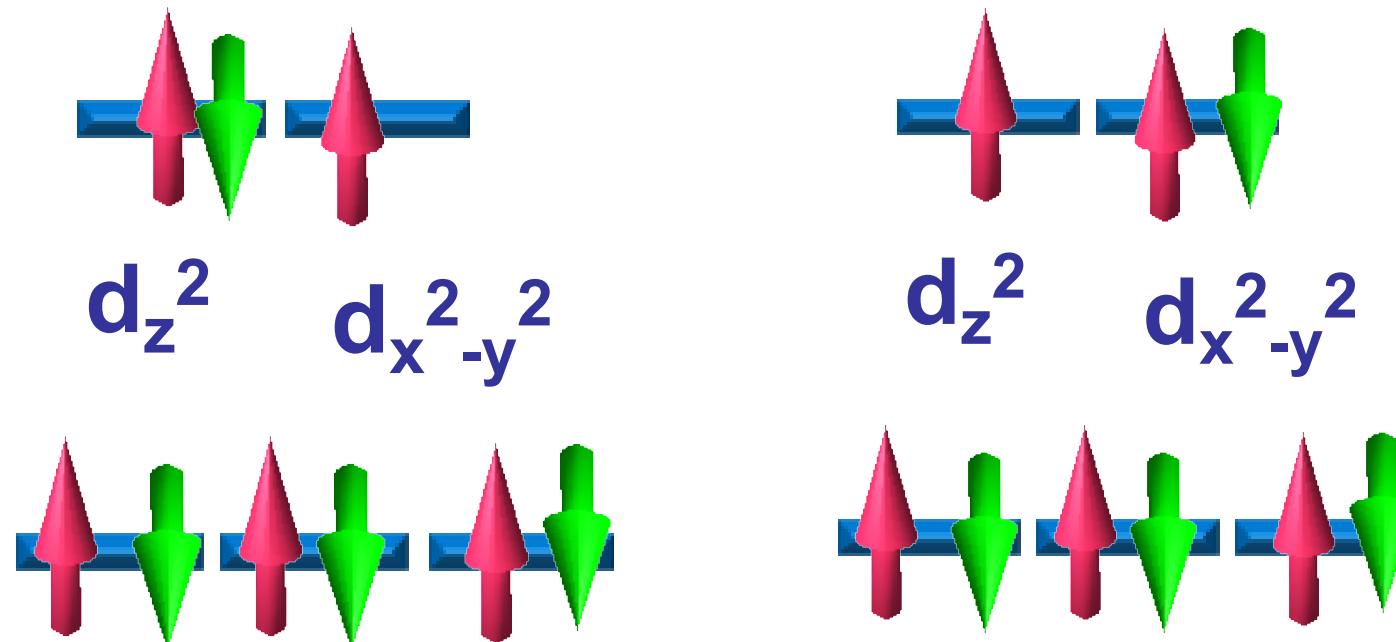


## Case of degeneracy: Jahn-Teller distortion

### Jahn-Teller Distortion:

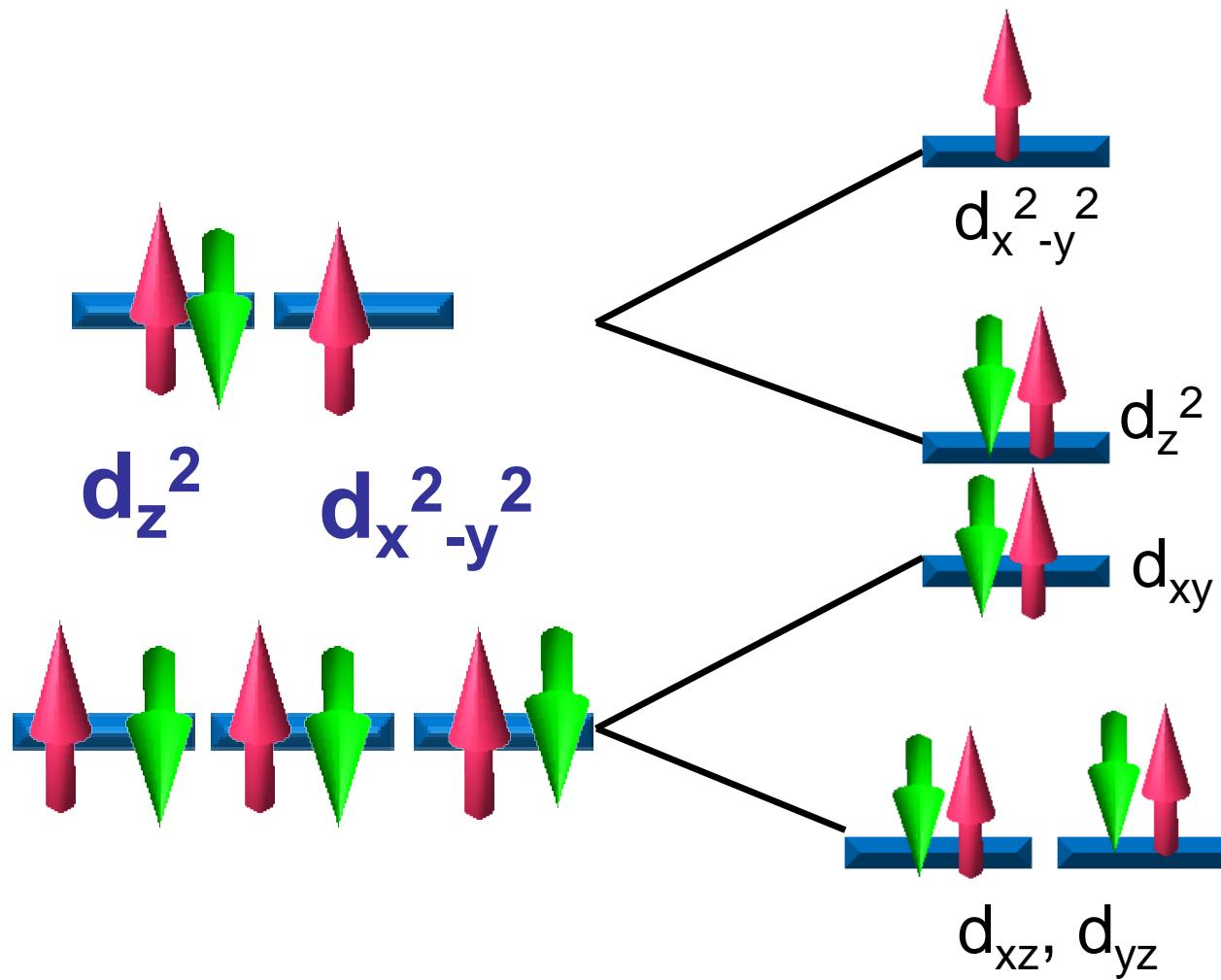
Any non-linear molecular system in a degenerate electronic state will be unstable and will undergo distortion to form a system of lower symmetry and lower energy thereby removing the degeneracy.

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



**Degenerate electronic state:** Complex undergoes distortion

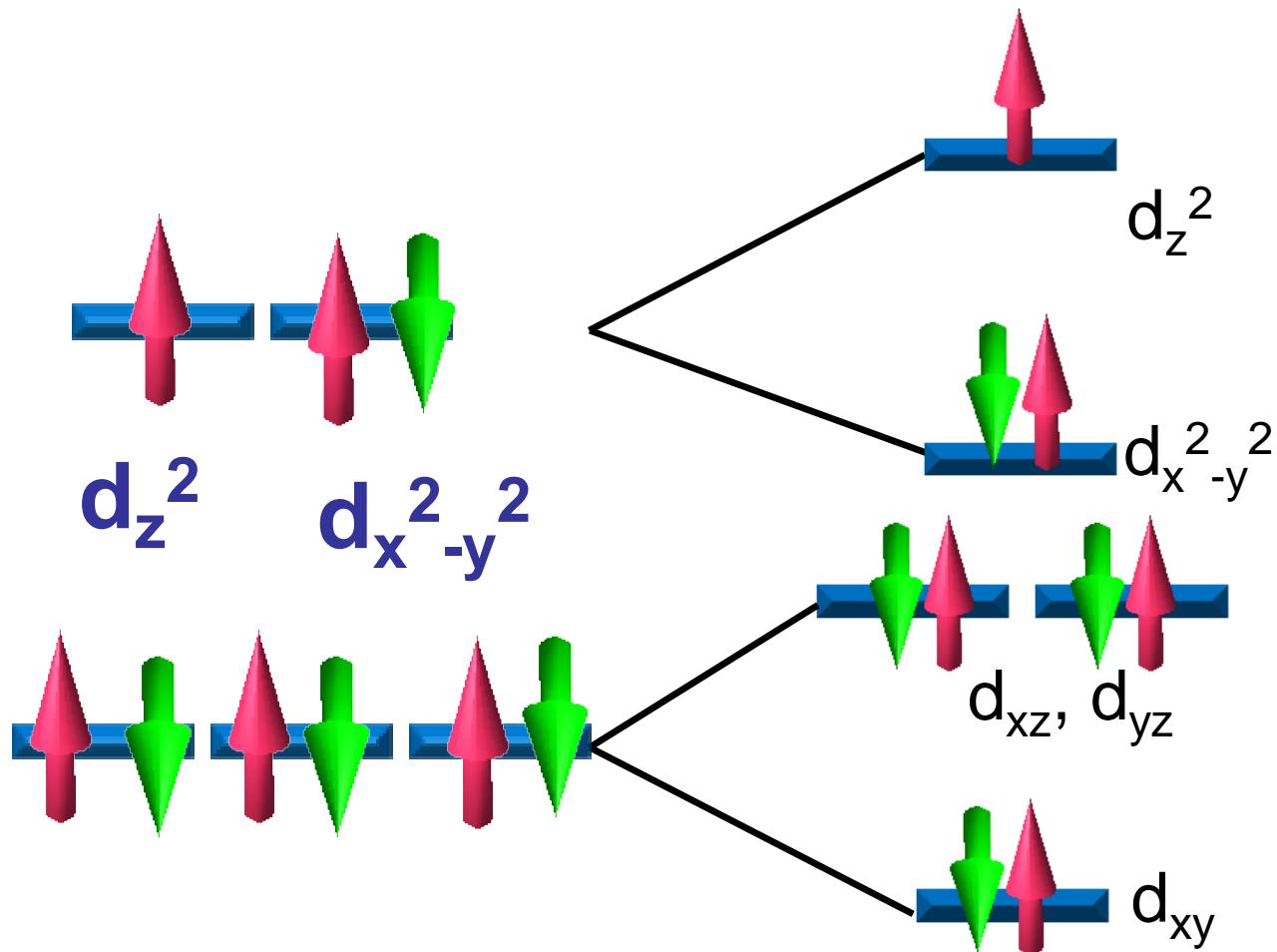
# Axial elongation: Jahn-Teller distortion



**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  $d_x^2 - y^2$  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

