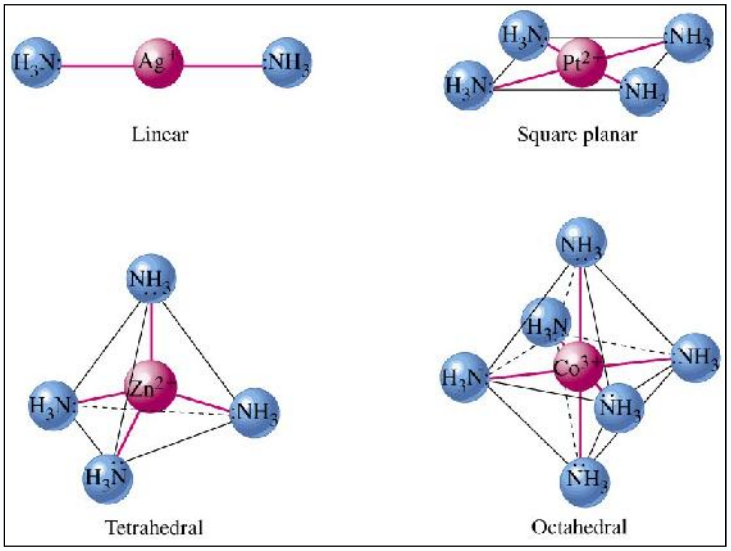
Bonding in coordination compounds

Nobel prize 1913

- **Alfred Werner - 1893**
- **VBT**
- **Crystal Field Theory (CFT)**
- **Modified CFT, known as Ligand Field Theory**
- **MOT**

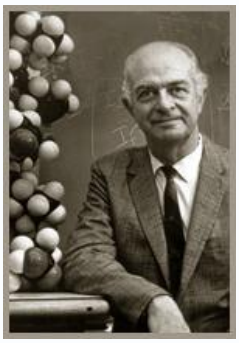
How & Why?



Valance Bond Theory

Basic Principle

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



Linus Carl Pauling
(1901–1994)
Nobel prizes: 1954, 196

Valance Bond Model

Ligand = Lewis base

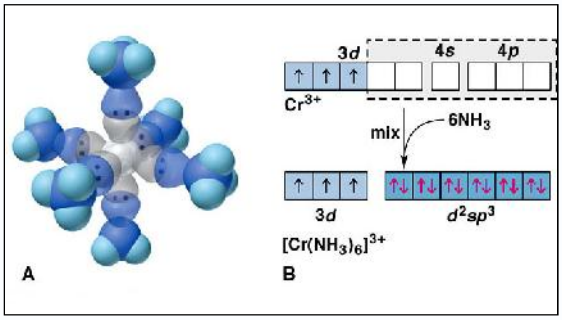
Metal = Lewis acid

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

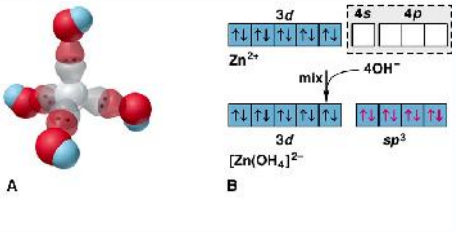
Number and type of M-L hybrid orbitals determines geometry of the complex

Octahedral Complex

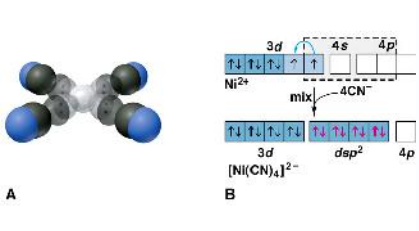
e.g. $[Cr(NH_3)_6]^{3+}$



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



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



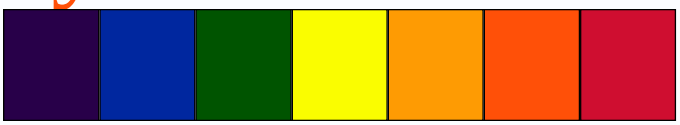
Limitations of VB theory

Cannot account for colour of complexes

May predict magnetism wrongly

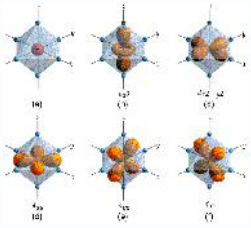
Cannot account for spectrochemical series

