Bonding in coordination compounds

Nobel prize 1913
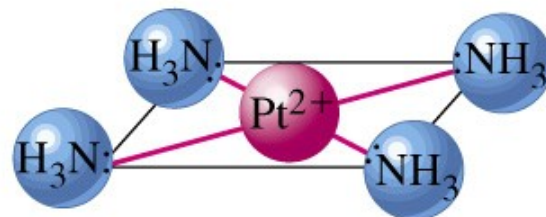

- **Alfred Werner - 1893**
- **VBT**
- **Crystal Field Theory (CFT)**
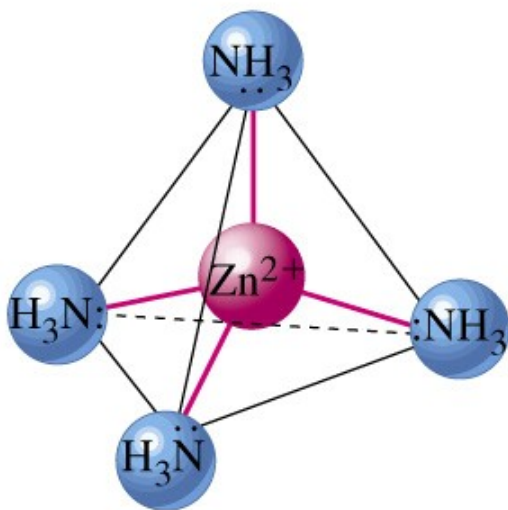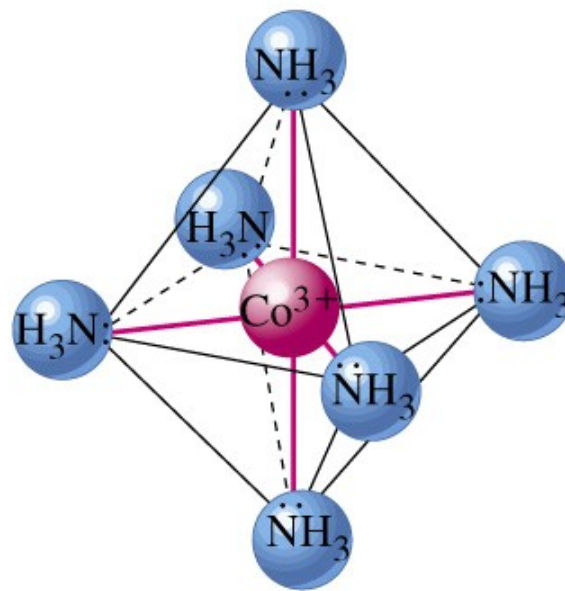- **Modified CFT, known as Ligand Field Theory**
- **MOT**

How & Why?

$H_3N:$ —— Ag^+ —— $:NH_3$

Linear

$H_3N:$ NH_3
Pt^{2+}
$H_3N:$ NH_3

Square planar

NH_3
$H_3N:$ Zn^{2+} $:NH_3$
$H_3\overset{..}{N}$

Tetrahedral

NH_3
H_3N Co^{3+} $:NH_3$
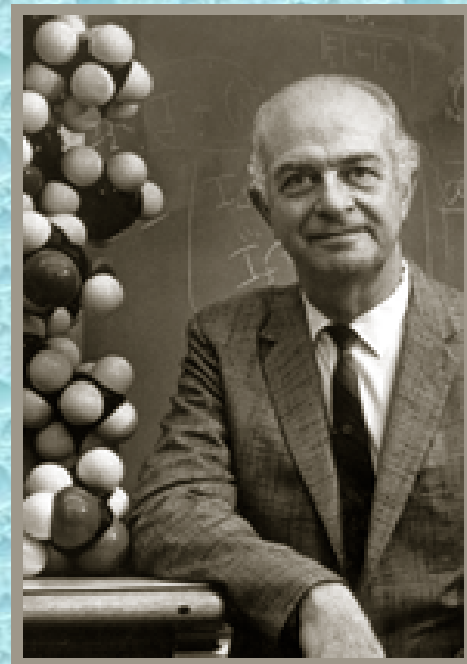$H_3N:$ $\overset{.}{N}H_3$
$\overset{..}{N}H_3$