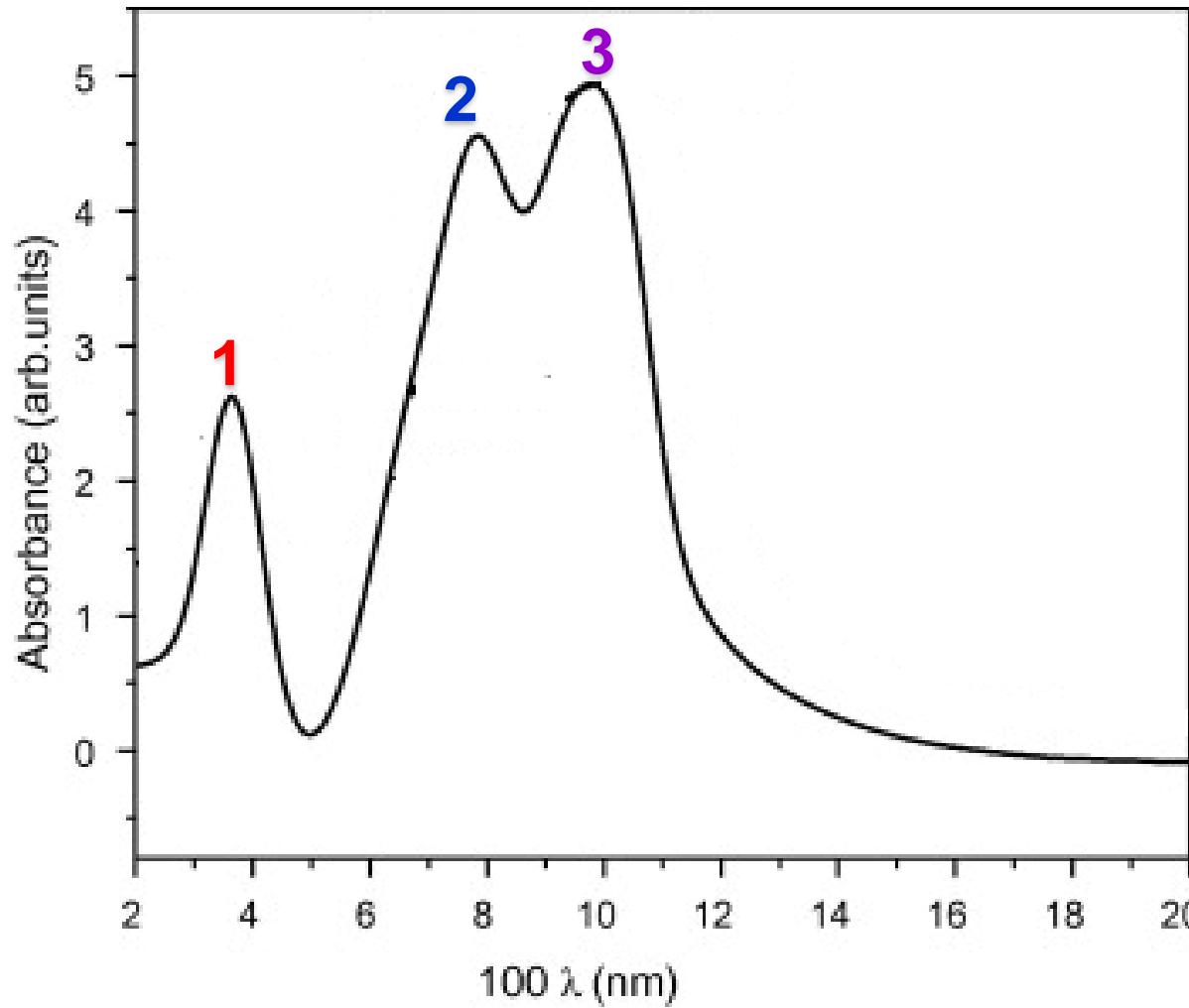
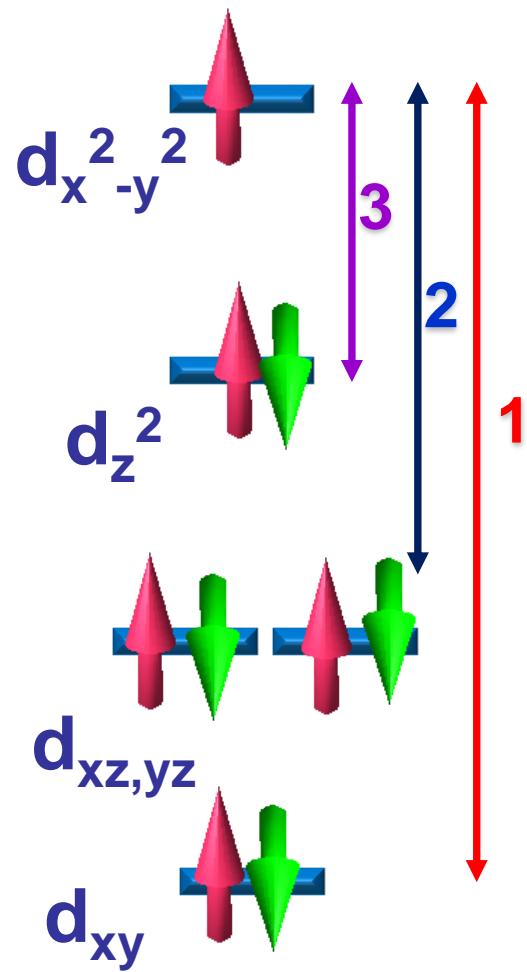


**As ligands approached along the axis in  $\text{O}_\text{h}$**

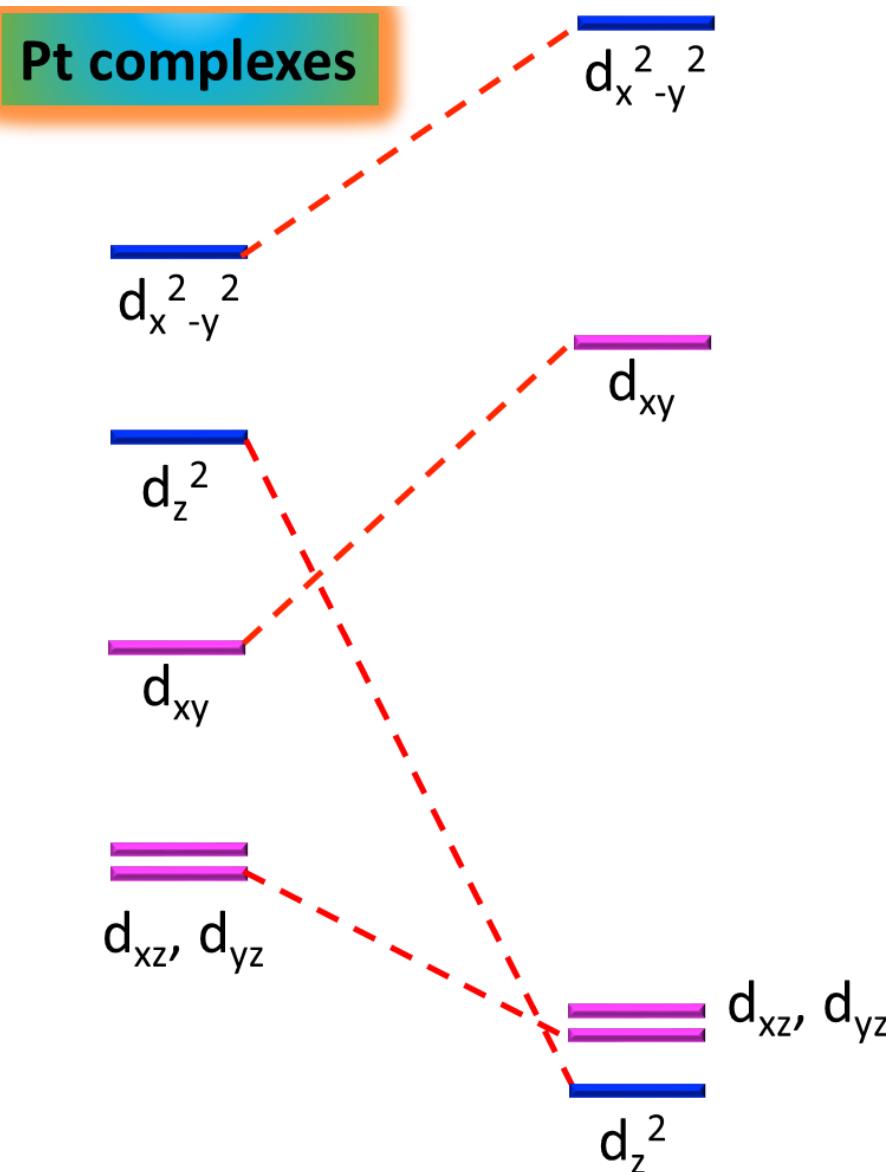
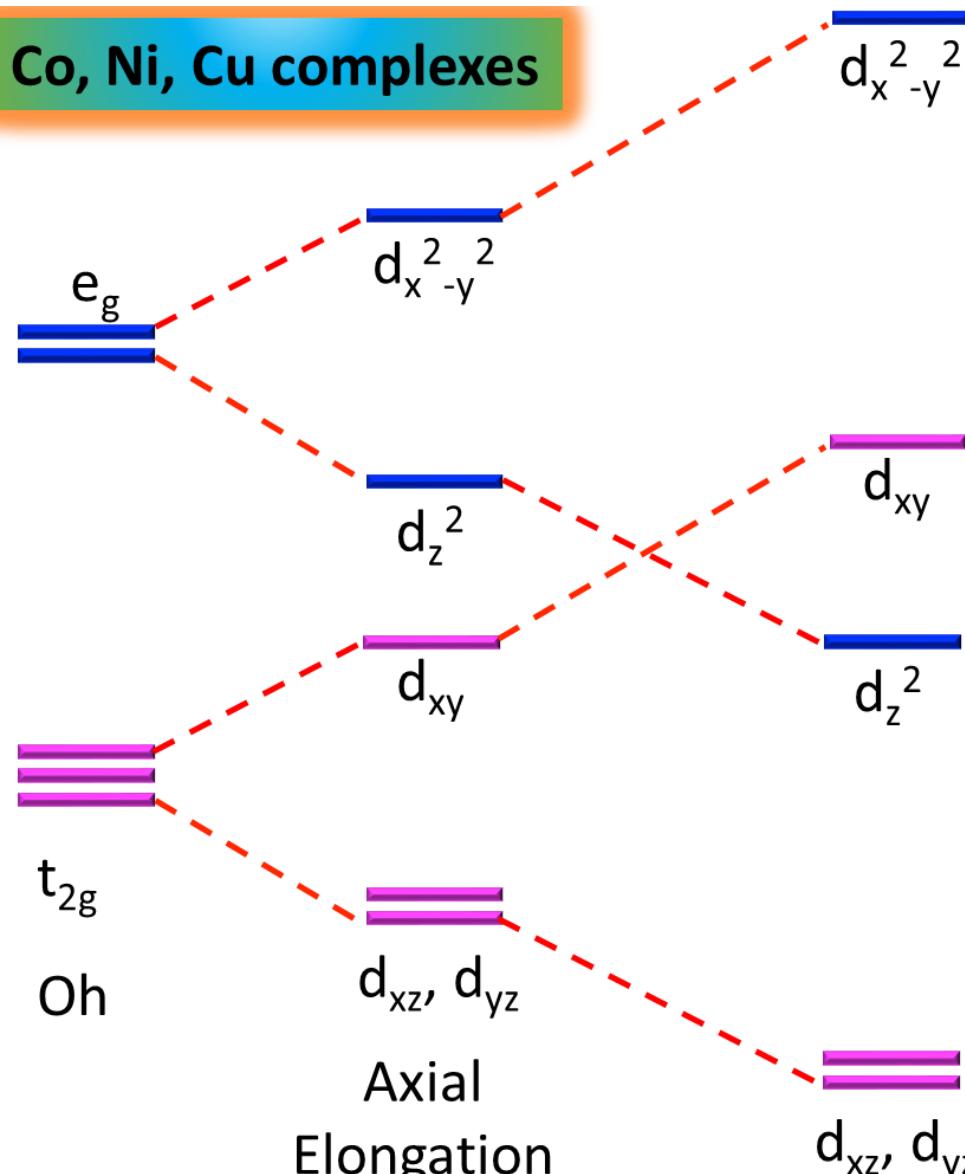
- ❖ The ligands can not approach  $\text{Cu}(\text{II})$  ion closely along  $xy$ -plane because  $d_{x^2-y^2}$  orbital contains two electron (i.e. due to the ligand  $e^-$  and metal  $e^-$  repulsion)
- ❖ While along  $d_{z^2}$  axis ligands can approach toward  $\text{Cu}(\text{II})$  ion much more 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  $\text{Cu}(\text{II})\text{-L}$  bond lengths along z-axis is shorter than  $\text{Cu}(\text{II})\text{-L}$  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

