

Lecture 3

Ligands and Bonding and Electron
Counting in Organo-Transition Metal
Compounds

Classification of Ligands: II

The L, X, Z approach

Malcolm Green : The CBC Method for Covalent Bond Classification used extensively in organometallic chemistry.

- L** ligands are derived from charge-neutral precursors: NH_3 , amines, N-heterocycles such as pyridine, PR_3 , CO, alkenes etc.
- X** ligands are derived from anionic precursors: halides, hydroxide, alkoxide alkyls—species that are one-electron neutral ligands, but two electron donors as anionic ligands. [EDTA](#)⁴⁻ is classified as an L_2X_4 ligand, features four anions and two neutral donor sites. C_5H_5 is classified an L_2X ligand.
- Z** ligands are RARE. They accept two electrons from the metal center. They donate none. The “ligand” is a Lewis Acid that accepts electrons rather than the Lewis Bases of the X and L ligands that donate electrons.

Table 3-1 Electron Counting Schemes for Common Ligands

Ligand	Method A	Method B
H	2 (:H^-)	1
F, Cl, Br, I	2 (:X^-)	1
OH	2 (:OH^-)	1
CN	2 ($\text{:C}\equiv\text{N:}^-$)	1
CH_3	2 (:CH_3^-)	1
NO (bent M–N–O)	2 (:N=O:^-)	1
<u>CO, PR_3</u>	2	2
NH_3 , H_2O	2	2
$=\text{CRR}'$ (carbene)	2	2
$\text{H}_2\text{C}=\text{CH}_2$	2	2
$=\text{O}$, $=\text{S}$	4 (:O^{2-} , :S^{2-})	2
NO (linear M–N–O)	2 ($\text{:N}\equiv\text{O:}^+$)	3
$\eta^3\text{-C}_3\text{H}_5$ (allyl)	2 (C_3H_5^+)	3
$\equiv\text{CR}$ (carbyne)	3	3
$\equiv\text{N}$	6 (N^{3-})	3
$\eta^4\text{-C}_4\text{H}_6$ (butadiene)	4	4
<u>$\eta^5\text{-C}_5\text{H}_5$</u> (cyclopentadienyl)	6 (C_5H_5^-)	5
$\eta^6\text{-C}_6\text{H}_6$ (benzene)	6	6
$\eta^7\text{-C}_7\text{H}_7$ (tropylium ion)	6 (C_7H_7^+)	7

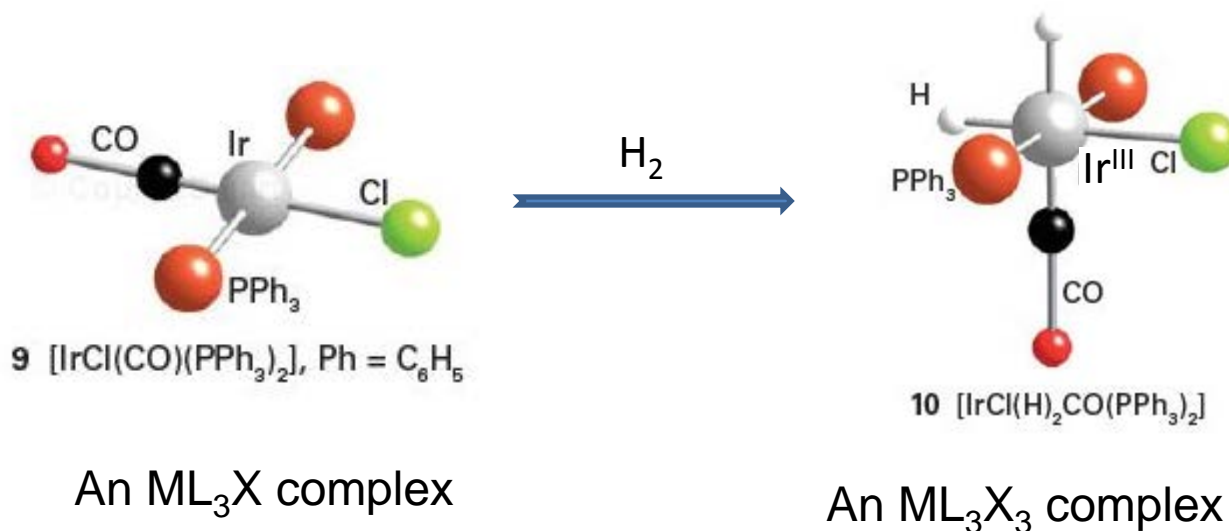
Illustration from page 57

Where are the electrons?

Show me the electrons!!

*Electron counting and the 18-electron "Rule"
(Guide is better. It is the "octet" rule for
transition metals—but not
so rigorously obeyed.)*

Oxidative addition of H_2 to chloro carbonyl bis triphenylphosphine Iridium(I) yields Chloro-dihydrido-carbonyl bis-triphenylphosphine Iridium(III). Note the neutral precursor, H_2 , becomes two X^- ligands once added to Ir.



Electron count: 16 e

18 e

$\text{Ir(I)} \text{ d}^8 = 8 \text{ e}$

$\text{Ir(III)} \text{ d}^6 = 6 \text{ e}$

L ligands: $2 \times (2) + 2 = 6$

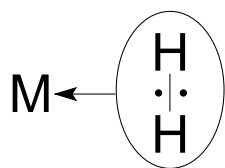
3 L ligands: $3 \times 2 = 6$

X- ligand: 2

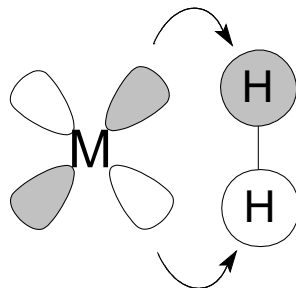
3 X⁻ ligands: $3 \times 2 = 6$

The $\eta^2\text{-H}_2$ Complexes

- Typically d^6 , Oh structures of Cr^0 , Mo^0 , W^0 , Fe^{II} , Ru^{II} , Ir^{III} .
- Bonding: Delicate Balance Required for Stability



σ - donor



σ^* acceptor



$\text{M}^{2+}(\text{H}^-)_2$



Kubas, LANL

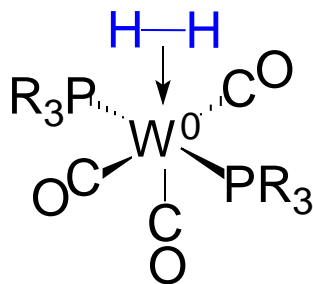


Morris, U. Toronto

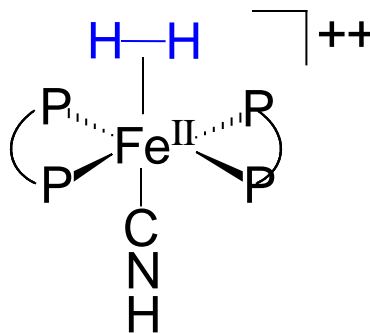


Crabtree, Yale

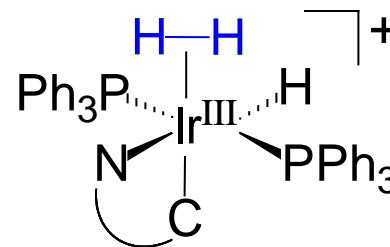
- Examples of $\eta^2\text{-H}_2$ complexes