Crystal Field Theory



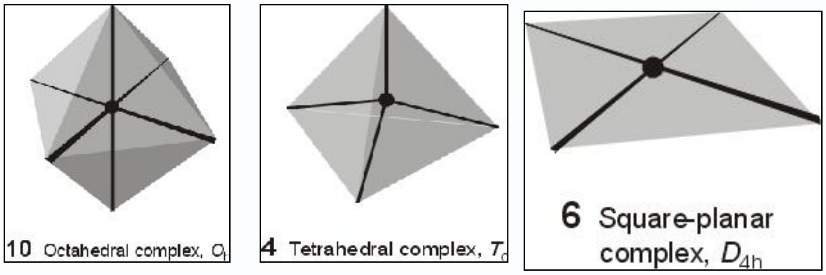
400 500 600 800

- **The relationship between colors and complex metal ions**

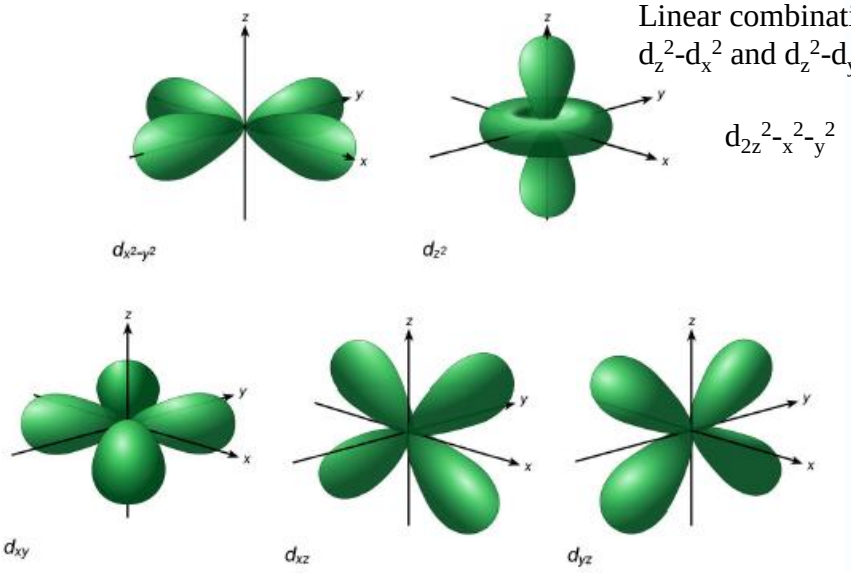


Crystal Field Model

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



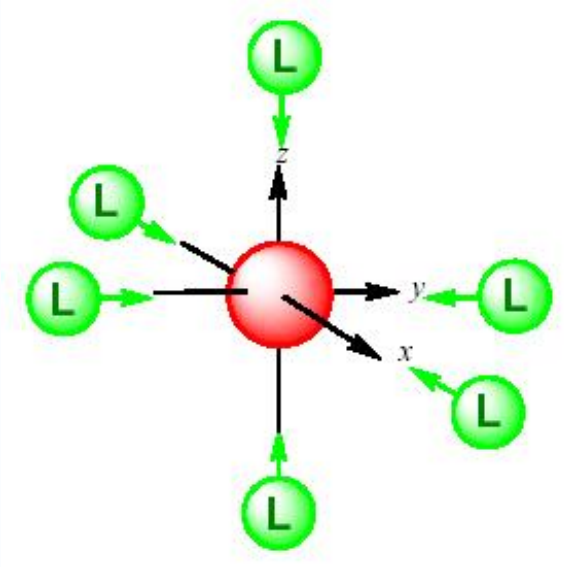
d-orbitals: look attentively along the axis



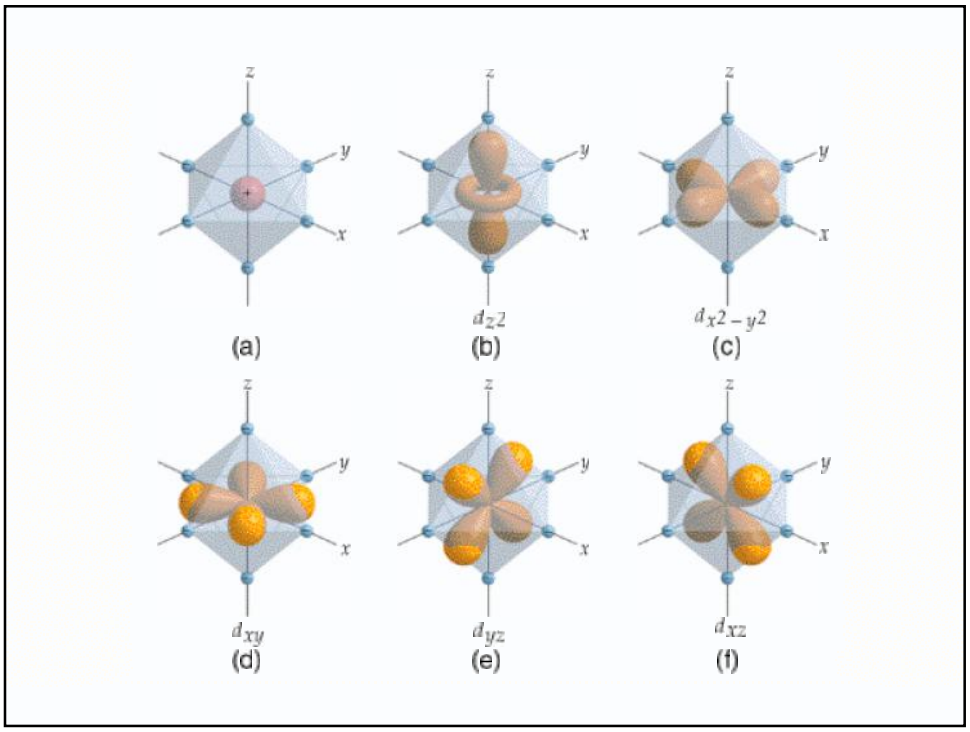
Linear combination of d_z^2-d_x^2 and d_z^2-d_y^2

