Coordination Chemistry-II:

Crystal Field Theory, Magnetochemistry and Origin of Colours in Transition Metal Chemistry

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Crystal Field Theory (CFT)

- ☐ A purely ionic model for transition metal complexes.
- ☐ Ligands are considered as point charge or point dipole.
- ☐ Predicts the pattern of splitting of d-orbitals.
- ☐ Used to rationalize spectroscopic and magnetic properties.

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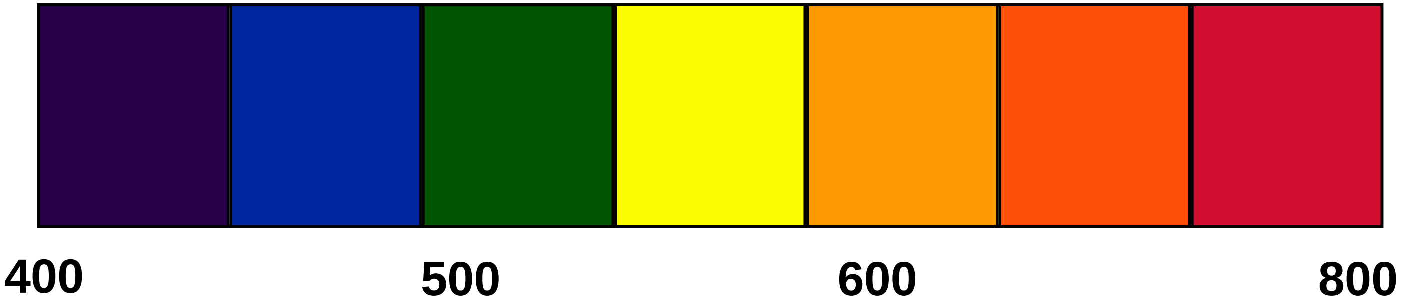
- **Alfred Werner - 1893**

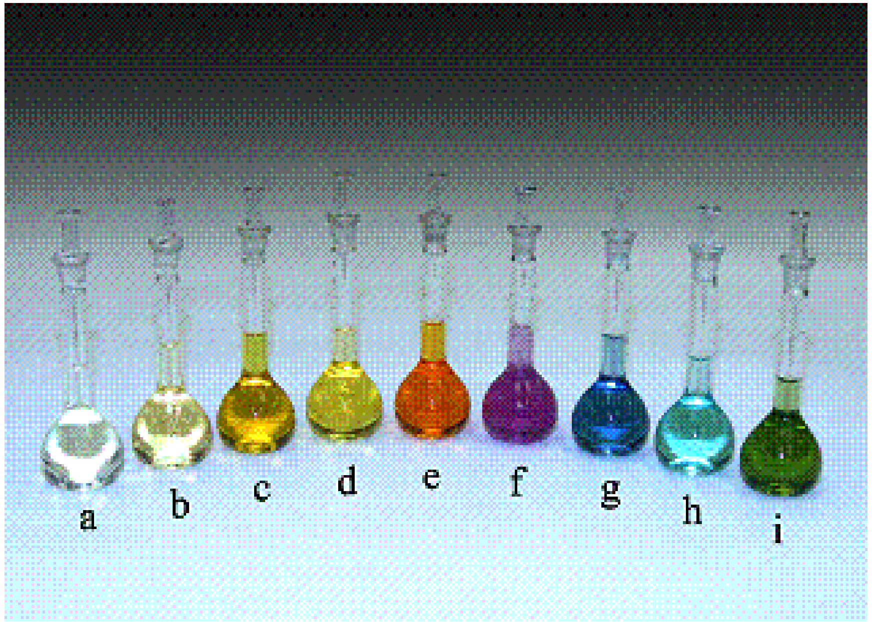
Nobel prize 1913

Crystal Field Theory:

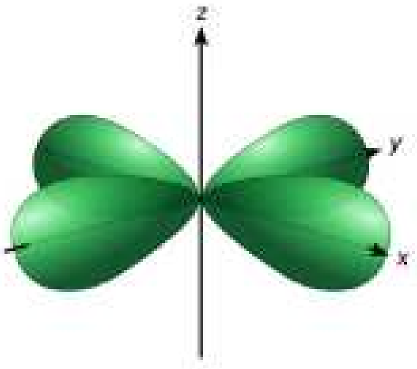
The relationship between colors and complex metal ions



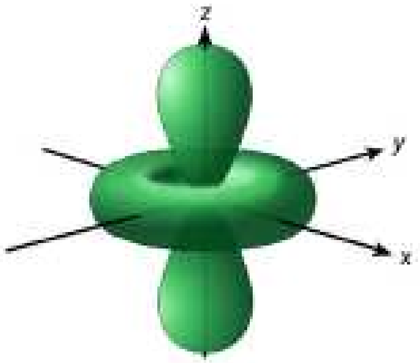
- (a) CN^-, (b) NO_2^-, (c) phen, (d) en, (e) NH_3, (f) gly, (g) H_2O, (h) ox^{2-}, (i) CO_3



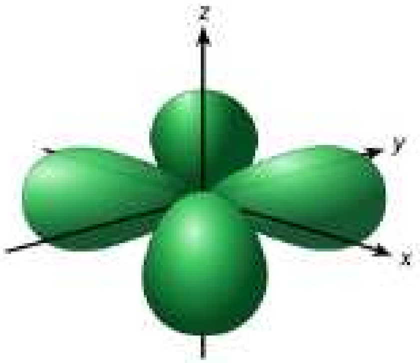
Shape of d-orbitals:
look attentively along the axis



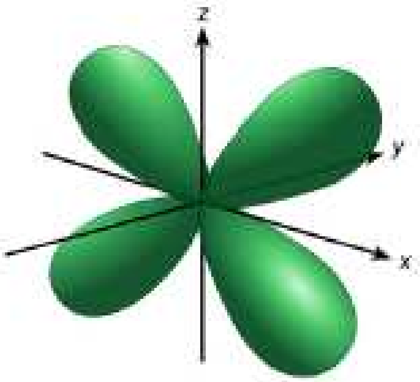
$d_{x^2-y^2}$



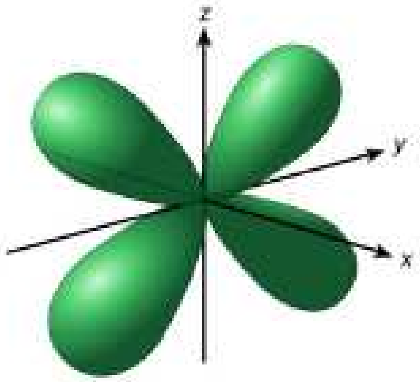
d_{z^2}



d_{xy}

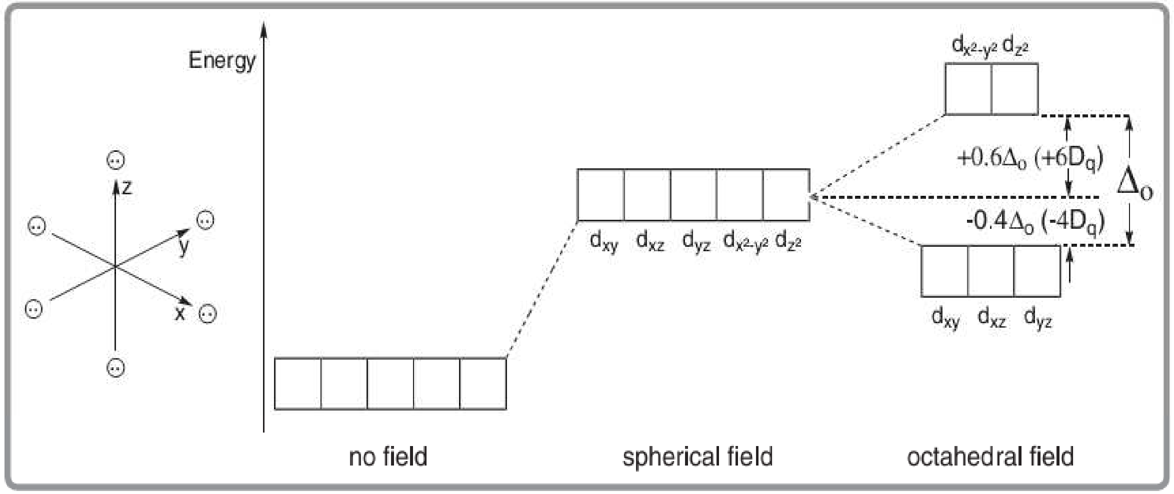


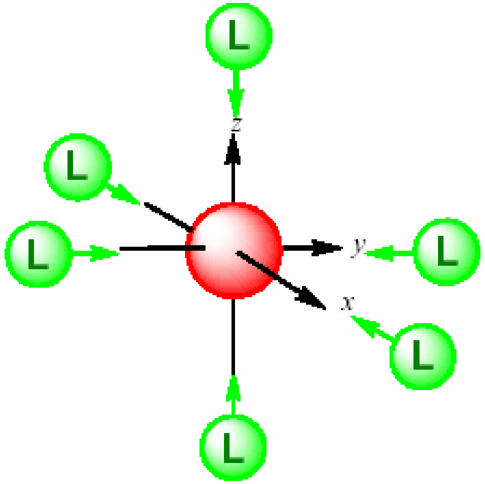
d_{xz}

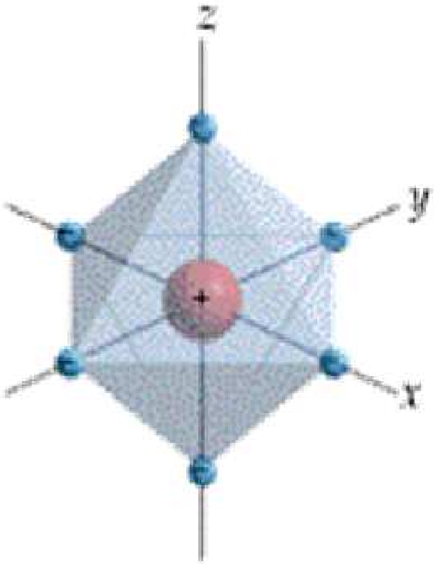


d_{yz}

Octahedral Field:
d-orbital Splitting



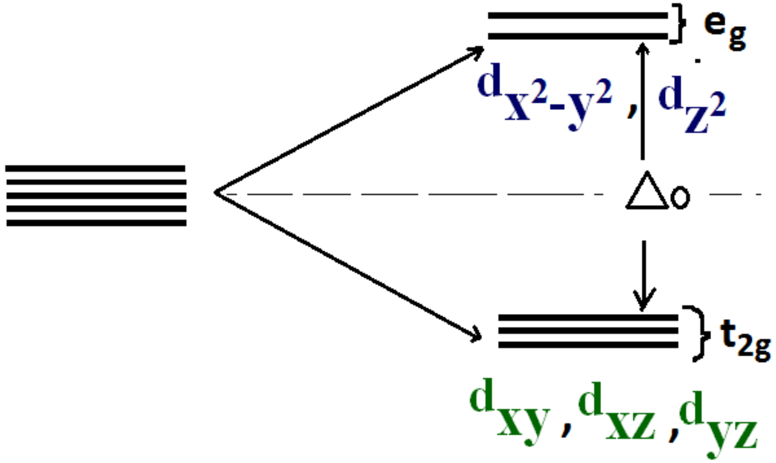


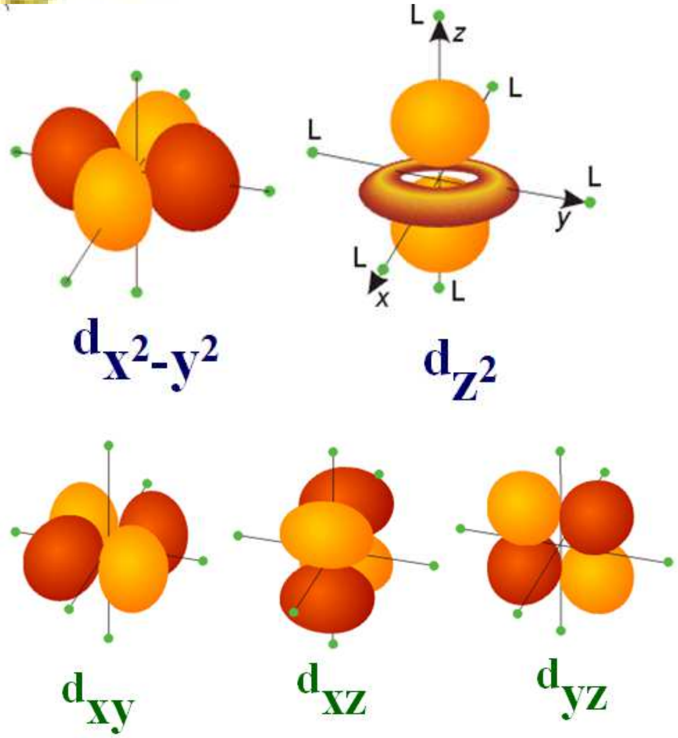


$D = 35ze/4a^5$ $q = 2er^4/105$
z = charge of the ligand,
a = metal-ligand distance ,
R = distance of the electron from the nucleus