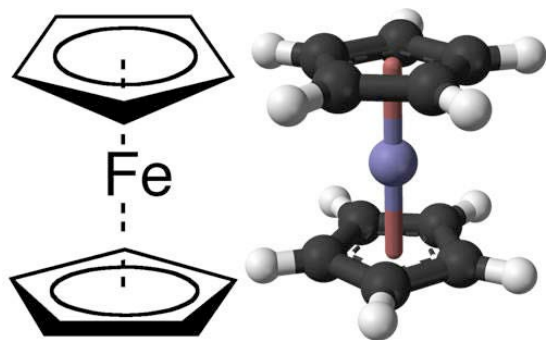
Kubas



Morris

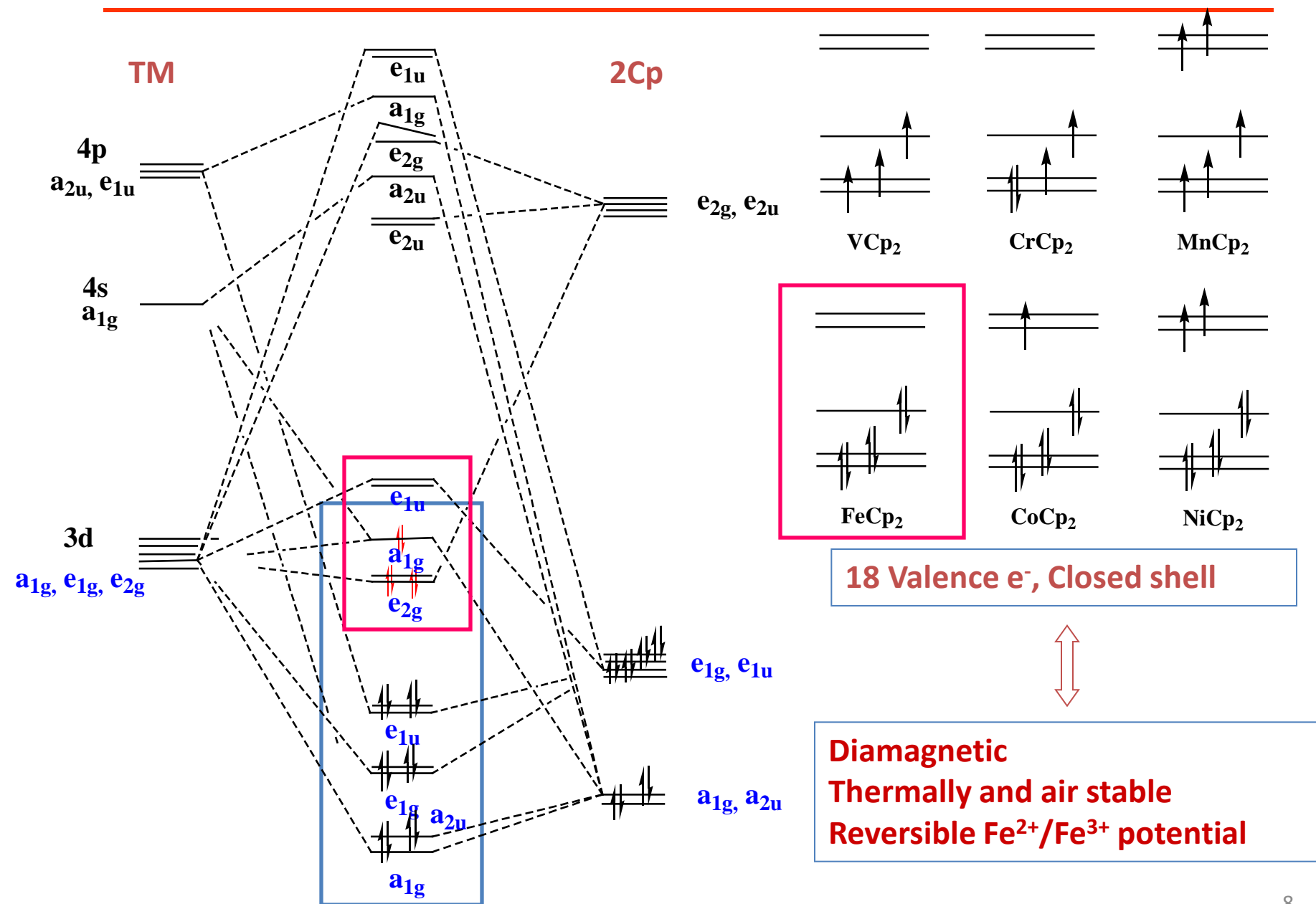


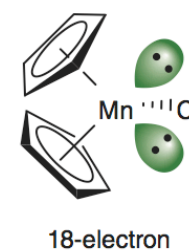
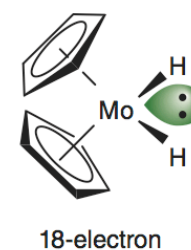
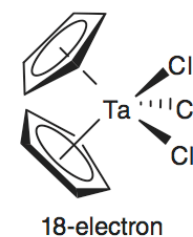
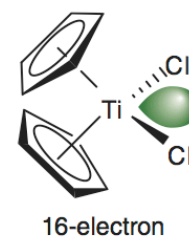
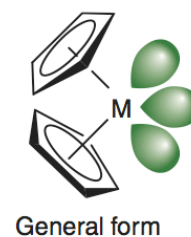
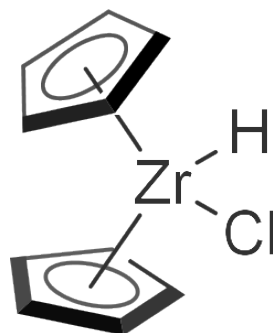
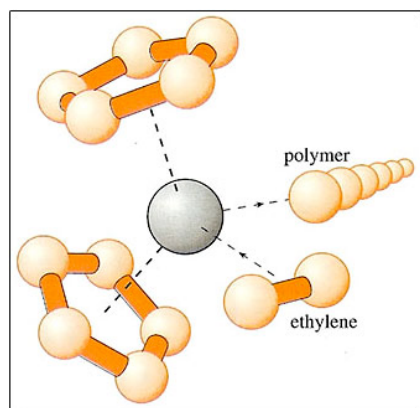
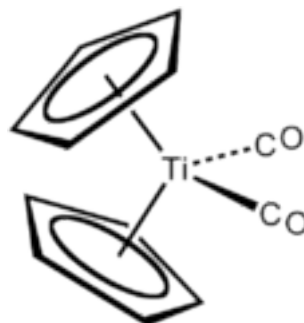
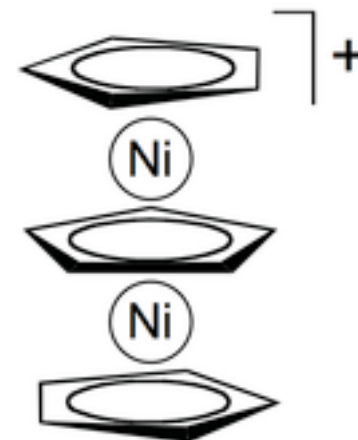
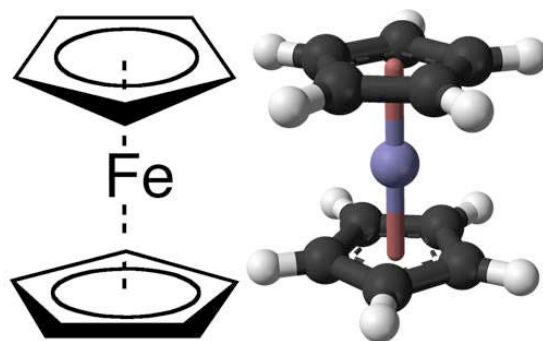
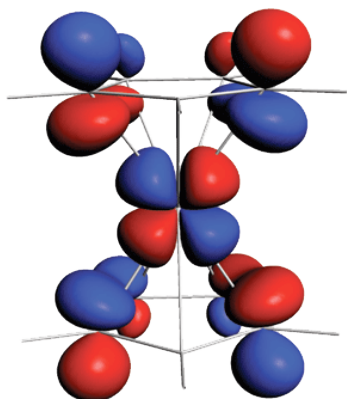
Crabtree



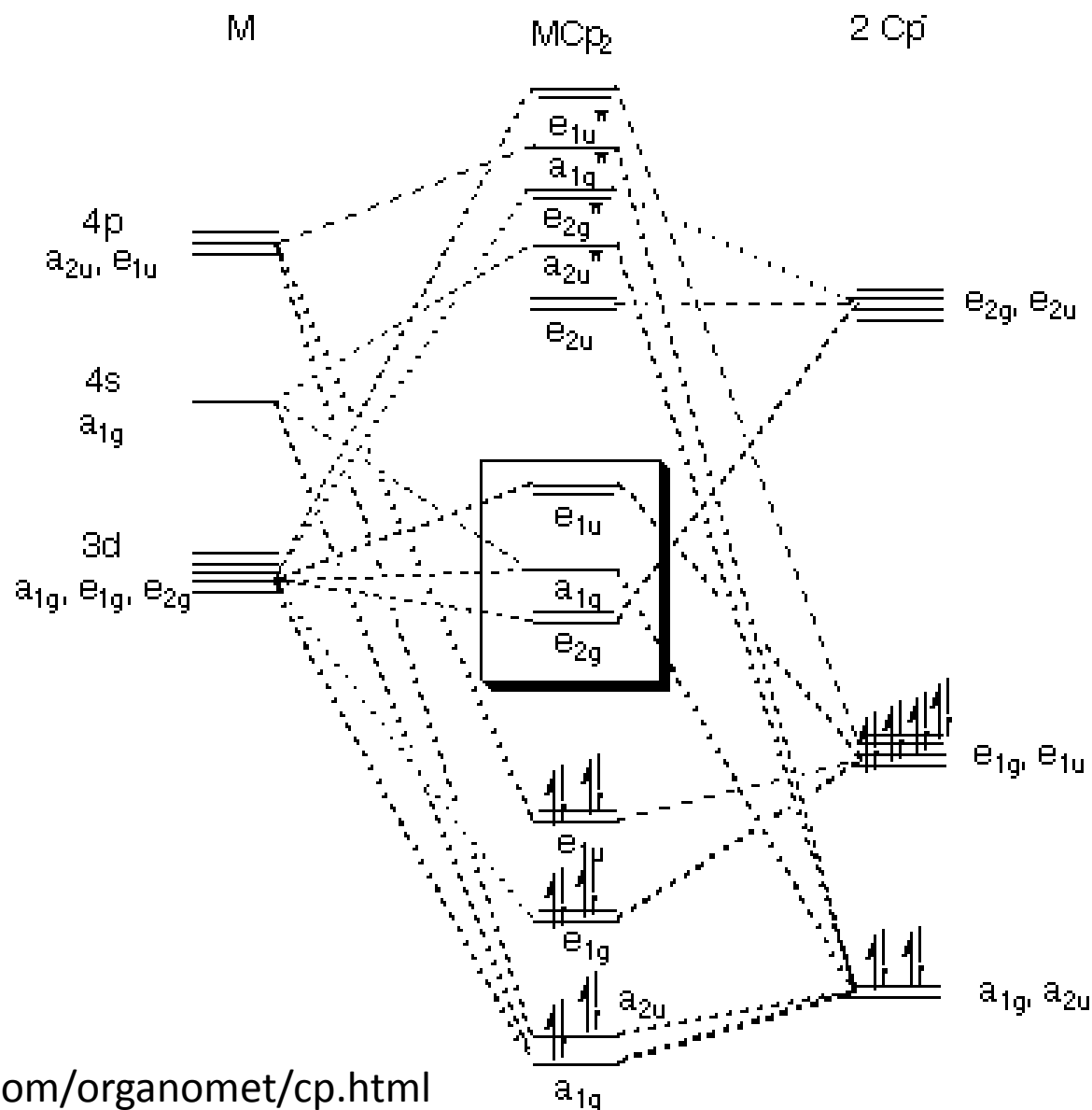
Questions/classwork

Electronic structure and properties



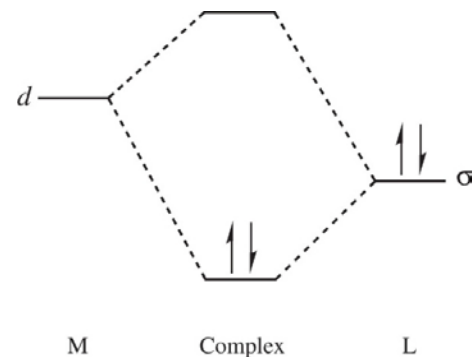
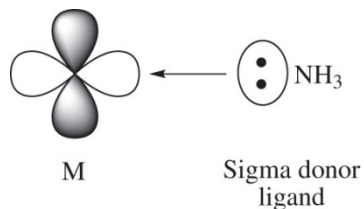