d_{2z}^2-$_x^2$-$_y^2$

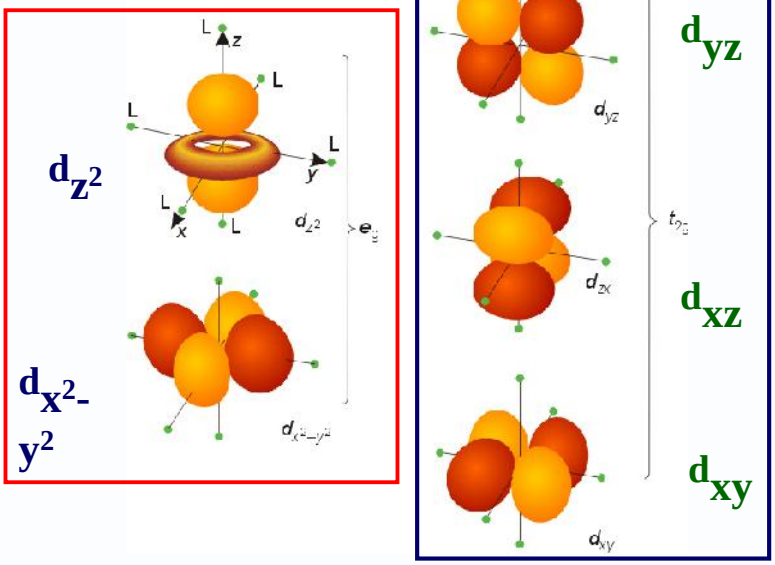
Octahedral Field

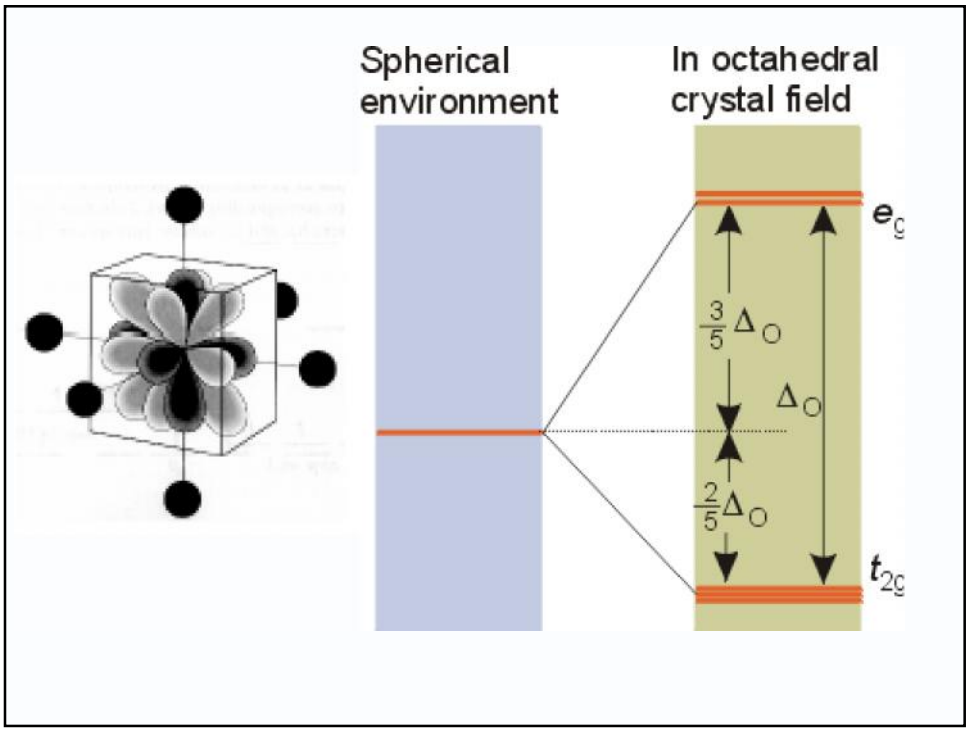


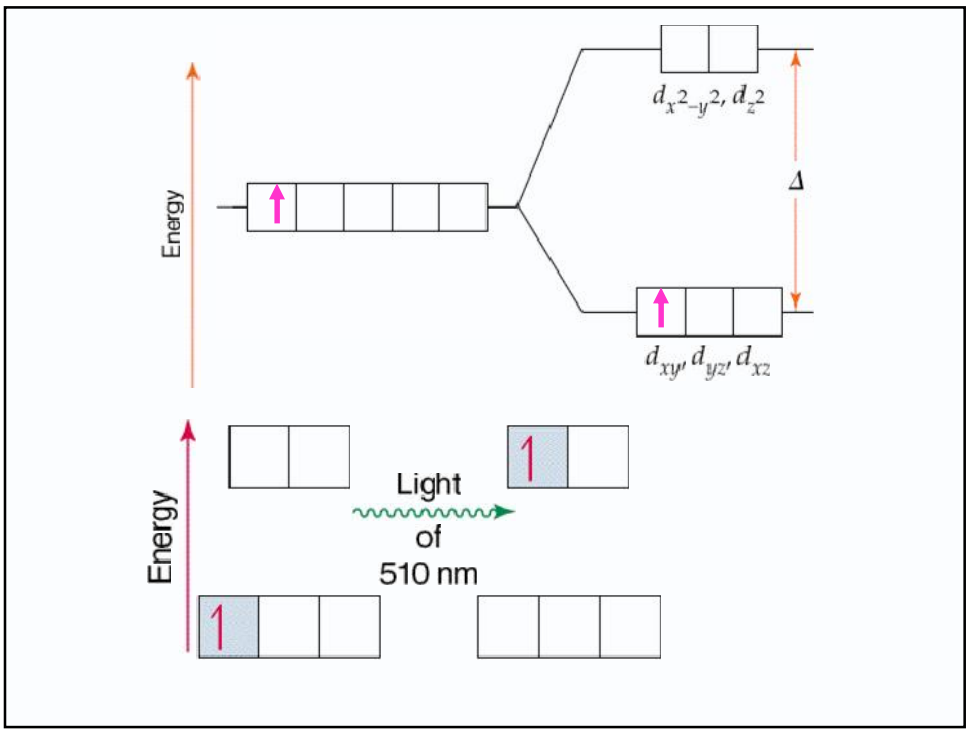
- **We assume an octahedral array of negative charges placed around the metal ion (which is positive).**
- **The ligand and orbitals lie on the same axes as negative charges.**
  - **Therefore, there is a large, unfavorable interaction between ligand (-) and these orbitals.**
  - **These orbitals form the degenerate high energy pair of energy levels.**
- **The d_{xy}, d_{yz}, and d_{xz} orbitals bisect the negative charges.**
  - **Therefore, there is a smaller repulsion between ligand and metal for these orbitals.**
  - **These orbitals form the degenerate low energy set of energy levels.**



