Bonding in coordination compounds

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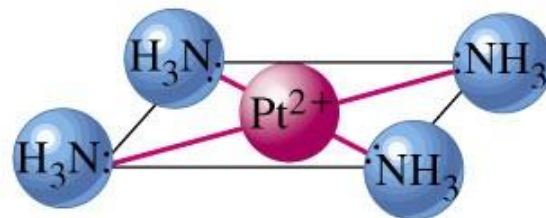- **Modified CFT, known as Ligand Field Theory**
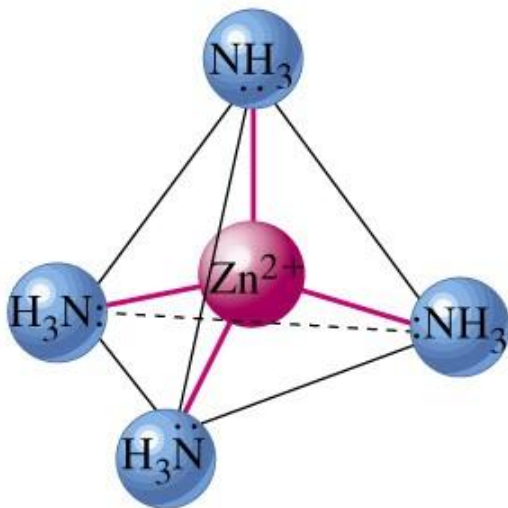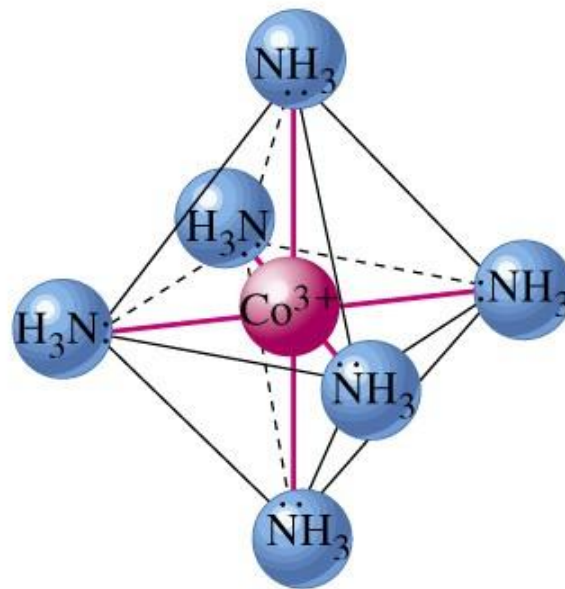- **MOT**

Nobel prize 1913

How & Why?

Linear

Square planar

Tetrahedral

Octahedral
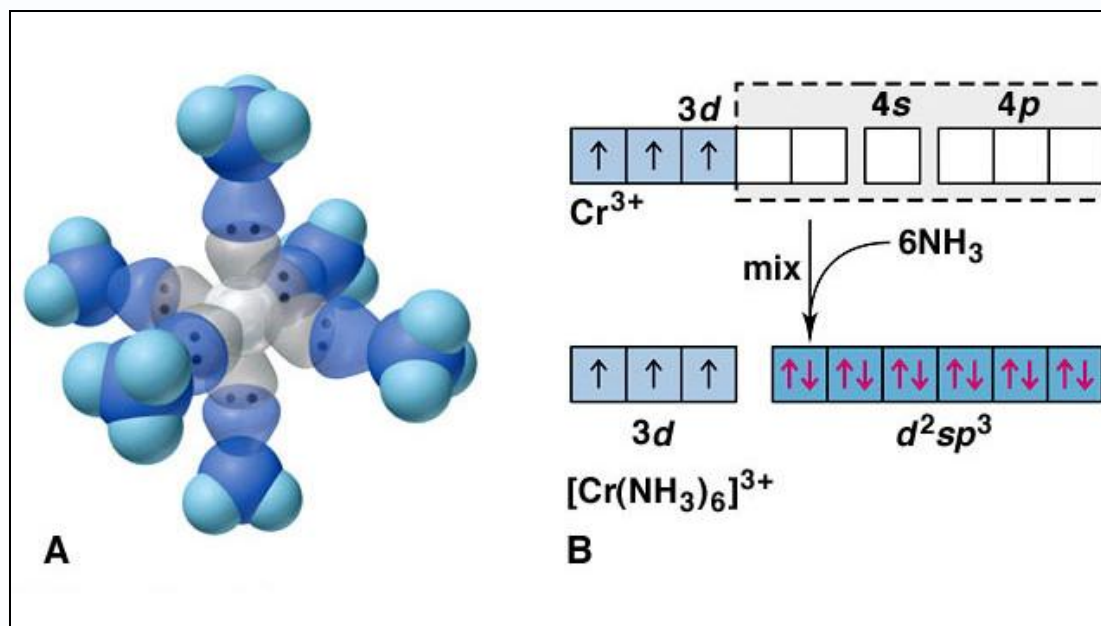
Valance Bond Model

Ligand = Lewis base

Metal = Lewis acid

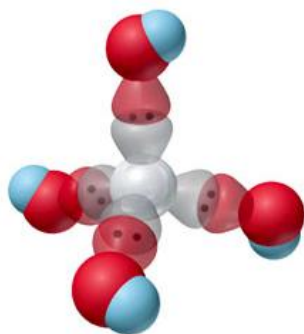s, p and d orbitals give hybrid orbitals with specific geometries

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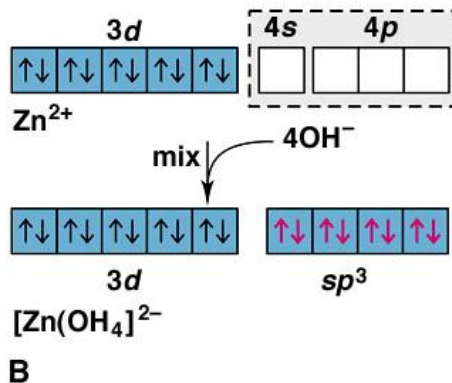
Octahedral Complex

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

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

A

3d | 4s | 4p

Zn^{2+}

mix — 4OH$^-$

3d | sp^3

[Zn(OH$_4$]$^{2-}$

B

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

A

3d | 4s | 4p

Ni^{2+}

mix — 4CN$^-$

3d | dsp^2 | 4p

[Ni(CN)$_4$]$^{2-}$

B
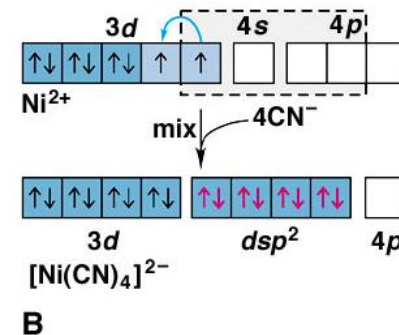
Limitations of VB theory

Can not account for colour of complexes

May predict magnetism wrongly

Can not account for spectrochemical series
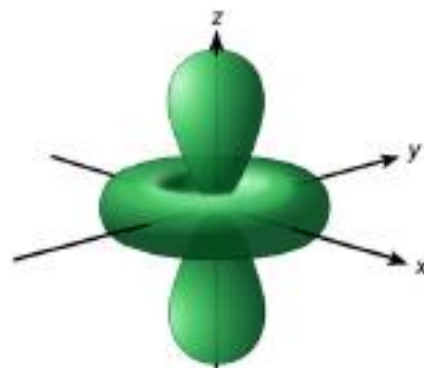
Crystal Field Model

- **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.**

10 Octahedral complex, O_h

4 Tetrahedral complex, T_c

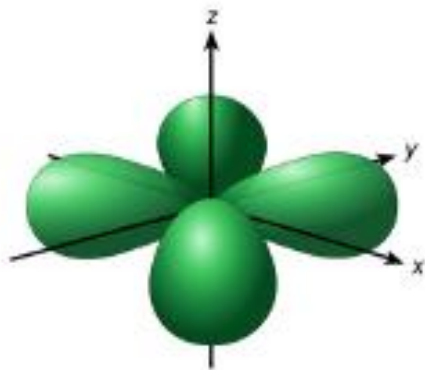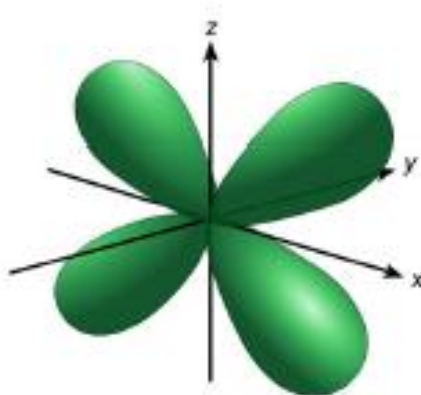6 Square-planar complex, D_{4h}
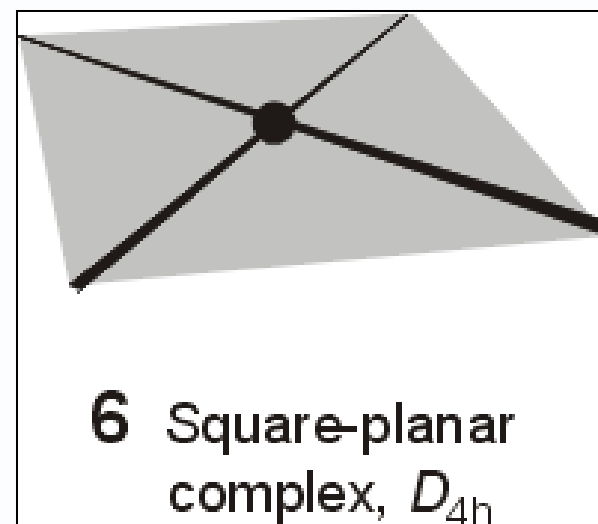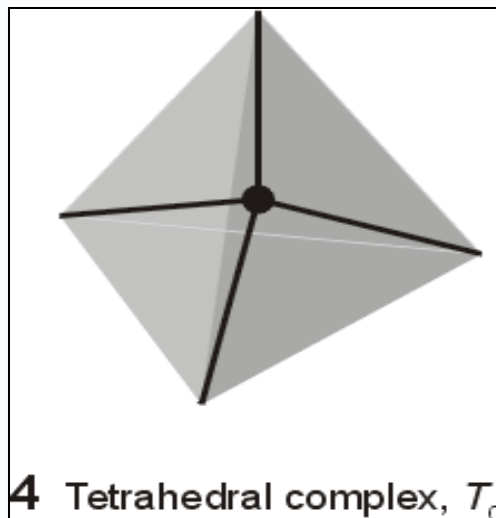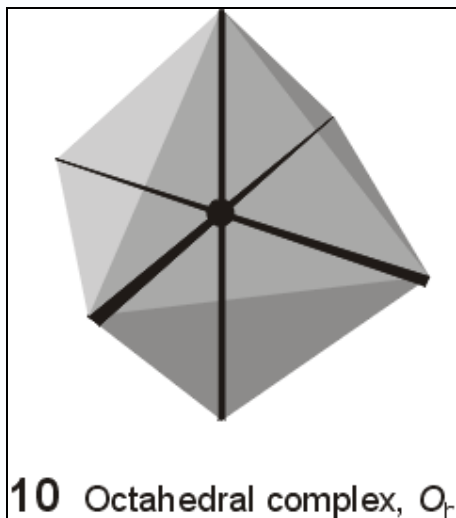
d-orbitals: look attentively along the axis
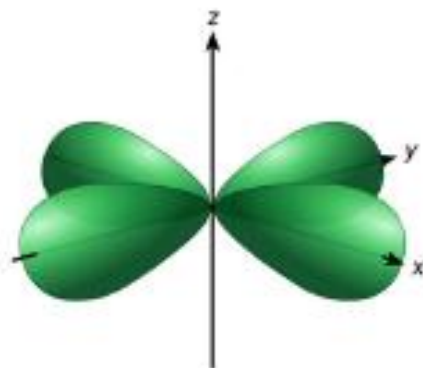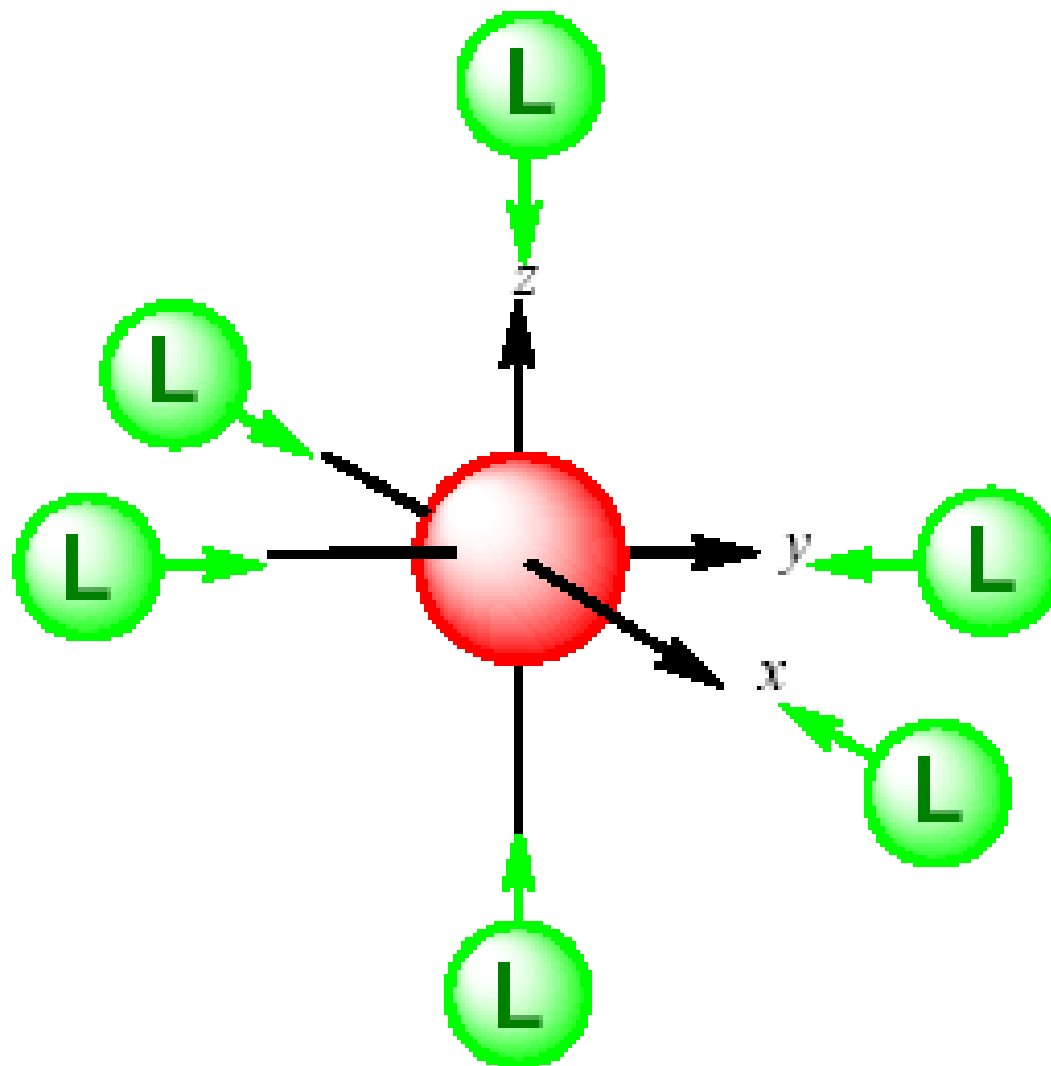