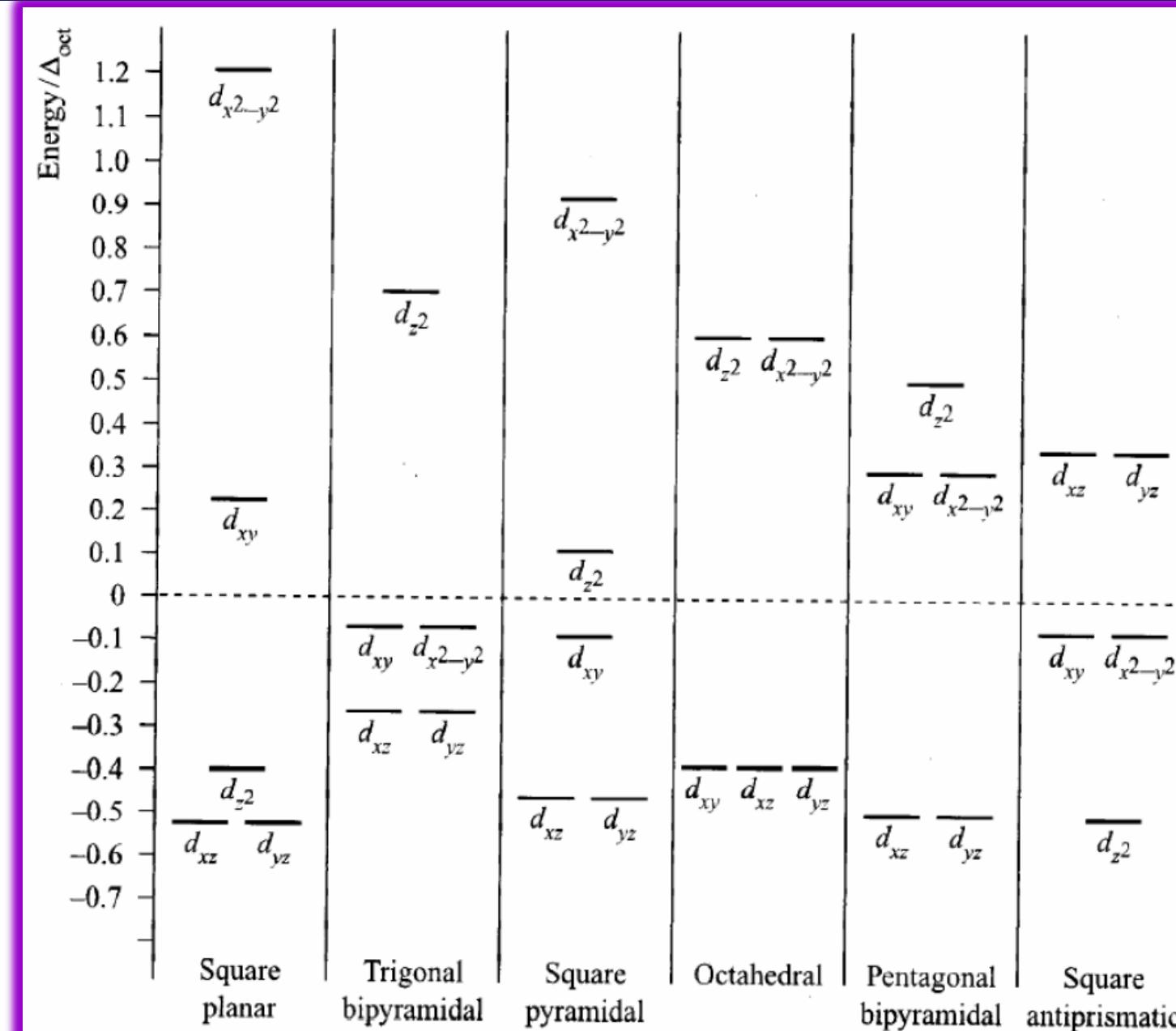
## Rationale for 3 transitions!



# Crystal field splitting for square planar complexes



# Crystal field splitting for other geometries

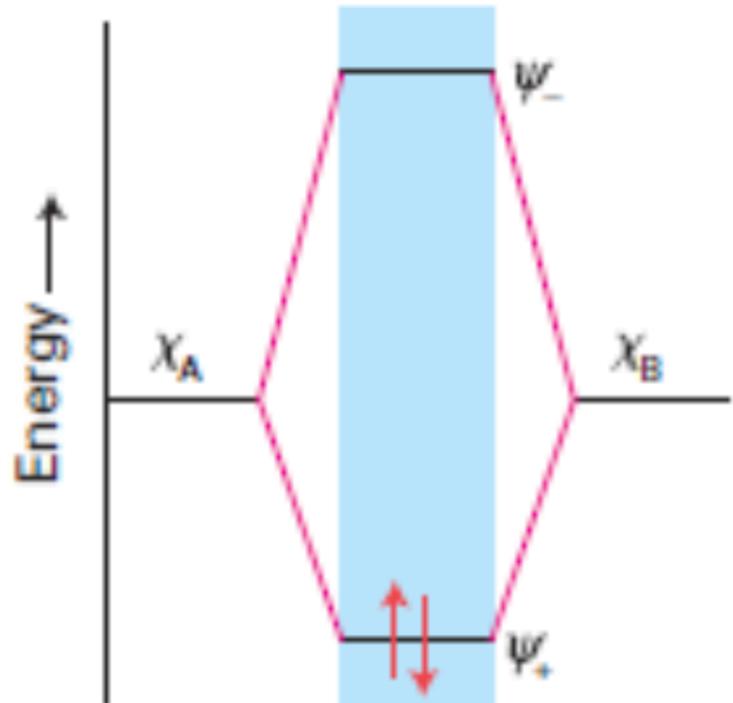


## Limitation of CFT

- ✓ The ligand spectrochemical series was not explained by CFT
- ✓ CFT could not account for the M-L covalancy

## Ligand Field Theory (Molecular Orbital Theory)

The building up principle is used in conjunction with a **molecular orbital energy level** constructed from **metal orbital** and **Linear Combinations** of ligand orbitals



Schematic representation of molecular orbital construction using the linear combination of atomic orbitals ( $\chi_A$  and  $\chi_B$ )

# Linear combination of atomic orbitals (LCAO)

LCAO:

This modelling of a molecular orbital in terms of contributing atomic orbitals is called the linear combination of atomic orbitals (LCAO) approximation i.e. **only the valence shell atomic orbitals are used to form molecular orbitals.**

Simple example: Molecular orbitals of  $\text{H}_2$  molecule

$$\Psi = c_A \chi_A + c_B \chi_B$$

Where

$\chi_A$  = Hydrogen atomic orbital ( $1s$ ) of atom A

$\chi_B$  = Hydrogen atomic orbital ( $1s$ ) of atom B

$c$  = Coefficient in the linear combination extent to which each atomic orbital contributes to molecular orbital

- ❖ Greater the  $c$  value, greater the contribution of atomic orbital to the molecular orbital

# Bonding and Anti-bonding molecular orbital

$$\Psi = c_A \chi_A + c_B \chi_B$$

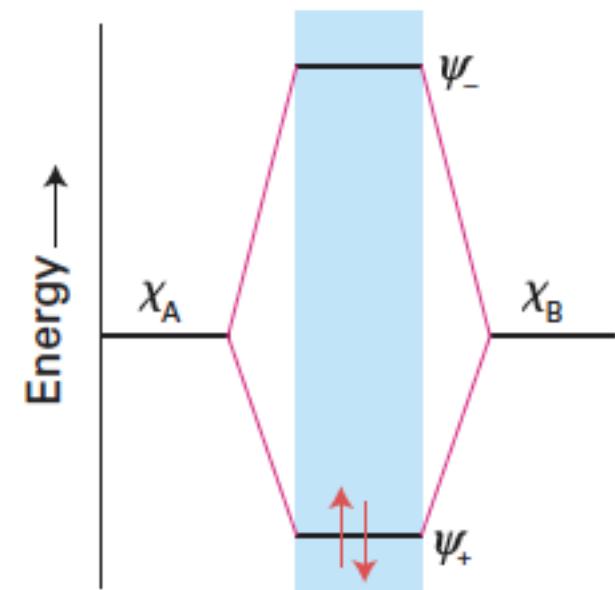
$\chi_A$  and  $\chi_B$  in the above equation represent 1s orbital of hydrogen, both atomic orbitals contribute equally to the molecular orbital

Under this situation

$$\Psi_{\pm} = \chi_A \pm \chi_B$$

$\Psi_+ = \chi_A + \chi_B \Rightarrow$  **Constructive interference** of two atomic orbitals (**Energy of the molecule lowered compared to the atomic orbital**) (**Bonding MO**)

$\Psi_- = \chi_A - \chi_B =$  **Destructive interference** of two atomic orbitals (**Energy of the molecule increased compared to the atomic orbital**) (**Antibonding MO**)



**Fig. 2.10** The molecular orbital energy level diagram for  $H_2$  and analogous molecules.

# Non-Bonding orbital

## Nonbonding molecular orbital

It is a molecular orbital that has the same energy as the initial atomic orbitals. In this case, occupation of this orbital neither stabilizes nor destabilizes the molecule and so it is described as a **nonbonding orbital**.