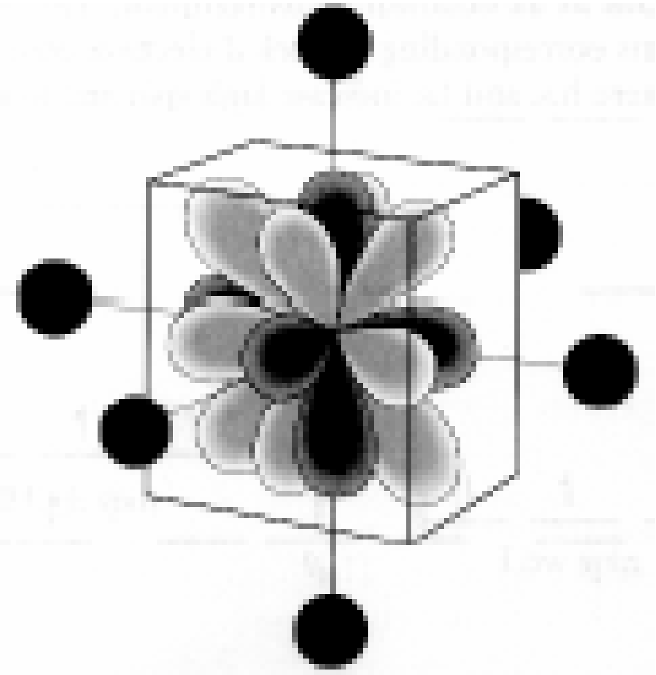
Effect of Octahedral Field

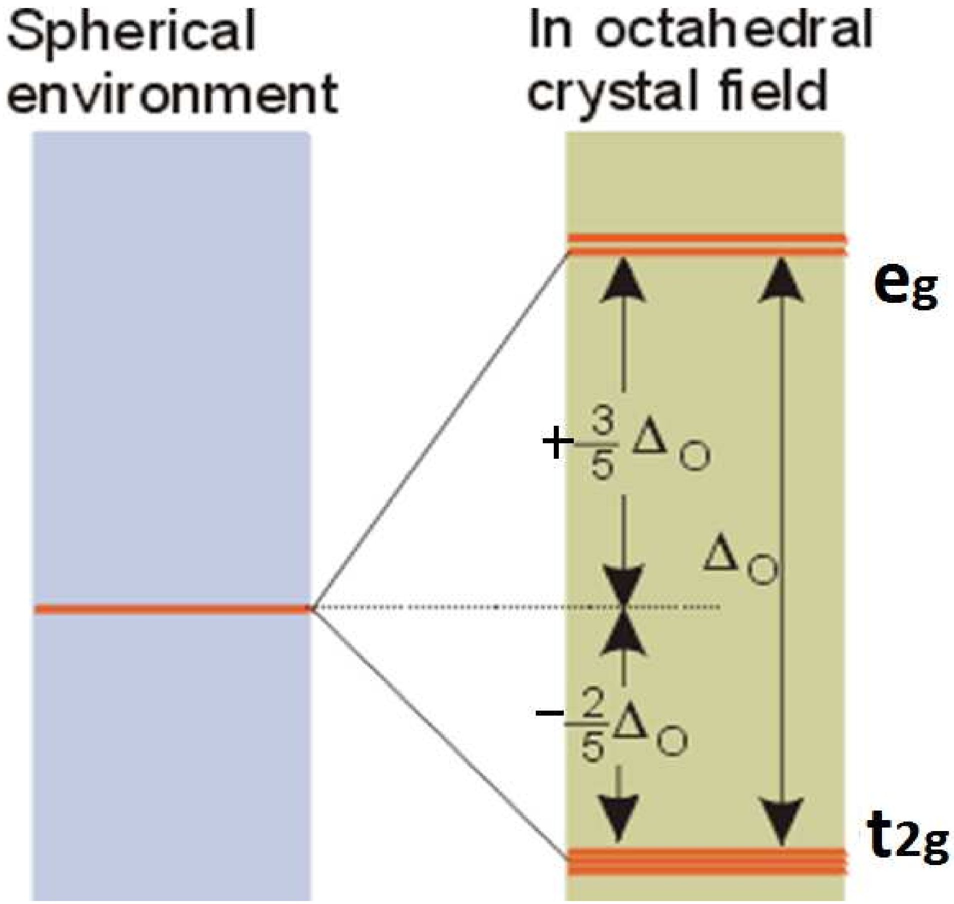
- The orbitals along axes strongly are strongly repelled and becomes high energy
- The d_{xy}, d_{yz}, and d_{xz} orbitals bisect the negative charges and experiences smaller repulsion become low energy set of orbitals



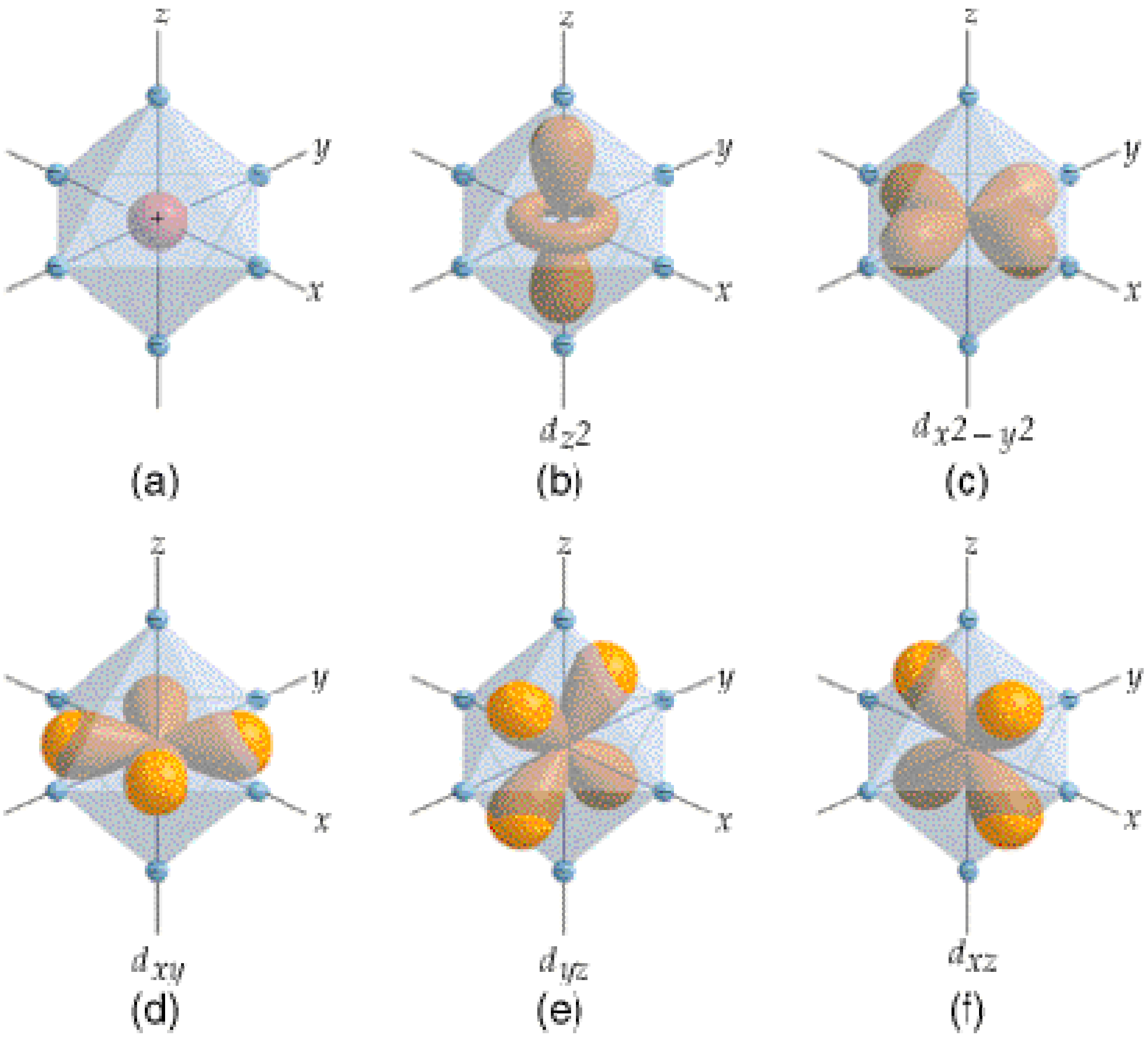


Octahedral field





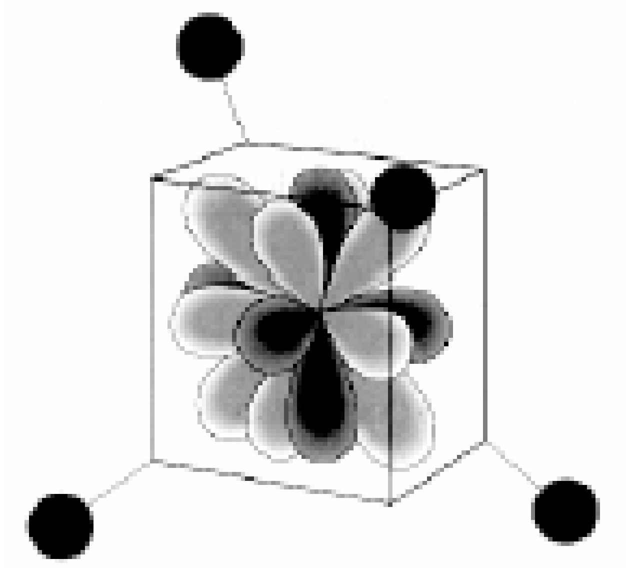
Orientation of 5 d-orbitals in Octahedral Geometry

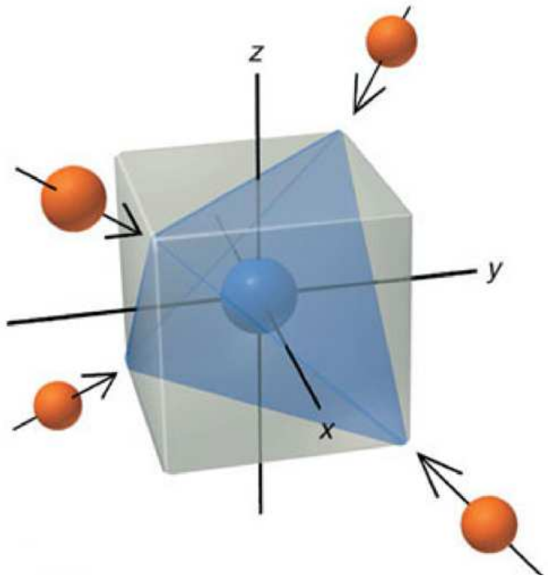


4 - Coordinate Complexes

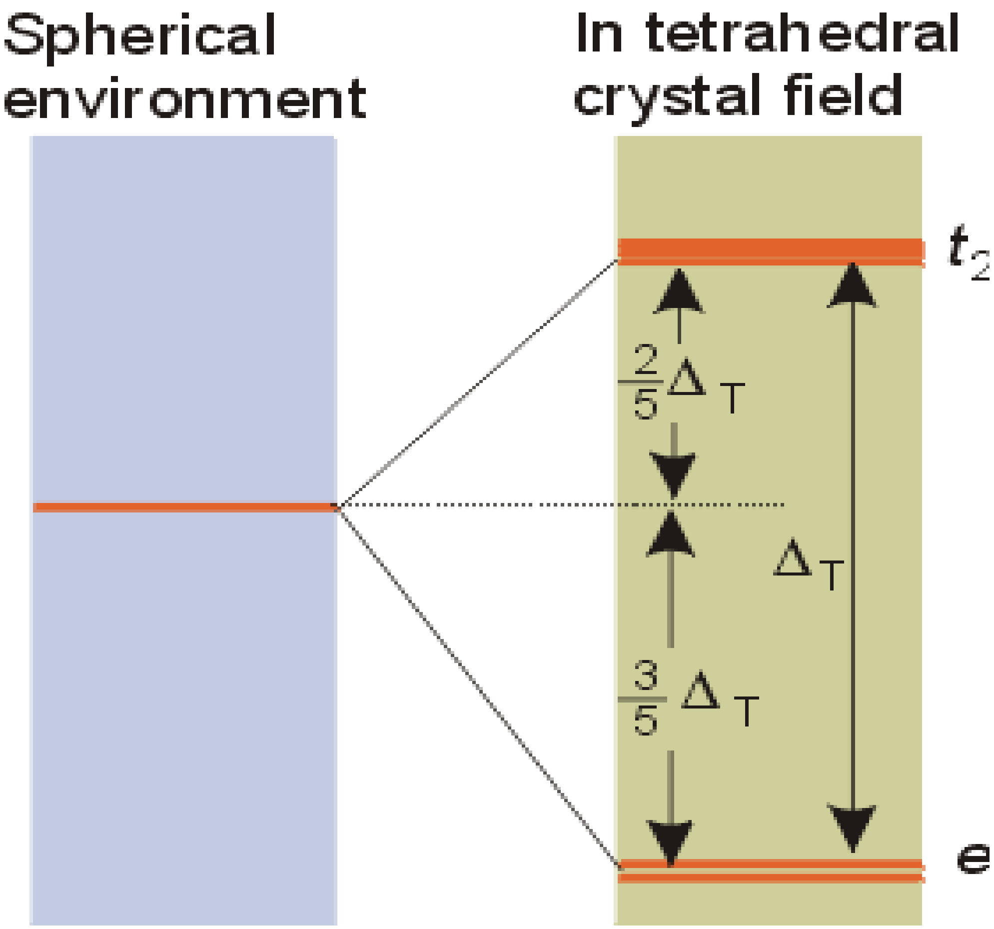
Square planar and tetrahedral complexes are quite common for certain transition metals.

The splitting patterns of the *d* orbitals on the metal will differ depending on the geometry of the complex.





Tetrahedral Complexes



In general,

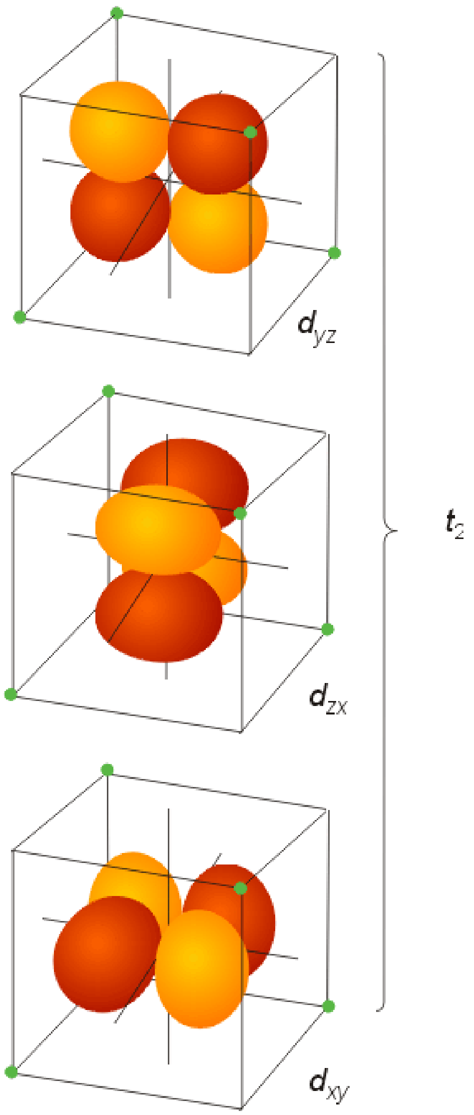
$\Delta_T \approx 4/9\ \Delta_o$.

Since the splitting is smaller, all tetrahedral complexes are weak-field, high-spin cases.

Tetrahedral Complexes

The size of the splitting, Δ_T, is considerable smaller than with comparable octahedral complexes.

This is because only 4 bonds are formed, and the metal orbitals used in bonding don't point right at the ligands as they do in octahedral complexes.

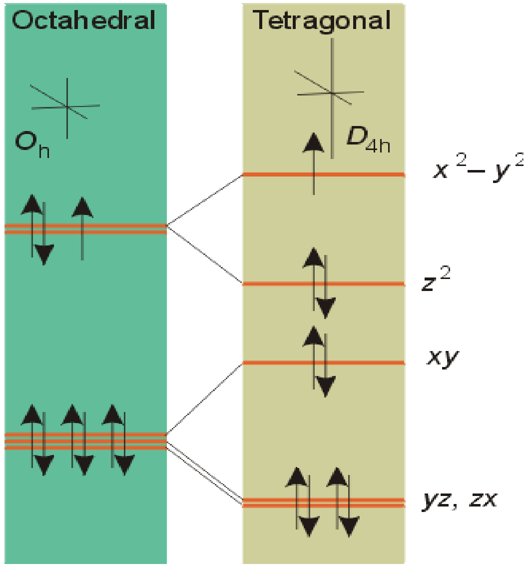


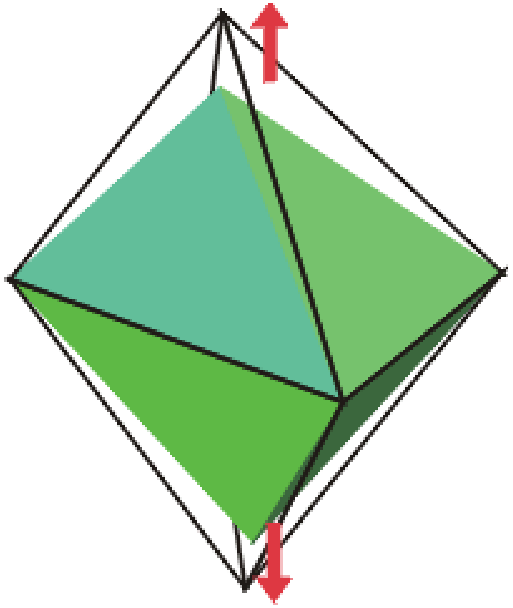
Tetragonal Complexes

Six coordinate complexes, notably those of Cu^{2+}, distort from octahedral geometry.