$d_{x^2-y^2}$

d_{z^2}

d_{xy}

d_{xz}
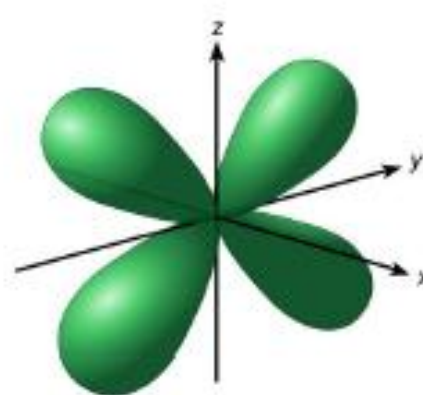
d_{yz}

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.**
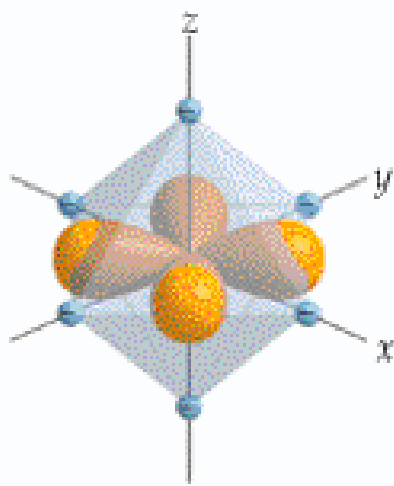
d_{z^2}

(a) (b) (c)

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

d_{xy} d_{yz} d_{xz}
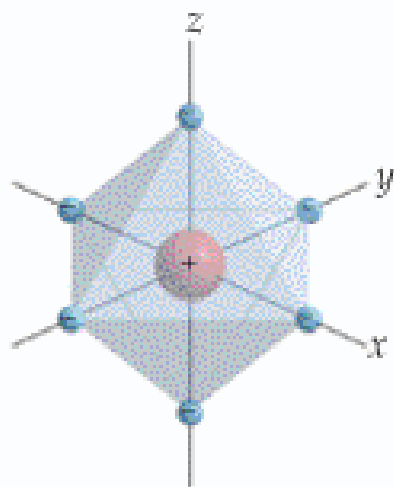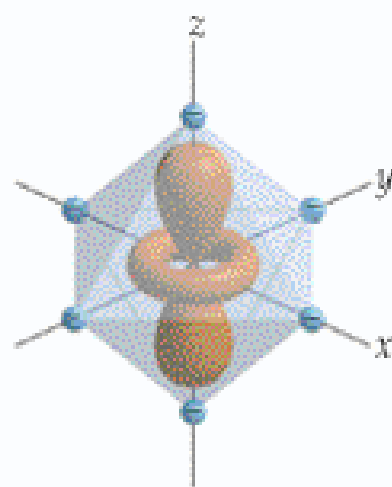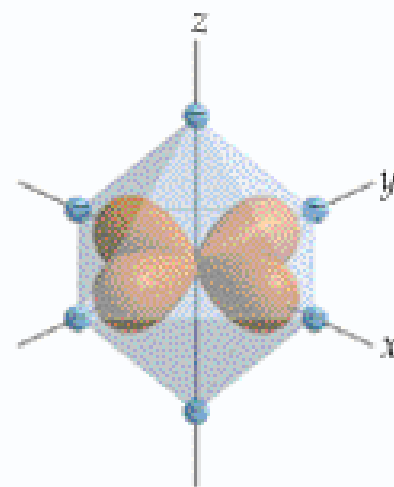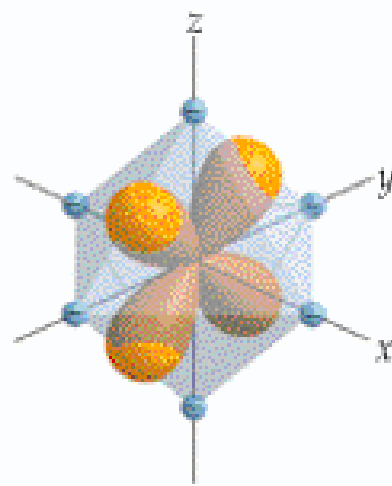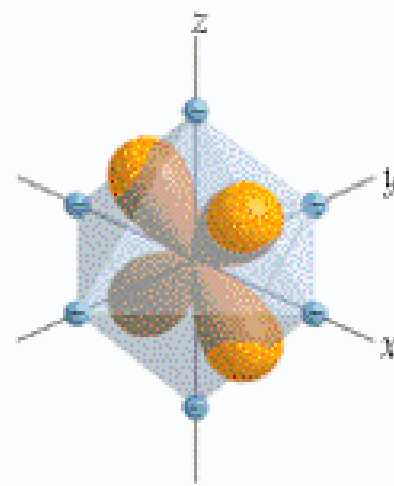
(d) (e) (f)

In Octahedral Field
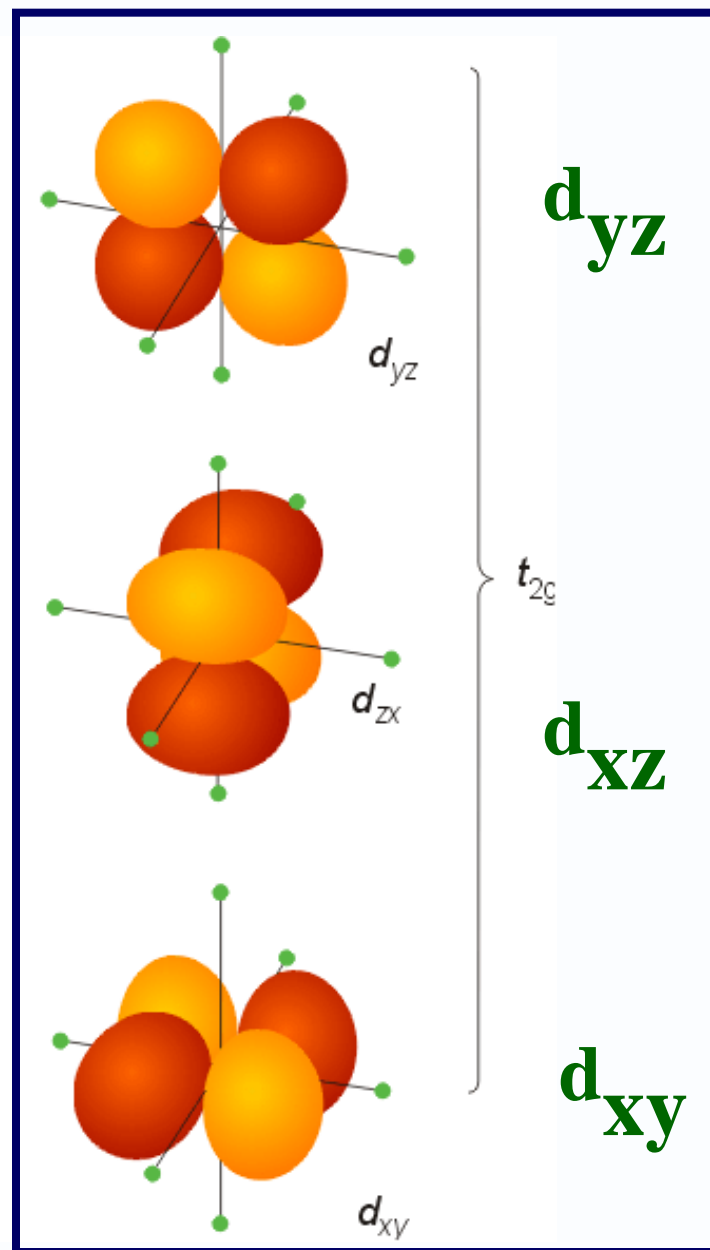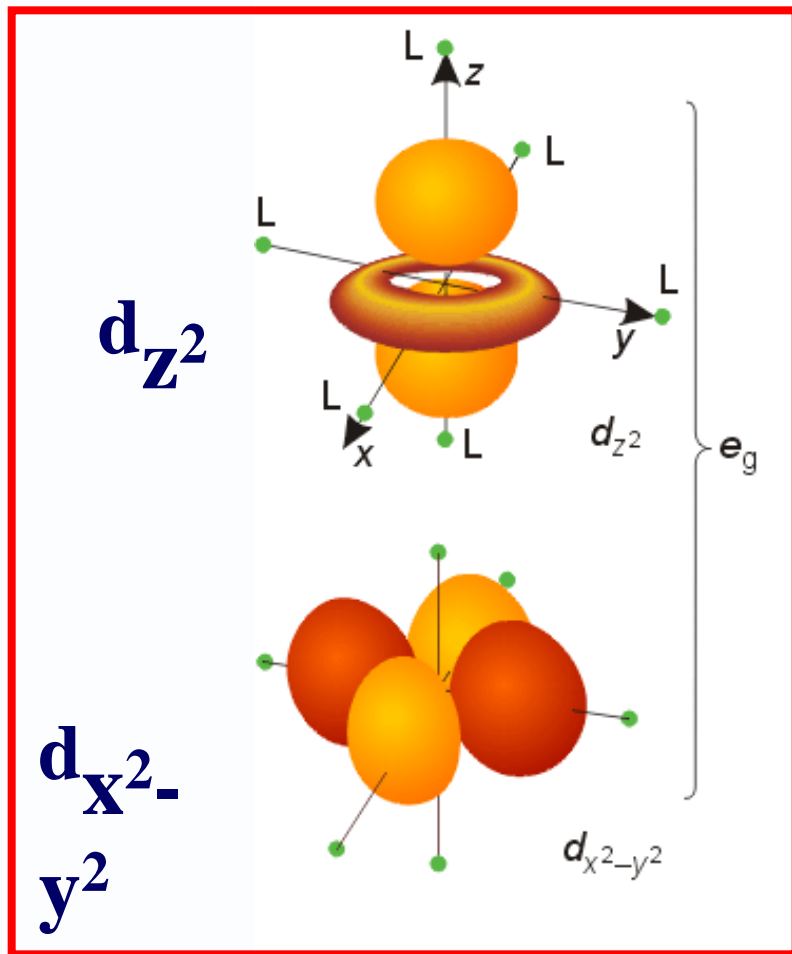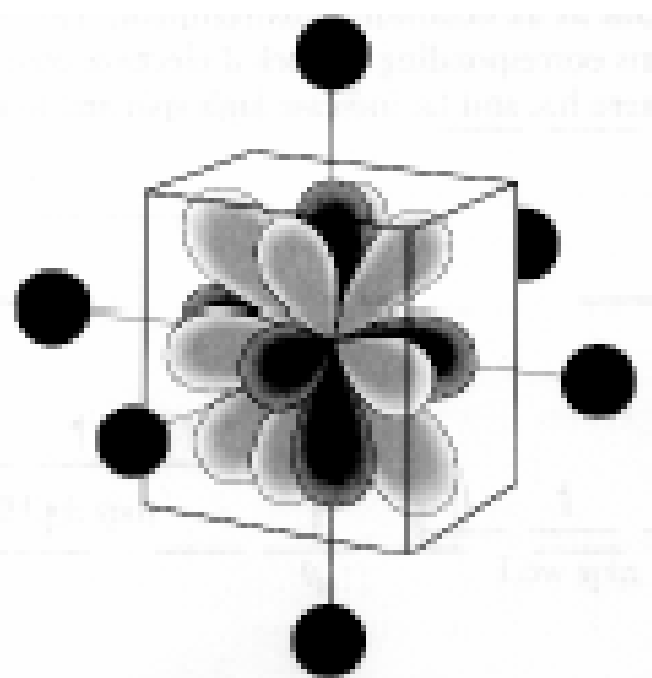
Spherical environment