MO Energy Level Diagram for ferrocene and related metallocenes

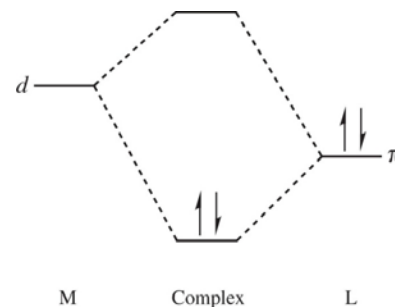
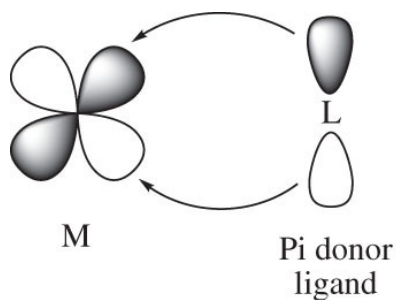


Types of ligands: σ -donor, π -donating and π -accepting

σ -donor



π -donor



π -accepting

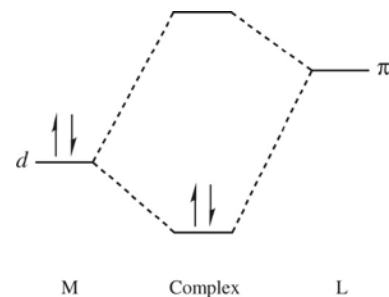
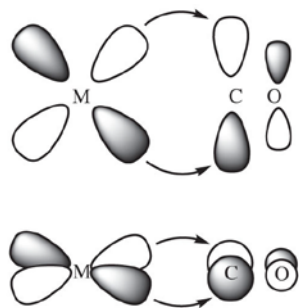


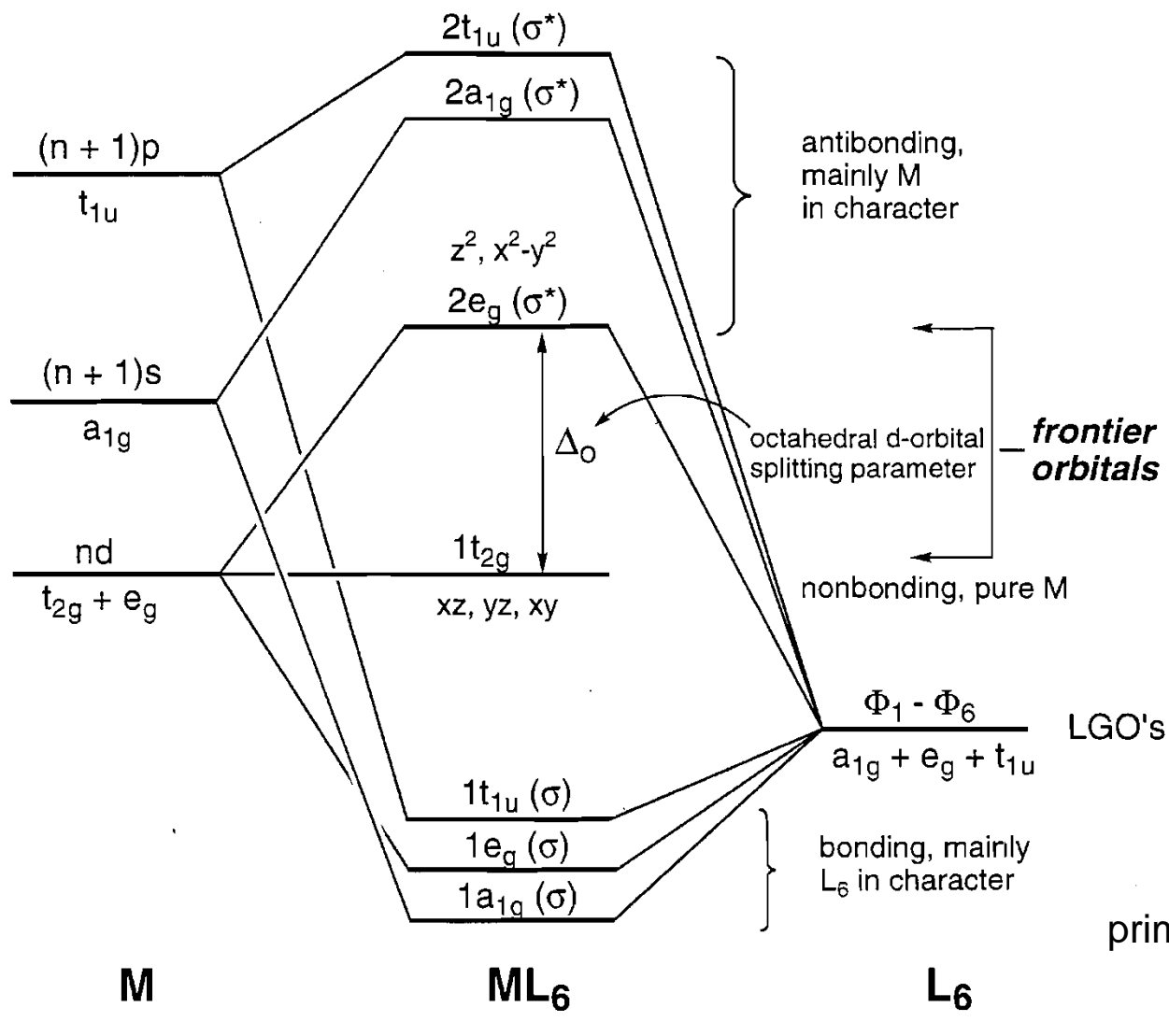
Table 3-2 Examples of Donor and Acceptor Ligands.

σ Donor	π Donor ^a	π Acceptor ^a
NH ₃	OH ⁻	CO
H ₂ O	Cl ⁻	CN ⁻
H ⁻	RCO ₂ ⁻	PR ₃

^aThese ligands also act as σ donors.

Illustration from page 64

To explain magnetism and colors, need electronic configuration of the Transition Metal Complex: MO diagram for σ -donor ligand in octahedral complex



Simplified MO energy level diagram for $\text{Cr}(\text{CO})_6$. Note the empty π^* orbitals. Only three are involved in overlap with metal d orbitals.