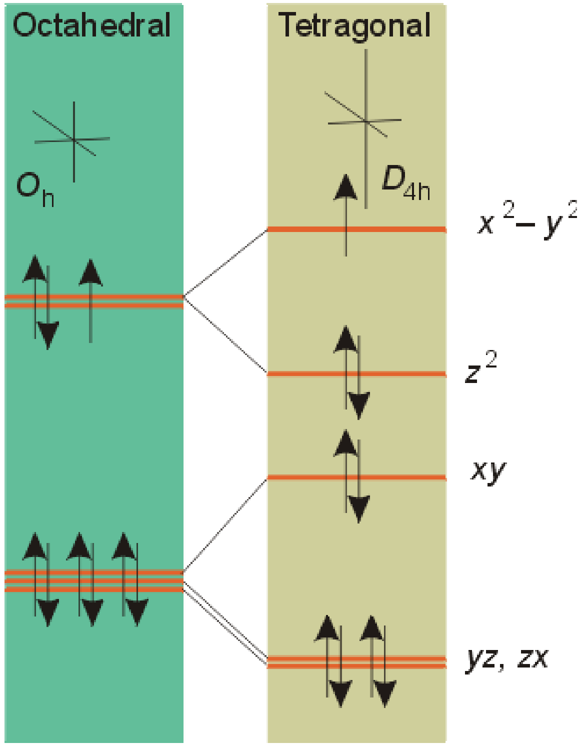
One such distortion is called *tetragonal distortion*, in which the bonds along one axis elongate, with compression of the bond distances along the other two axes.

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.



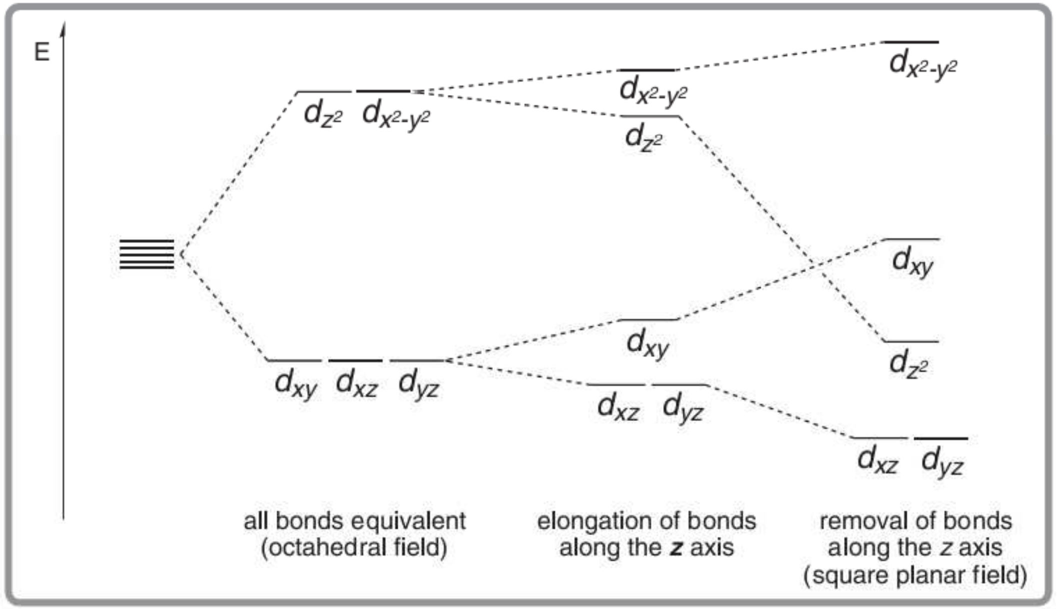


Tetragonal Complexes

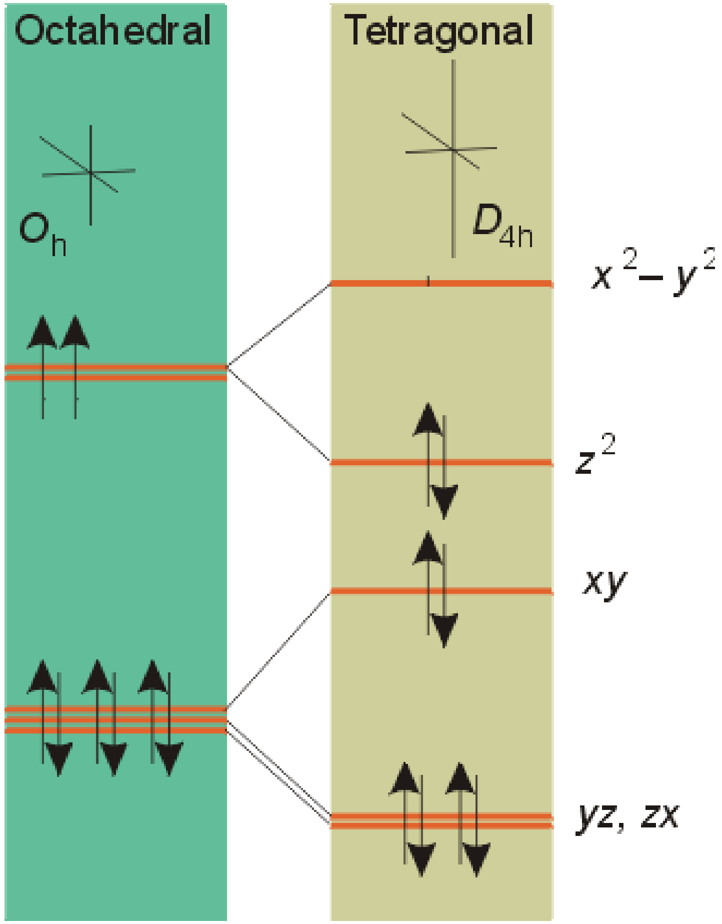


For complexes with 1-3 electrons in the e_g set of orbitals,

This type of tetragonal distortion may lower the energy of the complex.

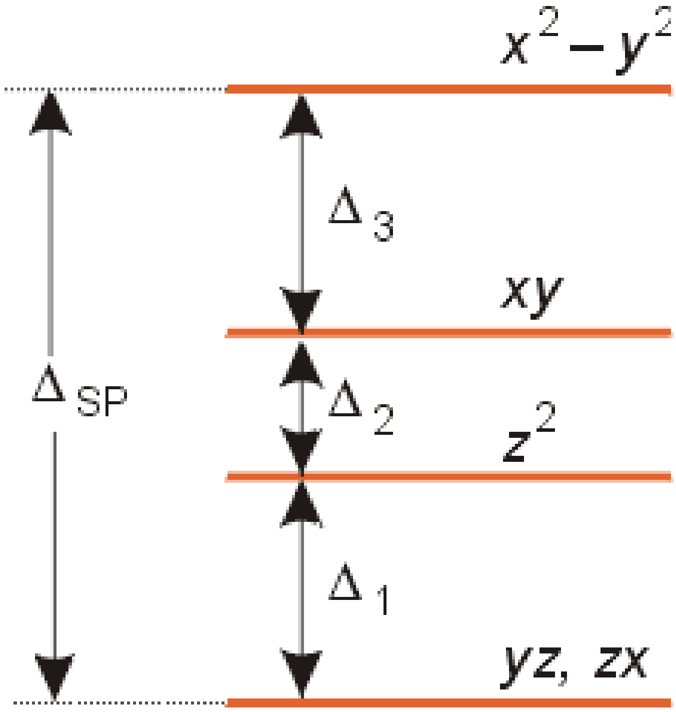


Square Planar Complexes



For complexes with 2 electrons in the e_g set of orbitals, a d^8 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.

Square Planar Complexes



Square planar complexes are quite common for the d^8 metals in the 4th and 5th periods: Rh(I), Ir(I), Pt(II), Pd(II) and Au(III).

The lower transition metals have large ligand field stabilization energies, favoring four-coordinate complexes.

Square planar complexes are rare for the 3rd period metals.

Ni(II) generally forms tetrahedral complexes.

Only with very strong ligands such as CN^-, is square planar geometry seen with Ni(II).

The value of Δ_{sp} for a given metal, ligands and bond length is approximately 1.3(Δ_o).

The Jahn-Teller Effect

If the ground electronic configuration of a non-linear complex is orbitally degenerate, the complex will distort so as to remove the degeneracy and achieve a lower energy.

- 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 orbital that point directly towards the ligands.

The Jahn-Teller Effect

In octahedral complexes, the effect is most pronounced in high spin d^4, low spin d^7 and d^9 configurations, as the degeneracy occurs in the e_g set of orbitals.

The Jahn–Teller Effect

The strength of the Jahn-Teller effect is tabulated below: (w=weak, s=strong)

# e^-	1	2	3	4	5	6	7	8	9	10
High spin	*	*	*	s	-	w	w	*	*	*
Low spin	w	w	-	w	w	-	s	-	s	-

*There is only one possible ground state configuration.

- No Jahn-Teller distortion is expected.

Crystal Field Splitting Energy (CFSE)

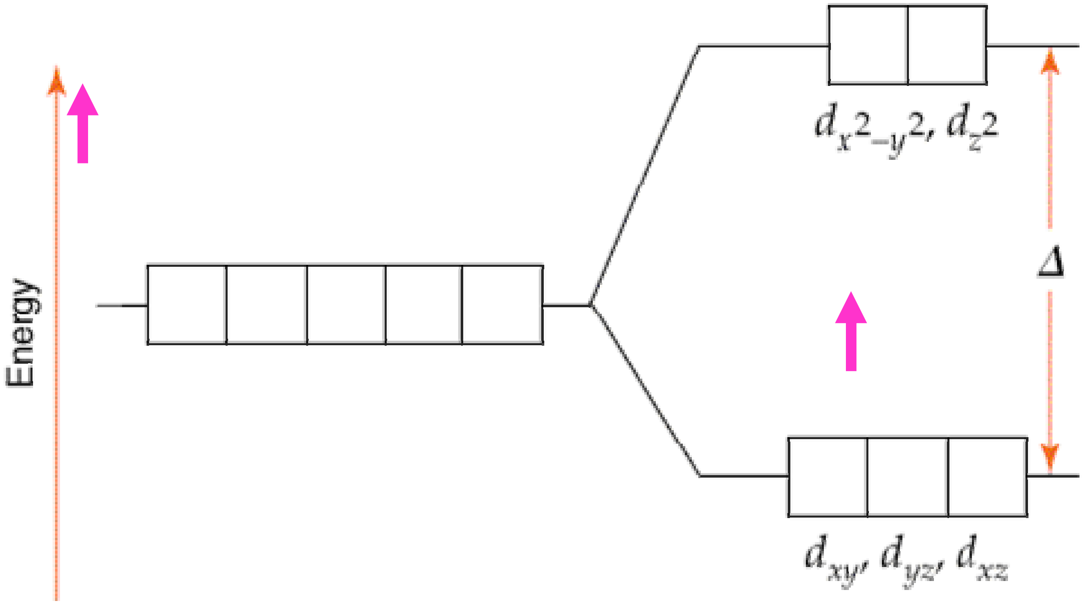
- In Octahedral field, configuration is: $t_{2g}^{x}\, e_{g}^{y}$
- Net energy of the configuration relative to the average energy of the orbitals is: $= (-0.4x + 0.6y)\Delta_O$

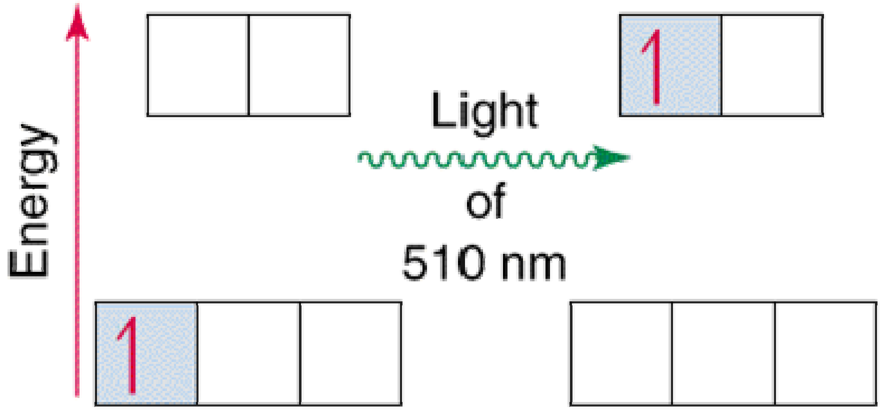
$\Delta_O = 10\ Dq$

BEYOND d^3

- In weak field: $\Delta_O < P$, => $t_{2g}^{3} e_{g}^{1}$
- In strong field $\Delta_O > P$, => t_{2g}^{4}
- P - paring energy

Ground-state Electronic Configuration, Magnetic Properties and Colour

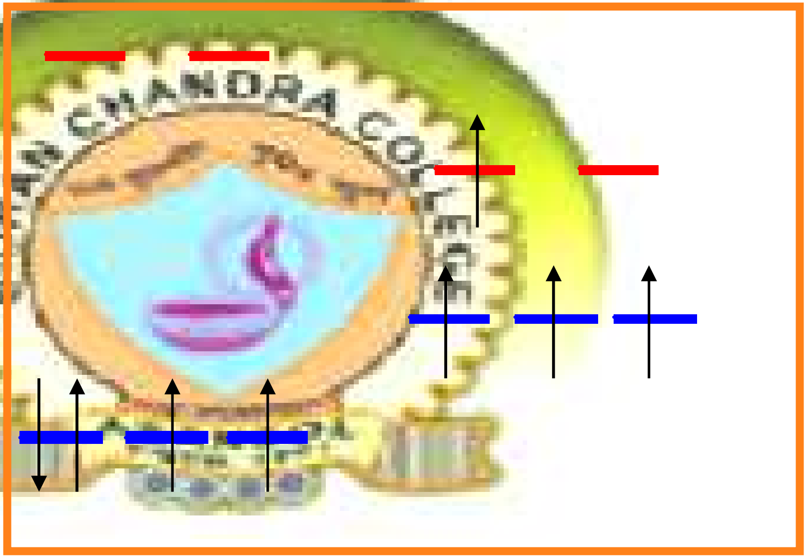




Field strength and Ground-state electronic configuration

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

d^4



Strong field =
Low spin
(2 unpaired)

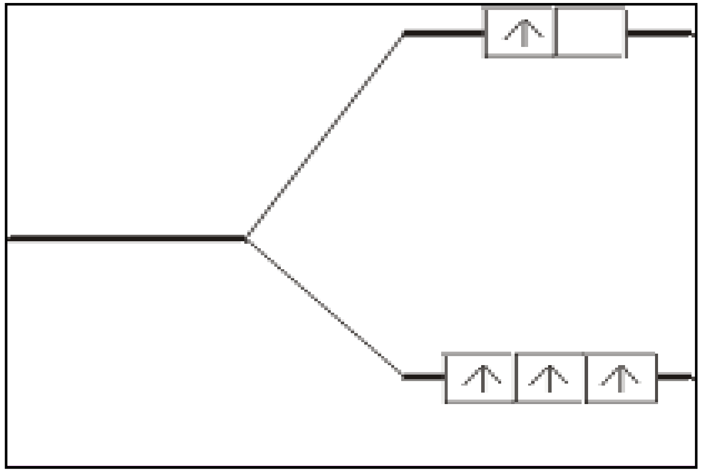
Weak field =
High spin
(4 unpaired)

$P < \Delta_o$

$P > \Delta_o$

In high spin complexes, the size of Δ_o is less than the pairing energy of the electrons.