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
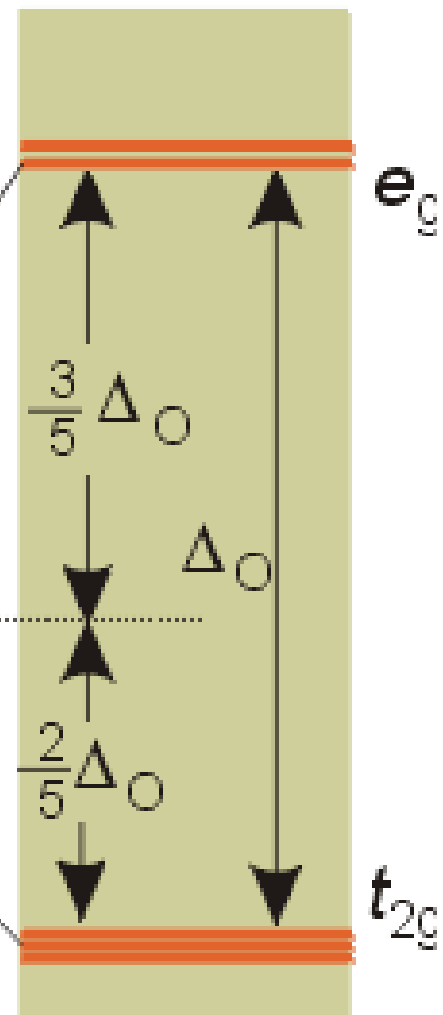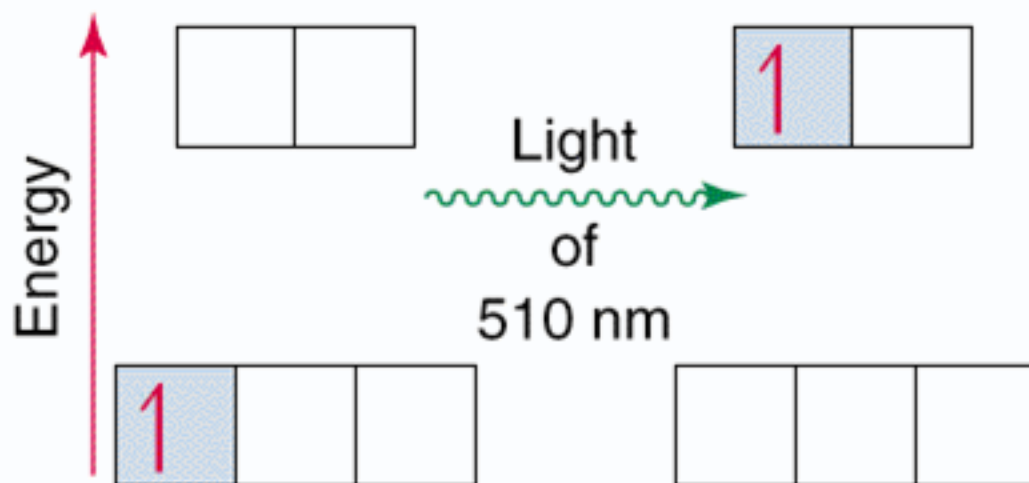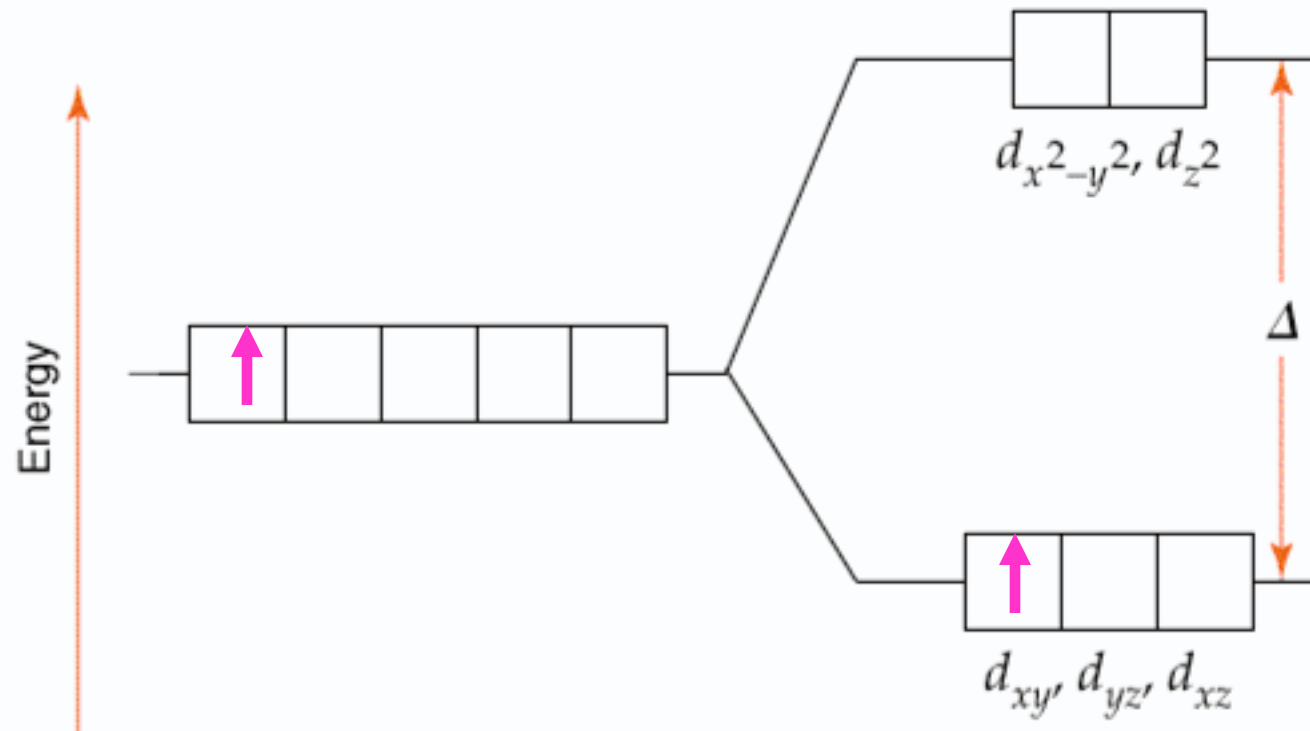
In Tetrahedral Field
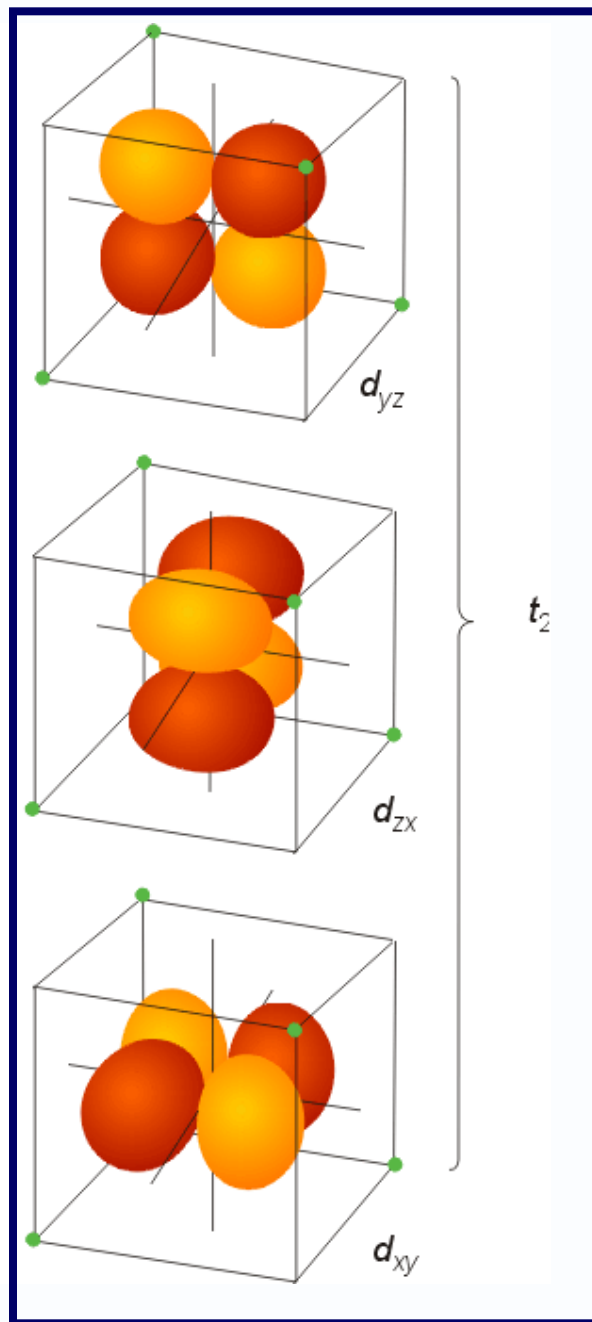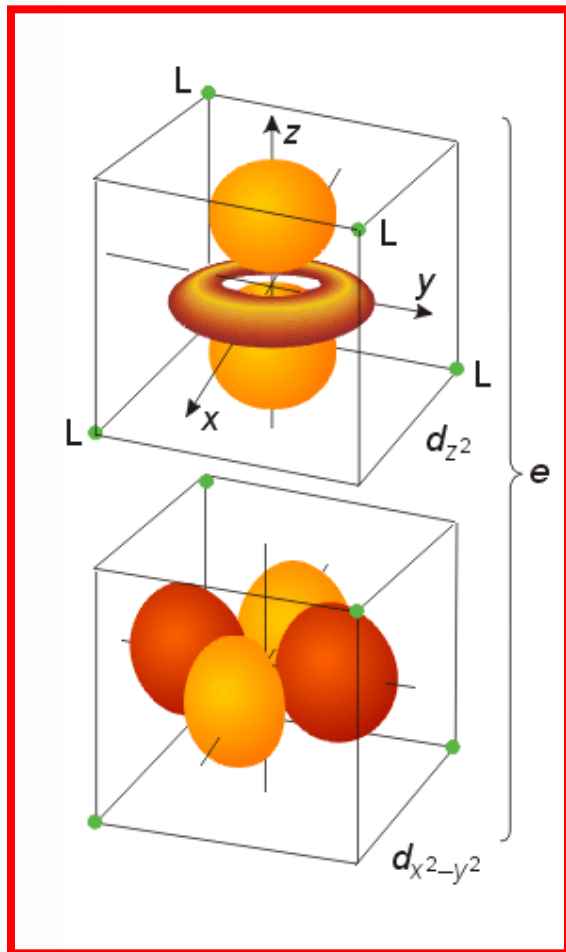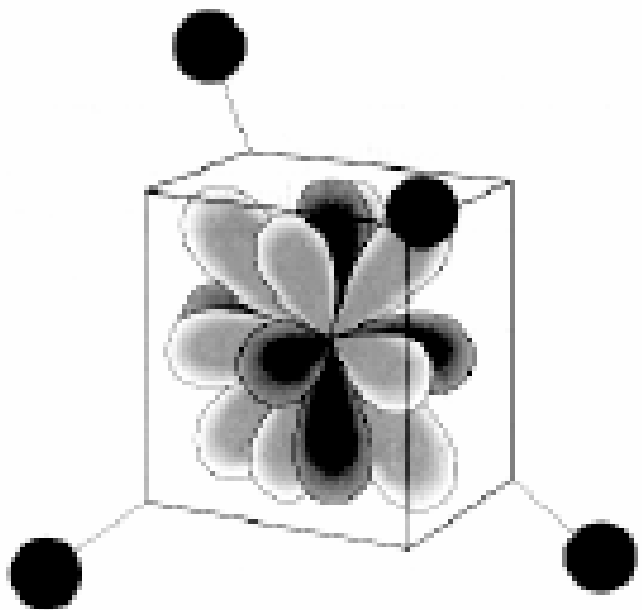
Spherical environment
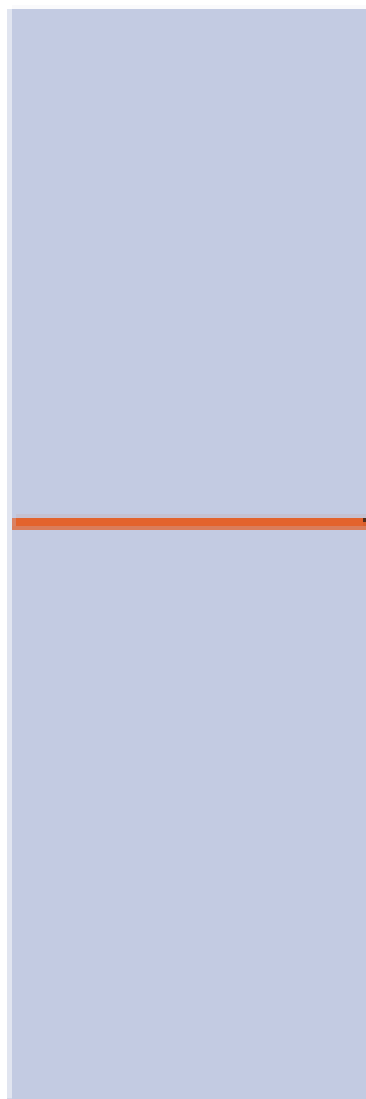
In tetrahedral crystal field
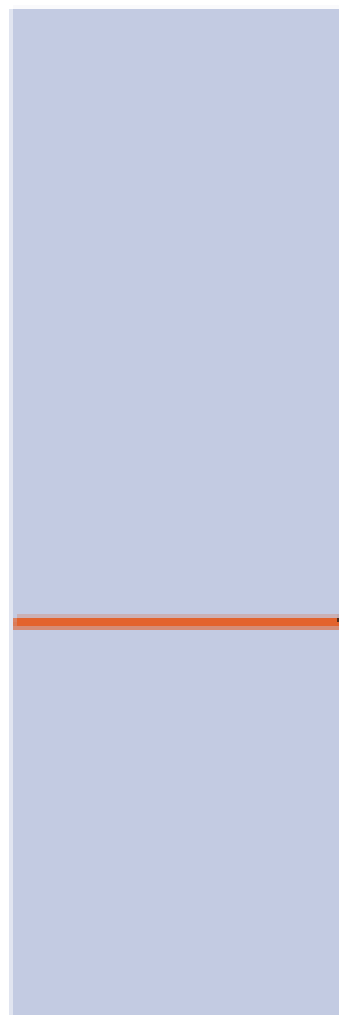
t_2