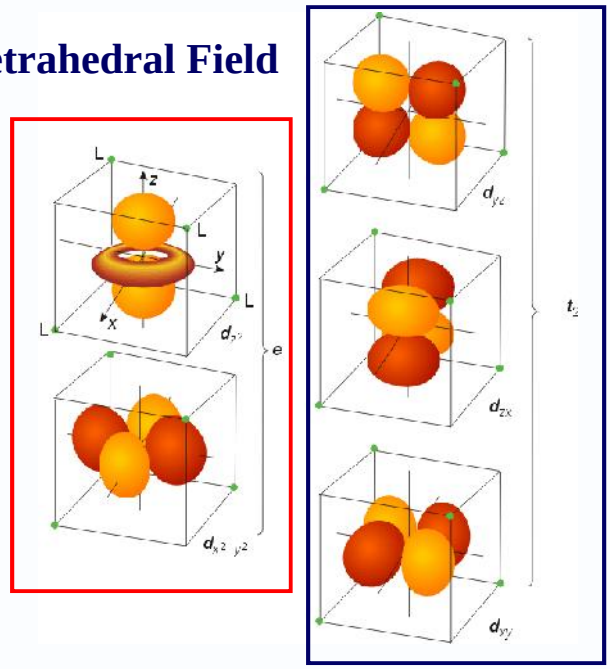
In Octahedral Field

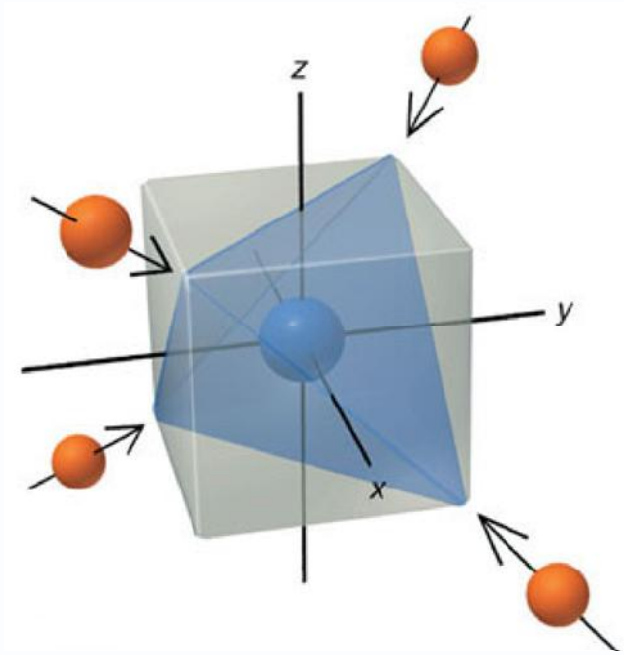


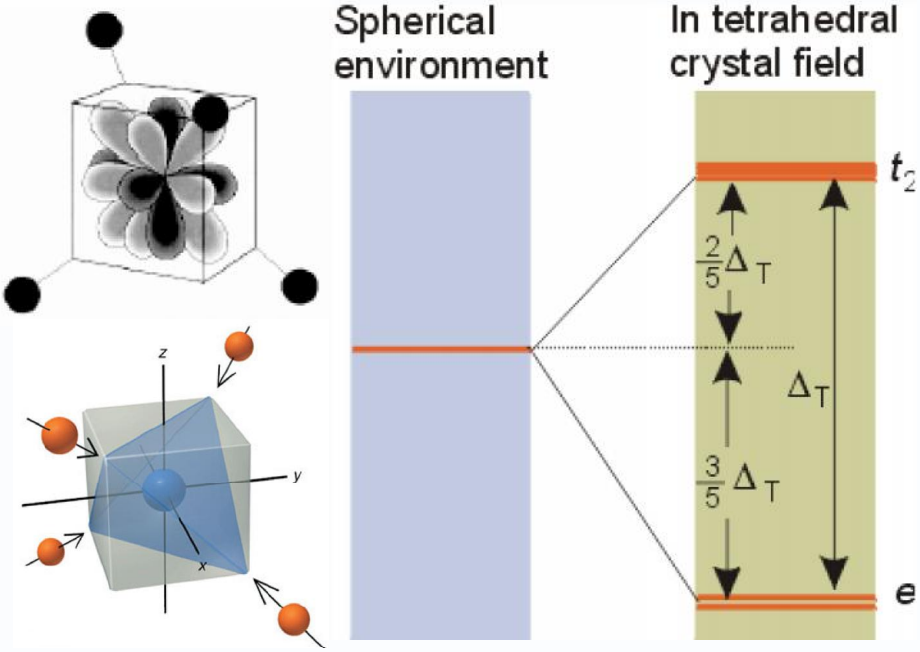

Spherical environment
In octahedral crystal field
e_g
$\frac{3}{5}\Delta_O$
Δ_O
$\frac{2}{5}\Delta_O$
t_{2g}


Energy
$d_{x^2-y^2}, d_{z^2}$
Δ
d_{xy}, d_{yz}, d_{xz}
Energy
Light
of
510 nm
1
1

In Tetrahedral Field







Magnitude of a

Oxidation state of the metal ion

$[Ru(H_2O)_6]^{2+}$ 19800 cm^{-1}

$[Ru(H_2O)_6]^{3+}$ 28600 cm^{-1}

Number of ligands and geometry

$a_t < a_o$ $a_t = 4/9 a_o$

Nature of the ligand

$I^- < S^{2-} < SCN^- < Cl^- < NO_3^- < N_3^- < F^- < OH^- < C_2O_4^{2-} < H_2O < \ldots.. CN^- < CO$