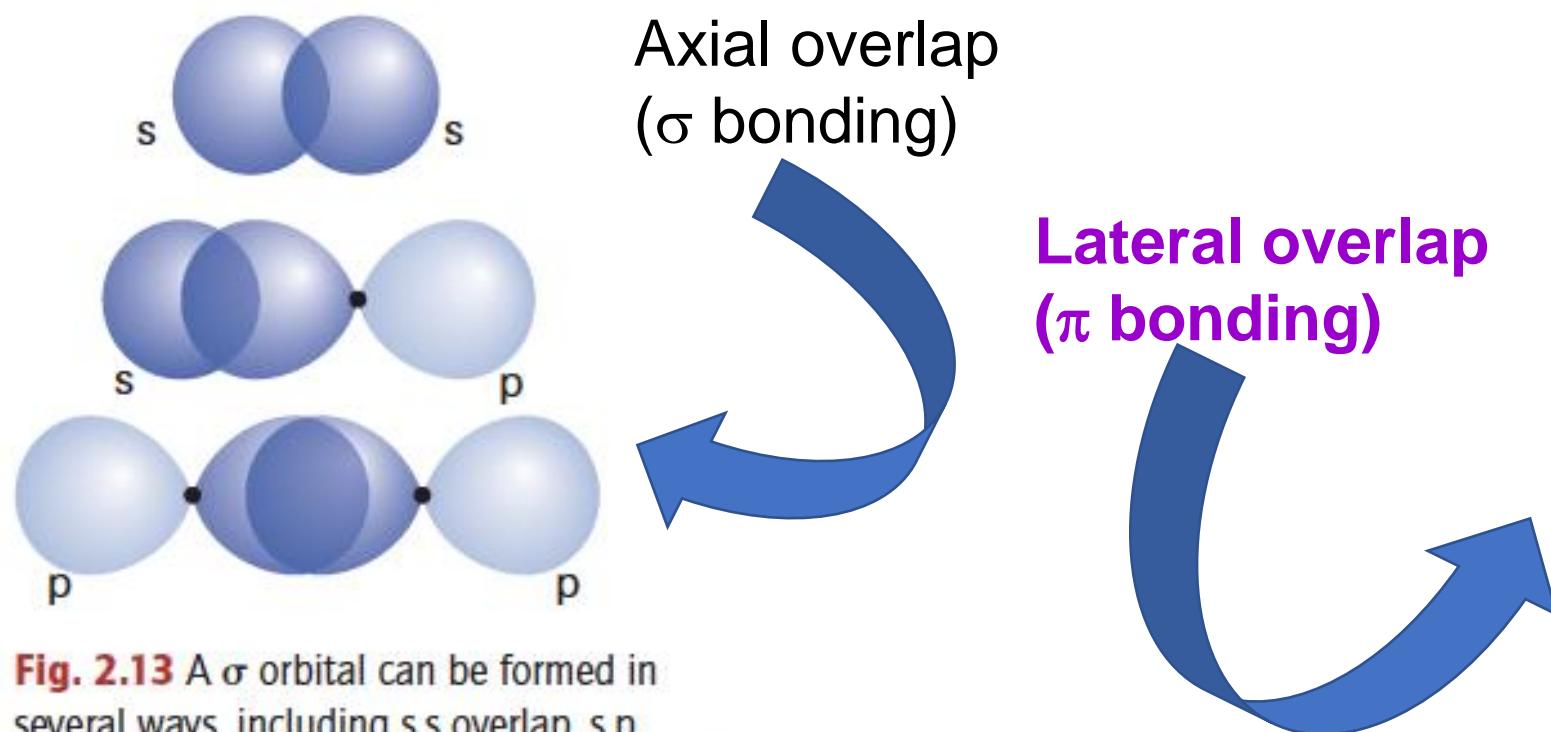
## $\sigma$ and $\pi$ Orbital

Molecular orbitals are classified as  $\sigma$  or  $\pi$  according to their rotational symmetry about the internuclear axis, and (in centrosymmetric species) as g or u according to their symmetry with respect to inversion.

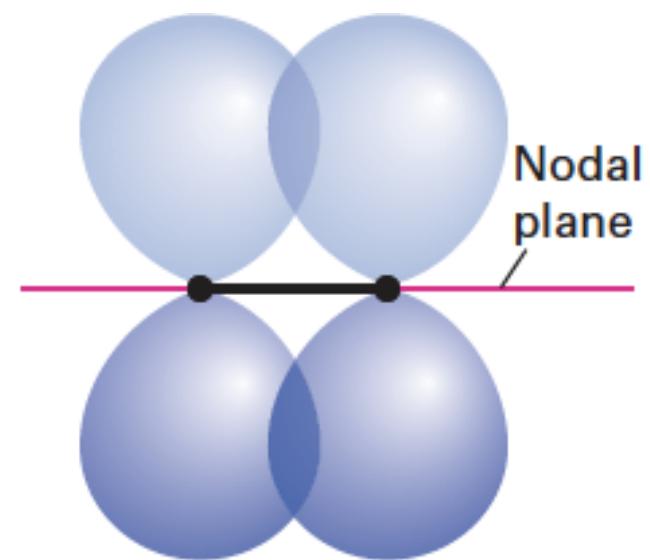
# $\sigma$ and $\pi$ Orbital

## $\sigma$ Orbital

$\sigma$  orbitals formed by allowing overlap between atomic orbitals that have cylindrical symmetry around the internuclear axis, which is conventionally labelled z.



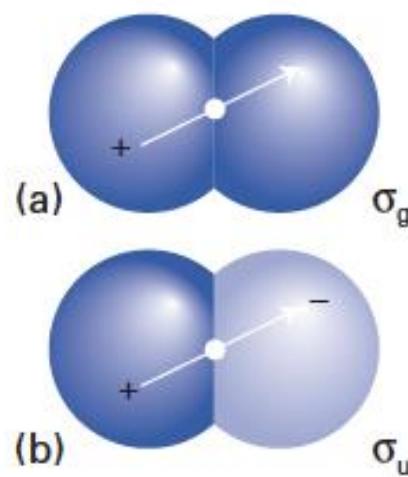
**Fig. 2.13** A  $\sigma$  orbital can be formed in several ways, including s,s overlap, s,p overlap, and p,p overlap, with the p orbitals directed along the internuclear axis.



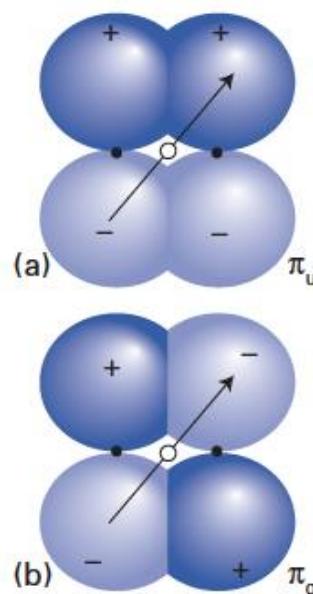
**Fig. 2.14** Two p orbitals can overlap to form a  $\pi$  orbital. The orbital has a nodal plane passing through the internuclear axis, shown here from the side.

## **g and u formalism (with respect to inversion symmetry)**

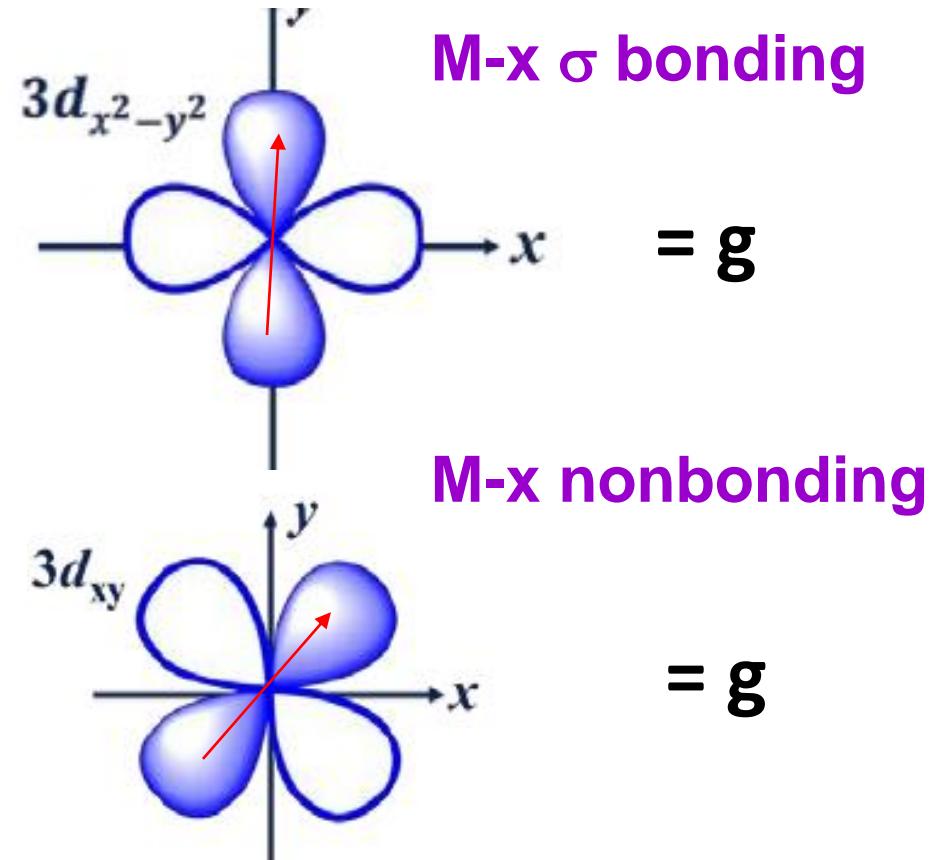
The operation of inversion consists of starting at an arbitrary point in the molecule, travelling in a straight line to the centre of the molecule, and then continuing an equal distance out on the other side of the centre. This procedure is indicated by the arrows in Figs 2.15 and 2.16. The orbital is designated g (for gerade, even) if it is identical under inversion, and u (for ungerade, odd) if it changes sign.



**Fig 2.15** (a) Bonding and (b) antibonding  $\sigma$  interactions with the arrow indicating the inversions.



**Fig 2.16** (a) Bonding and (b) antibonding  $\pi$  interactions with the arrow indicating the inversions.



# Molecular Orbital of heterodiatomic molecule

The molecular orbitals of heteronuclear diatomic molecules differ from those of homonuclear diatomic molecules in having unequal contributions from each atomic orbital.

$$\psi = c_A \chi_A + c_B \chi_B \quad \text{But } c_A^2 > c_B^2 \text{ OR } c_A^2 < c_B^2$$

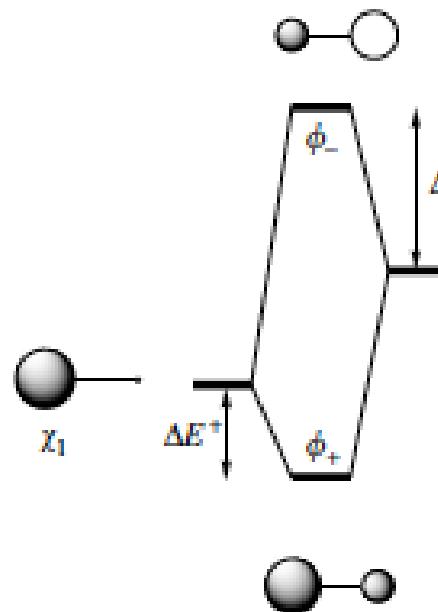


Figure 1.2. Interaction diagram for two orbitals with different energies.

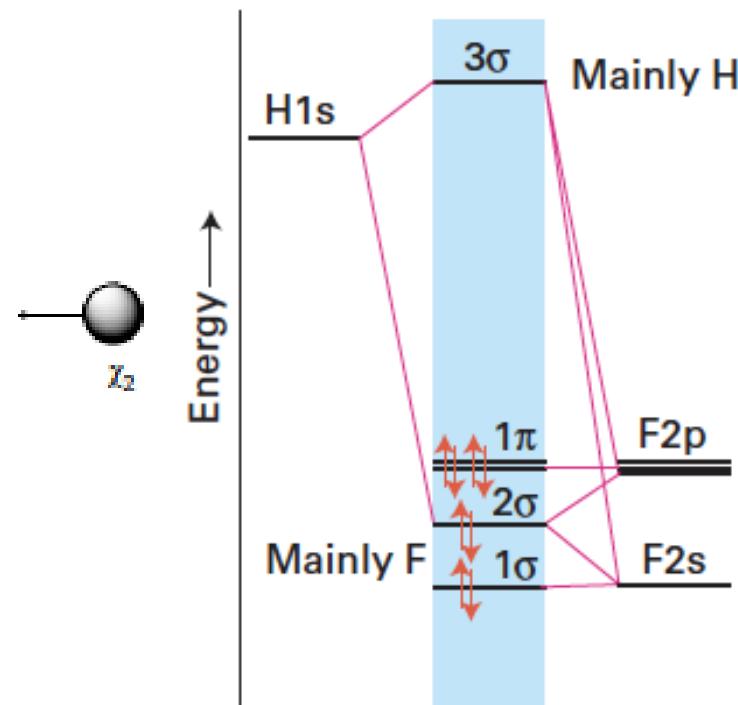


Fig. 2.21 The molecular orbital energy level diagram for HF. The relative positions of the atomic orbitals reflect the ionization energies of the atoms.

The  $1\sigma$  bonding orbital is predominantly F2s in character as the energy difference between it and the H1s orbital is large. It is, therefore, confined mainly to the F atom and essentially nonbonding.

The  $2\sigma$  orbital is more bonding than the  $1\sigma$  orbital and has both H1s and F2p character.

The  $3\sigma$  orbital is antibonding, and principally H1s in character: the 1s orbital has a relatively high energy (compared with the fluorine orbitals) and hence contributes predominantly to the high energy antibonding molecular orbital.