$\frac{2}{5}\Delta_T$

Δ_T

$\frac{3}{5}\Delta_T$

e
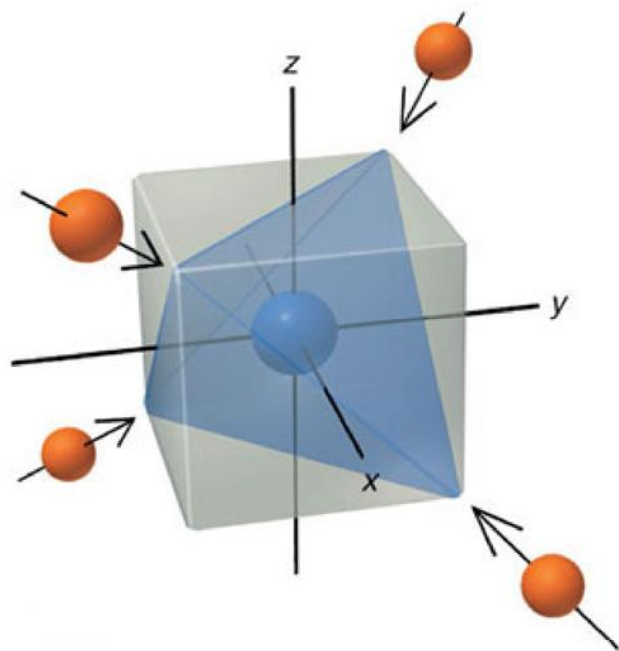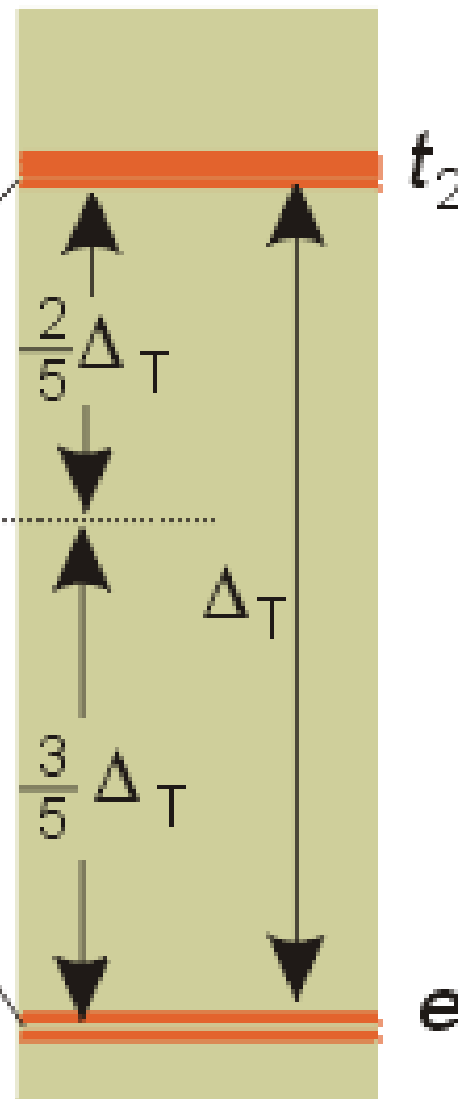
Crystal Field Splitting Energy (CFSE)

- **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:

$$= (-0.4x + 0.6y)\Delta_O$$

BEYOND d^3

- In weak field: $\Delta_O < P, \Rightarrow t_{2g}^3 e_g^1$

- In strong field $\Delta_O > P, \Rightarrow t_{2g}^4$

- P - paring energy

Magnitude of Δ

Oxidation state of the metal ion

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

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

Nature of the metal ion

3d<4d<5d

Number and geometry of the ligand
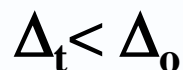
$\Delta_t < \Delta_o$

Nature of the ligand

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

Ground-state Electronic Configuration, Magnetic Properties and Colour

42 d^2

45 Weak-field d^4

43 d^3

44 Strong-field d^4

Ground-state Electronic Configuration, Magnetic Properties and Colour

45 Weak-field d^4

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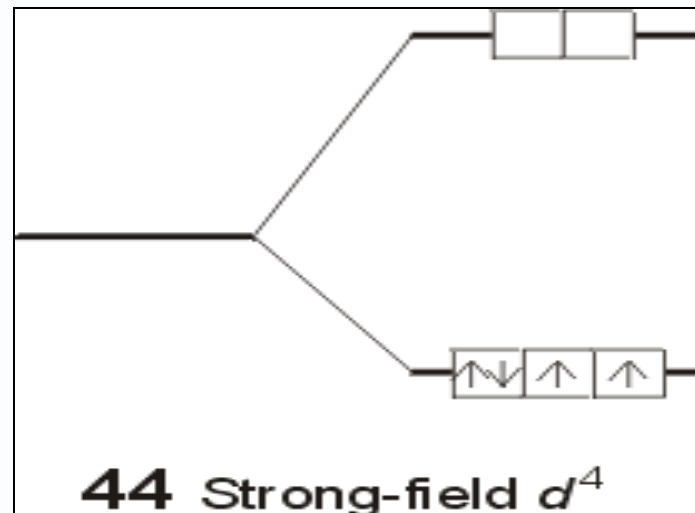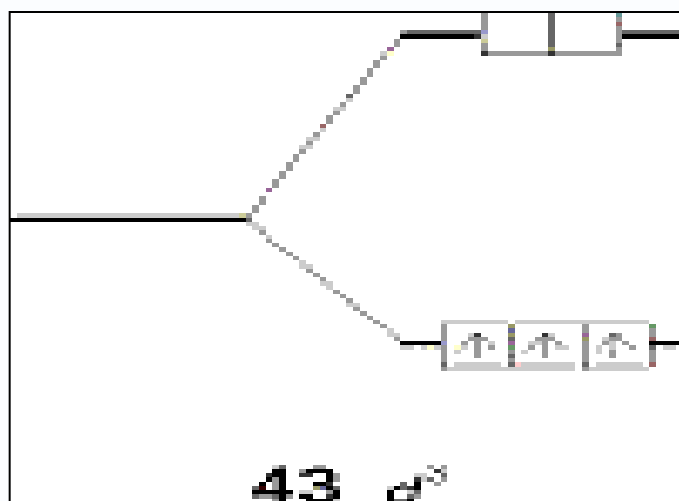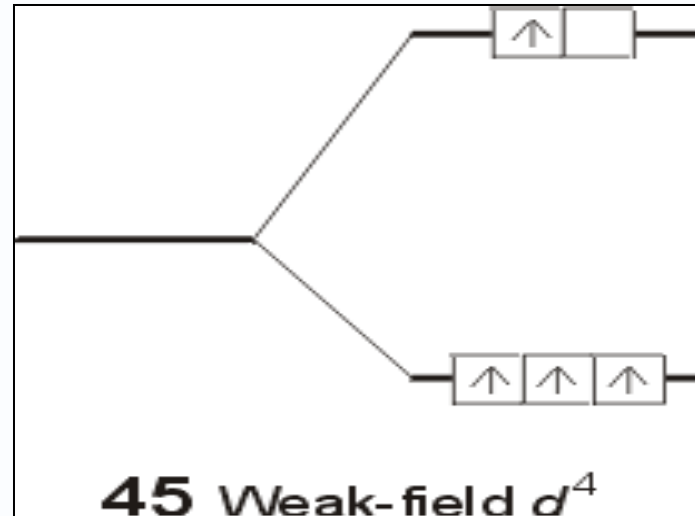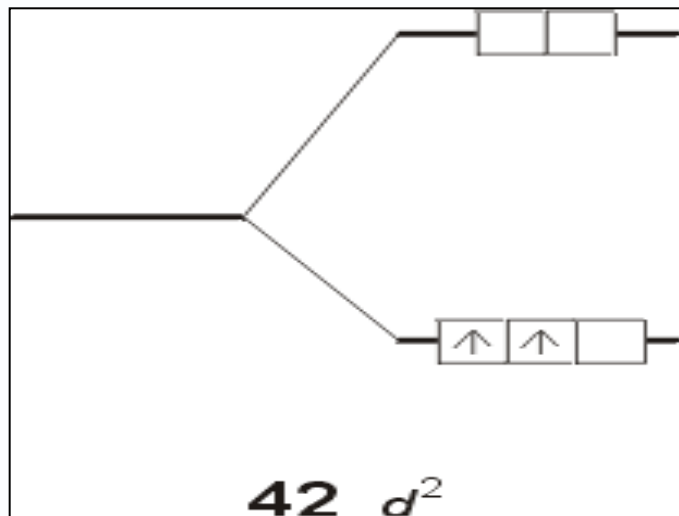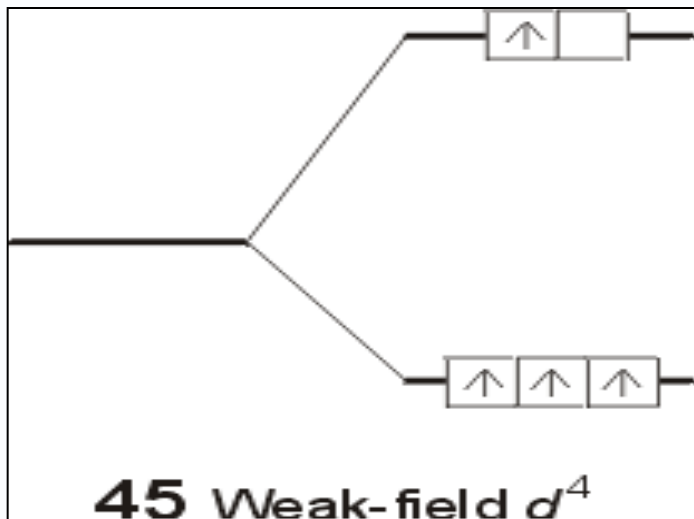
Weak Field Complex