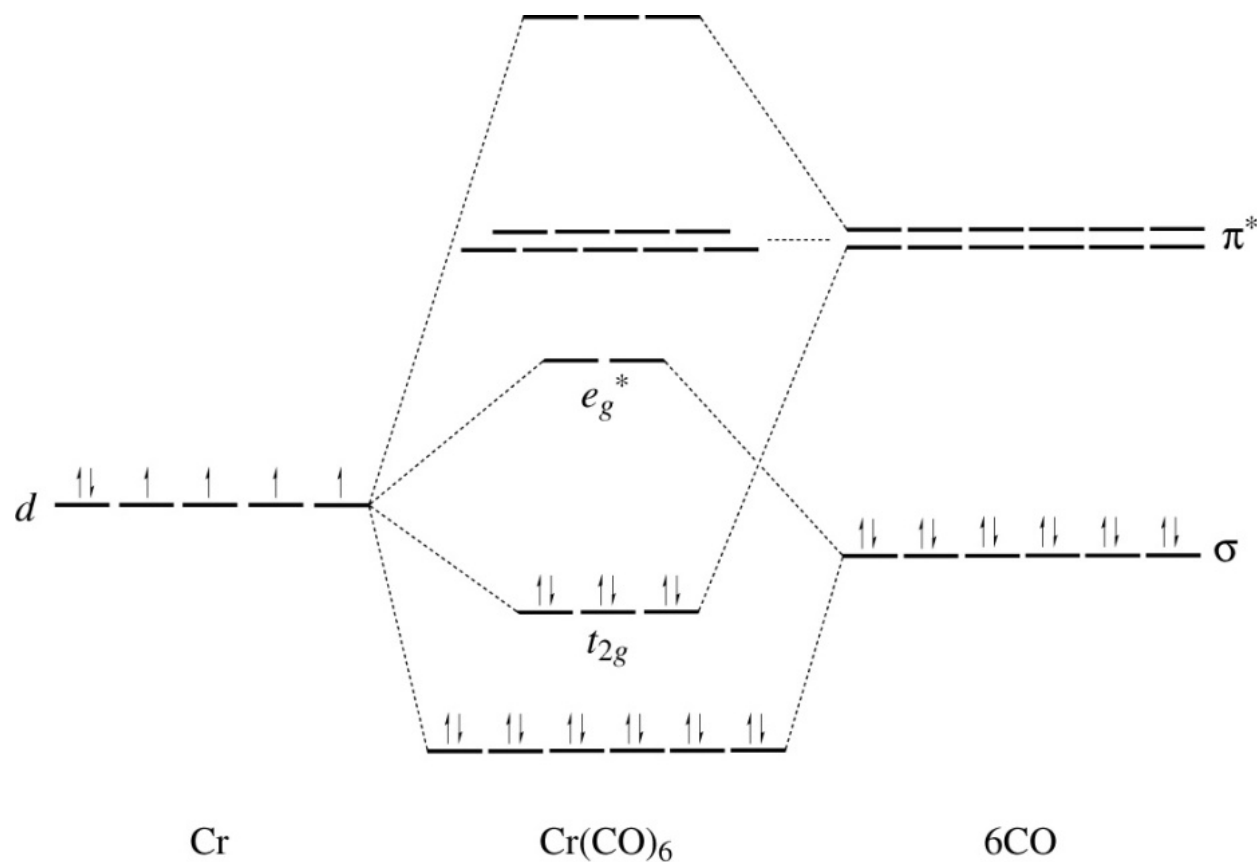
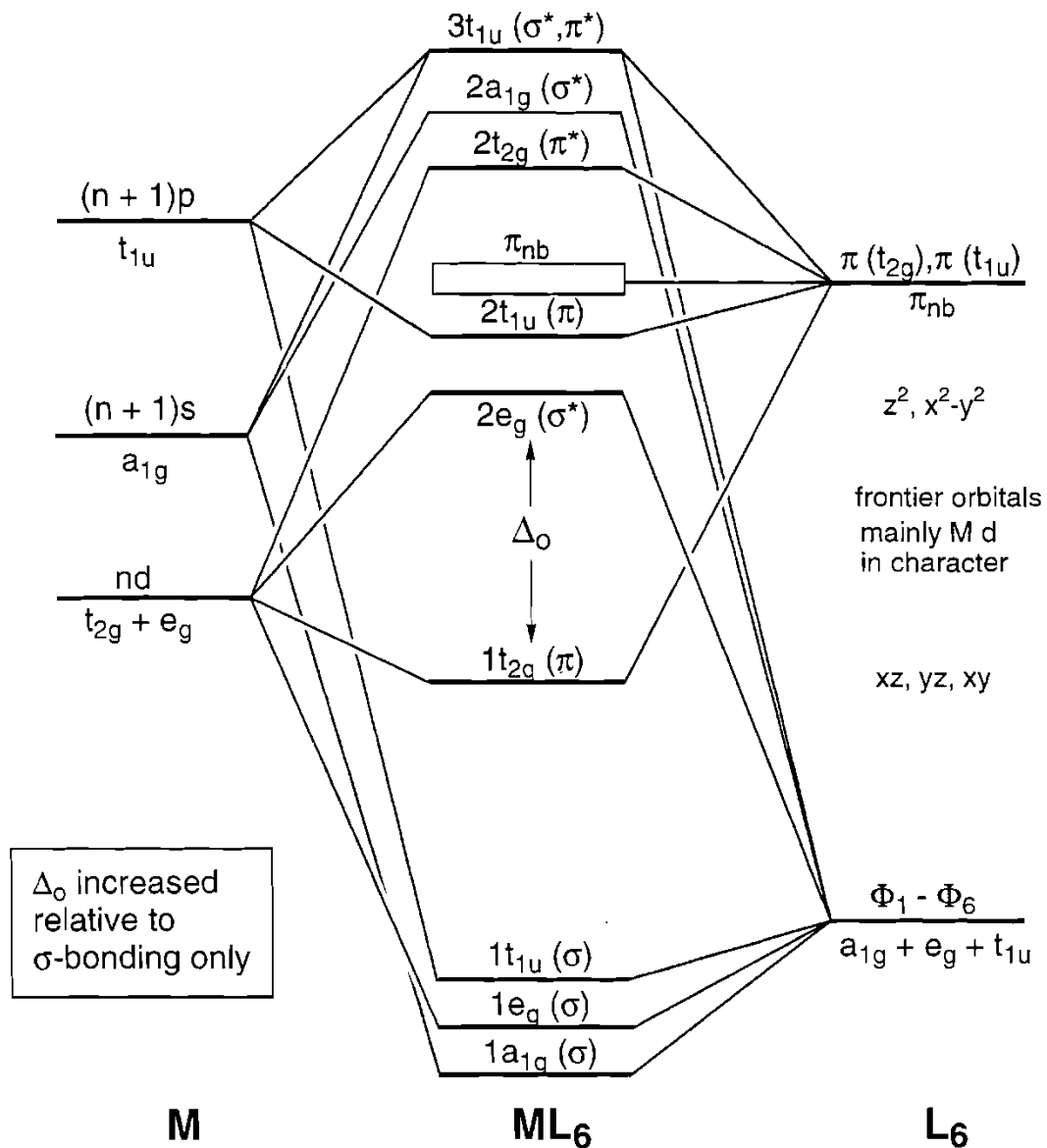


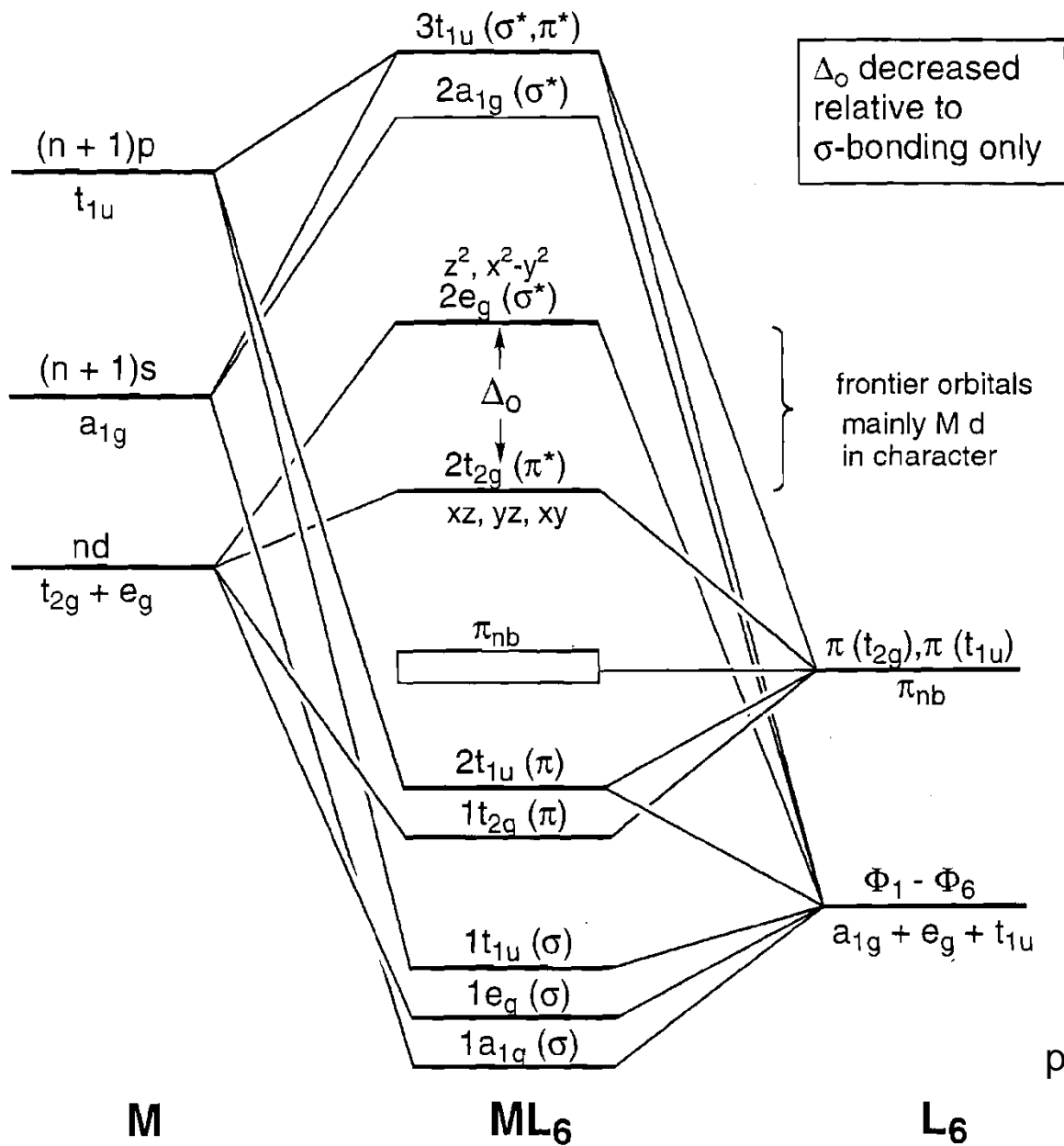
Figure 3-1 Molecular orbitals of $\text{Cr}(\text{CO})_6$ (Only interactions between Ligand (σ - and π^*) orbitals and metal d-orbitals are shown.)

Case 2. $L\pi$ orbitals vacant and less stable than $d\pi$ orbitals
(L is a π -acceptor)

A more accurate MO energy level diagram for $\text{Cr}(\text{CO})_6$.



Case 1. $L\pi$ orbitals filled and more stable than $d\pi$ orbitals
(L is a π -donor)