Ground-state Electronic Configuration, Magnetic Properties

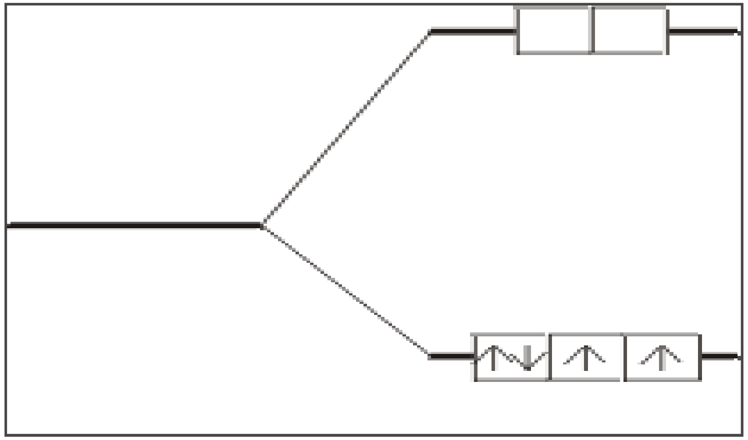


$[Mn(H_2O)_6]^{3+}$

Weak Field Complex

the total spin is 4 × ½ = 2

High Spin Complex



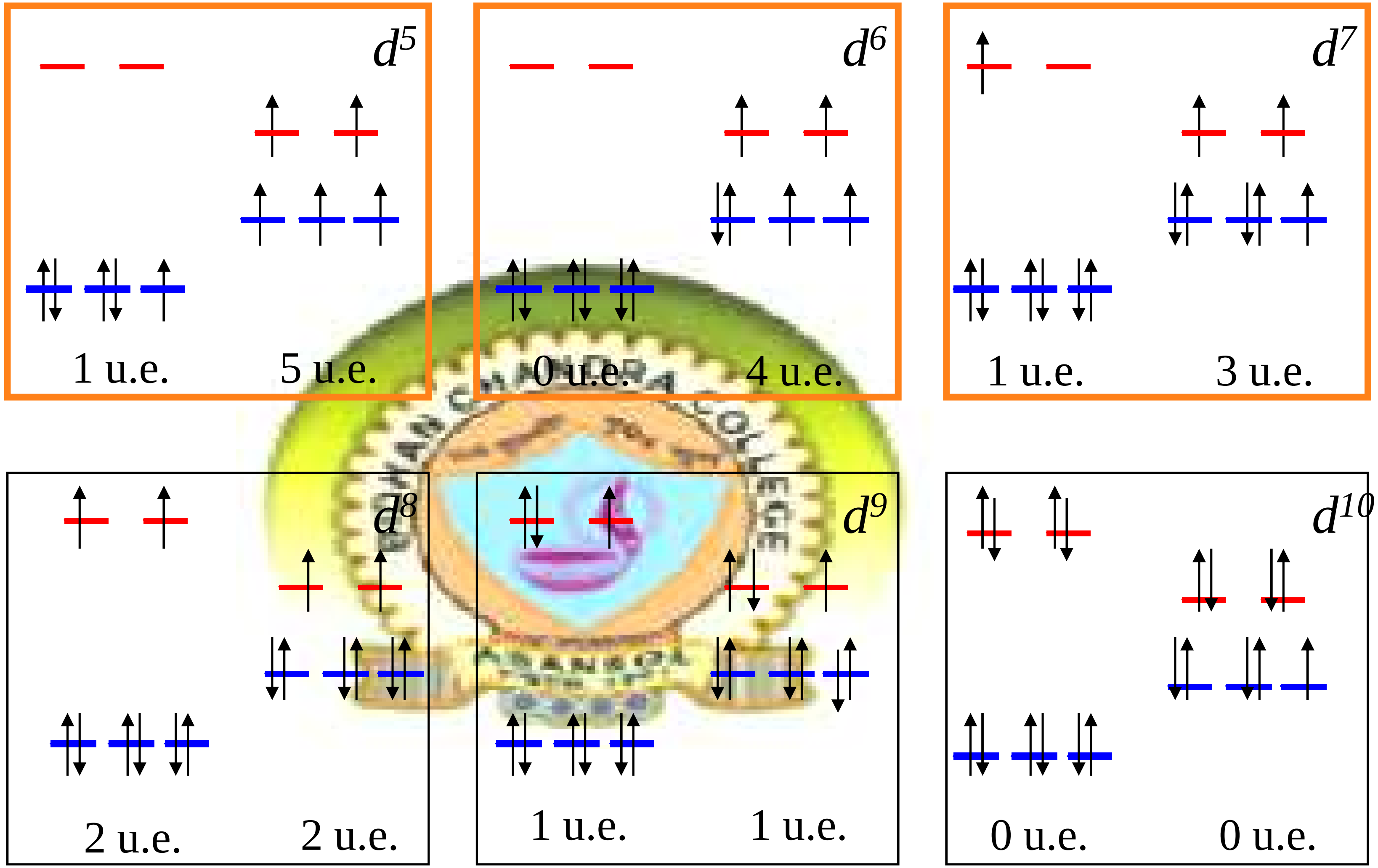
$[Mn(CN)_6]^{3-}$

Strong field Complex

total spin is 2 × ½ = 1

Low Spin Complex

Electrons in d orbitals in weak and strong ligand field

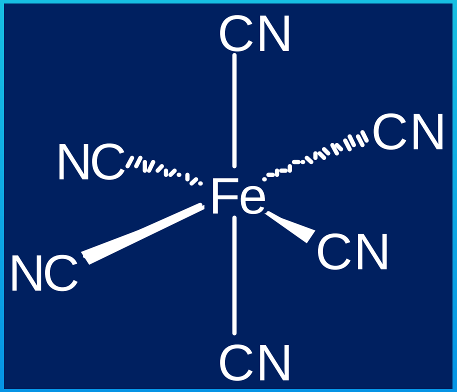


CFSE Calculation

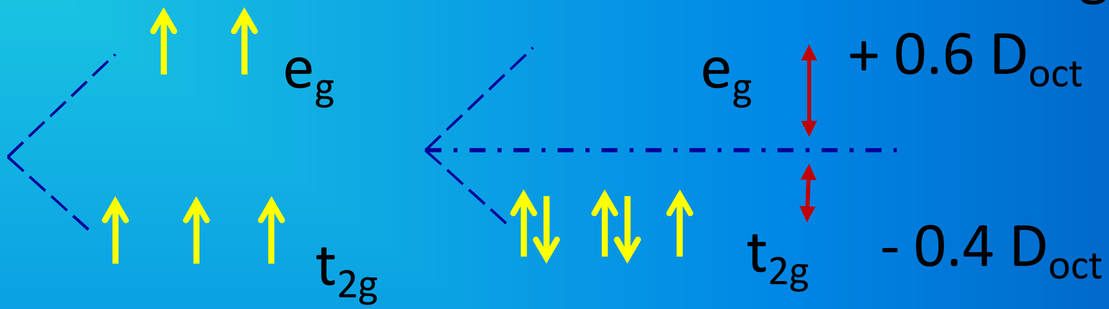
What is the CFSE of $[Fe(CN)_6]^{3-}$?

C.N. = 6 ∴ O_h Fe(III) ∴ d^5 H.S. L.S.

CN^- = strong ligand.



3-



↑ ↑ e_g

↑ ↑ ↑ t_{2g}

e_g + 0.6 D_{oct}

↑↓ ↑↓ ↑ t_{2g} - 0.4 D_{oct}

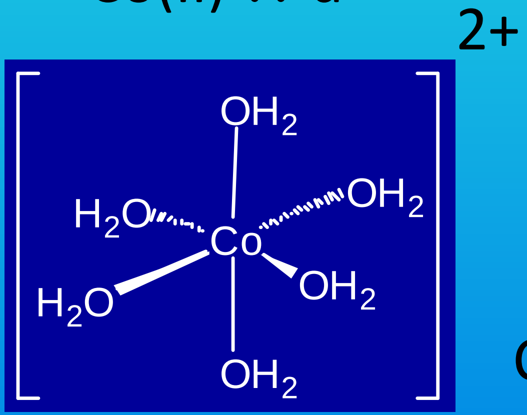
CFSE = 5 x - 0.4 D_{oct} + 2P = - 2.0 D_{oct} + 2P

CFSE Calculation

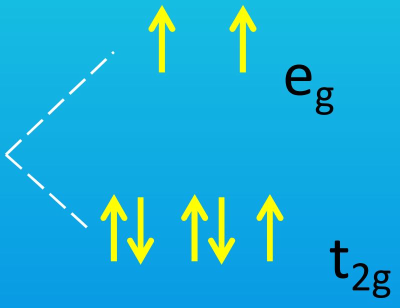
If the CFSE of $[Co(H_2O)_6]^{2+}$ is $-0.8\ D_{oct}$, what spin state is it in?

C.N. = 6 $\therefore$ O_h

Co(II) $\therefore$ d^7

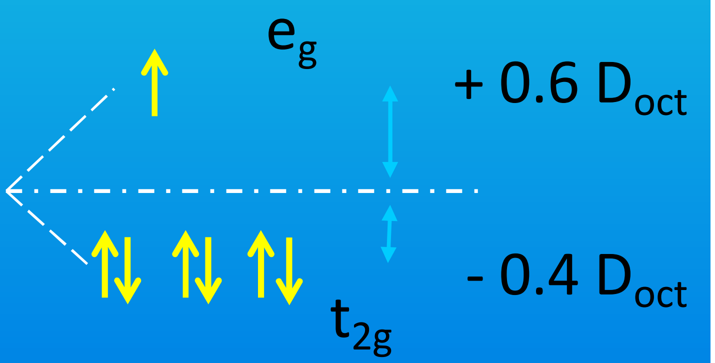


h.s.



$$CFSE = (5 \times -0.4\ D_{oct}) + (2 \times 0.6\ D_{oct}) = -0.8\ D_{oct}$$

L.S.



$$CFSE = (6 \times -0.4\ D_{oct}) + (0.6\ D_{oct}) + 3P = -1.8\ D_{oct} + P$$

Experimental Evidence for d-Orbital Splitting

- Several tools are used to confirm the splitting of the t_{2g} and e_g molecular orbitals.

- The broad range in colors of transition metal complexes arises from electronic transitions as seen in the UV/visible spectra of complexes.

- Additional information is gained from measuring the magnetic moments of the complexes.

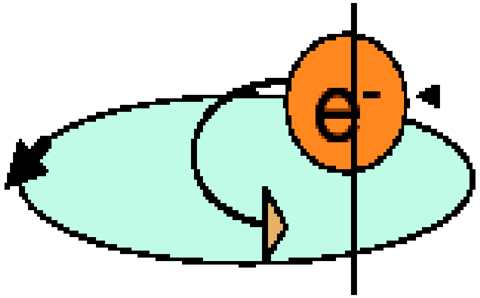
Magnetochemistry

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

Magnetic Moment Calculation

- The magnetic moment μ of a complex with total spin quantum number S is:
- $\mu = 2\{S(S+1)\}^{1/2}\ \mu_B$ (μ_B is the Bohr magneton)

- $\mu_B = eh/4\pi m_e = 9.274 \times 10^{-24}$ J T^{-1}

- Since each unpaired electron has a spin ½,
- S = (½)n, where n = no. of unpaired electrons
- $\mu = \{n(n+2)\}^{1/2}\ \mu_B$

Magnetic Moment Calculation

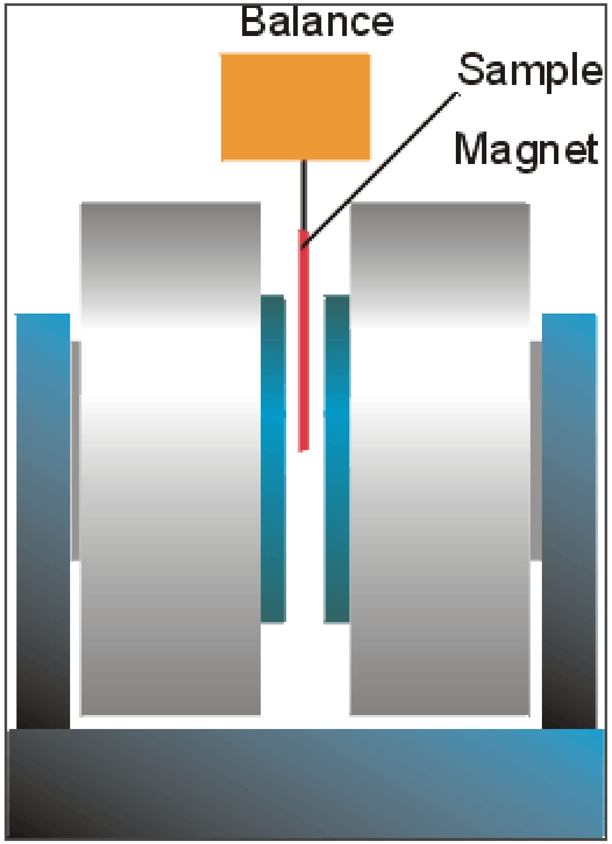
- In d^4, d^5, d^6, and d^7 octahedral complexes, magnetic measurements can very easily predict weak versus strong field.
- Tetrahedral complexes - only high spin complexes result, for $\Delta_t << \Delta_o$.