the total spin is $4 \times \frac{1}{2} = 2$
High Spin Complex

44 Strong-field d^4

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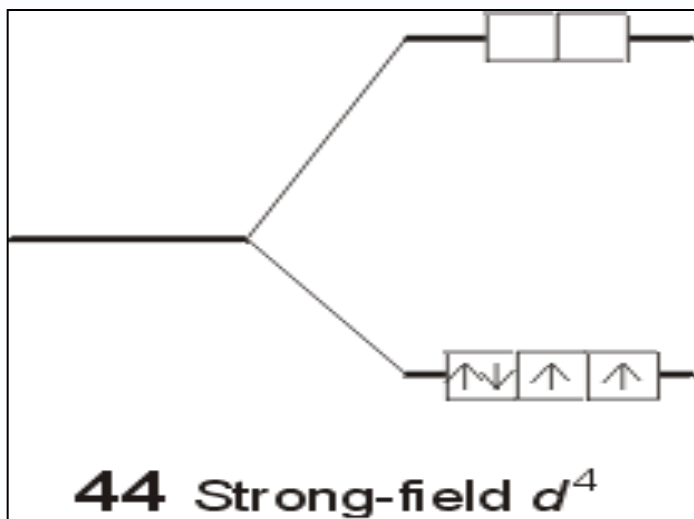
Strong field Complex

total spin is $2 \times \frac{1}{2} = 1$
Low Spin Complex

Ground-state Electronic Configuration, Magnetic Properties and Colour

d^5 ions, O_h field

e_g

$+ 0.6\ \Delta_{oct}$

$- 0.4\ \Delta_{oct}$

t_{2g}
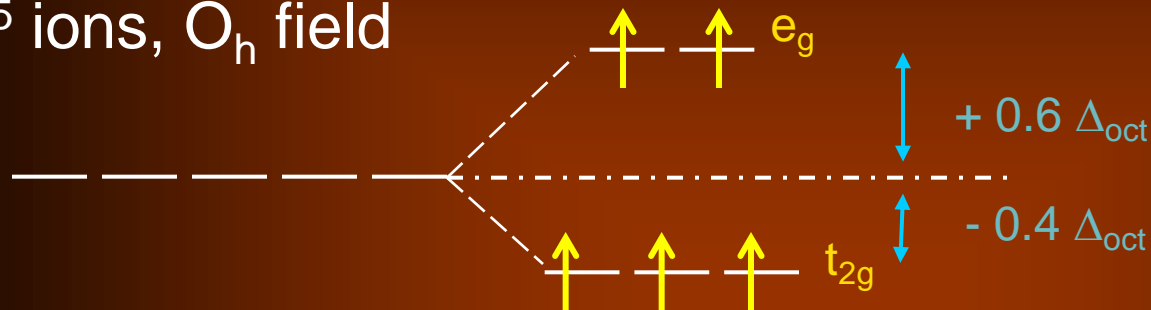
High Spin

CFSE = 0

5 u.p.e$^-$

e_g

$+ 0.6\ \Delta_{oct}$

$- 0.4\ \Delta_{oct}$

t_{2g}
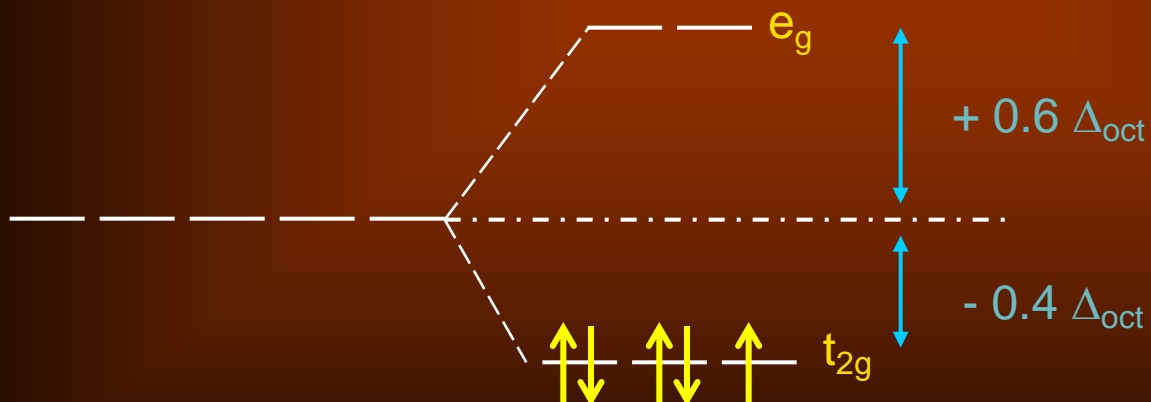
Low Spin

CFSE =

$5 \times - 0.4\ \Delta_{oct} + 2P$

$= - 2.0\ \Delta_{oct} + 2P$

1 u.p.e$^-$

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

CN⁻ = s.f.l.

C.N. = 6 ∴ O_h Fe(III) ∴ d^5 h.s.   l.s.

$$CFSE = 5 \times -0.4 \Delta_{oct} + 2P = -2.0 \Delta_{oct} + 2P$$

+ 0.6 Δ_{oct}

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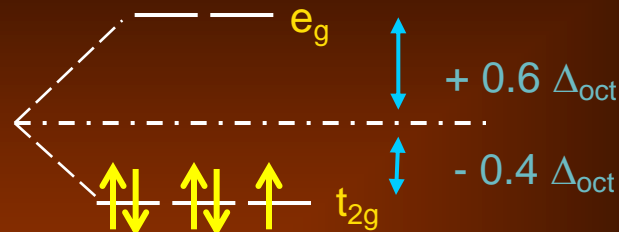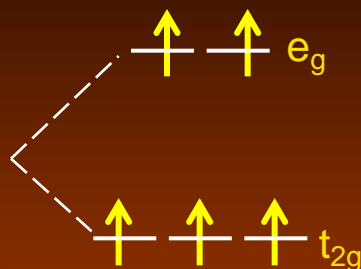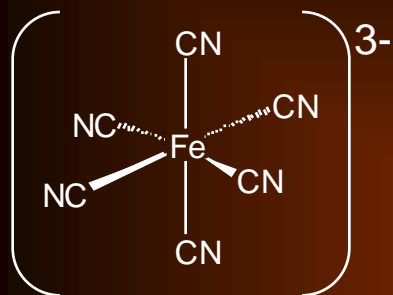
If the CFSE of $[Co(H_2O)_6]^{2+}$ is -0.8 Δ_{oct}, what spin state is it in?

C.N. = 6 ∴ O_h Co(II) ∴ d^7 h.s.   l.s.

+ 0.6 Δ_{oct}

- 0.4 Δ_{oct}
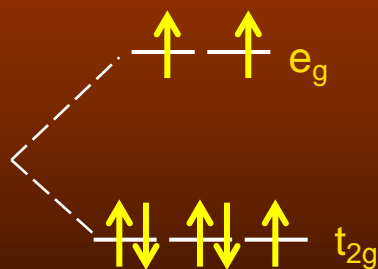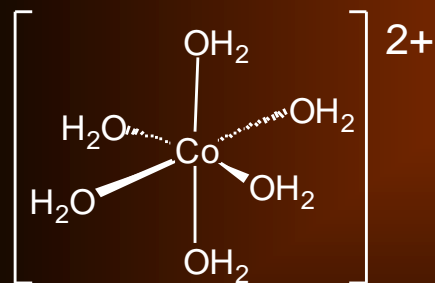
$$CFSE = (5 \times -0.4 \Delta_{oct}) + (2 \times 0.6 \Delta_{oct}) = -0.8 \Delta_{oct}$$
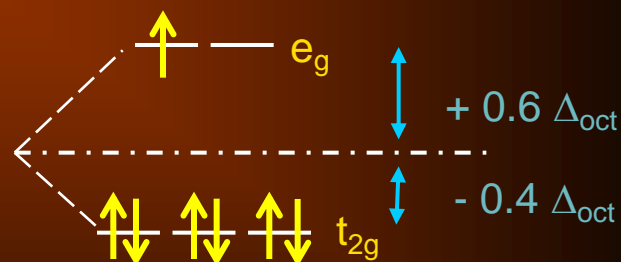
$$CFSE = (6 \times -0.4 \Delta_{oct}) + (0.6 \Delta_{oct}) + P = -1.8 \Delta_{oct} + P$$

Magnetism

Each electron has a magnetic moment owing to its:

spin angular momentum   orbital angular momentum
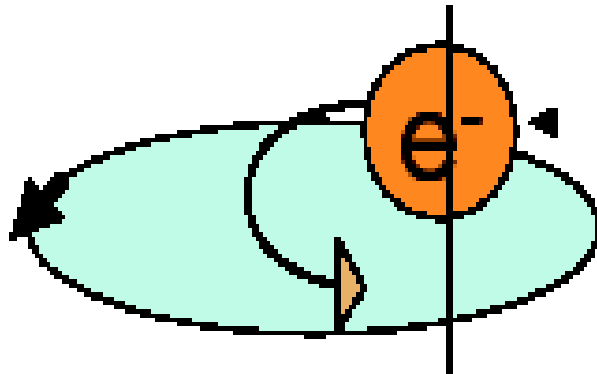
Orbital motion of e generates current and magnetic field

Spin motion of e about its own Axis also generates a magnetic field

- The magnetic moment 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

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

- 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 $\Delta_t << \Delta_O$.

n = no. of unpaired electrons

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

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

**Similar Calculation can be done for Low-spin Complex**
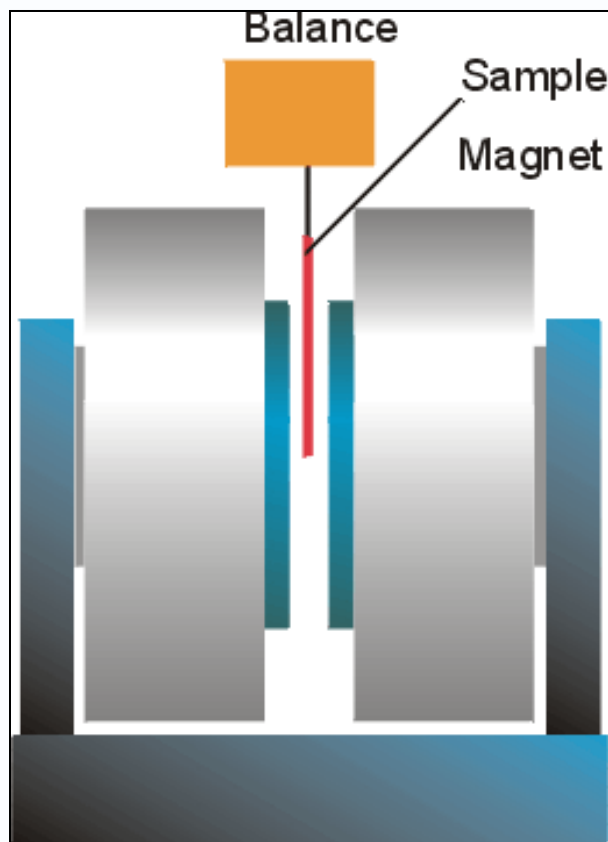
Gouy balance to measure the magnetic susceptibilities