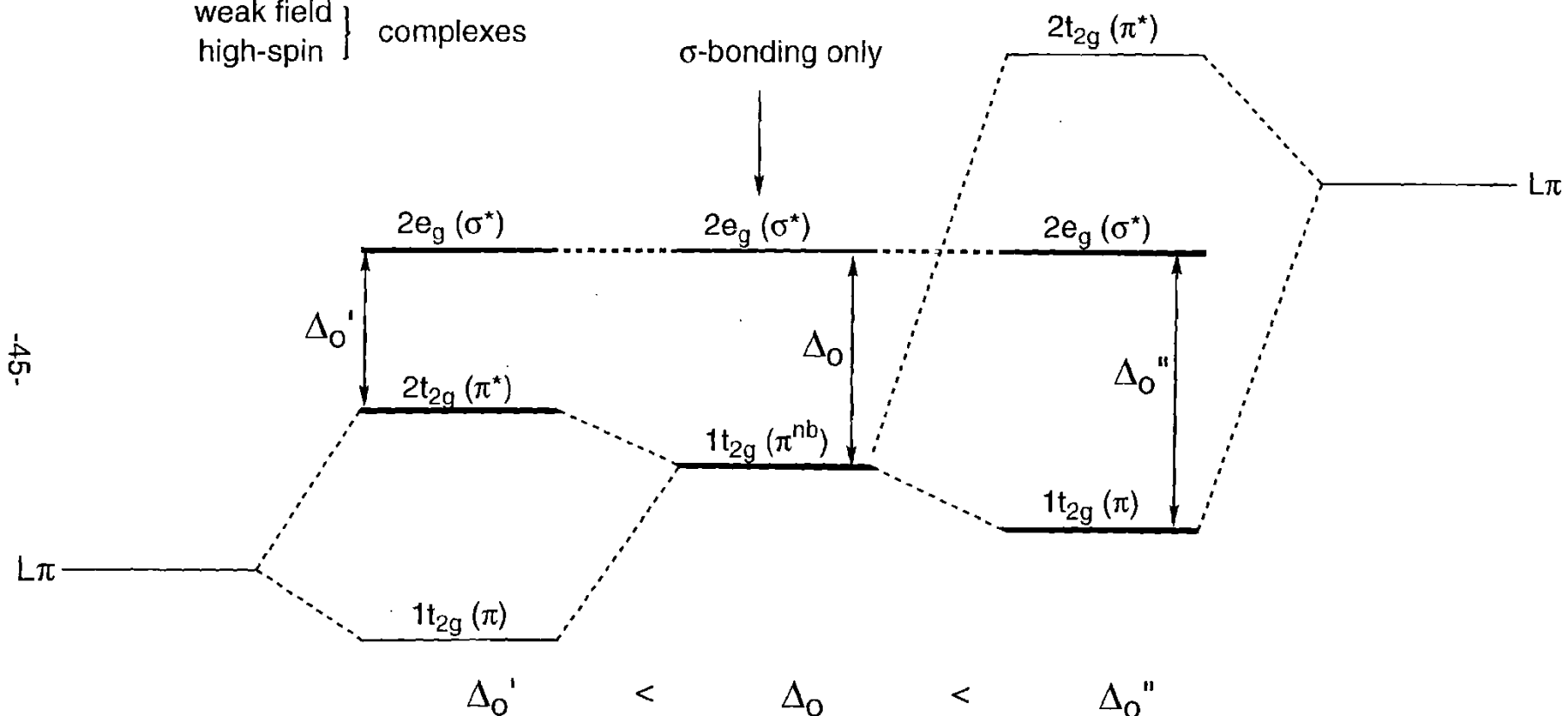
Important Cases of d-Orbital Splittings in Octahedral Complexes

Case 1. $L\pi$ orbitals filled and more stable than $d\pi$ orbitals. L are π -donors.

— mainly M orbitals
 — mainly L orbitals

Case 2. $L\pi$ orbitals vacant and less stable than $d\pi$ orbitals. L are π -acceptors.

weak field } complexes
 high-spin }



$L_{\pi\text{-donor}} = F^-, Cl^-, Br^-, I^-, H_2O, OH^-,$
 $RS^-, S^{2-}, NCS^-, NCO^-, \dots$

(virtually any ligand which, after forming
 M-L σ -bonds, has lone pairs)

$L_{\sigma} = NR_3$

PR_3

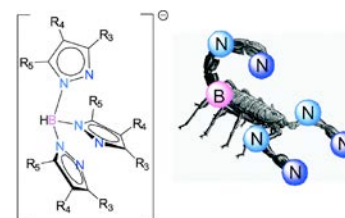
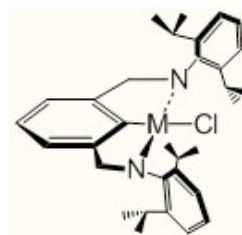
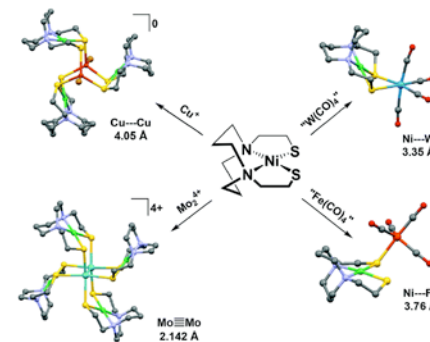
$L_{\pi\text{-acceptor}} = CO, NO, CN^-, N_2, \text{bipy}, \text{phen},$
 $RNC, C_5H_5^-, \text{alkenes}, \text{alkynes}$

(virtually any ligand with vacant
 π^* MO's)

Classification of Ligands: III

Terminology and description of properties

- ❑ Strong Field/Weak Field Ligands
- ❑ Chelating Ligands and Denticity
 - ❖ Polydentate: bi-, tri-, tetra, penta-
 - ❖ Hexadentate, etc.
- ❑ Bridging Ligands
 - ❖ 4-electron bridge; 3 center, 4 electrons
 - ❖ 2-electron bridge; 3-center, 2 electrons
- ❑ Ambidentate Ligands
- ❑ Bulky Ligands
- ❑ Chiral Ligands
- ❑ Hemi-labile Ligands
- ❑ Non-innocent Ligands
- ❑ Spectator Ligands
- ❑ Designer Ligands
 - ◆ Pincer
 - ◆ Scorpionate
 - ◆ Metallodithiolates



So, how do we mix and match these ligands and metals with their various oxidation states to get stable molecules?

1. Hard/Soft Acid Base approach to stability

2. Knowledge of preferred coordination numbers and geometries

The Chemical Bond:

- a) The sharing of an electron pair between two atoms.
- b) A mixture of electrostatic and covalent interactions.

Together these interactions lead to stable molecules.

Now, How about those colors and the magnetism in Werner type complexes?

Where are the electrons? Show me the electrons!!

Color: *Electronic transitions due to energy levels whose gaps are in the visible range of the electromagnetic spectrum.*

Magnetism: *partially filled orbitals, unpaired electrons.*

high spin: maximum no. of d electrons

unpaired

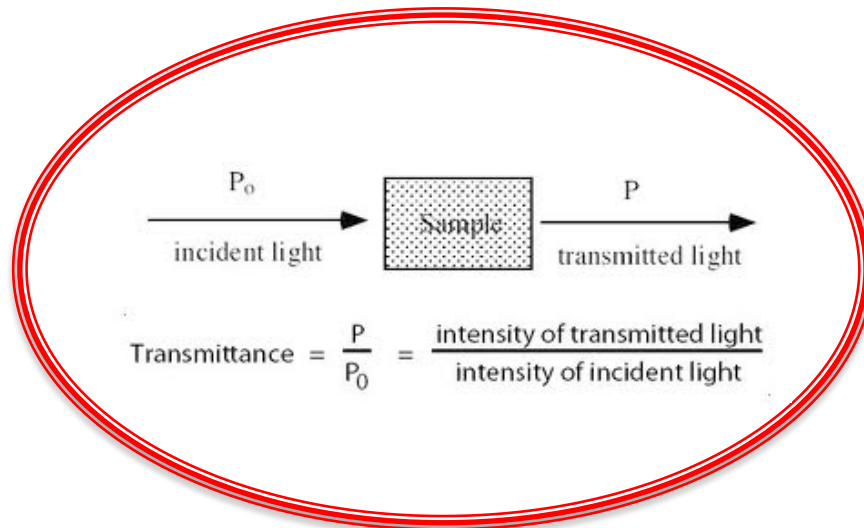
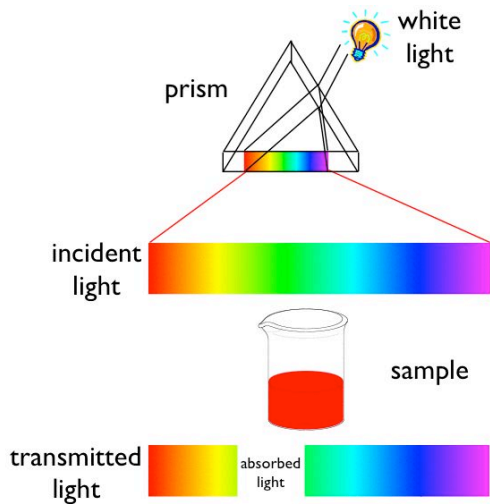
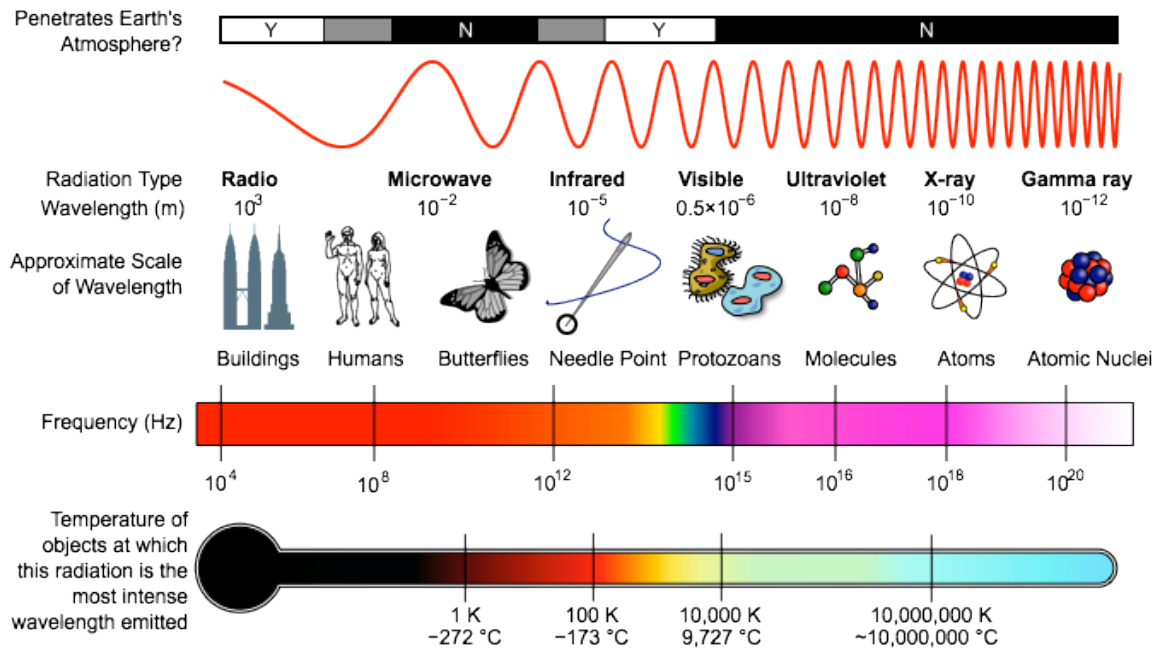
low spin: electrons paired up in d orbitals. WHY??