Octahedral

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)
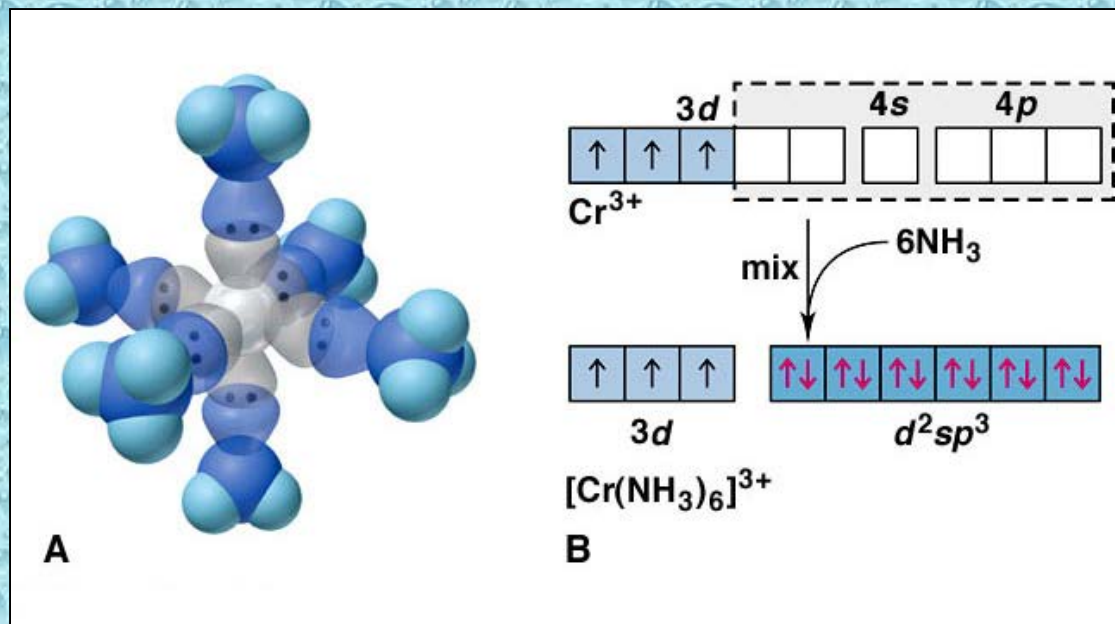Nobel prizes: 1954, 1962

Valance Bond Model

Ligand = Lewis base

Metal = Lewis acid

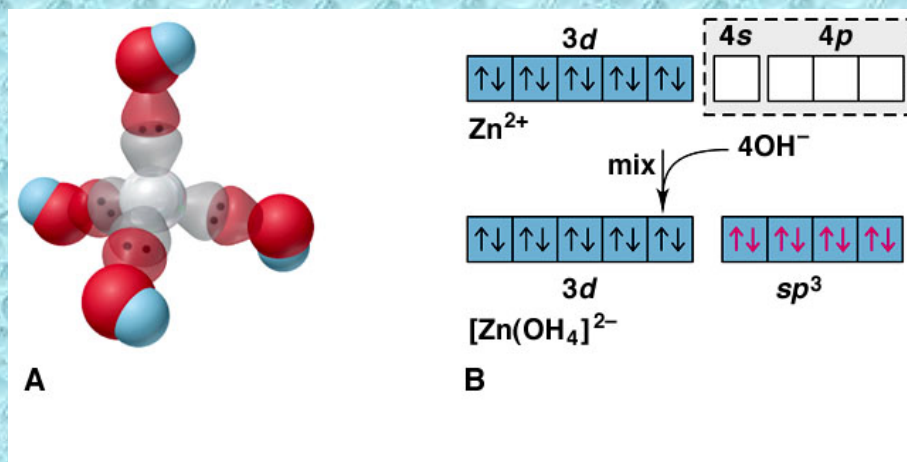**s, p and d orbitals give hybrid orbitals with specific geometries**

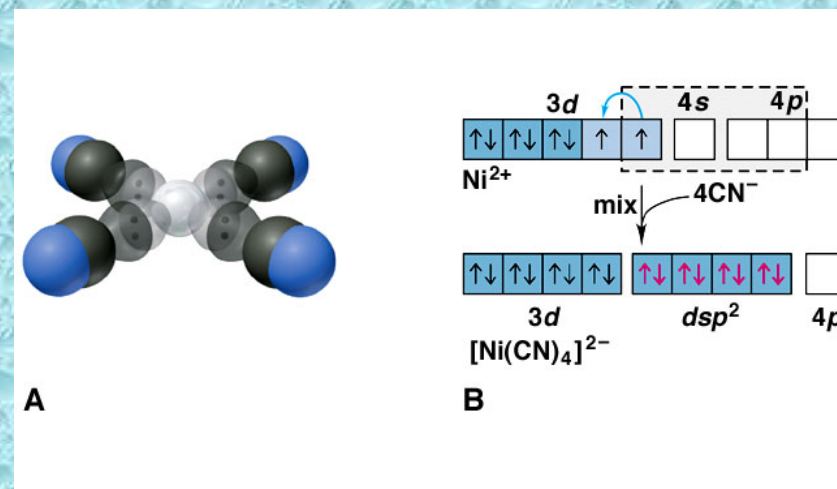**Number and type of M-L hybrid orbitals determines geometry of the complex**