- 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

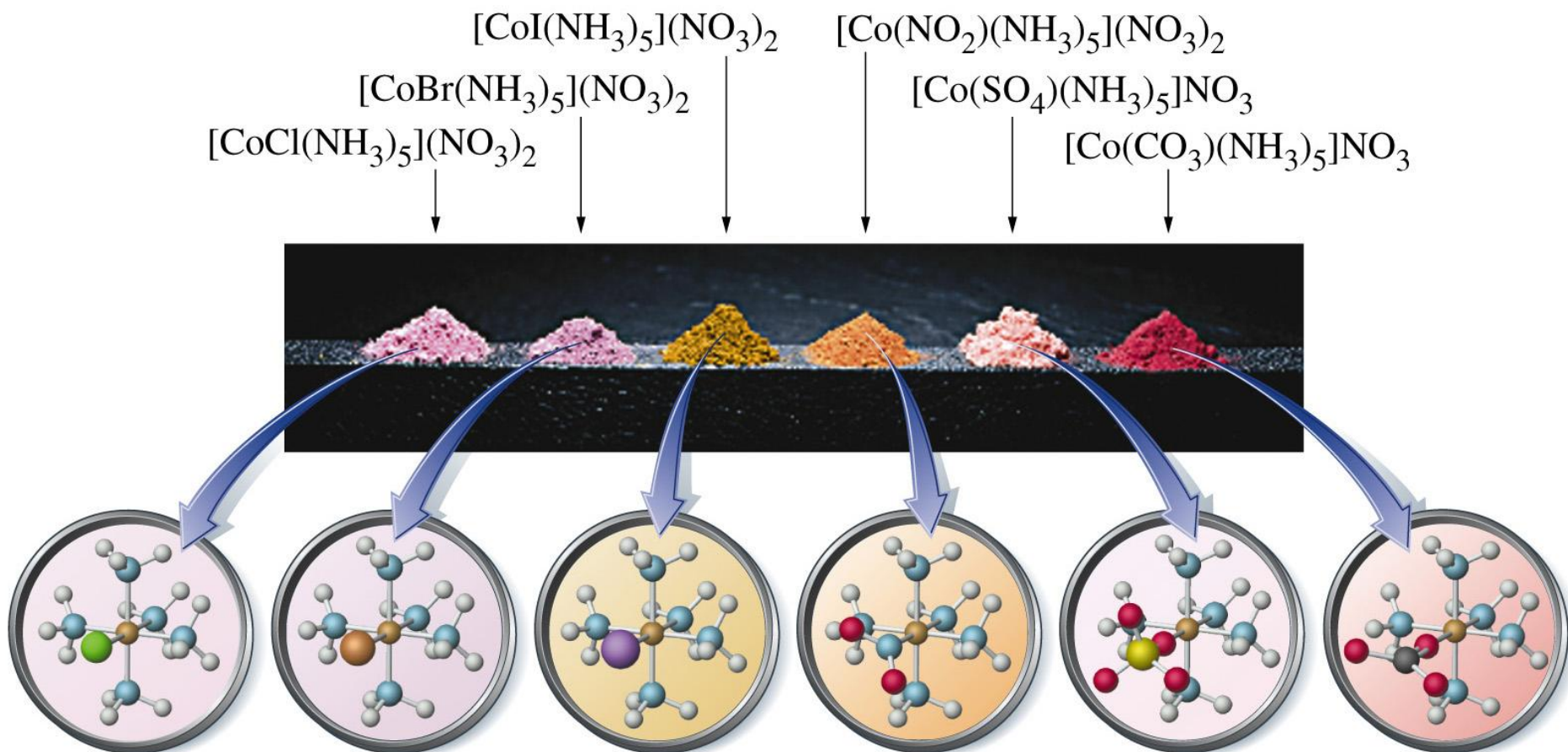# The origin of the color of the transition metal compounds
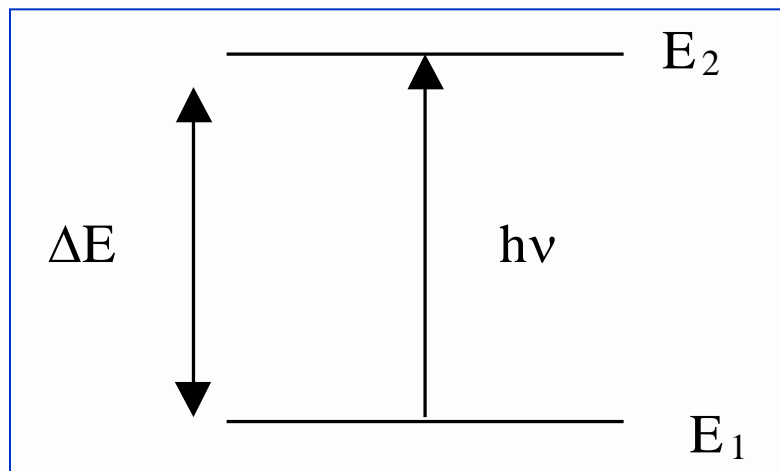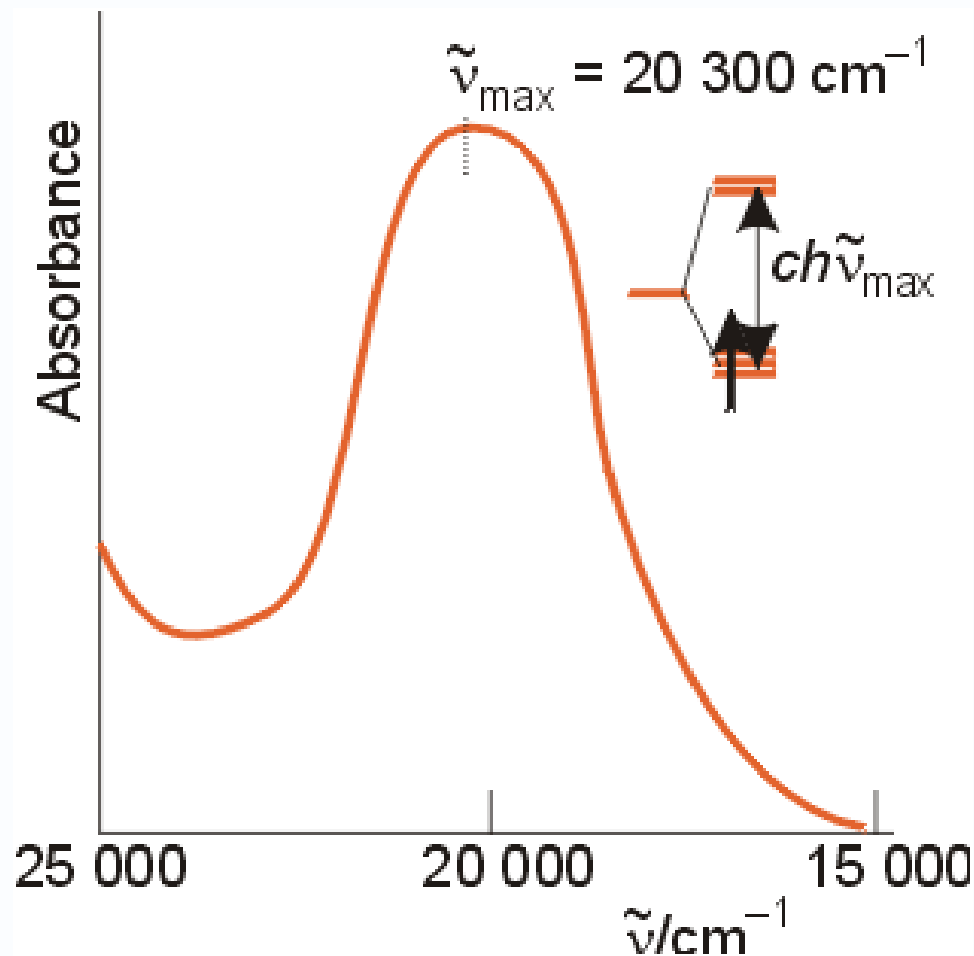

$$\Delta E = E_2 - E_1 = h\nu$$

Ligands influence Δ_O, therefore the colour

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

1. Metal charge
2. Ligand strength

$[CoI(NH_3)_5](NO_3)_2$

$[Co(NO_2)(NH_3)_5](NO_3)_2$

$[CoBr(NH_3)_5](NO_3)_2$

$[Co(SO_4)(NH_3)_5]NO_3$

$[CoCl(NH_3)_5](NO_3)_2$

$[Co(CO_3)(NH_3)_5]NO_3$

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

$\tilde{\nu}_{max} = 20\ 300\ cm^{-1}$

$ch\tilde{\nu}_{max}$

Absorbance

25 000   20 000   15 000

$\tilde{\nu}/cm^{-1}$
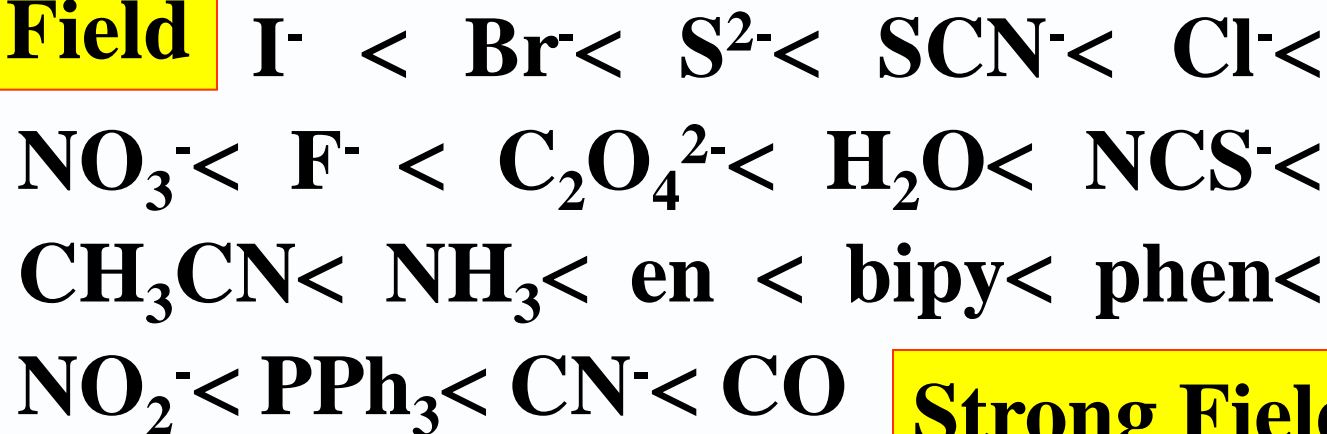
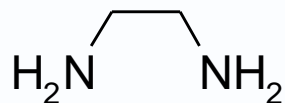**Assigned transition:**

$e_g \longrightarrow t_{2g}$

This corresponds to the energy gap

$\Delta_O = 243\ kJ\ mol^{-1}$

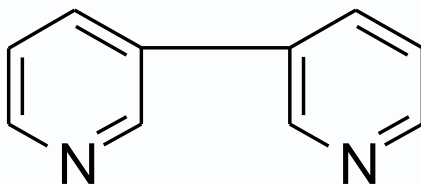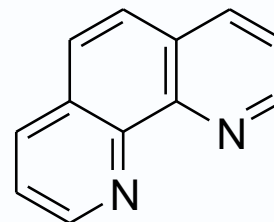- **Spectrochemical Series: An order of ligand field strength based on experiment:**