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:

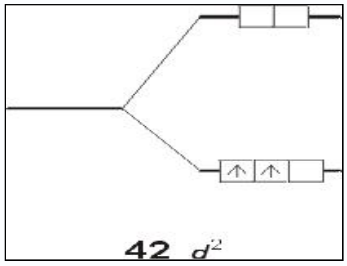
$$= (-0.4x + 0.6y)a_O$$

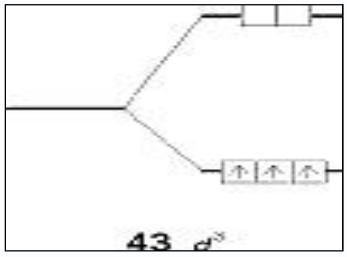
$$a_O = 10\ Dq$$

BEYOND d^3

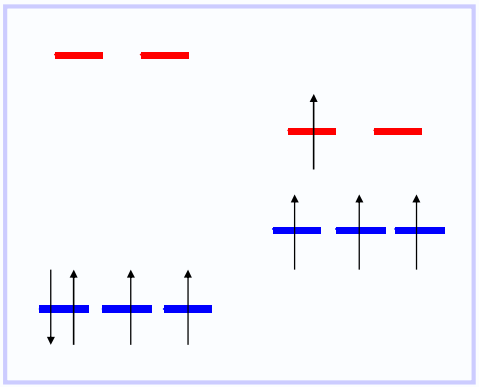
- In weak field: a_O < P, => $t_{2g}^{3} e_g^{1}$
- In strong field a_O > P, => t_{2g}^{4}
- P - paring energy

Ground-state Electronic Configuration, Magnetic Properties and Colour





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



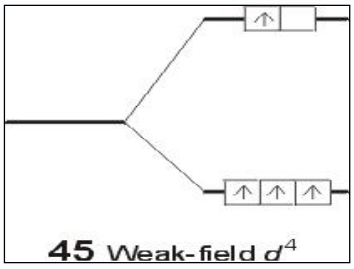
Strong field = Low spin (2 unpaired)

Weak field = High spin (4 unpaired)