## **Take home message from the MO's of simple diatomic molecules**

- ❖ MO's are constructed as linear combination of atomic orbitals (Valence orbitals)
- ❖ Each MO can accommodate maximum of two electrons (Pauli's exclusion principle and Hund's rule followed)
- ❖ From n-number atomic orbitals, n-number of molecular orbital can be constructed
- ❖ Electron filling up of MO's follows the same rules that are followed to fill the atomic orbitals (Hund's rule or building-up principle)

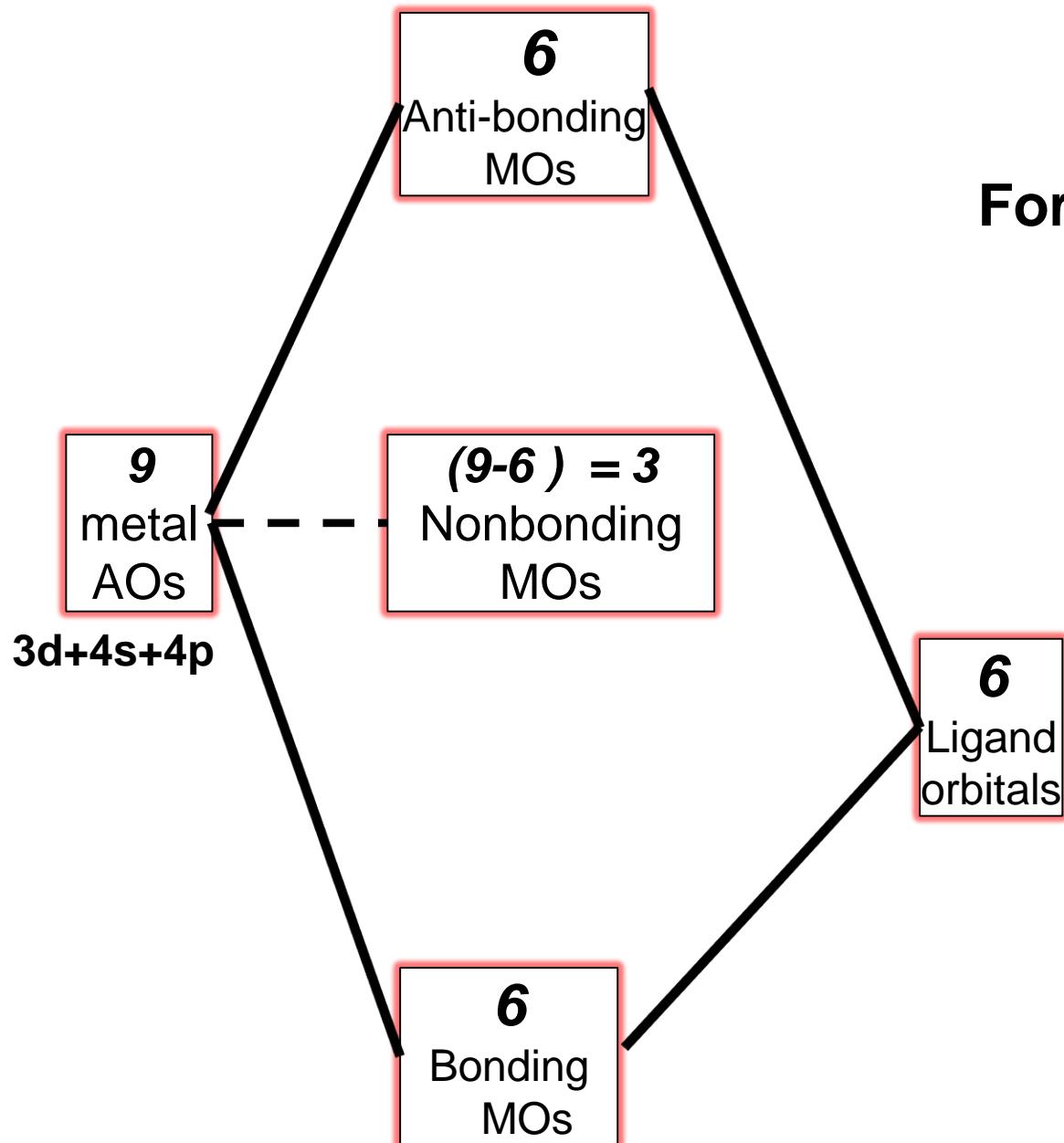
**WE WILL EXTEND THESE PRINCIPLES TO EXPLAIN THE ELECTRONIC STRUCTURE AND BONDING OF THE  $\text{ML}_6$  OCTAHEDRAL COMPLEXES**

# General consideration for constructing MO of $ML_6$ $\sigma$ -bonding

To construct MO:

- ❖ Valence atomic orbitals of 3d metal ions are considered (3d, 4s and 4p orbitals)
- ❖ Specific combination of atomic orbitals of ligands are used to build MO's of a given symmetry (called Symmetry Adopted Linear Combination (SALC)). In simpler terms, ligand orbitals are placed in certain symmetry so as to have maximum overlap with metal atomic orbitals.
- ❖ Energetic of MO's based on the overlap (metal and ligand atomic orbitals)
- ❖ Filling up of electrons into the MO's

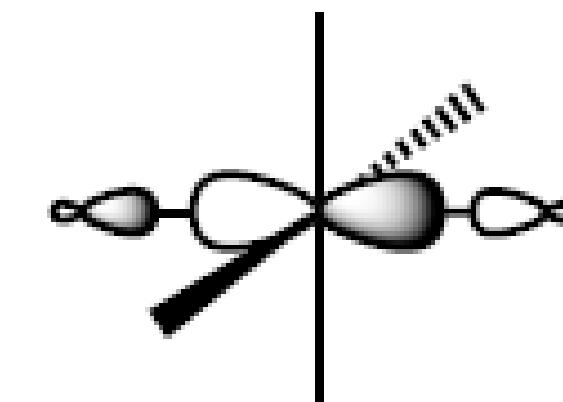
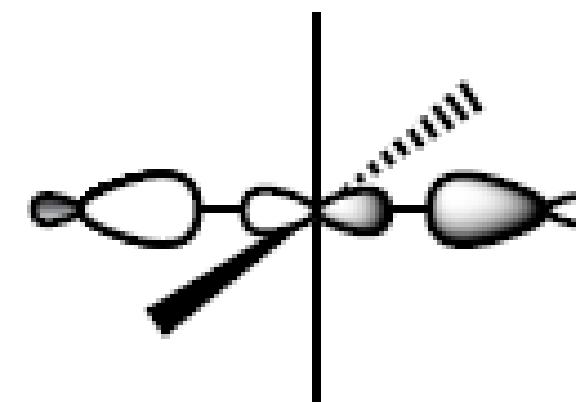
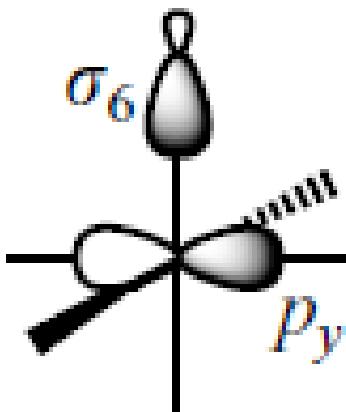
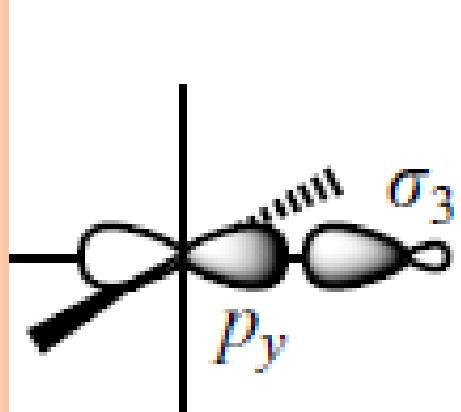
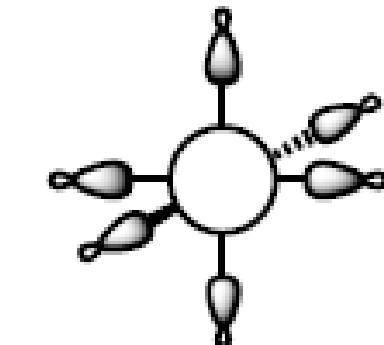
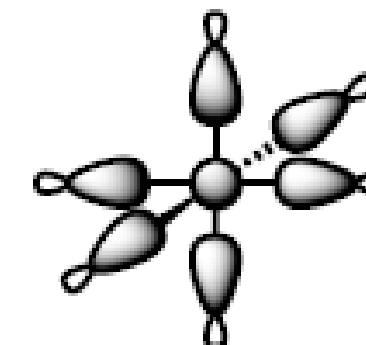
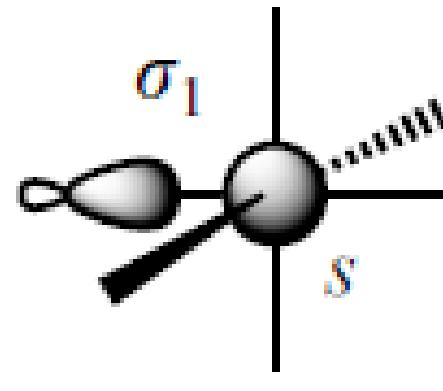
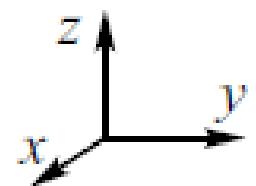
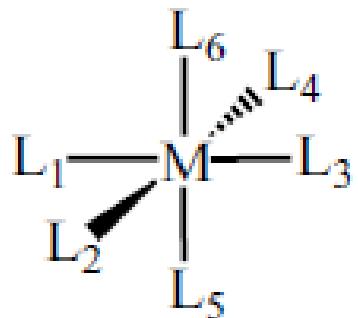
# General interaction diagram (M-L<sub>6</sub> σ bonding)