Ion	n	S	μ/μ_B Calculated	Experimental
Ti^{3+}	1	1/2	1.73	1.7 – 1.8
V^{3+}	2	1	2.83	2.7 – 2.9
Cr^{3+}	3	3/2	3.87	3.8
Mn^{3+}	4	2	4.90	4.8 – 4.9
Fe^{3+}	5	5/2	5.92	5.3

n = no. of unpaired electrons

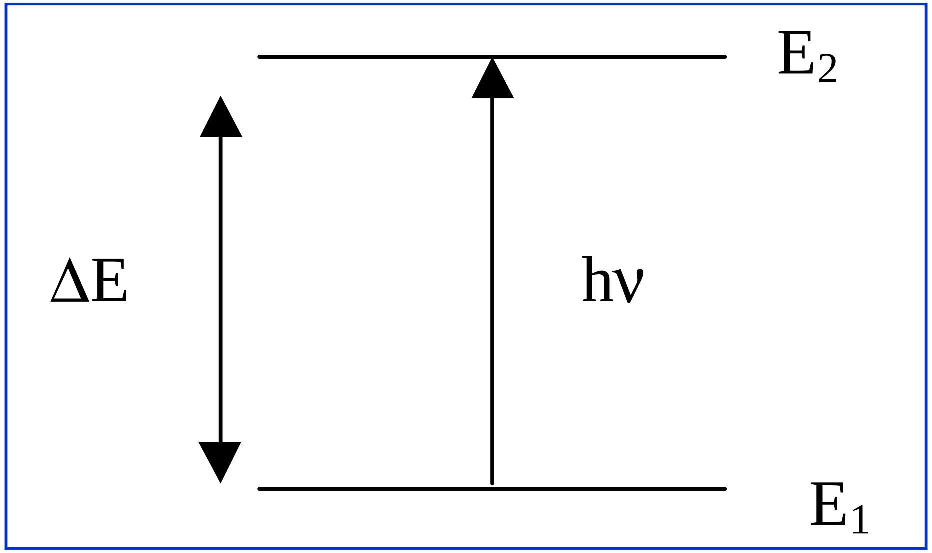
$\mu = \{n(n+2)\}^{1/2}\ \mu_B$

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

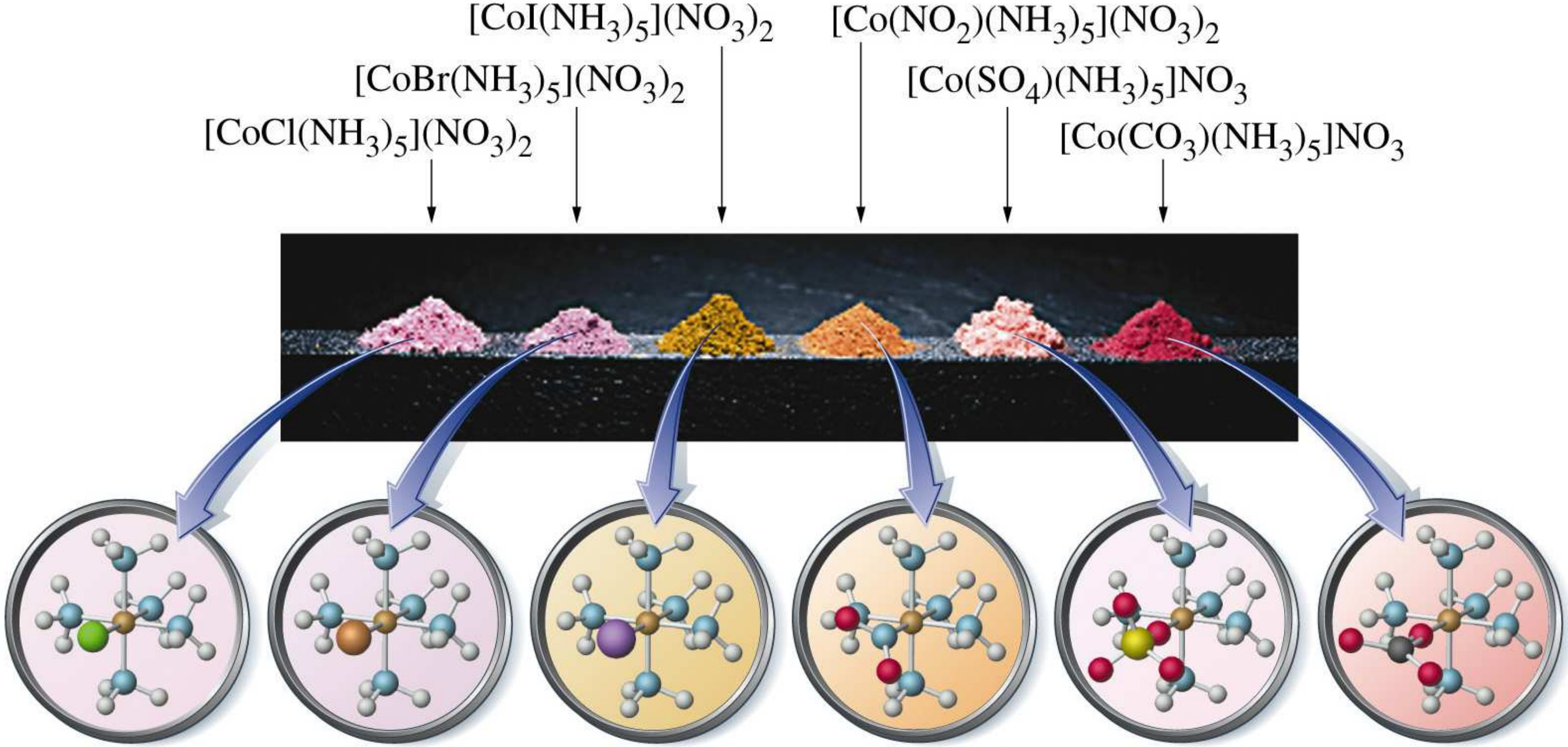
The origin of the color of the transition metal compounds



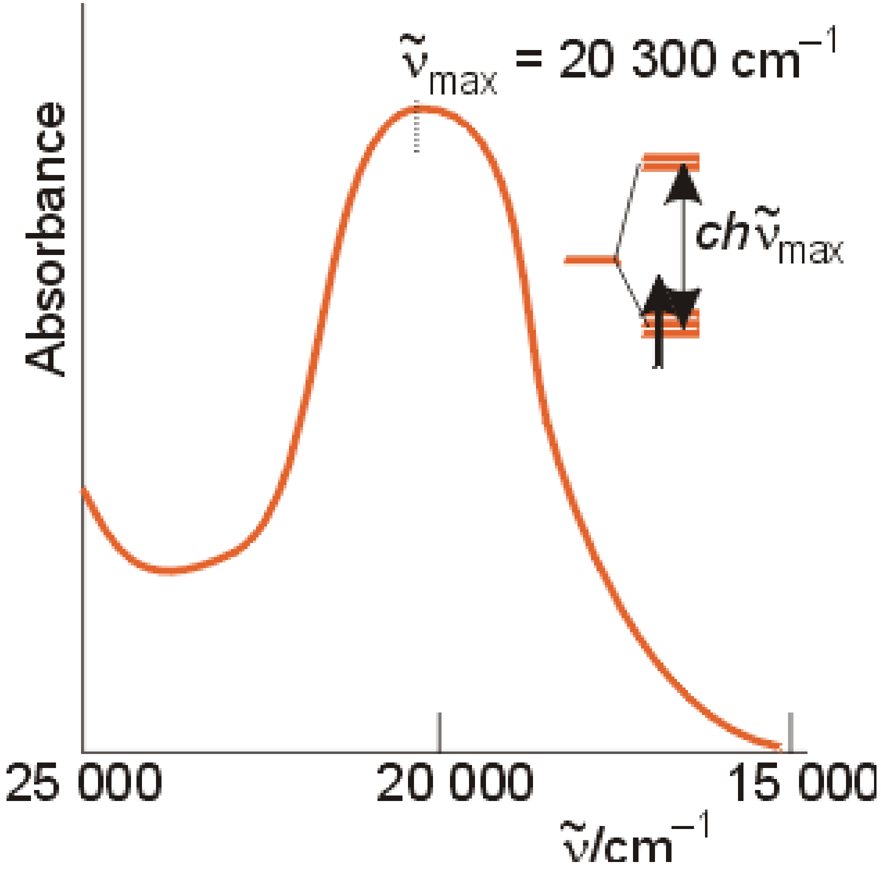
$$\Delta E = E_2 - E_1 = h\nu$$

Ligands influence Δ_o, therefore the colour originates

The colour depends on Charge of metal centre and Ligand field strength



The optical absorption spectrum of $[Ti(H_2O)_6]^{3+}$

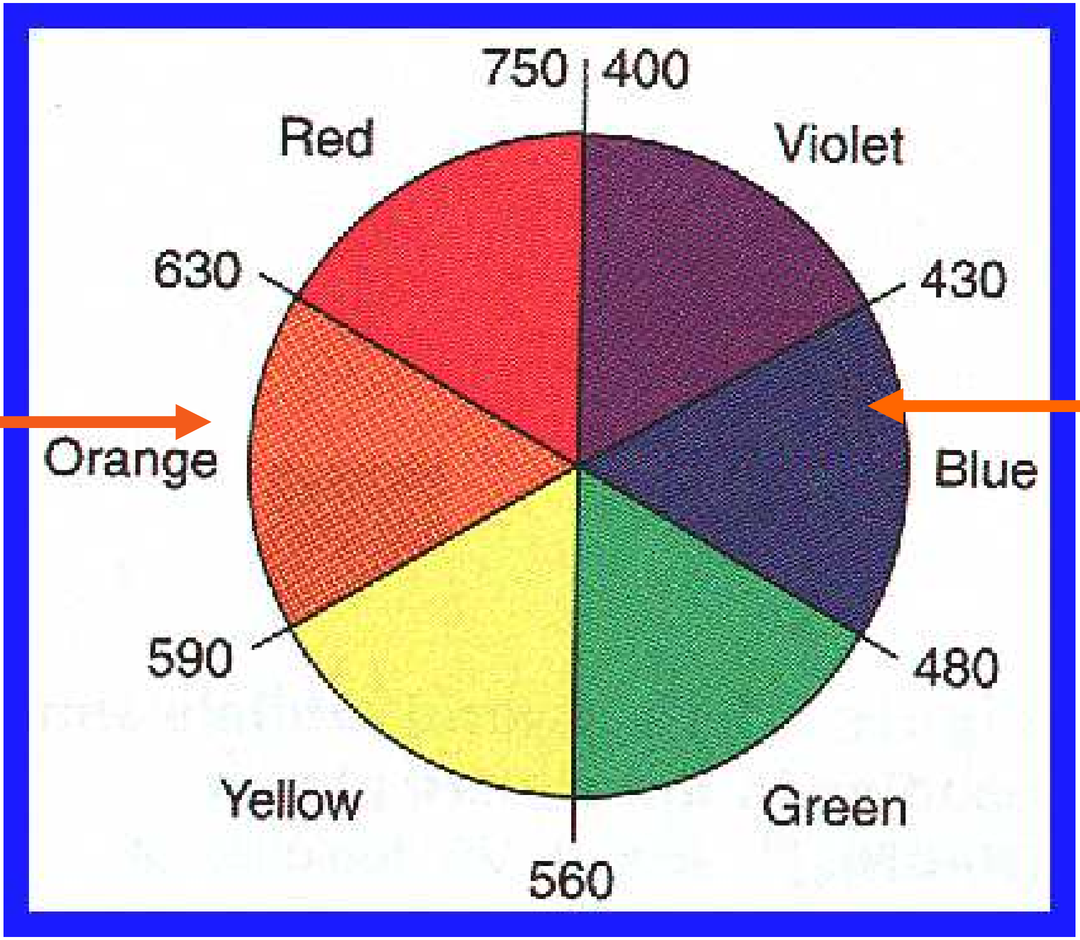


Assigned transition: $e_g \rightarrow t_{2g}$

This corresponds to the energy gap

Δ_O = 243 kJ mol^{-1}

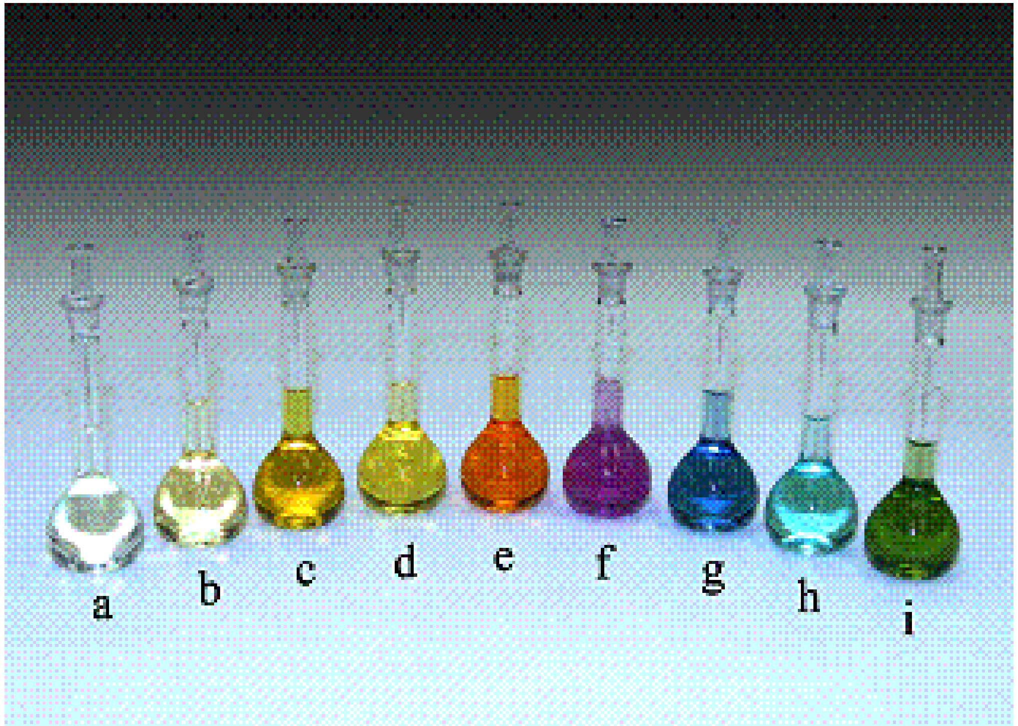
Complementary Color in optical absorption spectrum



absorbed
color

observed
color

CFT : The Spectrochemical Series



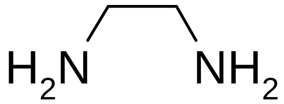
The complexes of cobalt (III) with different ligands.

(a) CN^-, (b) NO_2^-, (c) phen, (d) en, (e) NH_3, (f) gly, (g) H_2O, (h) ox^{2-}, (i) CO_3^{2-}.