Octahedral Complex

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

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

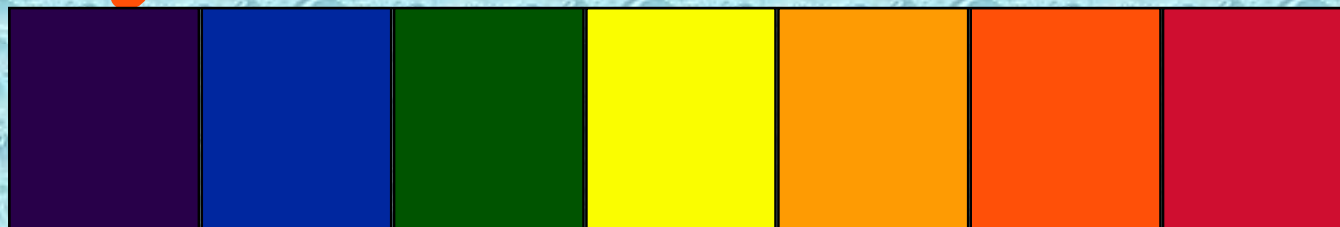**Square Planar *e.g.* [Ni(CN)$_4$]$^{2-}$**

Limitations of VB theory

Cannot account for colour of complexes

May predict magnetism wrongly

Cannot account for spectrochemical series
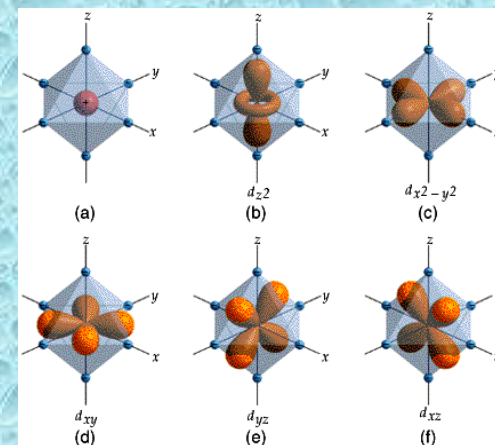
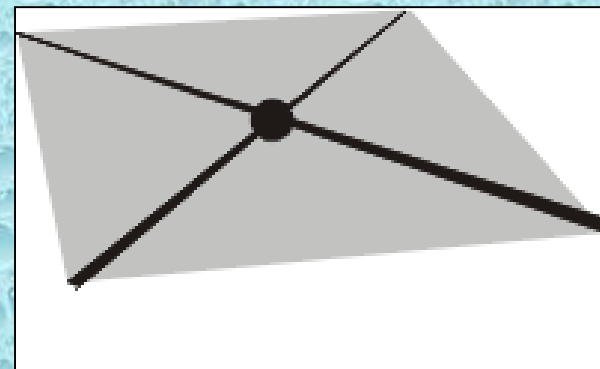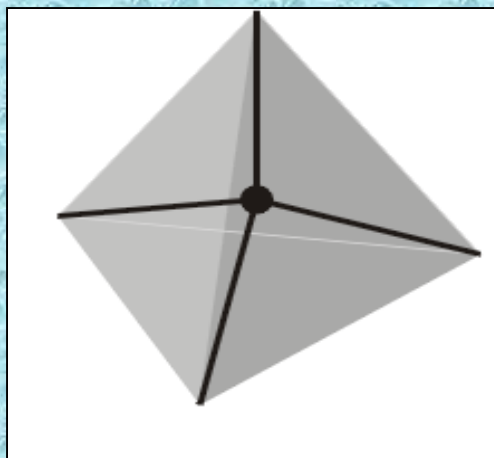# Crystal Field Theory