$I^- < Br^- < S^{2-} < SCN^- < Cl^- <$
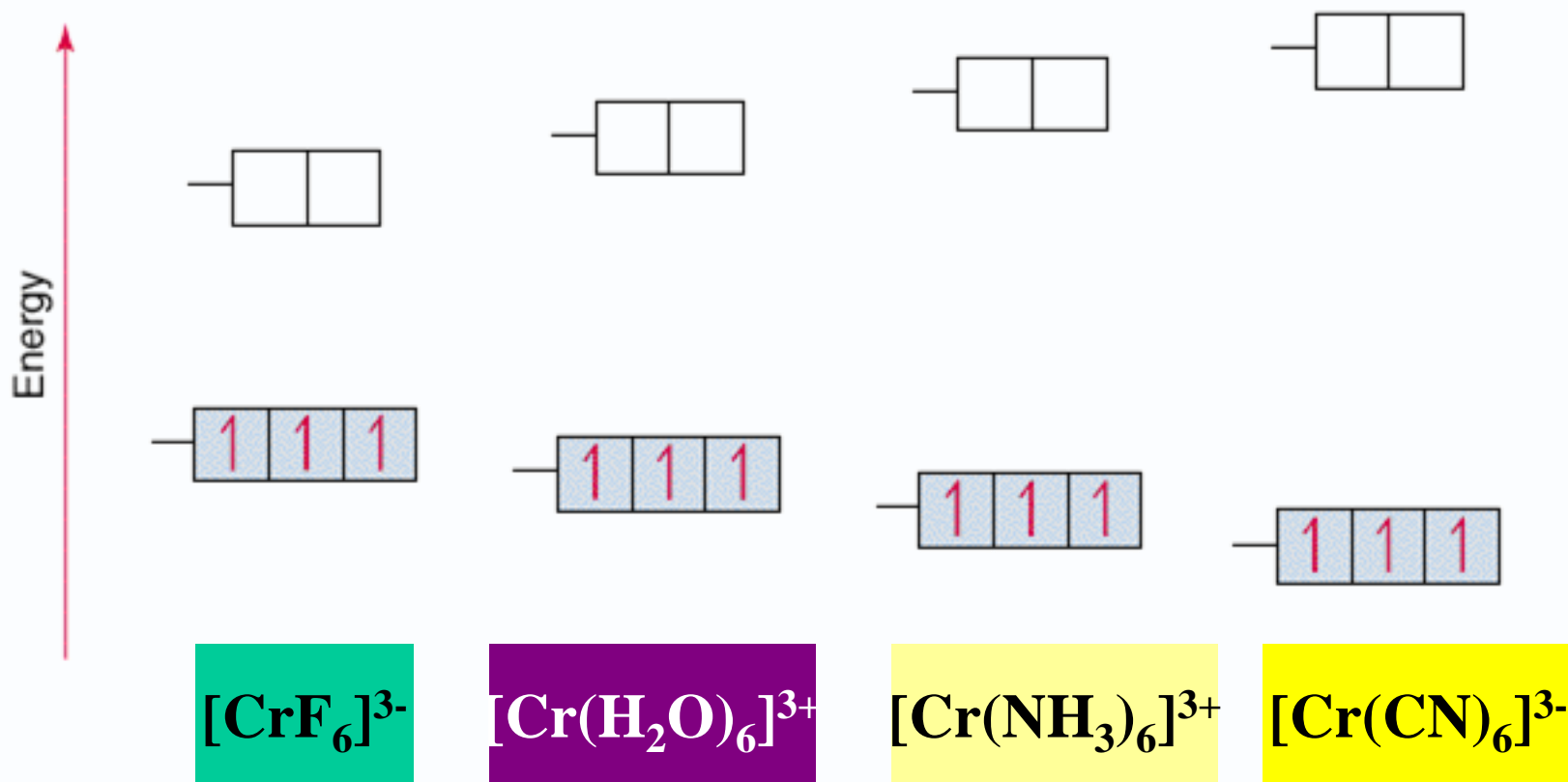
$NO_3^- < F^- < C_2O_4^{2-} < H_2O < NCS^- <$

$CH_3CN < NH_3 < en < bipy < phen <$

$NO_2^- < PPh_3 < CN^- < CO$

Ethylenediamine (en)

2,2'-bipyridine (bipy)

1.10 - penanthroline (phen)

[CrF₆]³⁻ **[Cr(H₂O)₆]³⁺** **[Cr(NH₃)₆]³⁺** **[Cr(CN)₆]³⁻**

As Cr³⁺ 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.
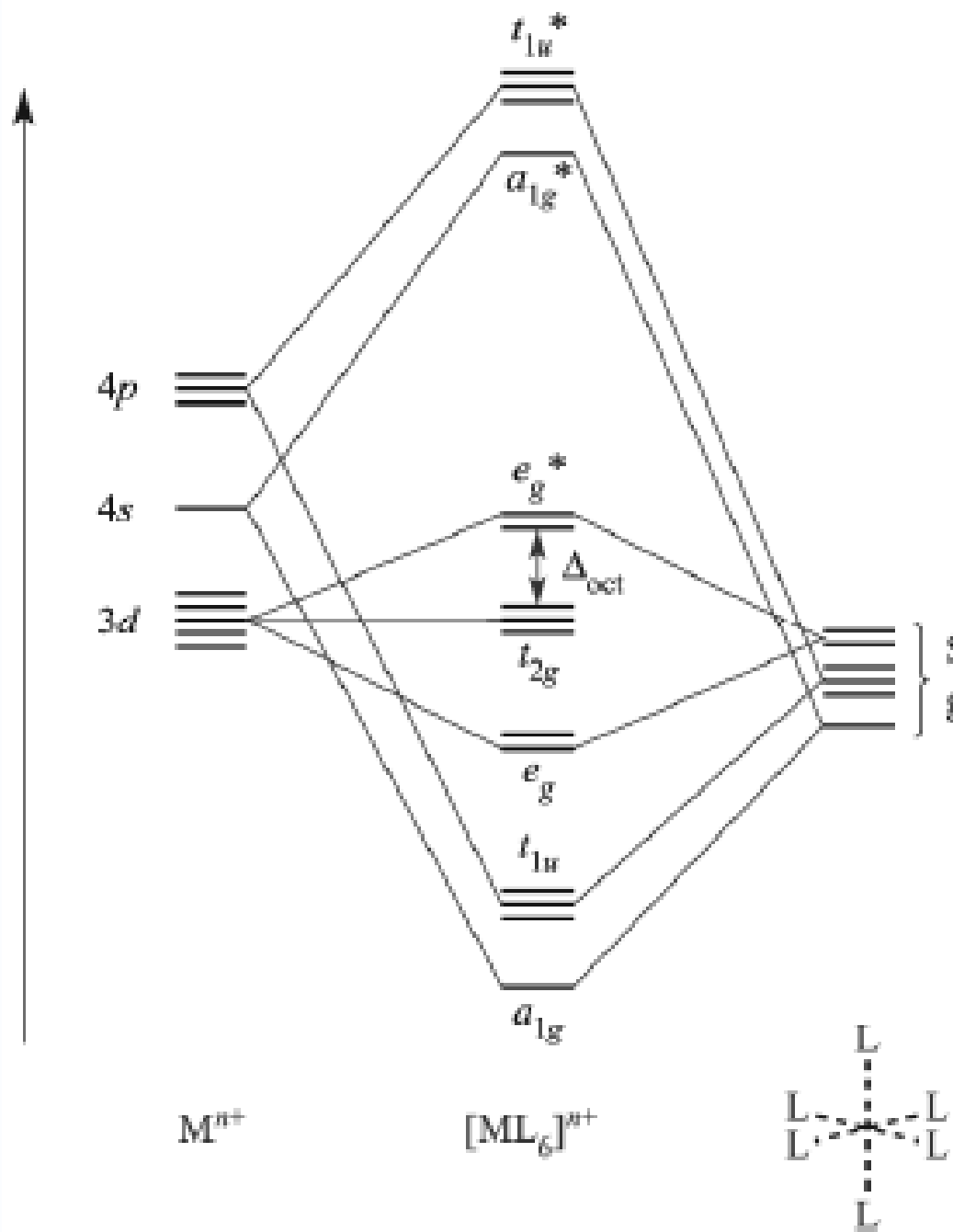
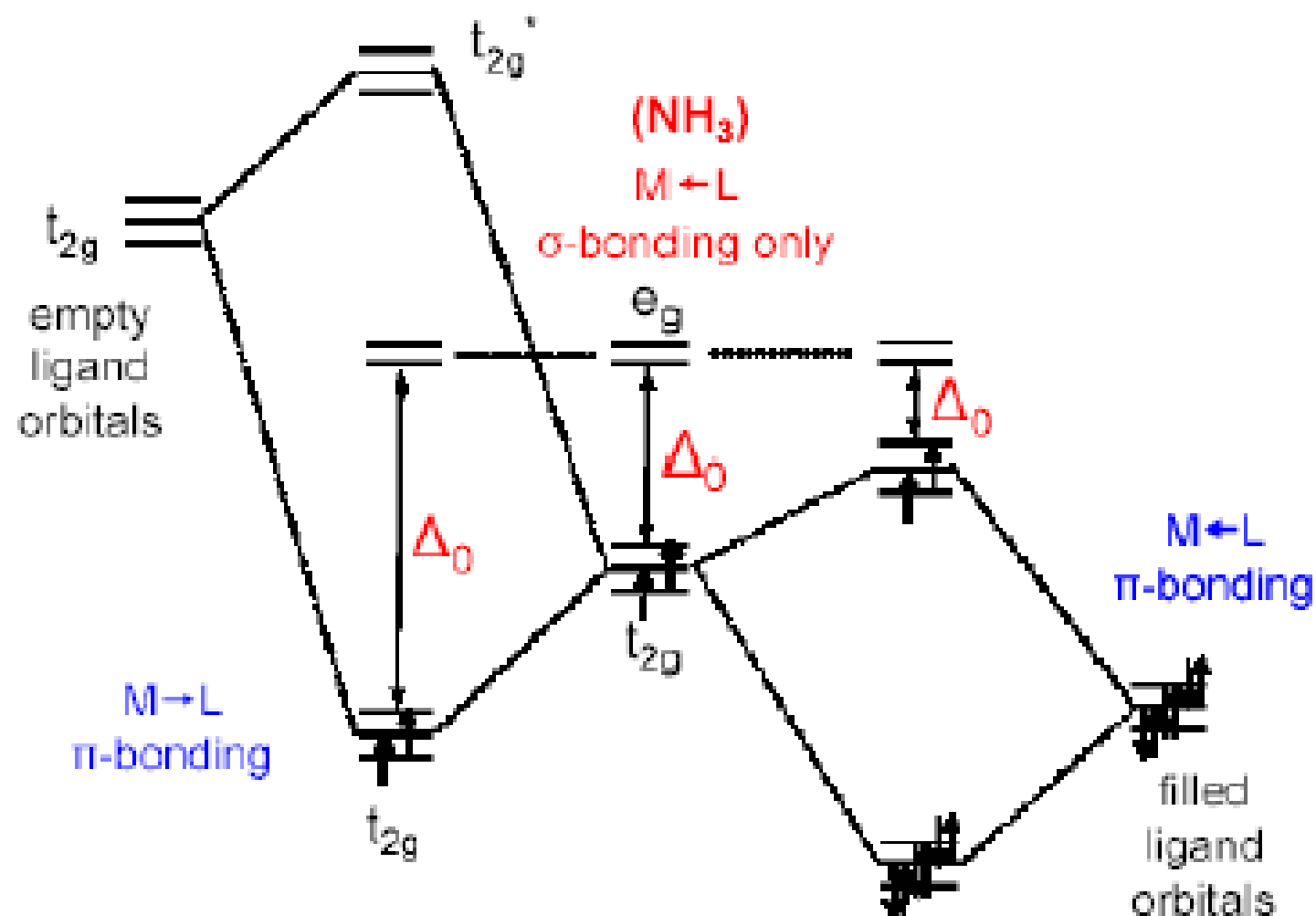## Limitations of CFT

Considers Ligand as Point charge/dipole only
Does not take into account overlap between 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