For stability, total number of electron desired is,

$$N_t = (2 \times 6) + 2 \times (9 - 6)$$
$$12 + 6 = 18 \text{ electrons}$$

# Metal-Ligand Combinations decided by overlap ( $S$ )



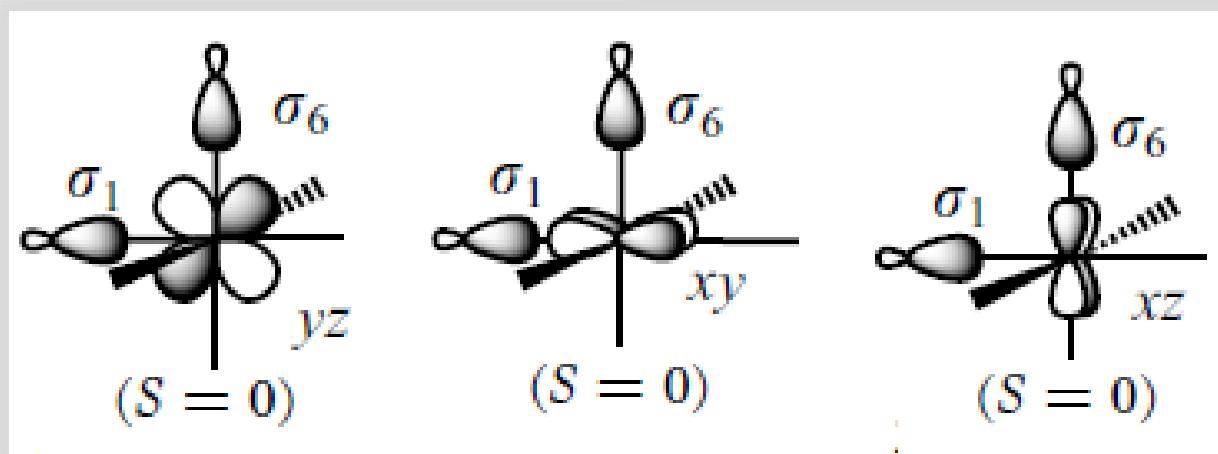
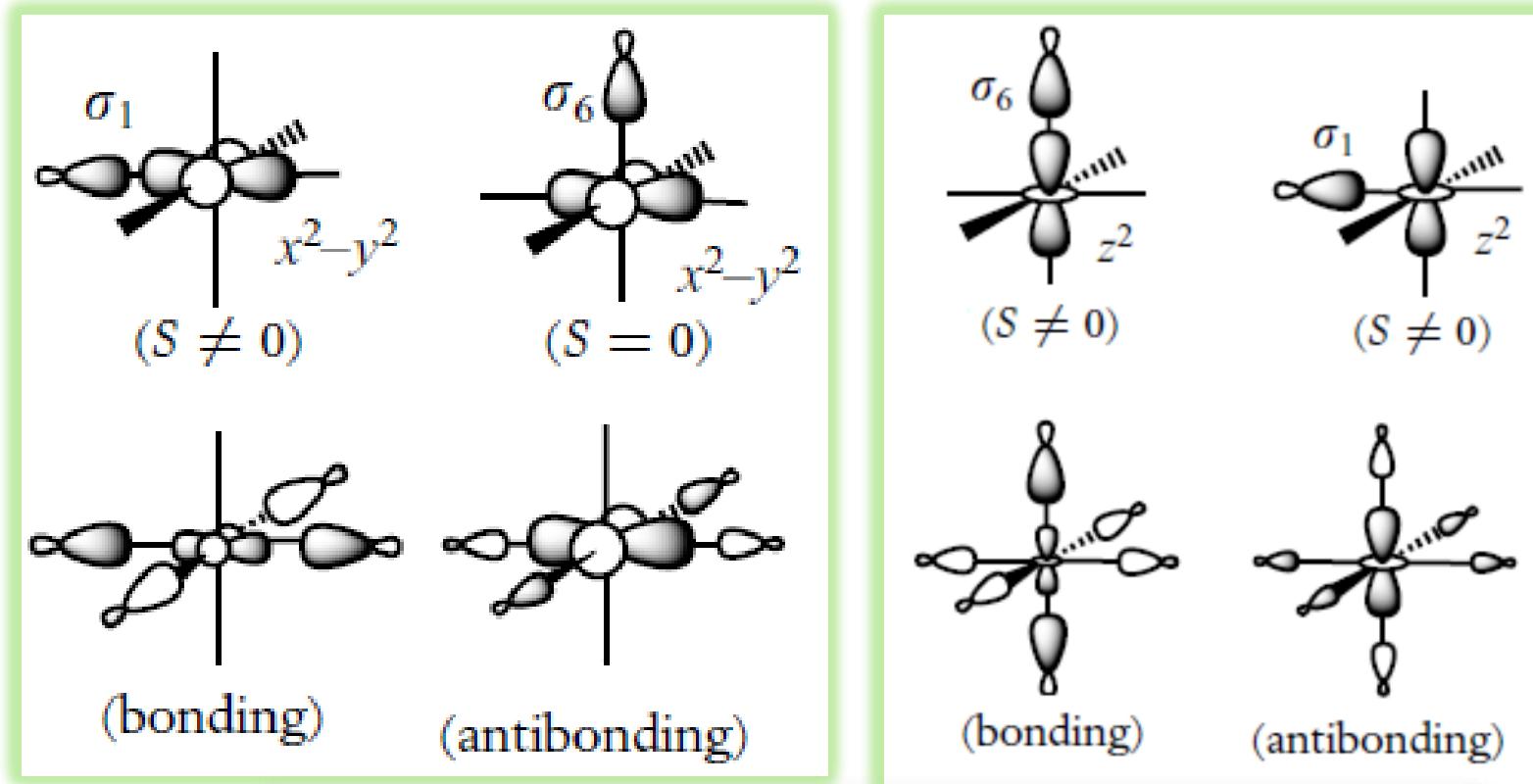
$(S \neq 0)$

$(S = 0)$

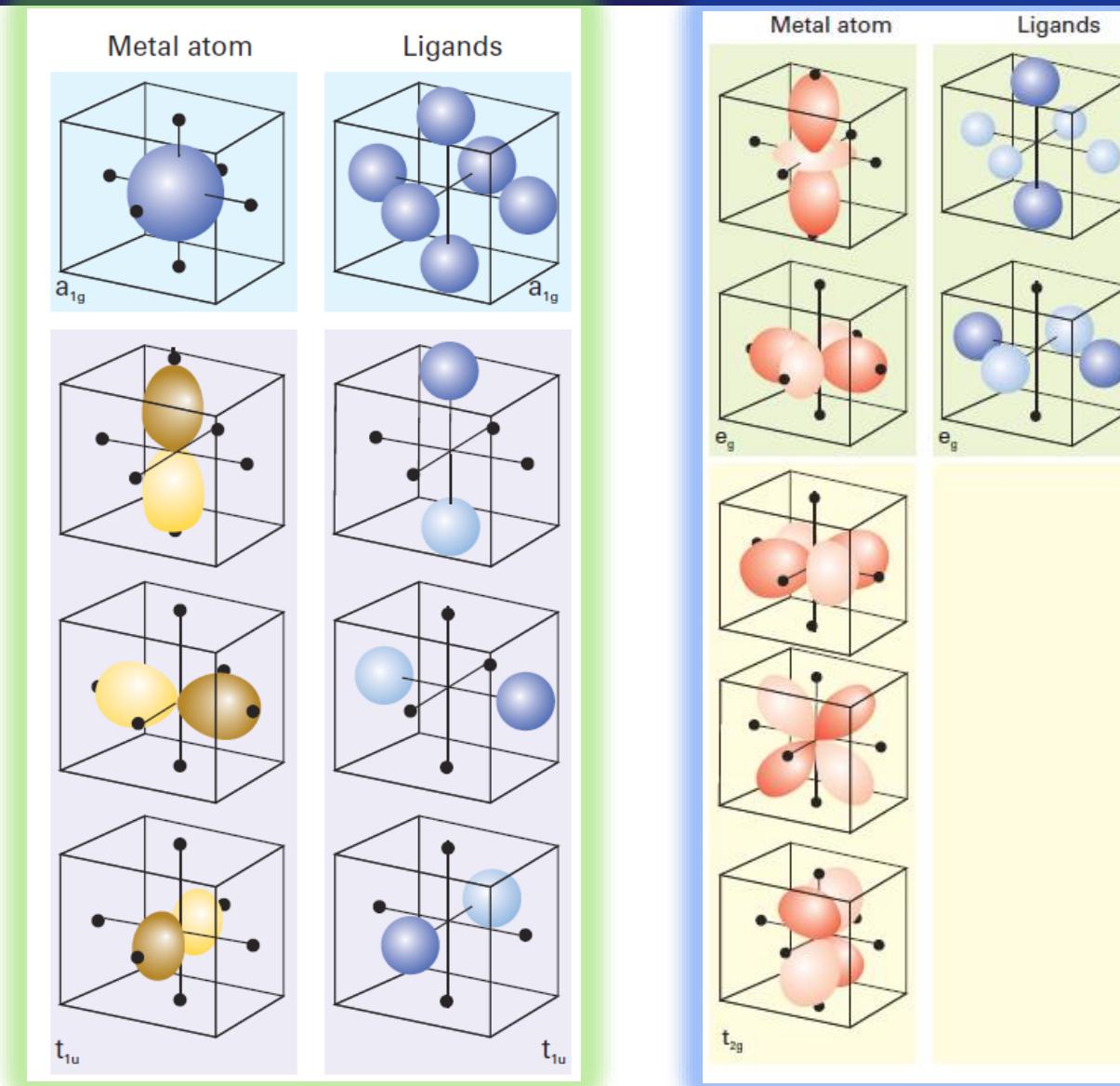
(bonding)

(antibonding)

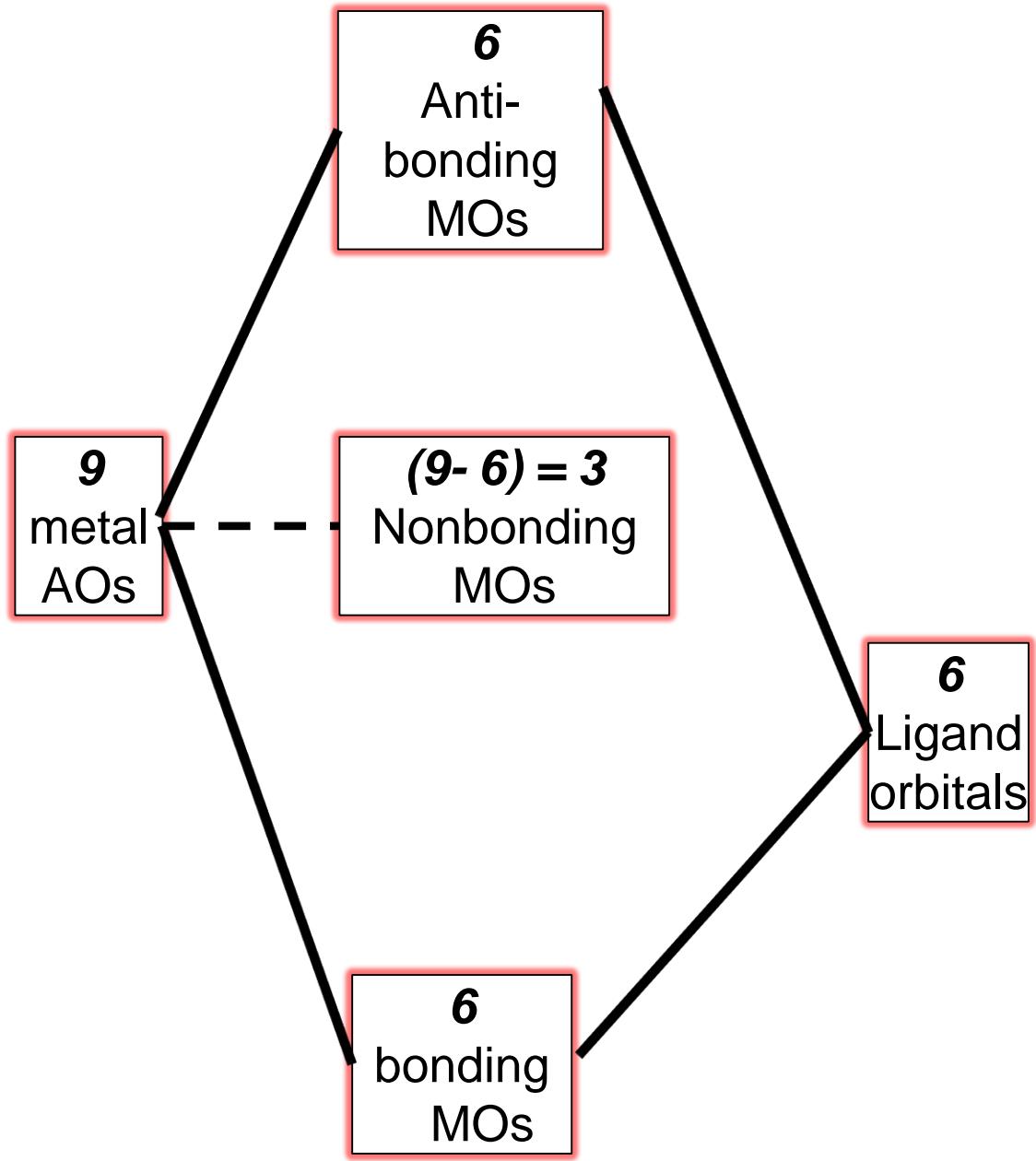
# Metal-Ligand Combinations decided by overlap ( $S$ )



# M-L $\rightarrow$ $\sigma$ -bonding



**Figure 20.15** Symmetry-adapted combinations of ligand orbitals (represented here by spheres) in an octahedral complex. For symmetry-adapted orbitals in other point groups, see *Resource section 5*.