$P < \Delta_o$ $P > \Delta_o$

Coulombic repulsion energy and exchange energy

Ground-state Electronic Configuration, Magnetic Properties and Colour

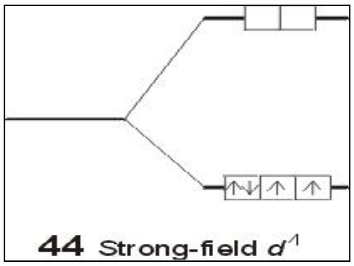


$[Mn(H_2O)_6]^{3+}$

Weak Field Complex

the total spin is $4 \times ½ = 2$

High Spin Complex



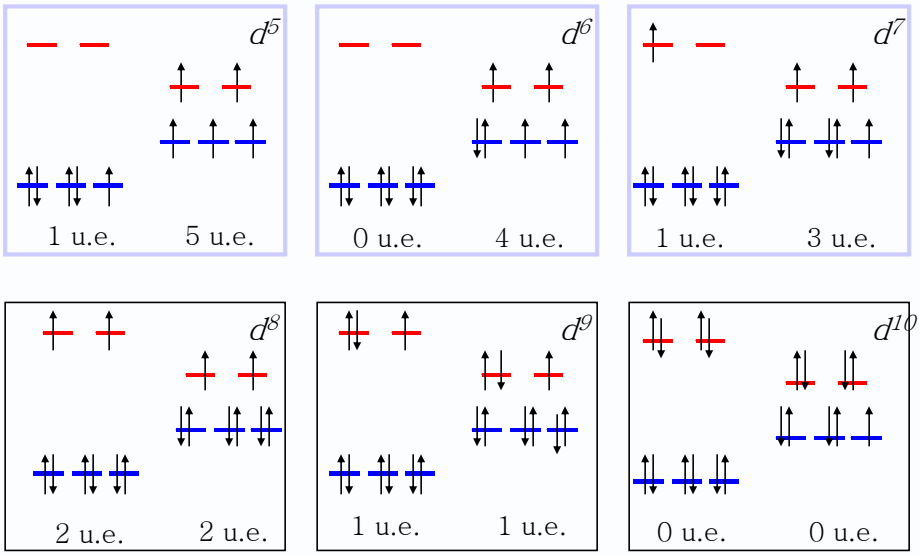
$[Mn(CN)_6]^{3-}$

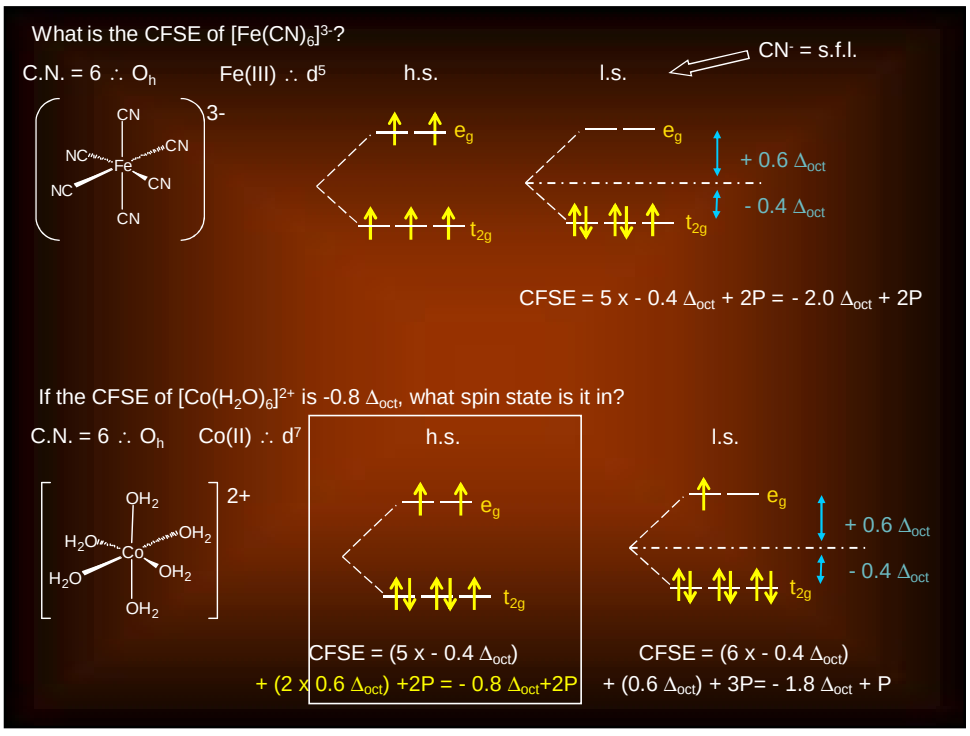
Strong field Complex

total spin is $2 \times ½ = 1$

Low Spin Complex

Placing electrons in d orbitals



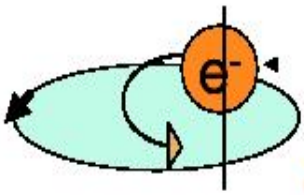


Magnetism

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

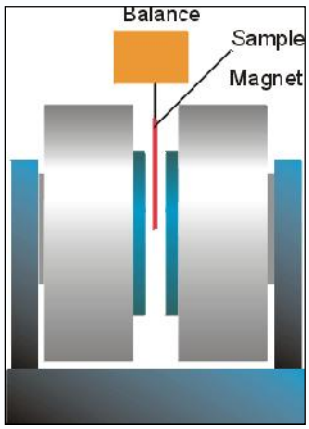
- The magnetic moment « of a complex with total spin quantum number S is:
- « = $2\{S(S+1)\}^{1/2}$ $«_B$ ($«_B$ is the Bohr magneton)
- $«_B = eh/4®m_e = 9.274$ ò10^{-24} J T^{-1}
- Since each unpaired electron has a spin ½,
- S = (½)n, where n = no. of unpaired electrons
- « = $\{n(n+2)\}^{1/2}$ $«_B$
- 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 a_t YY a_O.