t_{1u}^*

a_{1g}^*

$4p$

e_g^*

$4s$

Δ_{oct}

$3d$

t_{2g}

e_g

t_{1u}

a_{1g}

M^{n+}

$[ML_6]^{n+}$

σ

π

L

L   L

L   L

L

Summary of ligand effects on Δ_o

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.**
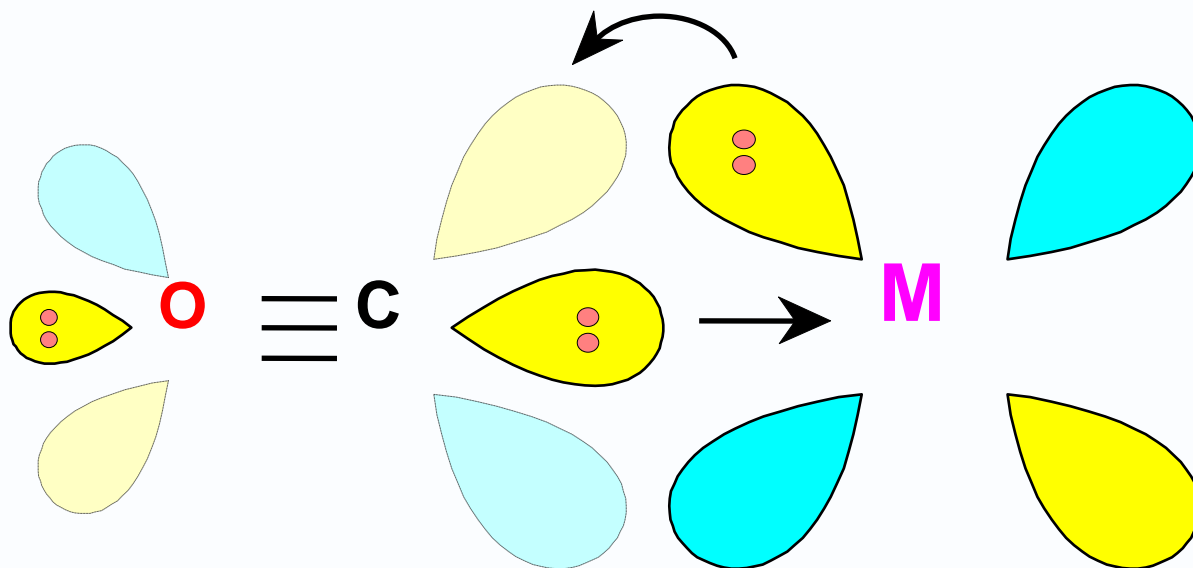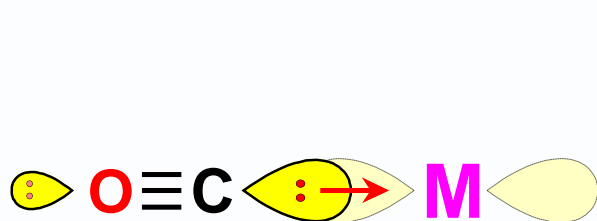
Stabilizing Low Oxidation State: CO Can Do the Job
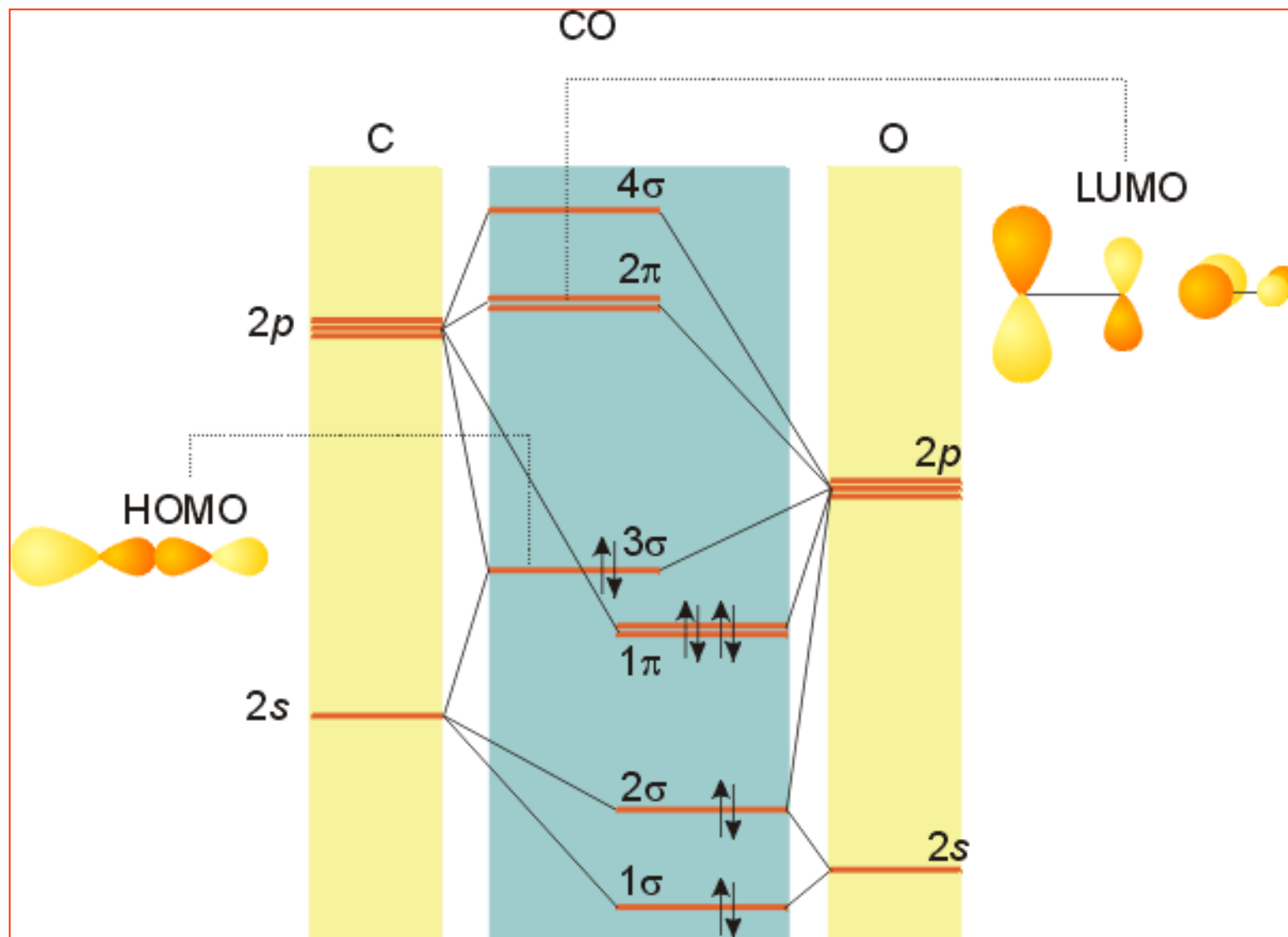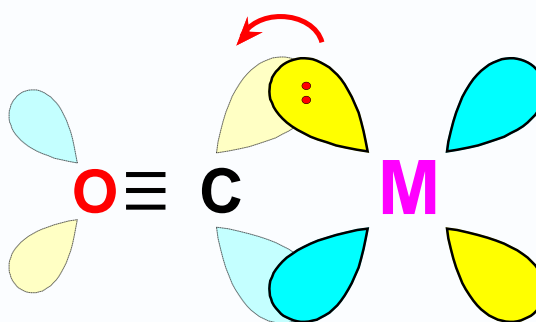
Stabilizing Low Oxidation State: CO Can Do the Job
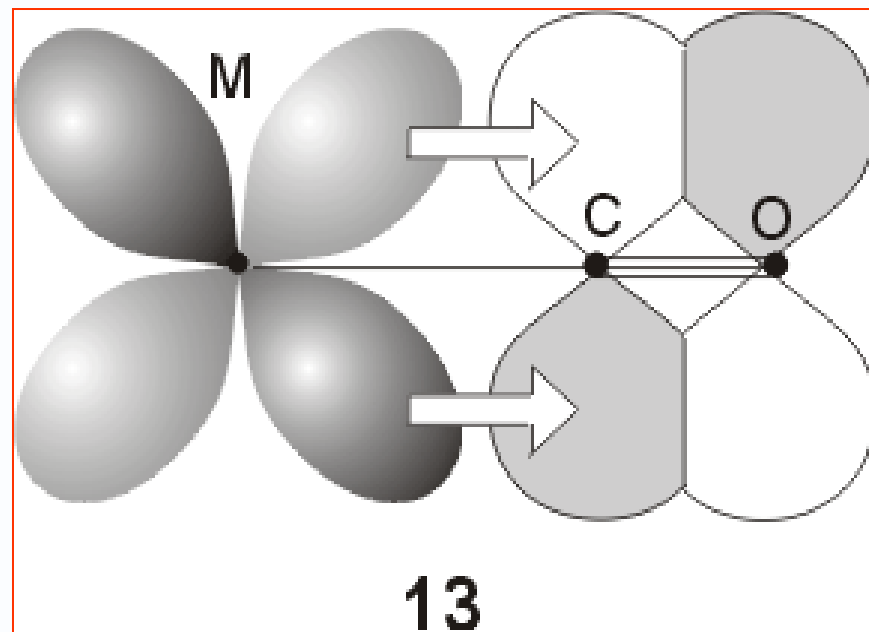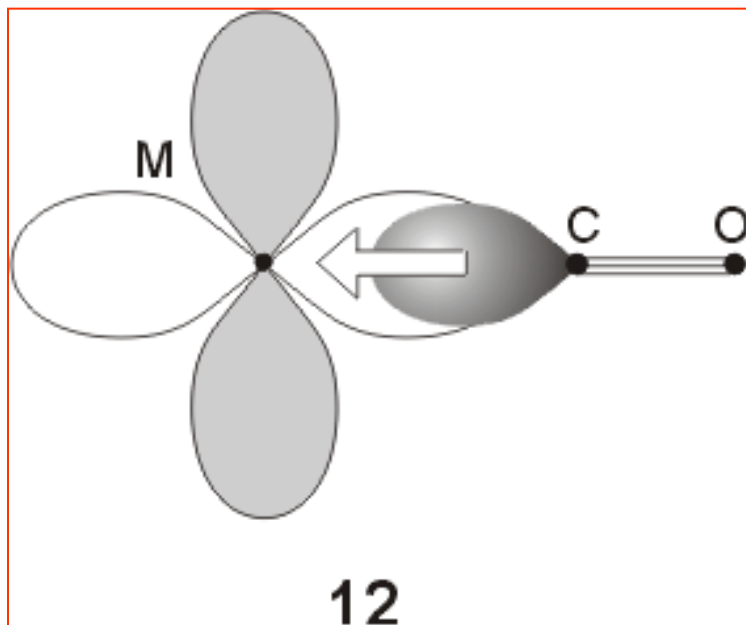
$Ni(CO)_4$], [$Fe(CO)_5$], [$Cr(CO)_6$], [$Mn_2(CO)_{10}$], [$Co_2(CO)_8$], $Na_2[Fe(CO)_4]$, $Na[Mn(CO)_5]$
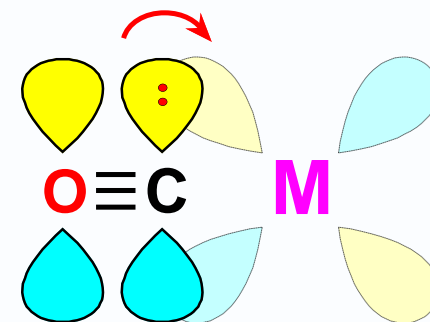
σ orbital serves as a very weak donor to a metal atom

CO-M sigma bond

M to CO pi backbonding

CO to M pi bonding
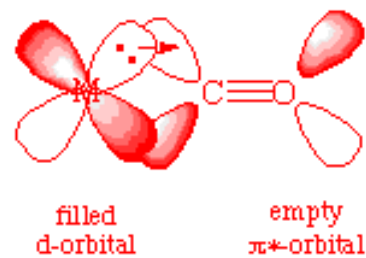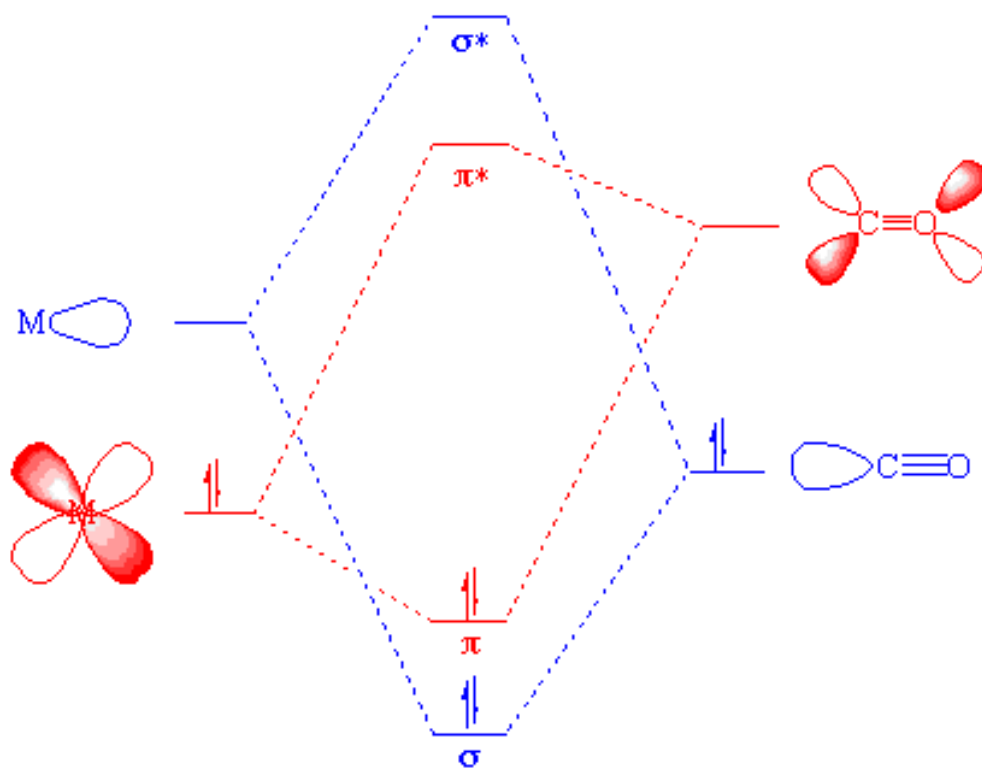*(rare)*

σ bond:

π backbond:

empty
d or p-orbital

filled
σ-orbital

filled
d-orbital

empty
π*-orbital

L_nM $L_nM(CO)$ CO

σ*

π*

π

σ

M

C≡O