# M-L $\rightarrow$ $\sigma$ -bonding

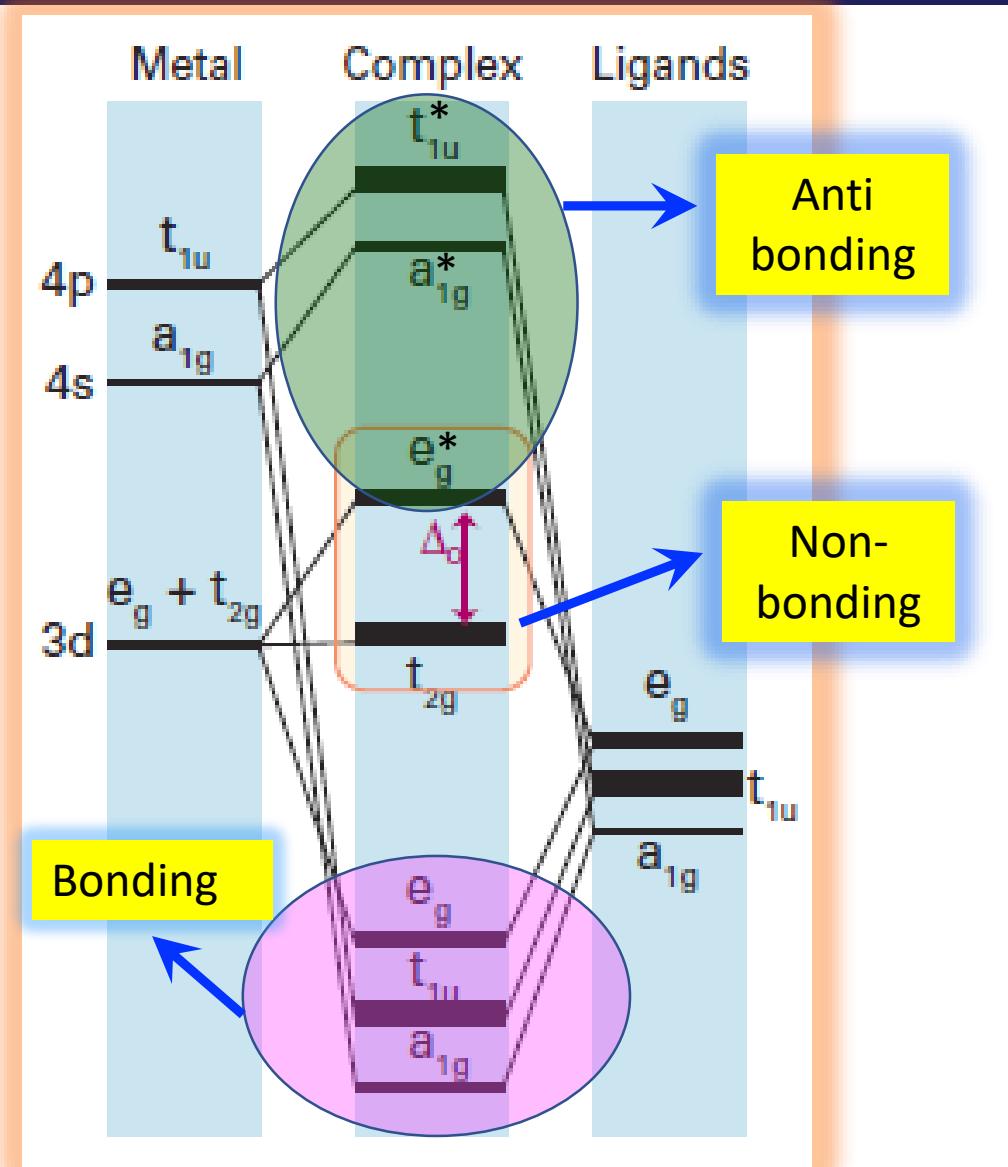
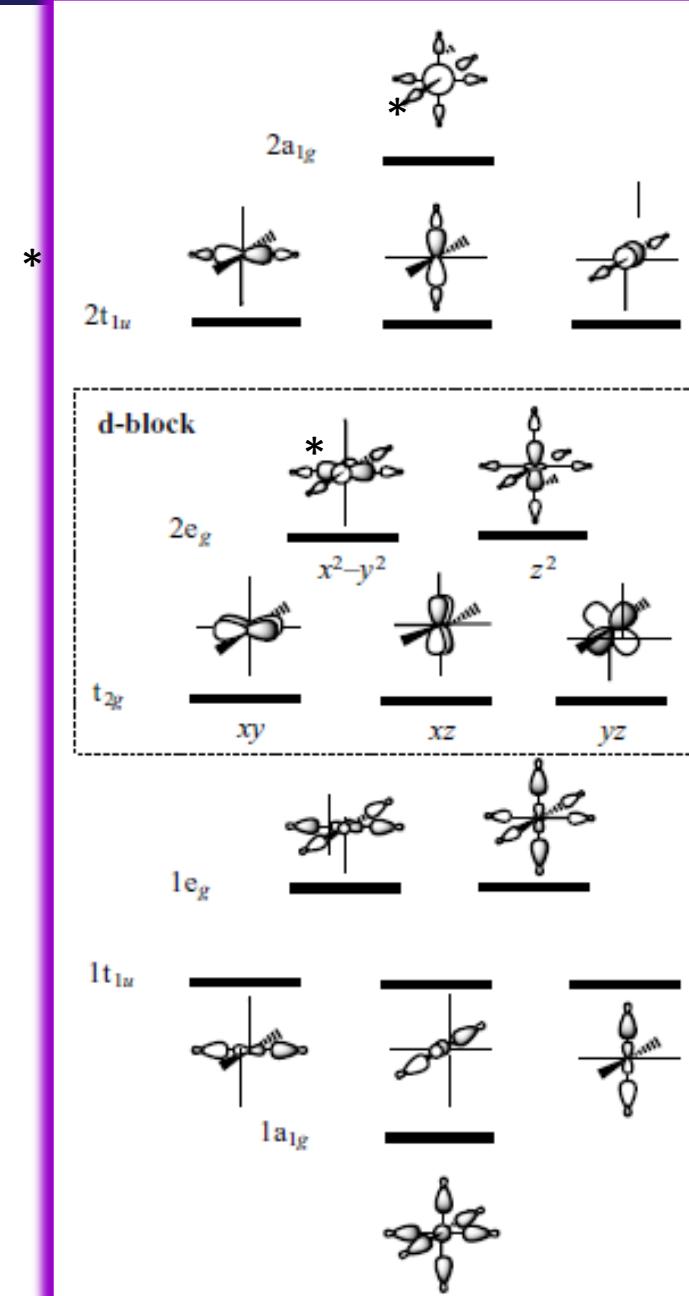
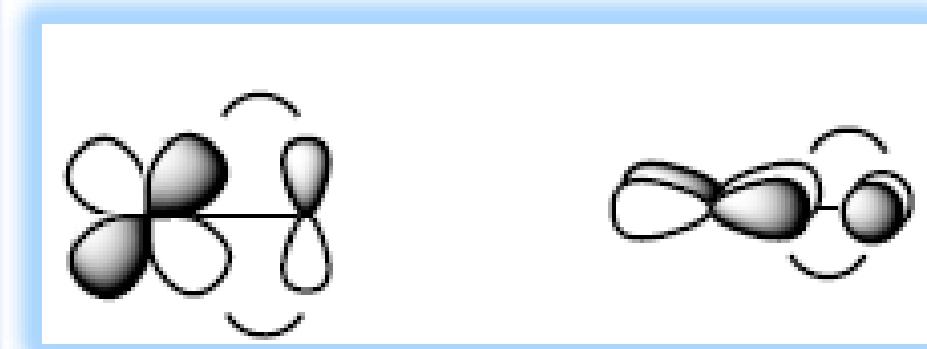
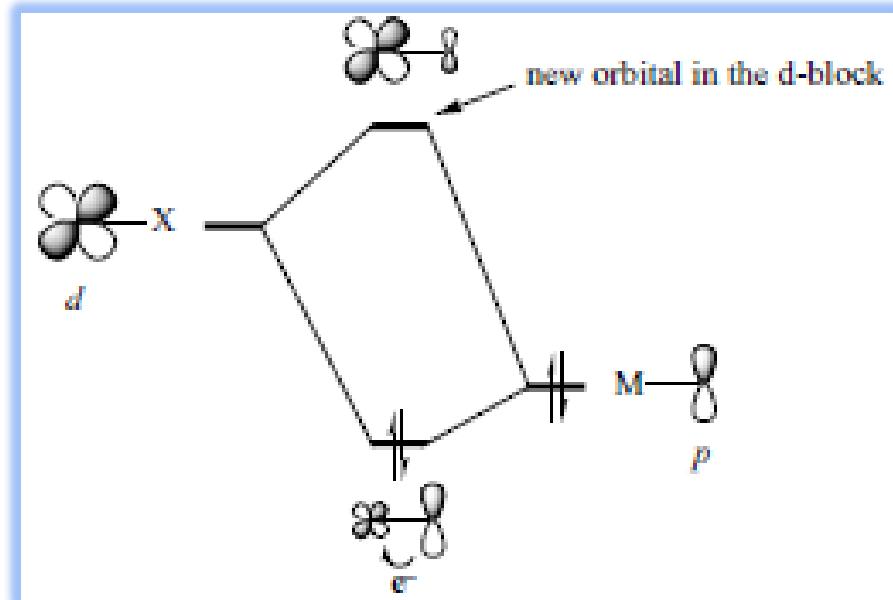


Figure 20.16 Molecular orbital energy levels of a typical octahedral complex. The frontier orbitals are inside the tinted box.



# Influence of $\pi$ -bonding on Non-bonding Orbital ( $t_{2g}$ ) in $O_h$ complexes

$\pi$ -Donor ligands decrease  $\Delta_o$  whereas  $\pi$ -acceptor ligands increase  $\Delta_o$ ; the spectrochemical series is largely a consequence of the effects of  $\pi$  bonding when such bonding is feasible.



In  $O_h$  geometry: The non-bonding d-orbital ( $t_{2g}$ ) will interact with the suitable ligand with  $\pi/\pi^*$  molecular orbital.