n = no. of unpaired electrons

« = {n(n+2)}$^{1/2}$ «$_B$

Ion	n	S	«/«$_B$ 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

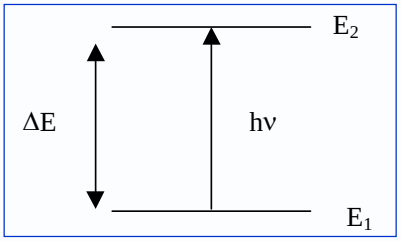
Similar Calculation can be done for Low-spin Complex



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

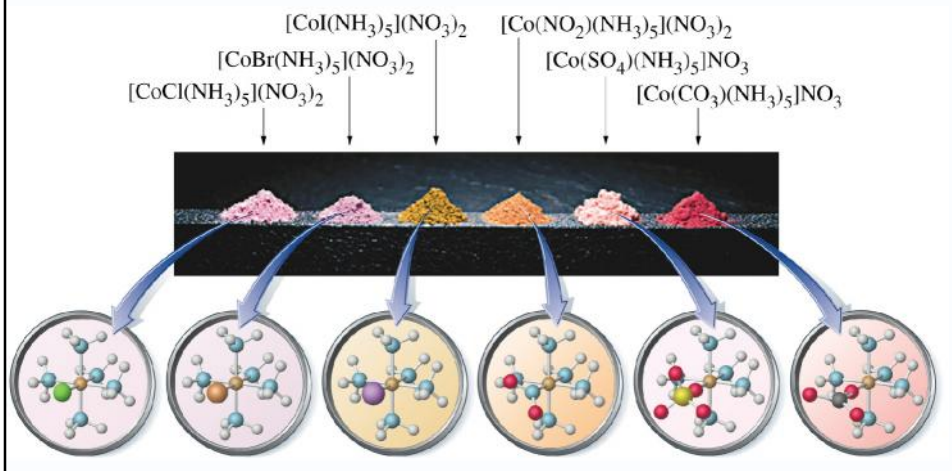


$$\Delta E = E_2 - E_1 = h\nu$$

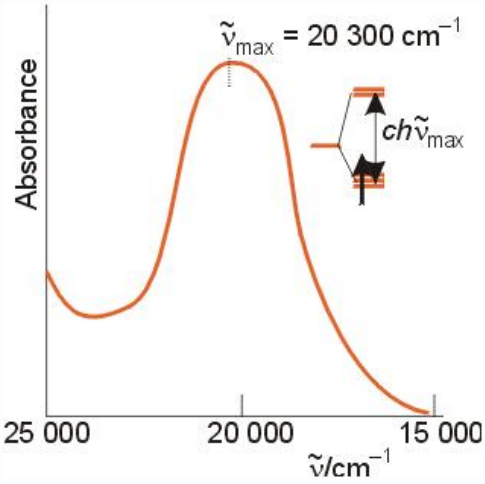
Ligands influence a_o, therefore the colour

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

1. Metal charge
2. Ligand strength



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

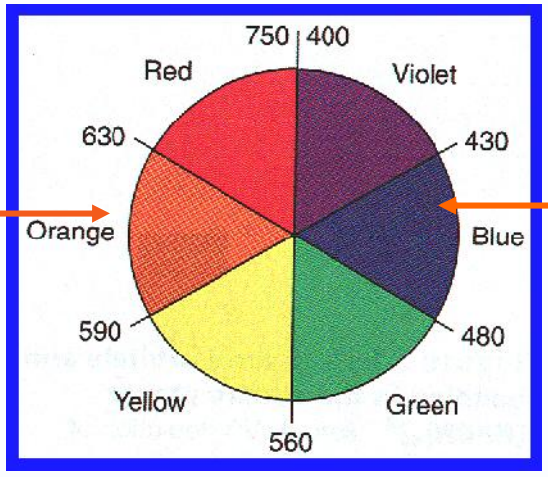


Assigned transition:

$e_g \rightarrow t_{2g}$

This corresponds to the energy gap

a_O = 243 kJ mol^{-1}

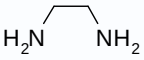


absorbed color

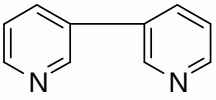
observed color

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

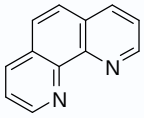
Weak Field I^- < Br^- < S^{2-} < SCN^- < Cl^- < NO_3^- < F^- < $C_2O_4^{2-}$ < H_2O < NCS^- < CH_3CN < NH_3 < en < bipy < phen < NO_2^- < PPh_3 < CN^- < CO **Strong Field**