Bonding models:

Valence bond (coordinate covalent bond needs empty orbitals on metal)

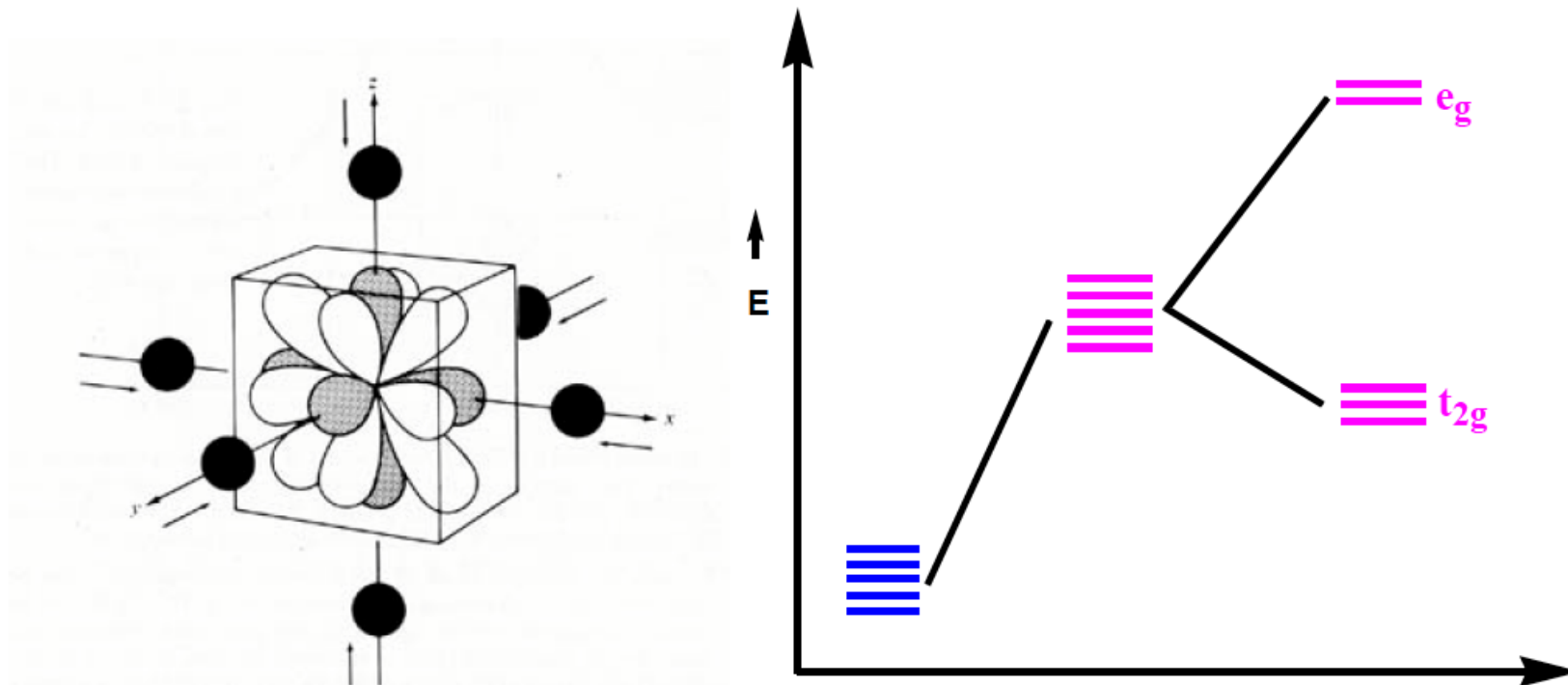
Crystal Field Theory (originally from ionic crystals; influence of ligand lone pair repulsion on d-orbitals)

Molecular Orbital Theory (all orbitals defined)



Octahedral Field

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



• Not all d orbitals will interact to the same extent with the six point charges located on the +x, -x, +y, -y, +z and -z axes respectively.

• The orbitals which lie along these axes (i.e. x^2-y^2 , z^2) will be destabilized more than the orbitals which lie in-between the axes (i.e. xy, xz, yz).

CFT-Octahedral Complexes

- For the O_h point group, the x^2-y^2 , z^2 orbitals belong to the E_g irreducible representation and xy , xz , yz belong to the T_{2g} representation.
- The extent to which these two sets of orbitals are split is denoted by Δ_o or alternatively $10Dq$. As the **baricenter** must be conserved on going from a spherical field to an octahedral field, the t_{2g} set must be stabilized as much as the e_g set is destabilized.

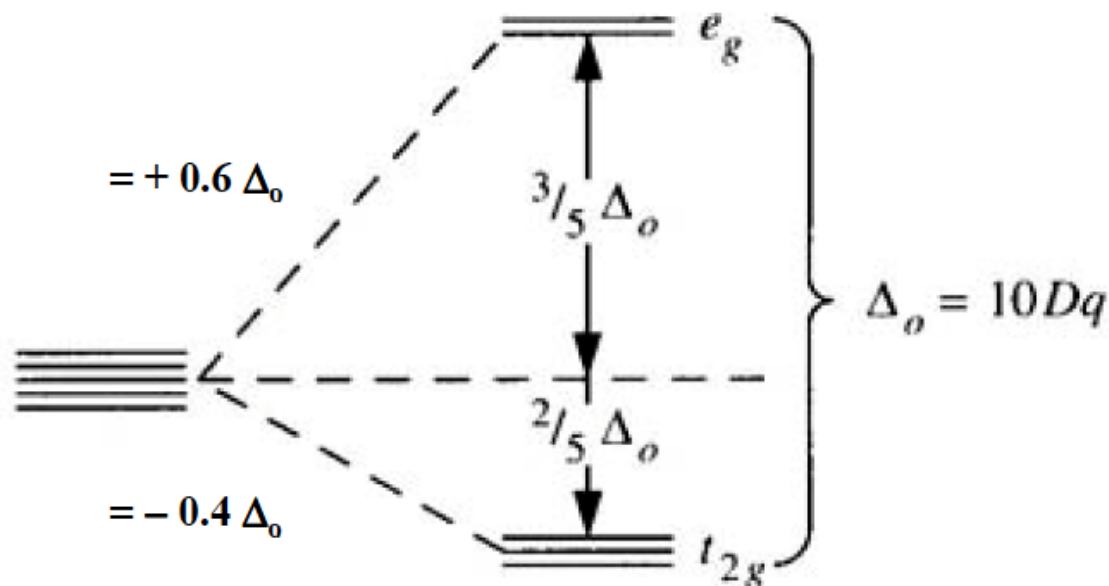
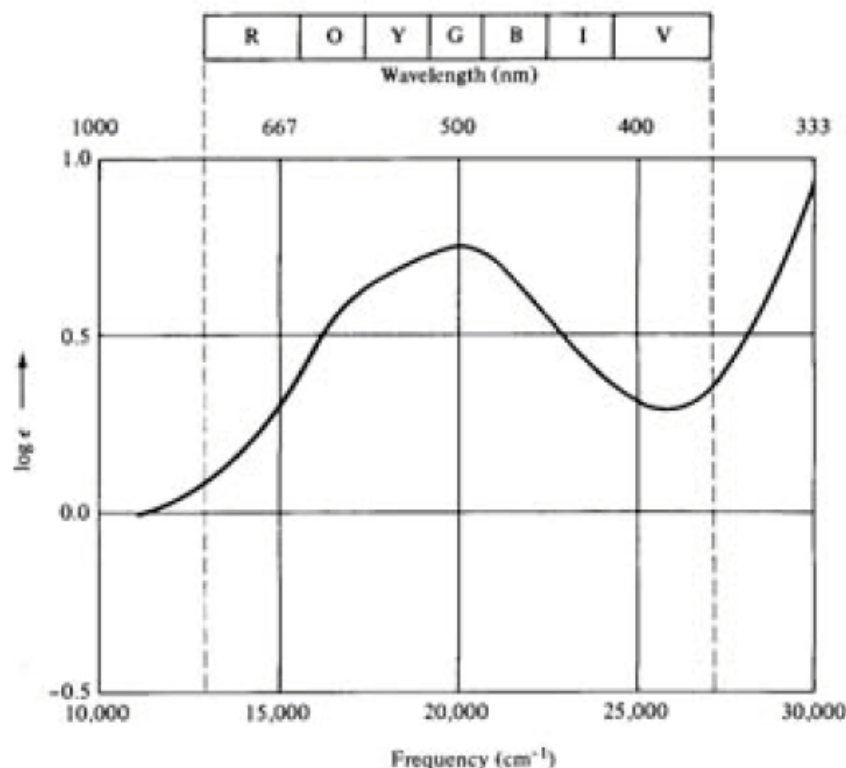


Illustration of CFSE

$[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$: a d^1 complex and the e^- occupies the lowest energy orbital, i.e. one of the three degenerate t_{2g} orbitals. The **purple colour** is a result of the absorption of light which results in the promotion of this t_{2g} electron into the e_g level. $t_{2g}^1 e_g^0 \rightarrow t_{2g}^0 e_g^1$



The UV-Vis absorption spectrum reveals that this transition occurs with a maximum at 20300 cm^{-1} which corresponds to Δ_o 243 kJ/mol.

(1000 cm^{-1} = 11.96 kJ/mol or
2.86 kcal/mol or
0.124 eV.)

Typical Δ_o values are of the same order of magnitude as the energy of a chemical bond.