## $\pi$ -Donors decreases $\Delta_o$

Example:  $[ML_5Cl]$  with only one  $\pi$ -donor

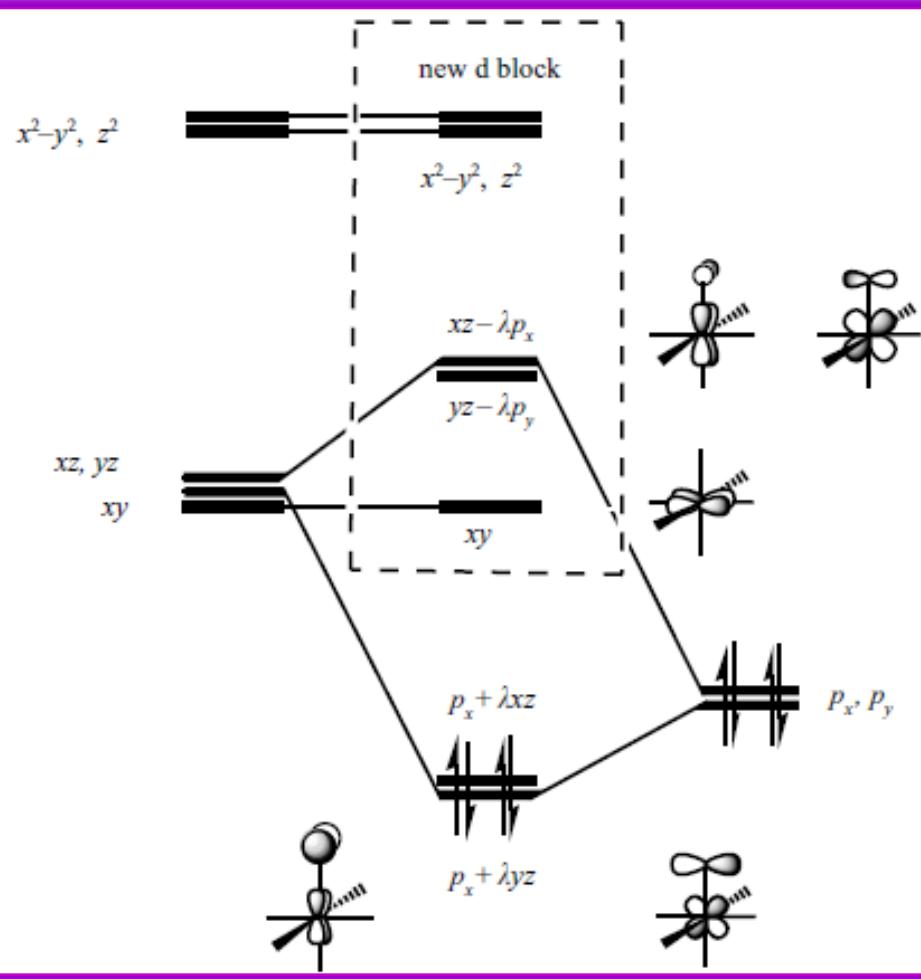
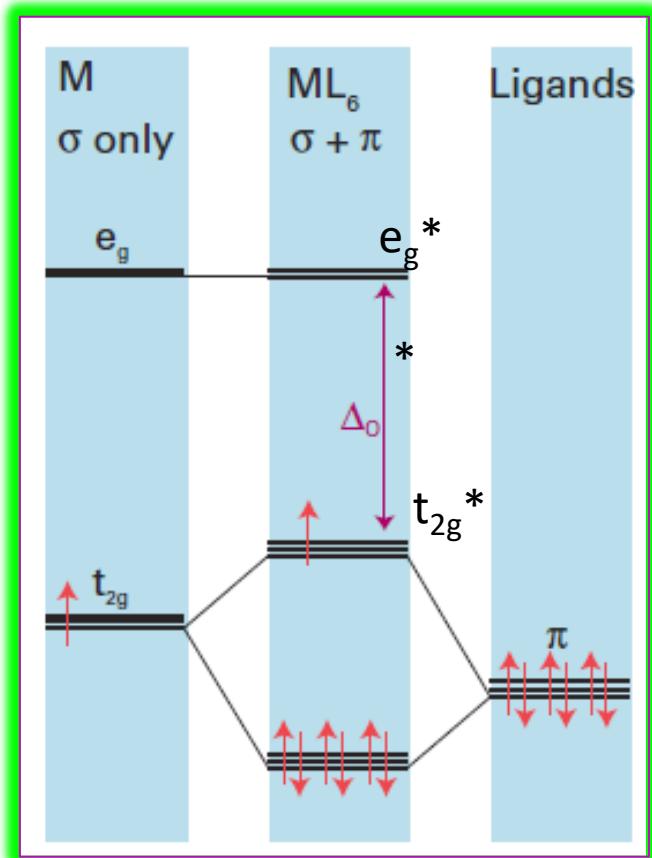


Figure 20.20 The effect of  $\pi$ -bonding on the ligand-field splitting parameter. Ligands that act as  $\pi$  donors decrease  $\Delta O$ . Only the  $\pi$  orbitals of the ligand are shown.

- ❖  $\pi$ - donor ligand (HOMO) of an atomic orbital energy will be lower than the energy of non-bonding  $t_{2g}$  molecular orbital.
- ❖ The interaction of  $\pi$ -donor with  $t_{2g}$  orbital lead to bonding (mostly ligand in character) and anti-bonding (mostly metal in character).
- ❖ The  $\pi$ - donor ligand raises the energy of non-bonding  $t_{2g}$  level to anti-bonding  $t_{2g}^*$  orbital.
- ❖ Consequently, the energy gap between the  $t_{2g}^*$  and  $e_g^*$  becomes small i.e  $\Delta_o$  is small.
- ❖ Examples: I<sup>-</sup>, Br<sup>-</sup>, Cl<sup>-</sup> and F<sup>-</sup>

# $\pi$ -Acceptors increases $\Delta_o$

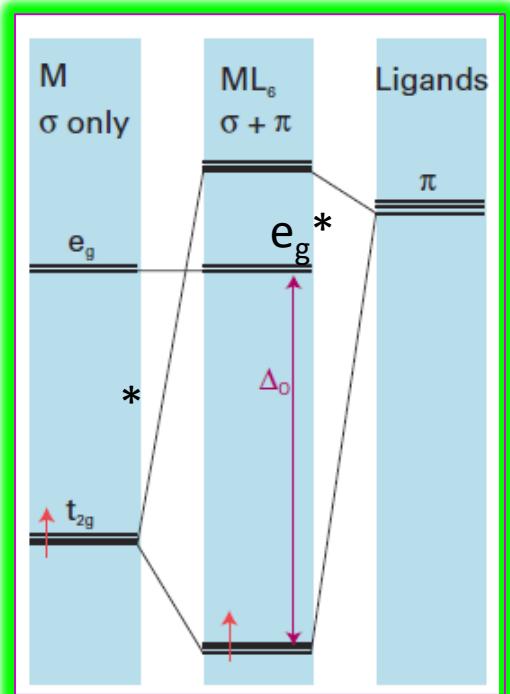
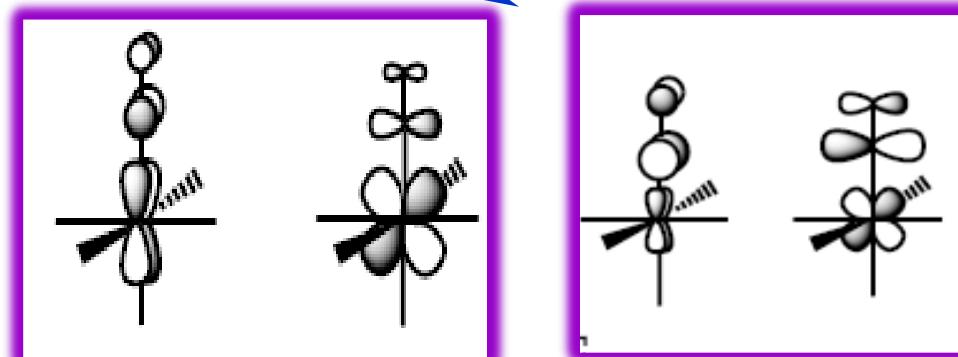
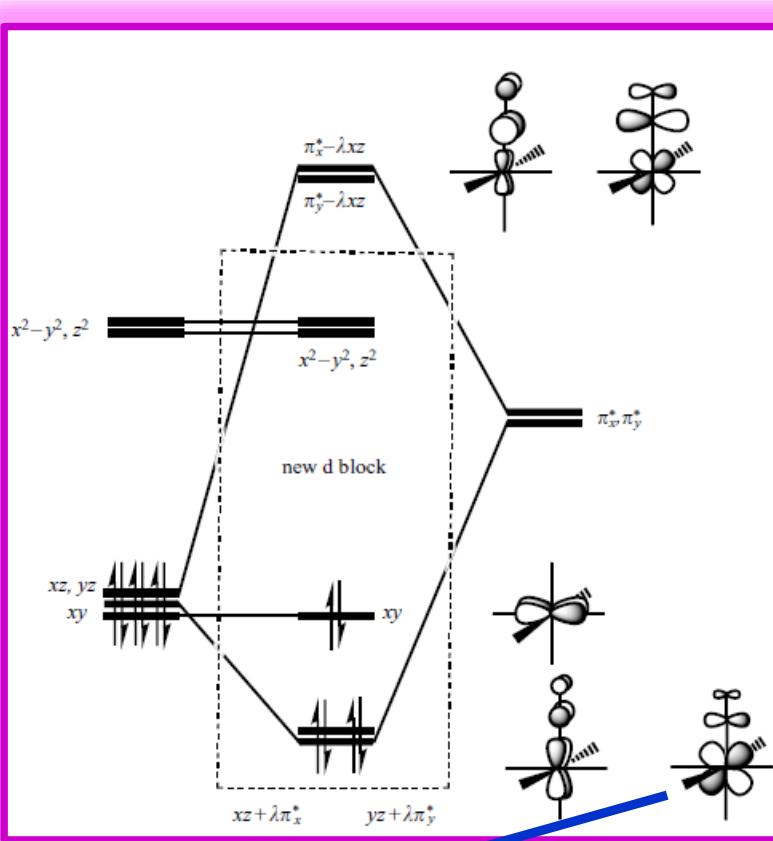


Figure 20.21 Ligands that act as  $\pi$ - acceptors increase  $\Delta_o$ . Only the  $\pi$  orbitals of the ligand are shown.



- ❖  $\pi$ - acceptor ligand (LUMO) of an atomic orbital energy will be higher than the energy of non-bonding  $t_{2g}$  molecular orbital.
- ❖ The interaction of  $\pi$ - acceptor with  $t_{2g}$  orbital lead to bonding (mostly metal in character) and anti-bonding (mostly ligand in character).
- ❖ The  $\pi$ - acceptor ligand lower the energy of non-bonding  $t_{2g}$  level.
- ❖ Consequently, the energy gap between the  $t_{2g}$  and  $e_g^*$  becomes large i.e  $\Delta_o$  is large.
- ❖ Examples: CO, CN, PR<sub>3</sub>

# Rationale for Spectro-chemical Series

$\pi$ -donor ligand

I<sup>-</sup>, Br<sup>-</sup>, S<sup>2-</sup>, SCN<sup>-</sup>, Cl<sup>-</sup>, N<sup>3-</sup>, F<sup>-</sup>

Weak  $\pi$ -donor ligand

Urea, OH<sup>-</sup>, Ox<sup>2-</sup>, O<sup>2-</sup>, H<sub>2</sub>O, NCS<sup>-</sup>, Py

No  $\pi$ -effect

NH<sub>3</sub>, en, bpy, phen, NO<sub>2</sub><sup>-</sup>, CH<sub>3</sub><sup>-</sup> and C<sub>6</sub>H<sub>5</sub><sup>-</sup>

$\pi$ -acceptor ligand

CN, CO, PR<sub>3</sub>

I<sup>-</sup> < Br<sup>-</sup> < S<sup>2-</sup> < SCN<sup>-</sup> < Cl<sup>-</sup> < N<sub>3</sub><sup>-</sup>, F<sup>-</sup> < urea, OH<sup>-</sup> < ox, O<sup>2-</sup> < H<sub>2</sub>O < NCS<sup>-</sup> < py, NH<sub>3</sub> < en < bpy, phen < NO<sub>2</sub><sup>-</sup> < CH<sub>3</sub><sup>-</sup>, C<sub>6</sub>H<sub>5</sub><sup>-</sup> < CN<sup>-</sup> < CO.

**$\pi$ -bases < weak  $\pi$  -bases < no  $\pi$  -effect <  $\pi$  -acids**

LFT:

- 1) Electronic structure and bonding
- 2) Spectroscopic properties
- 3) Magnetic properties etc.
- 4) Metal ligand covalency
- 5) Spectrochemical series