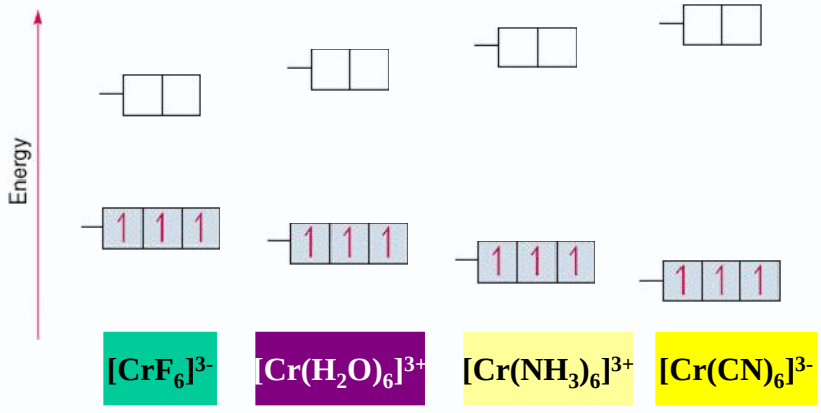
Ethylenediamine (en)



2,2'-bipyridine (bipy)



1.10 - penanthroline (phen)



As Cr^{3+} goes from being attached to a weak field ligand to a strong field ligand, a 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

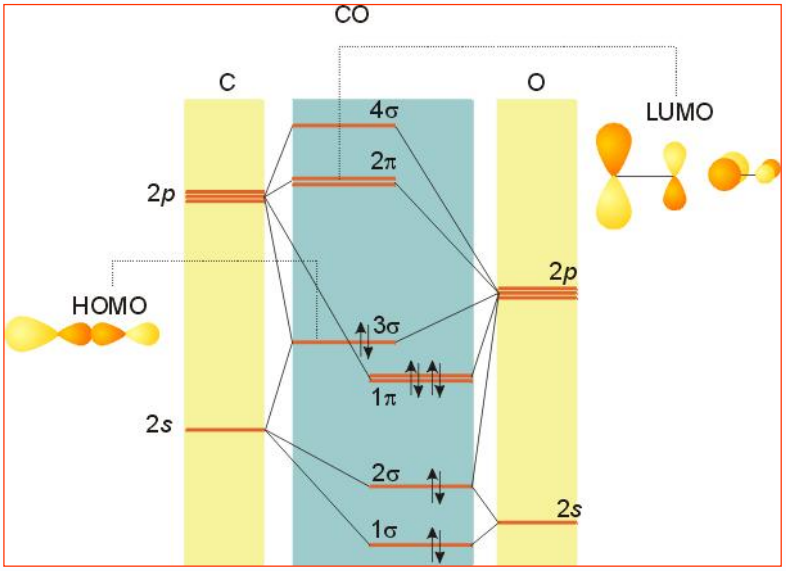
Consequence

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

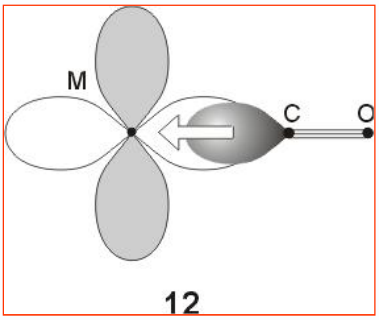
Metals in Low Oxidation States

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

Stabilizing Low Oxidation State: CO Can Do the Job



Stabilizing Low Oxidation State: CO Can Do the Job



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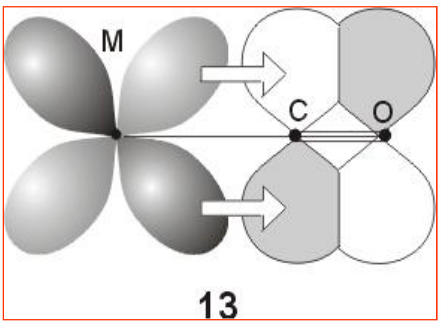
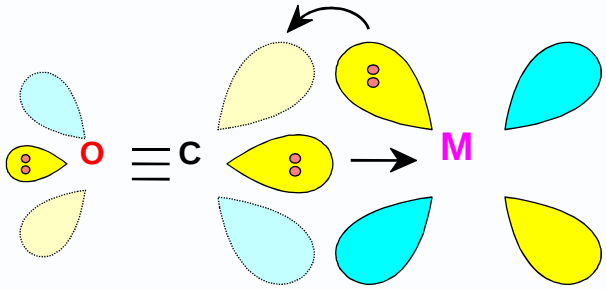
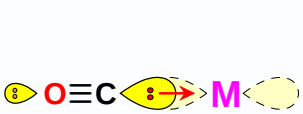


13

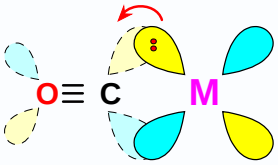
$Ni(CO)_4$], [$Fe(CO)_5$], [$Cr(CO)_6$], [$Mn_2(CO)_{10}$], [$Co_2(CO)_8$], Na_2[$Fe(CO)_4$], Na[$Mn(CO)_5$]



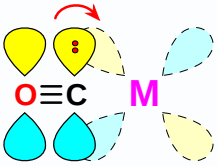
± orbital serves as a very weak donor to a metal atom



CO-M sigma bond



M to CO pi backbonding



CO to M pi bonding (rare)