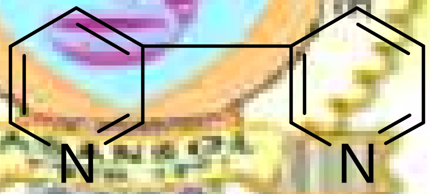
Spectrochemical Series:

An order of ligand field strength based on experiment

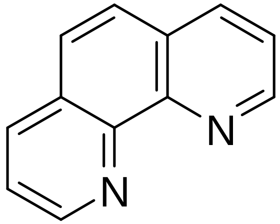
Weak Field $I^- < Br^- < S^{2-} < SCN^- < Cl^- < NO_3^- < F^- <$
$C_2O_4^{2-} < H_2O < NCS^- < CH_3CN < NH_3 <$ en $<$
bipy $<$ phen $< NO_2^- < PPh_3 < CN^- < CO$ **Strong Field**



Ethylenediamine (en)

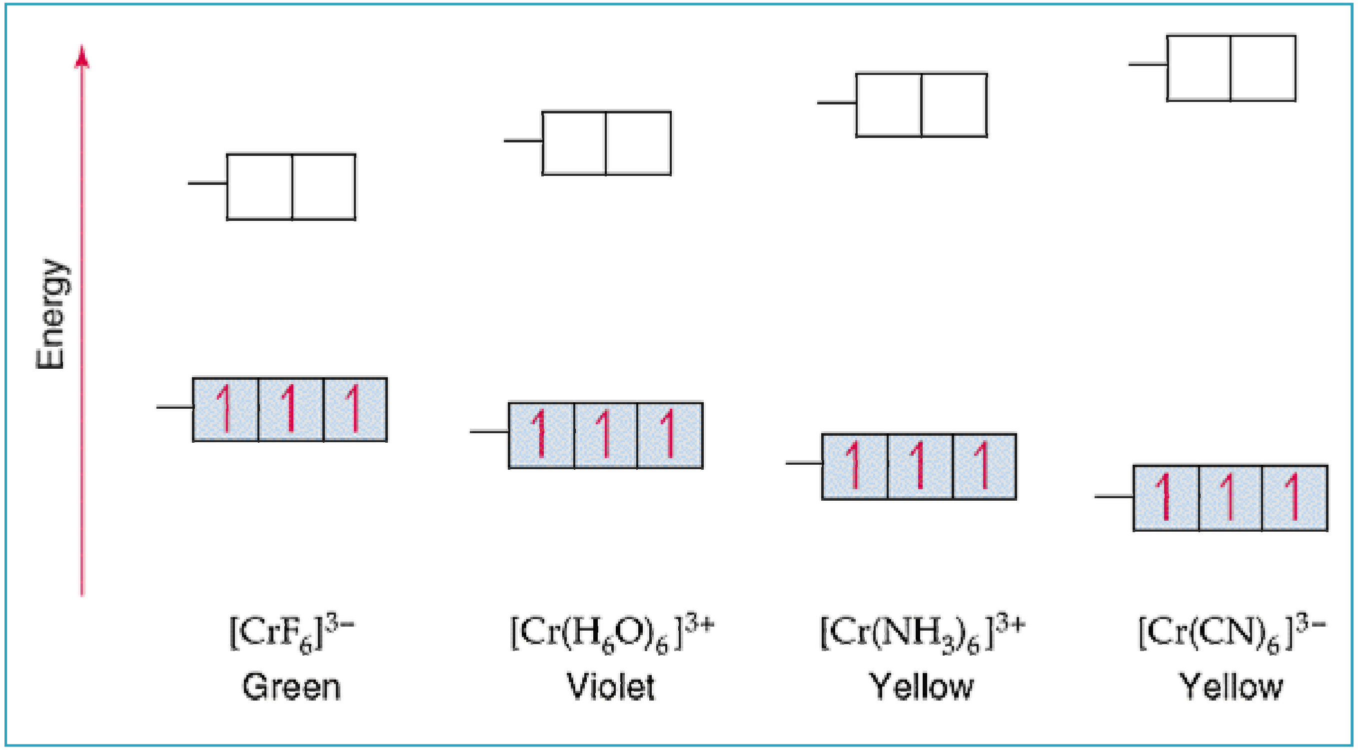


2,2'-bipyridine (bipy)



1.10 - penanthroline (phen)

Variation of color with ligand strength



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

Limitations of CFT

- Considers Ligand as Point charge/dipole only
- Does not take into account of the overlap of ligand and metal orbitals

Consequence

Fails to explain why CO is stronger ligand than CN^- in complexes having metal in low oxidation state

Ligand Field Strength Observations

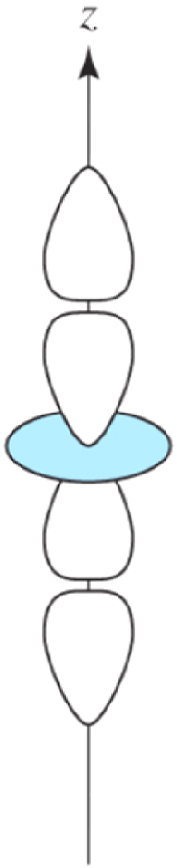
1. Δ_o increases with increasing oxidation number on the metal.

$$Mn^{+2}<Ni^{+2}<Co^{+2}<Fe^{+2}<V^{+2}<Fe^{+3}<Co^{+3}$$
$$<Mn^{+4}<Mo^{+3}<Rh^{+3}<Ru^{+3}<Pd^{+4}<Ir^{+3}<Pt^{+4}$$

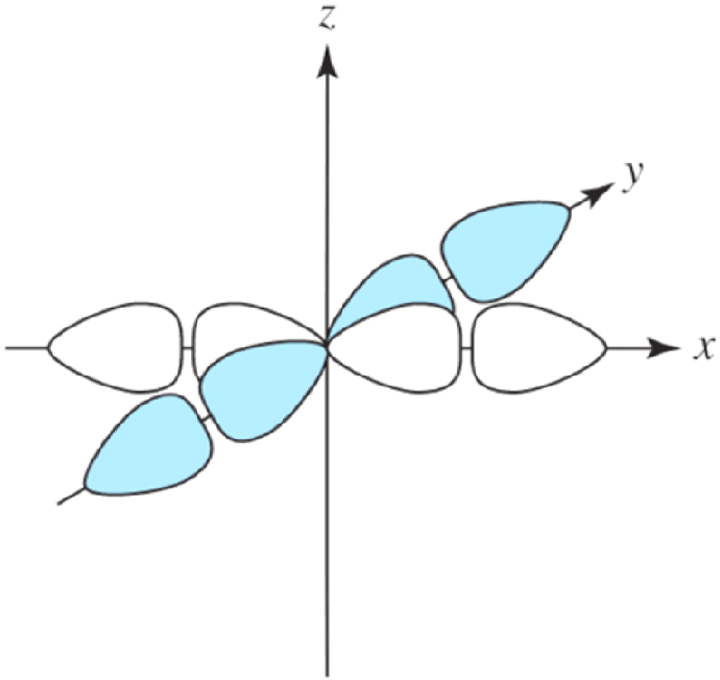
2. Δ_o increases with increases going down a group of metals.

- Crystal Field Theory completely ignores the nature of the ligand. As a result, it can not explain the spectrochemical series.
- Ligand Field Theory uses a molecular orbital approach. Initially, the ligands can be viewed as having a hybrid orbital or a *p* orbital pointing toward the metal to make σ bonds

Ligand Field Theory (LFT)



Sigma bonding interaction between two ligand orbitals and metal d_{z^2} orbital



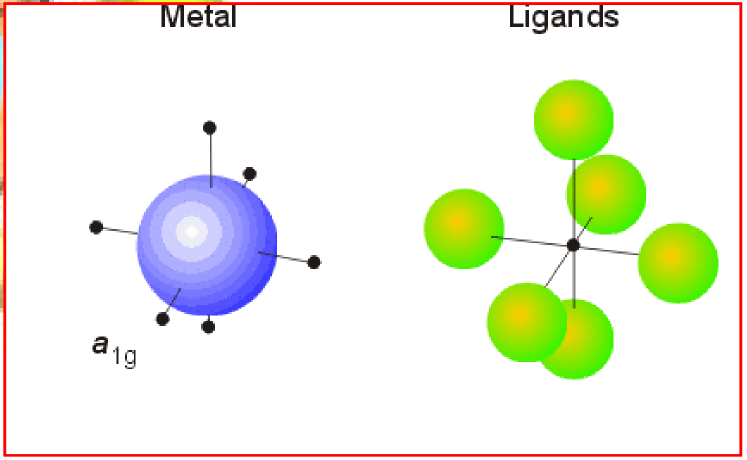
Sigma bonding interaction between four ligand orbitals and metal $d_{x^2-y^2}$ orbital

Ligand Field Theory

Consider the sigma bonds to all six ligands in octahedral geometry.

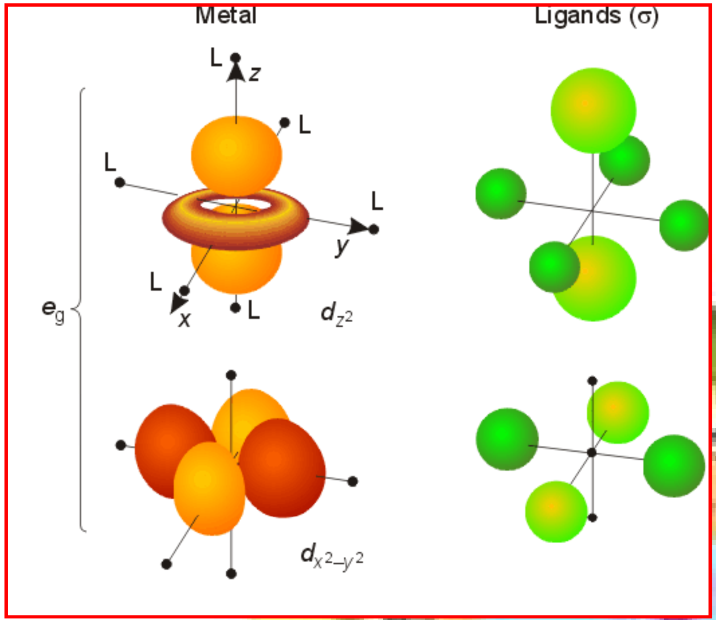
h	E	$8C_3$	$6C_2$	$6C_4$	$3C_2$ $(=C_4^2)$	i	$6S_4$	$8S_6$	$3\sigma_h$	$6\sigma_d$
Γ_σ	6	0	0	2	2	0	0	0	4	2

This reduces to $A_{1g} + E_g + T_{1u}$



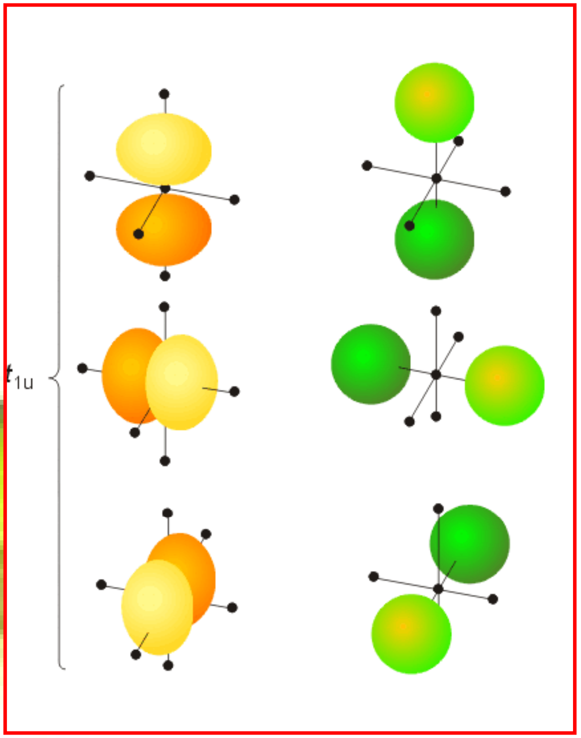
The A_{1g} group orbitals have the same symmetry as an *s* orbital on the central metal

Ligand Field Theory



The E_g group orbitals have the same symmetry as the d_z2 and $d_x2_{-y}2$ orbitals on the central metal.

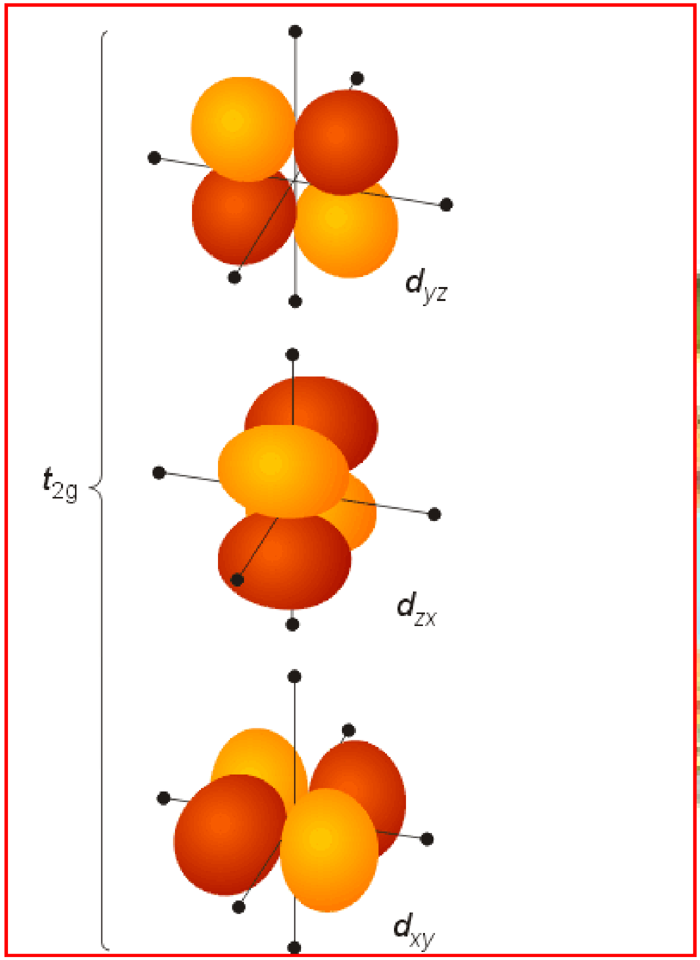
(E representations are doubly degenerate.)



The T_{1u} group orbitals have the same symmetry as the *p* orbitals on the central metal.

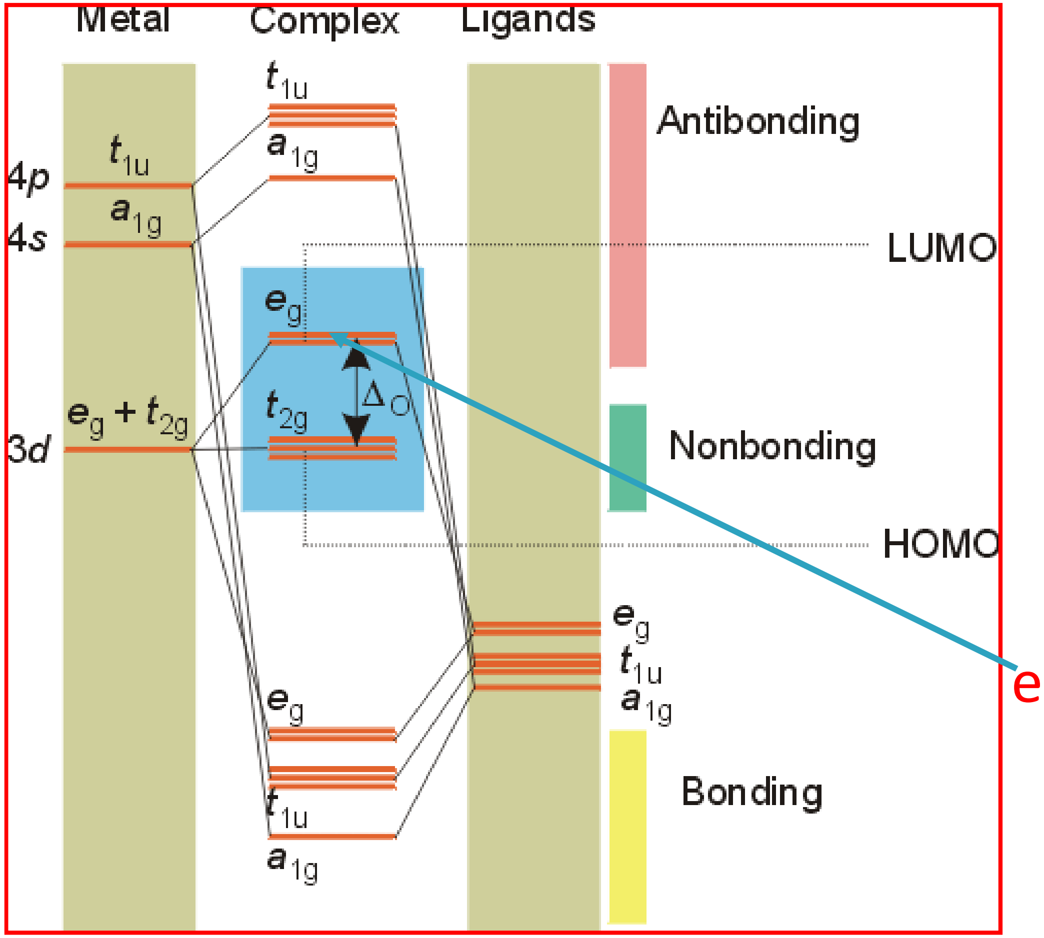
(T representations are triply degenerate.)