- What happens for more than 1 electron in d orbitals?
- The electron-electron interactions must be taken into account.
- For d^1 - d^3 systems: Hund's rule predicts that the electrons will not pair and occupy the t_{2g} set.
- For d^4 - d^7 systems (there are two possibilities): Either put the electrons in the t_{2g} set and therefore pair the electrons (**low spin case** or **strong field situation**. Or put the electrons in the e_g set, which lies higher in energy, but the electrons do not pair (**high spin case** or **weak field situation**).
- Therefore, there are two important parameters to consider: **The Pairing energy (P)**, and **the $e_g - t_{2g}$ Splitting (referred to as Δ_0 , $10Dq$ or CFSE)**
- For both the high spin (h.s.) and low spin (l.s.) situations, it is possible to compute the **CFSE**.

For an octahedral complex, 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 no. of electrons occupying the respective levels

If CFSE is very large, pairing occurs (i.e. $CFSE > P$)

If CFSE is rather small, no pairing occurs (i.e. $P > CFSE$)

d^5 system



Case I results in LS complex

Case II results in HS complex

Δ_o is dependent on:

- *Nature of the ligands*
- *The charge on the metal ion*
- *Whether the metal is a 3d, 4d, or 5d element*

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

Spectrochemical Series

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

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

$[\text{Co}(\text{NH}_3)_6]^{3+}$	24800 cm^{-1}	163 kJ/mol
$[\text{Rh}(\text{NH}_3)_6]^{3+}$	34000	213
$[\text{Ir}(\text{NH}_3)_6]^{3+}$	41000	314

Tetrahedral Field- Considerations

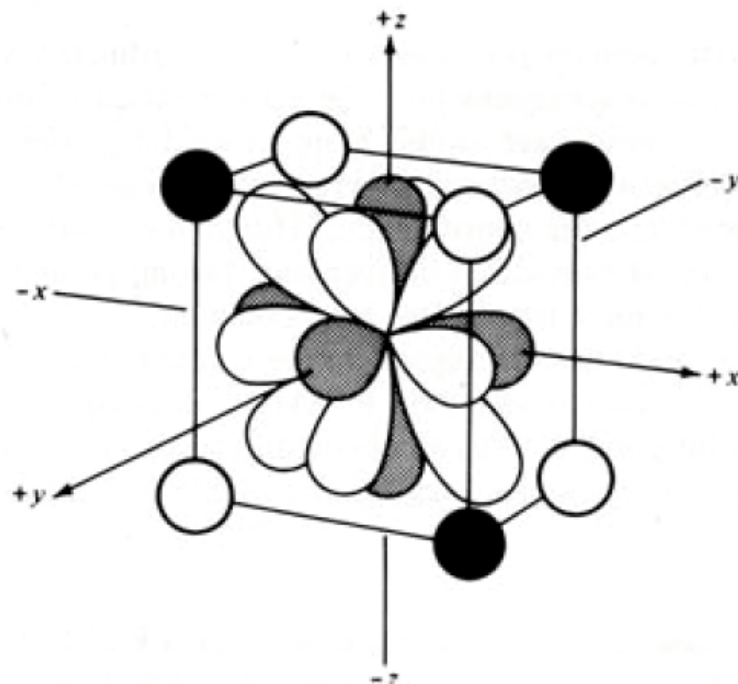
Imagine a tetrahedral molecule inside a cube with metal ions in the center of the cube. The ligands occupy the four alternate corners of the cube leaving the rest four corners empty.

The two 'e' orbitals point to the center of the face of the cube while the three 't₂' orbitals point to the center of the edges of the cube.

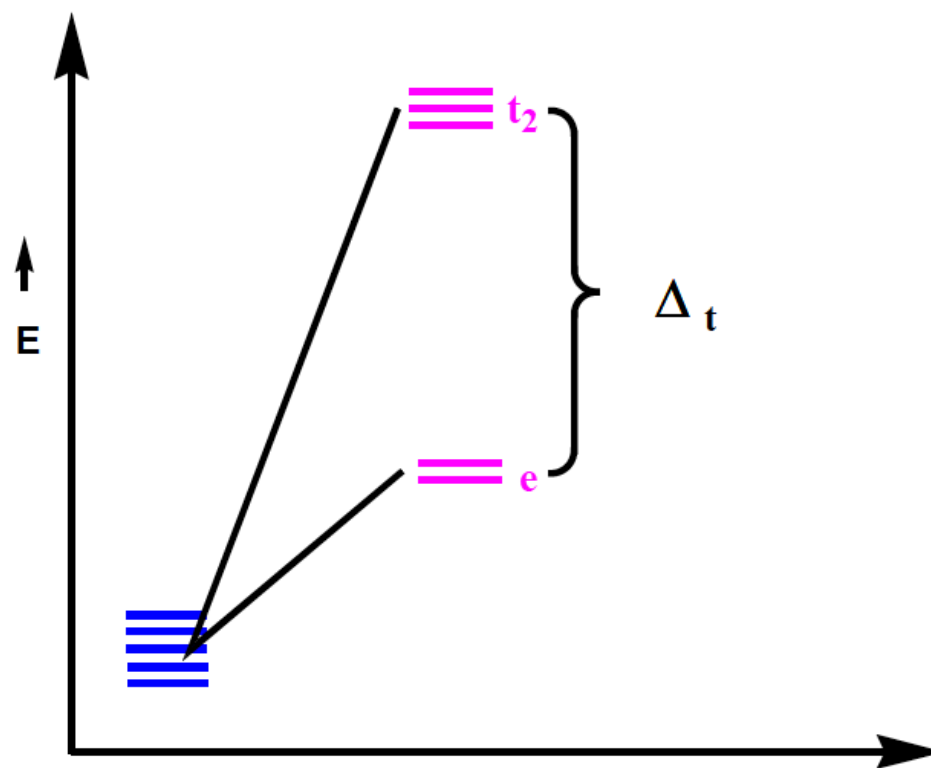
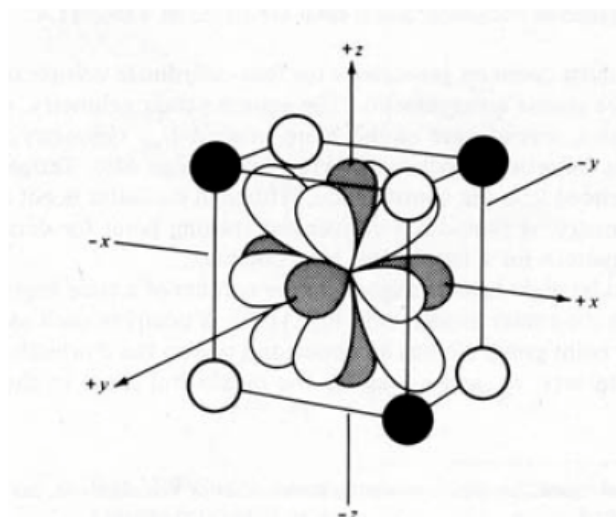
Therefore, the angle between the e-orbitals, metal and ligand is one-half of the tetrahedral angle, i.e. $109^{\circ}28' / 2 = 54^{\circ}44'$. But the angle between the t₂-orbitals, metal and ligand is one-third of the tetrahedral angle, i.e. $109^{\circ}28' / 3 = 35^{\circ}16'$.

Thus the t₂ orbitals are nearer to the direction of approach of the ligands than the e orbitals.

Hence, t₂ orbitals have higher energy compared to e-orbitals



Tetrahedral Field



$$\Delta_t < \Delta_o$$

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

There are only 4 ligands in the tetrahedral complex, and hence the ligand field is roughly 2/3 of the octahedral field.

The direction of ligand approach in tetrahedral complex does not coincide with the d-orbitals. This reduces the field by a factor of 2/3. Therefore Δ_t is roughly $2/3 \times 2/3 = 4/9$ of Δ_o .

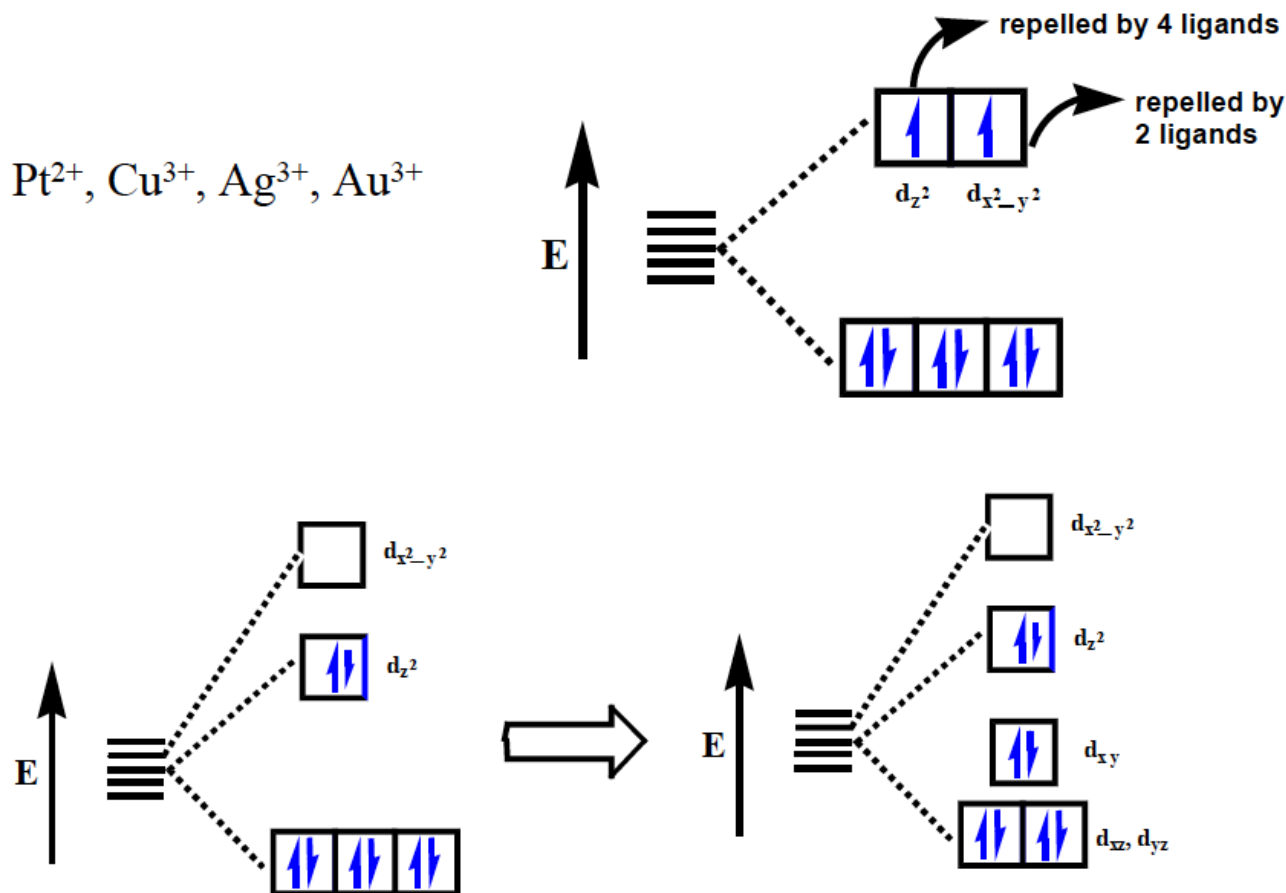
As a result, **all tetrahedral complexes are high-spin** since the CFSE is normally smaller than the pairing energy.

Hence low spin configurations are rarely observed. Usually, if a very strong field ligand is present, the square planar geometry will be favored.

Special case of d^8 Octahedral

Examples:

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



Square-planar complex is formed ; attempts to form octahedral complexes become impossible

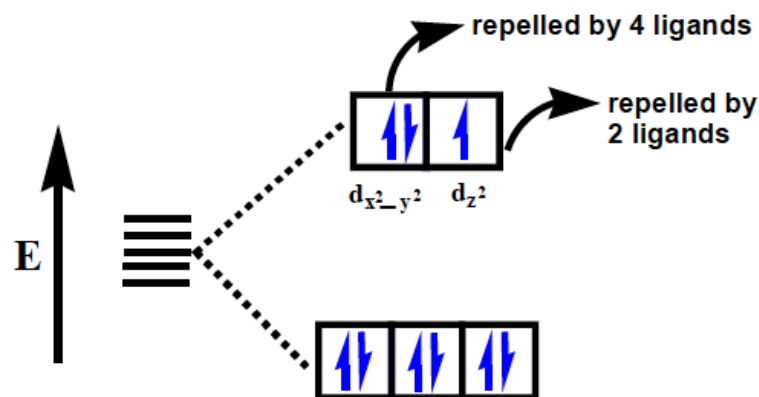
Special case II

Jahn-Teller Distortion

If both the e_g orbitals are symmetrically filled - all ligands are repelled equally.

Result: regular octahedron

If **asymmetrically** filled - some ligands are repelled more than the other. **Result:** Distorted octahedron



Consider e_g configuration: $(d_{z^2})^1 d_{x^2-y^2}^2$

Ligands along x, -x, y, -y will be repelled more and bonds elongated.
i.e. the octahedron will be compressed along the z axis.

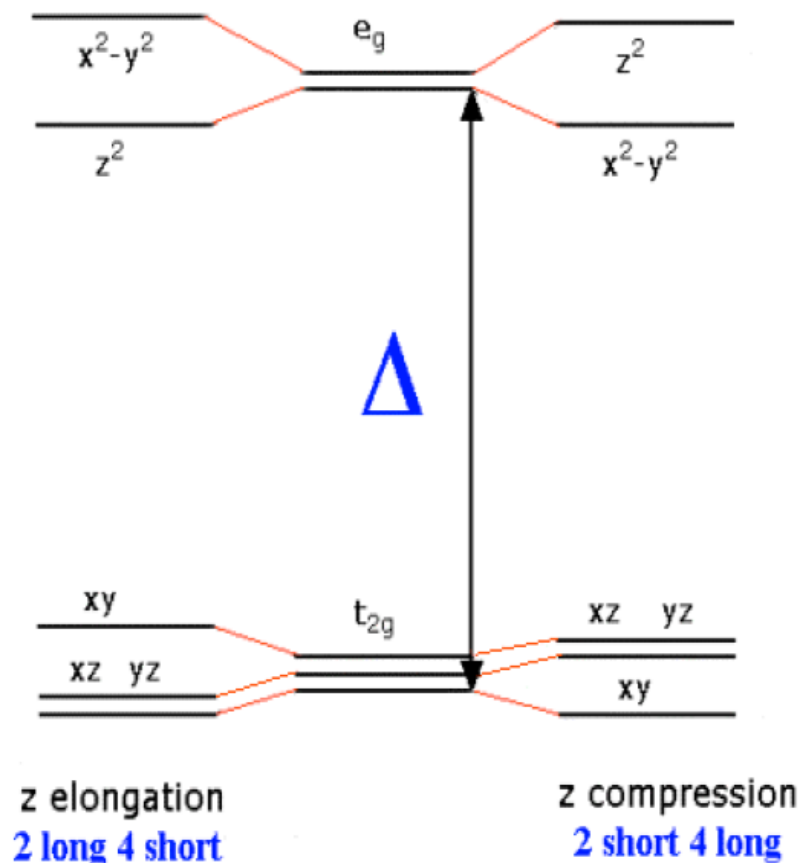
Consider e_g configuration: $(d_{z^2})^2 d_{x^2-y^2}^1$

Ligands along z, -z will be repelled more and bonds elongated. i.e.
the octahedron will be elongated along the z axis.

The Jahn-Teller Theorem was published in 1937 and states:

"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"

The e_g point along bond axes. The effect of JT distortions is best documented for Cu(II) complexes (with 3e in e_g) where the result is that most complexes are found to have elongation along the z-axis.



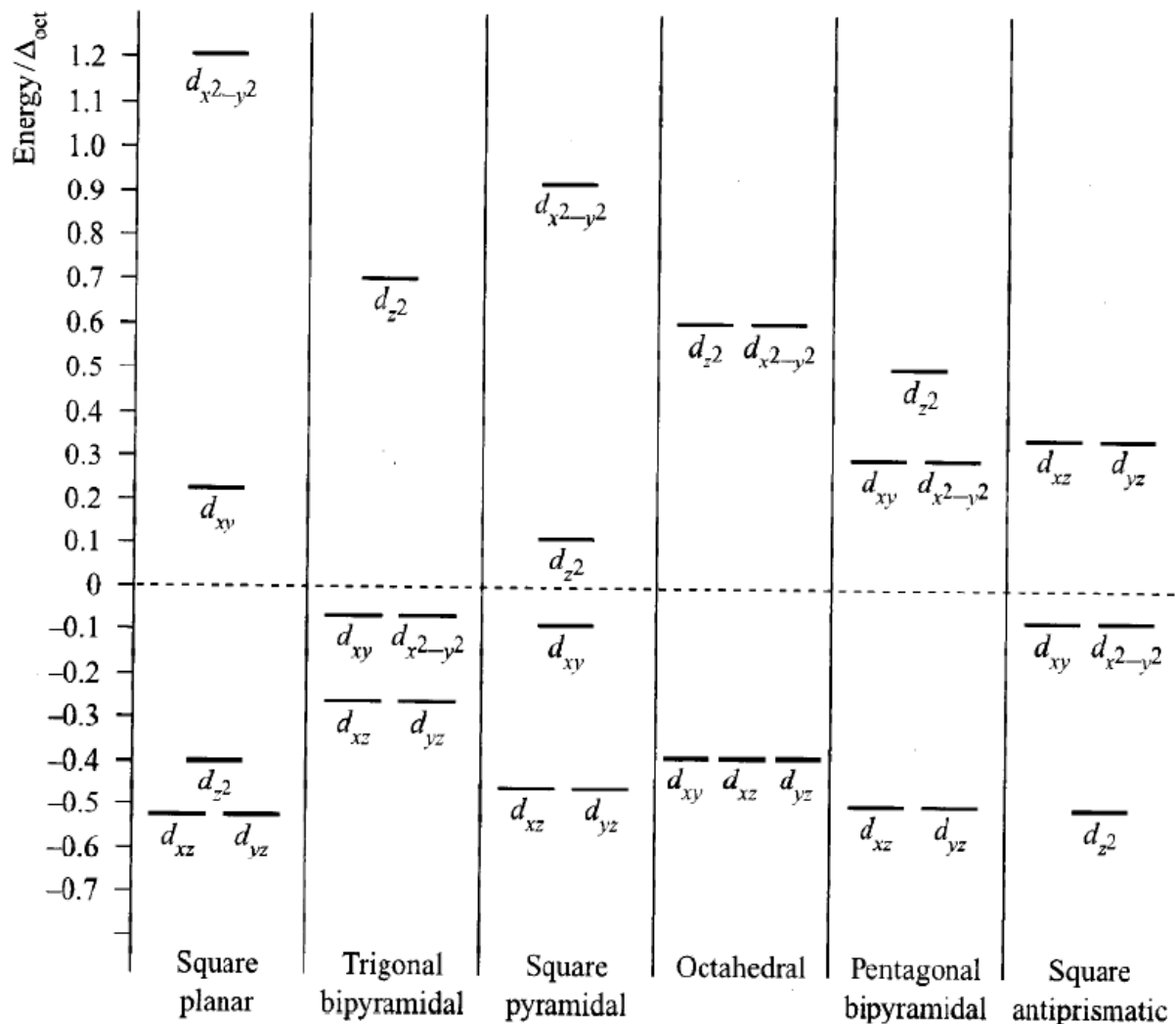


Figure 2 Crystal field splittings of d orbitals