Ligand Field Theory



Since the ligands don’t have a combination with t_{2g} symmetry, the d_{xy}, d_{yz} and d_{xy} orbitals on the metal will be non-bonding when considering σ bonding.

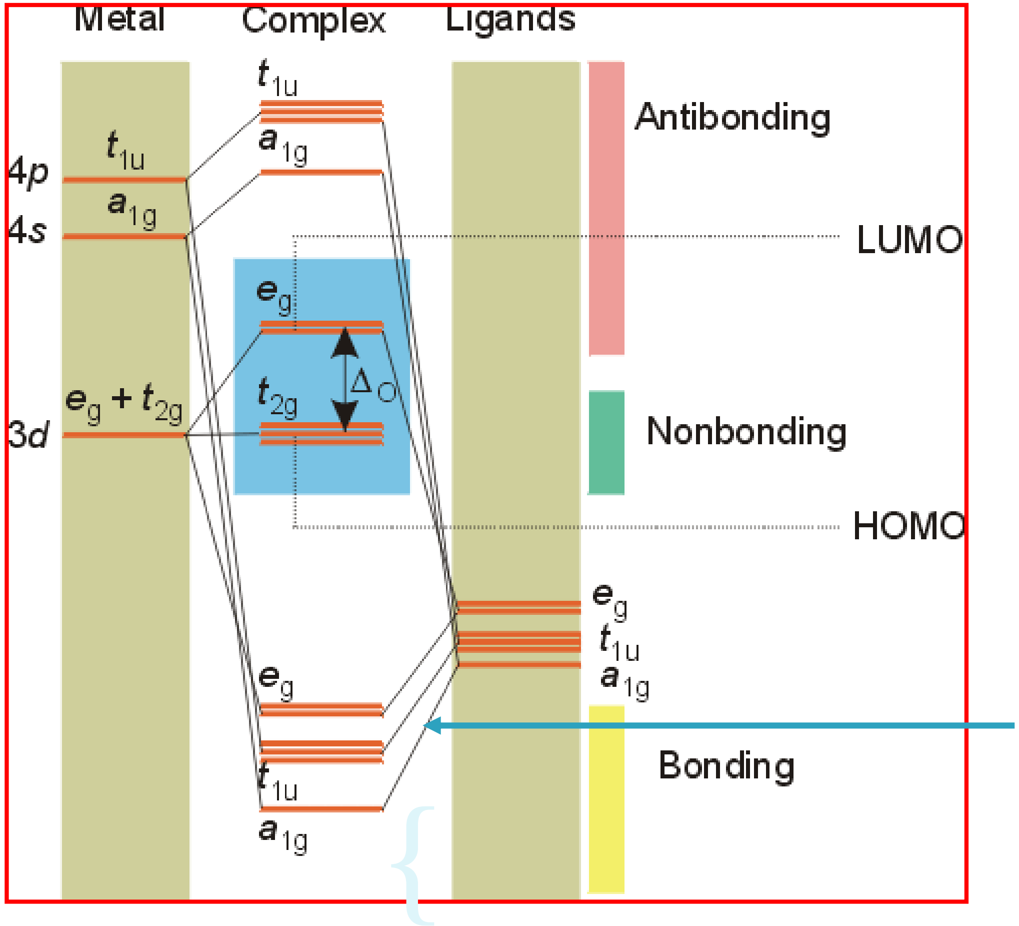
Ligand Field Theory



The molecular orbital diagram is consistent with the crystal field approach.

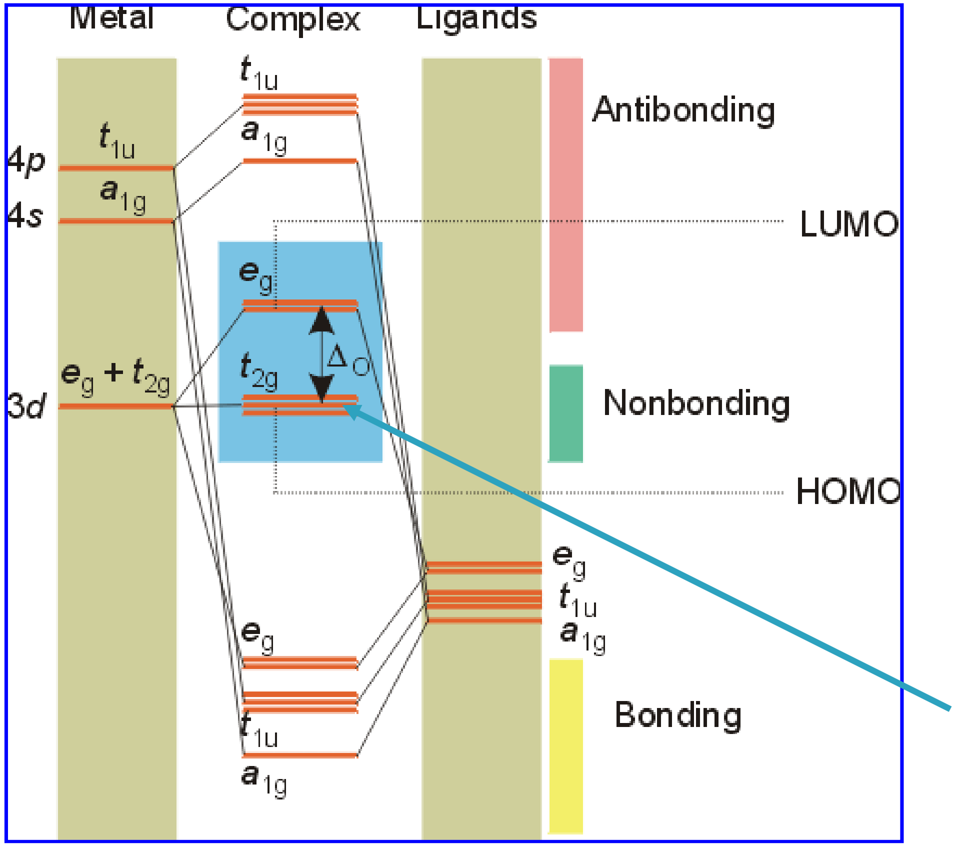
Note that the t_{2g} set of orbitals is non-bonding, and the e_g set of orbitals is antibonding.

Ligand Field Theory



The electrons from the ligands (12 electrons from 6 ligands in octahedral complexes) will fill the lower bonding orbitals.

Ligand Field Theory



The electrons from the 4s and 3d orbitals of the metal (in the first transition row) will occupy the middle portion of the diagram.

Nature of the Ligands

Crystal field theory and ligand field theory differ in that LFT considers the nature of the ligands.

Thus far, we have only viewed the ligands as electron pairs used for making σ bonds with the metal.

Many ligands can also form π bonds with the metal.

Considering π Bonding

- The LGOs symmetry are $T_{1g} + T_{2g} + T_{1u} + T_{2u}$.

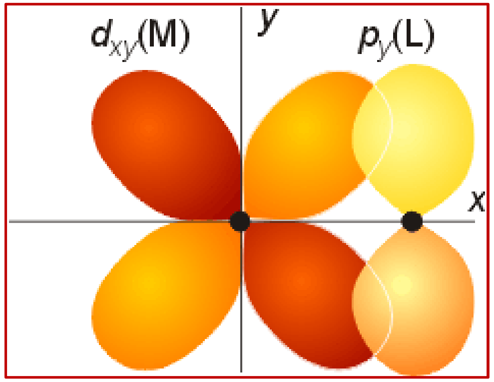
The T_{2g} set has the same symmetry as the d_{xy}, d_{yz} and d_{xz} orbitals on the metal.

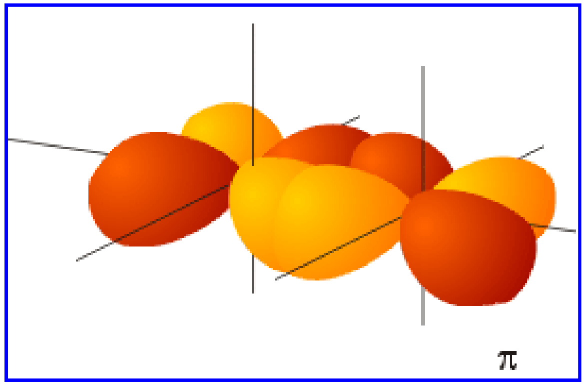
The T_{1u} set has the same symmetry as the p_x, p_y and p_z orbitals on the metal.

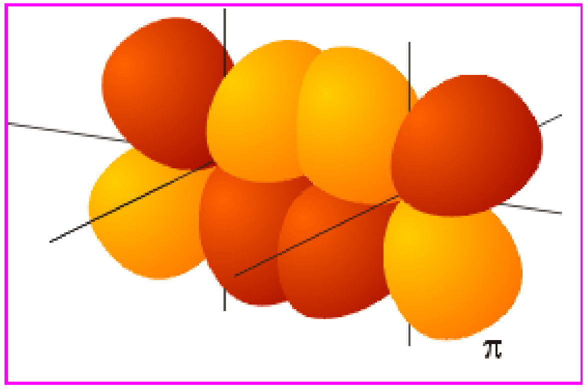
- The T_{1g} and T_{2u} group orbitals for the ligands don’t match the symmetry of any of the metal orbitals.
- The T_{1u} set has the same symmetry as the p_x, p_y and p_z orbitals on the metal. These orbitals are used primarily to make the σ bonds to the ligands.
- The T_{2g} set has the same symmetry as the d_{xy}, d_{yz} and d_{xz} orbitals on the metal.

π -Bonding

The main source of π bonding is between the d_{xy}, d_{yz} and d_{xz} orbitals on the metal and the d, p or π* orbitals on the ligand.





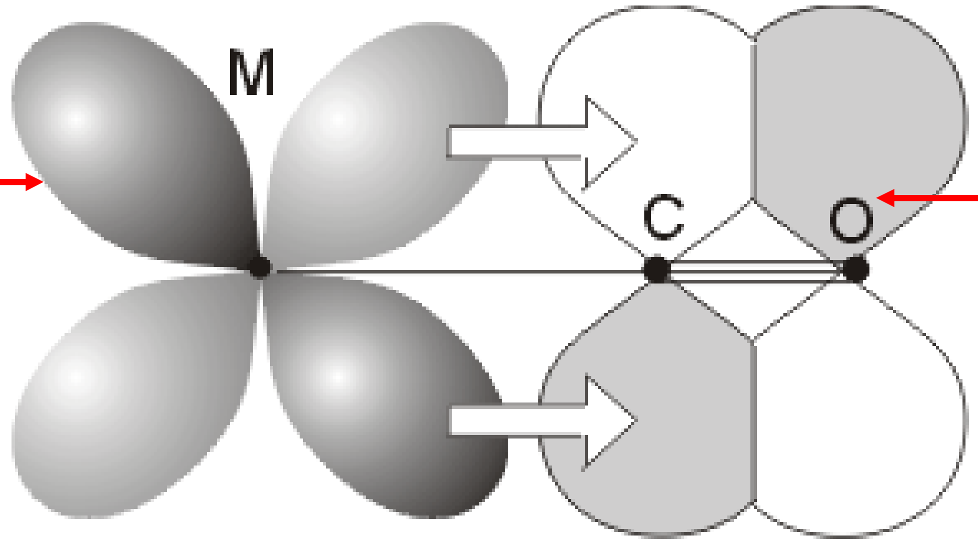


π -Bonding

- The ligand may have empty d or π* orbitals and serve as a *π acceptor* ligand, or full p or d orbitals and serve as a *π donor* ligand.

  - The empty π antibonding orbital on CO can accept electron density from a filled *d* orbital on the metal. CO is a *pi acceptor* ligand.

π- Bonding of CO molecule



filled

d -orbital

empty π*

orbital

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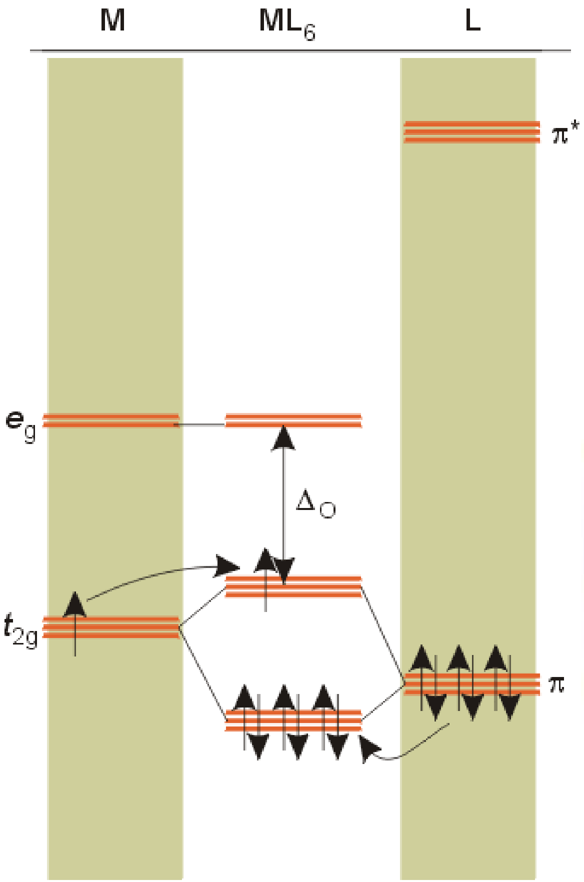
π - Donor Ligands (L→M)

All ligands are σ donors.

Ligands with filled *p* or *d* orbitals may also serve as pi donor ligands. Examples of π donor ligands are I^-, Cl^-, and S^{2-}.

The filled p or d orbitals on these ligands interact with the t_{2g} set of orbitals on the metal to form bonding and antibonding molecular orbitals.

π - Donor Ligands (L→M)



The bonding orbitals (lower in energy) are primarily filled with electrons from the ligand and the antibonding molecular orbitals are primarily occupied by electrons from the metal.

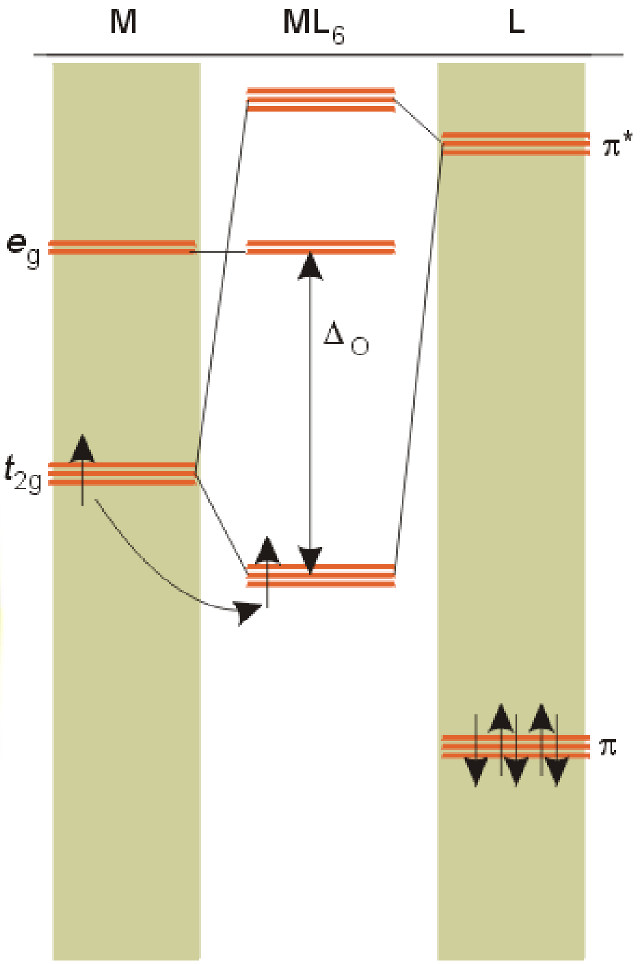
The Δ_o value decreases, since it is now between an antibonding t_{2g} orbital and the e_g* orbital. This is confirmed by the spectrochemical series. Weak field ligands are also pi donor ligands

π - Acceptor Ligands (M→L)

- Ligands such as CN^-, N_2 and CO have empty π antibonding orbitals of the proper symmetry and energy.
- The empty π antibonding orbitals interact with filled *d* orbitals on the metal
- The π* orbitals on the ligand are usually higher in energy than the d orbitals on the metal

π Acceptor Ligands (M→L)

The metal uses the t_{2g} set of orbitals pi bonding with the ligand π* orbitals usually higher in energy than the d orbitals on the metal.



The interaction lowers the energy of the t_{2g} bonding orbitals thus increasing the Δ_o value.

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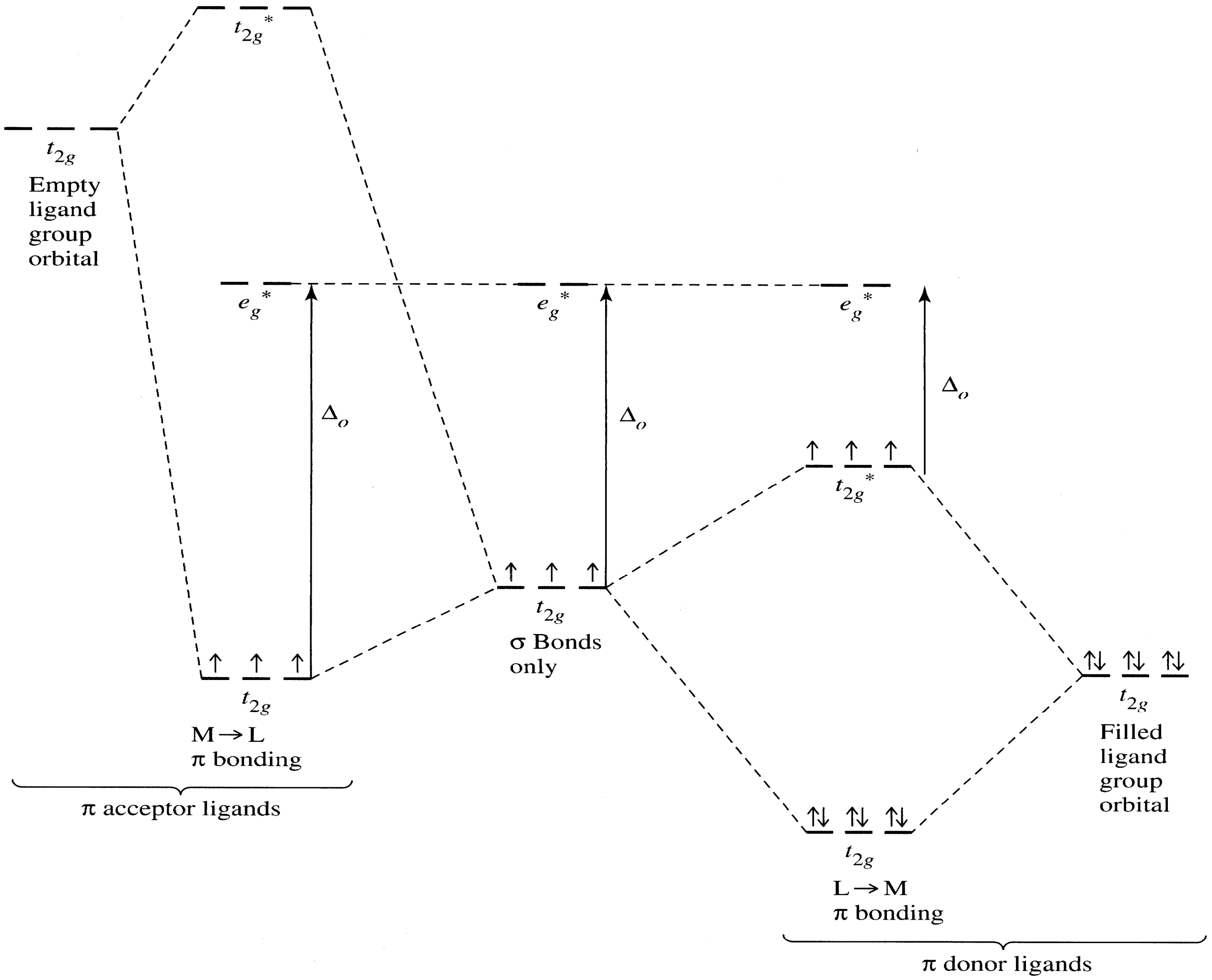
π- Acceptor (left) and π- Donor (right) Ligands



Summary

1. All ligands are σ donors. In general, ligand that engage solely in σ bonding are in the middle of the spectrochemical series. Some very strong σ donors, such as CH_3^- and H^- are found high in the series.

2. Ligands with filled *p* or *d* orbitals can also serve as π donors. This results in a smaller value of Δ_o.

3. Ligands with empty *p*, *d* or π* orbitals can also serve as π acceptors. This results in a larger value of Δ_o.

$$I^-<Br^-<Cl^-<F^-<H_2O<NH_3<PPh_3<CO$$

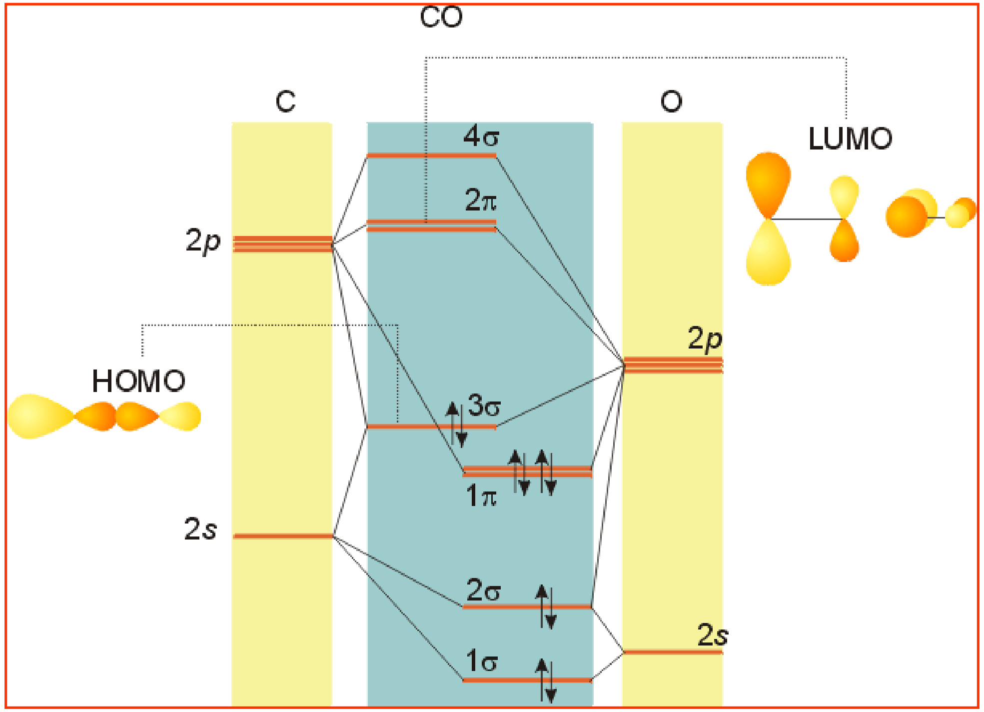
π donor< weak π donor<σ only< π acceptor

Metals in Low Oxidation States

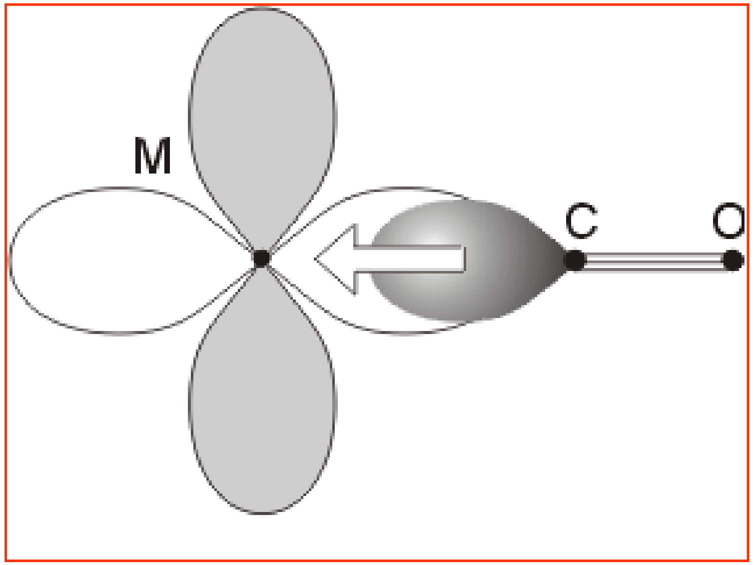
- In low oxidation states, the electron density on the metal ion is very high.
- To stabilize low oxidation states, we require ligands, which can simultaneously bind the metal center and also withdraw electron density from it.

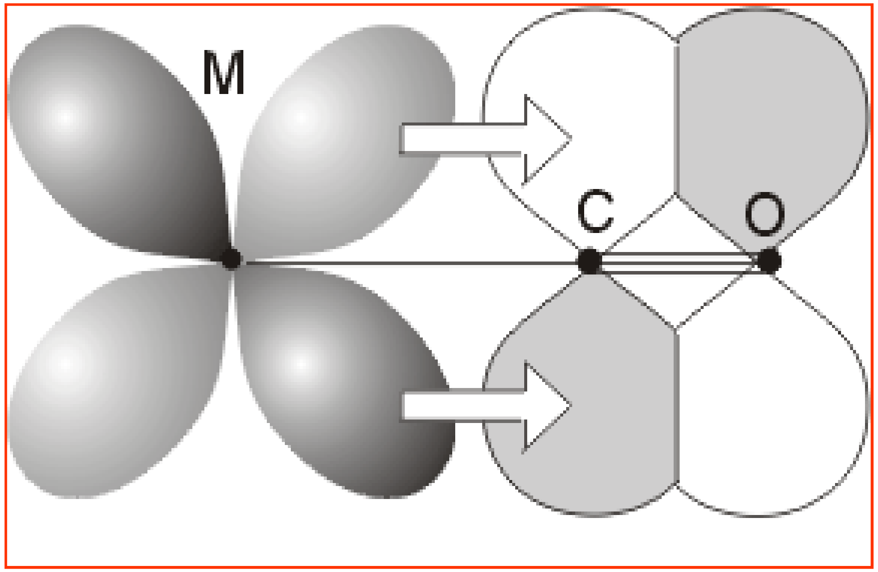
Stabilization of Low Oxidation State:

CO can do the Job



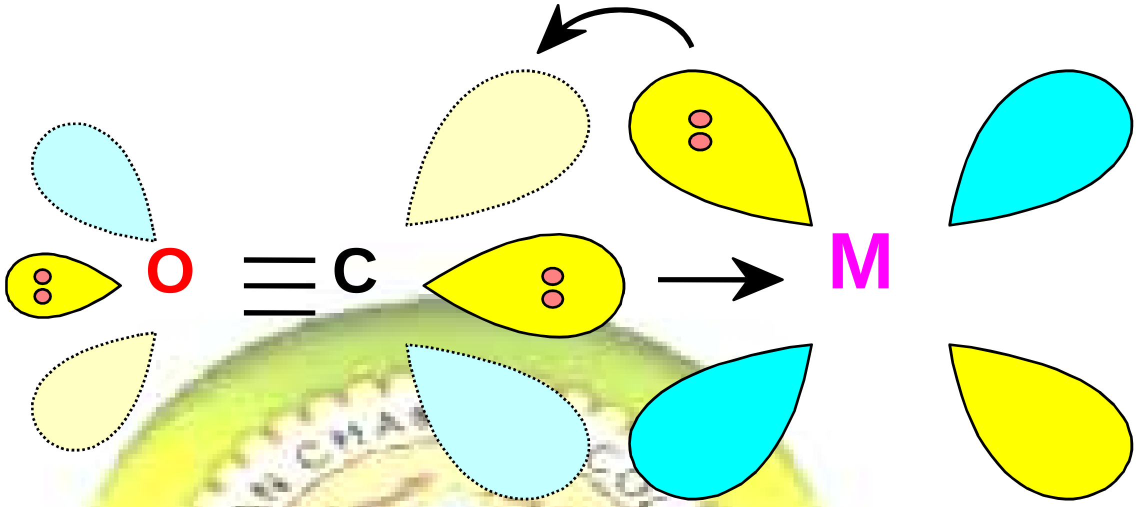
Stabilization of Low Oxidation State:



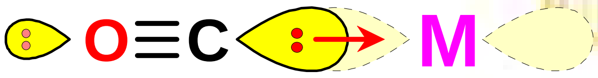


$Ni(CO)_4$], [$Fe(CO)_5$], [$Cr(CO)_6$], [$Mn_2(CO)_{10}$], [$Co_2(CO)_8$],
Na_2[$Fe(CO)_4$], Na[$Mn(CO)_5$]

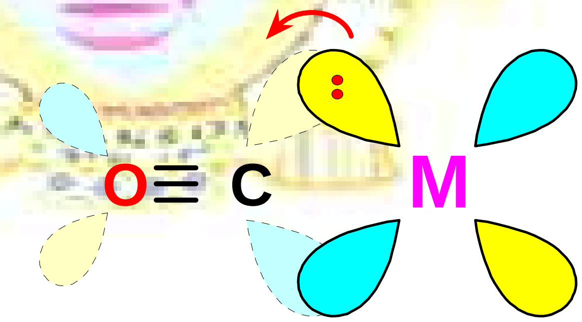
CO Ligand: σ (sigma) donor π (pi) acceptor



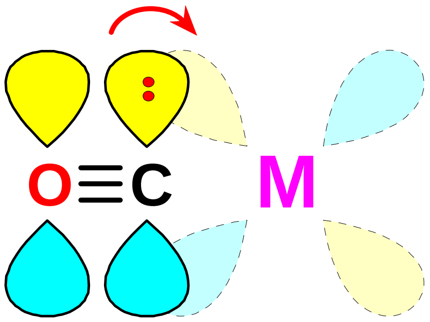
σ orbital serves as a very weak donor to a metal atom



CO-M sigma bond



M to CO pi backbonding



CO to M pi bonding
(rare)

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