400   500   600   800
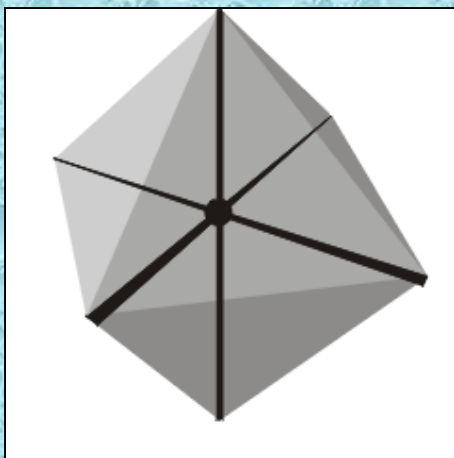
- The relationship between colors and complex metal ions
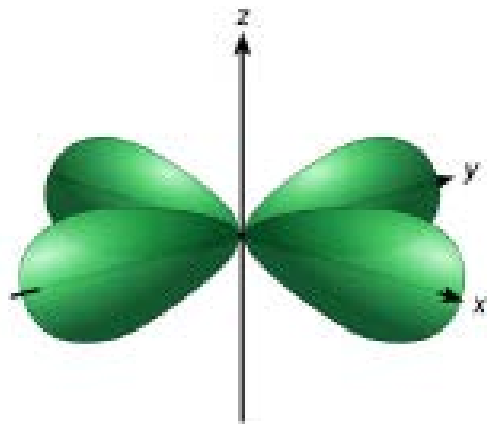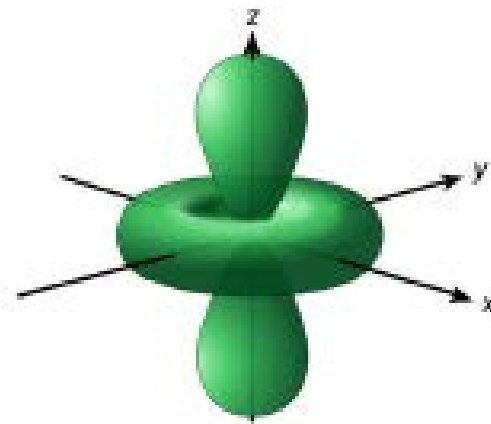
Crystal Field Model

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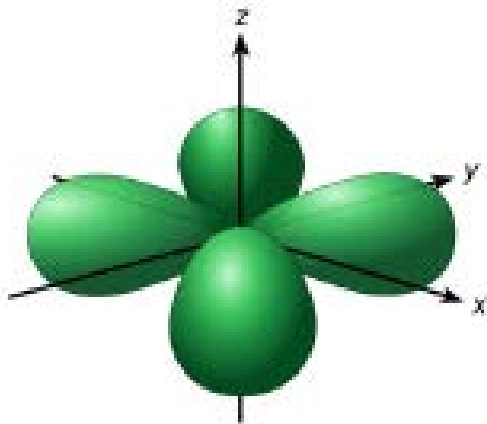- ➢ **Used to rationalize spectroscopic and magnetic properties.**
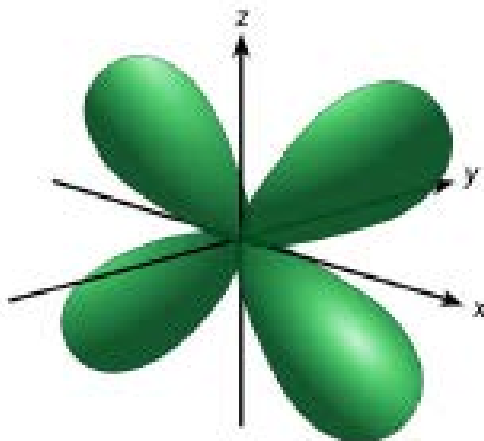
d-orbitals: look attentively along the axis

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

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 (d_{z^2} and $d_{x^2-y^2}$).**
  - **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.**
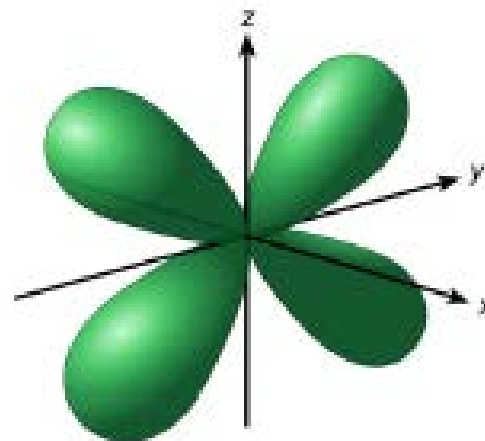 - **These orbitals form the degenerate low energy set of energy levels.**

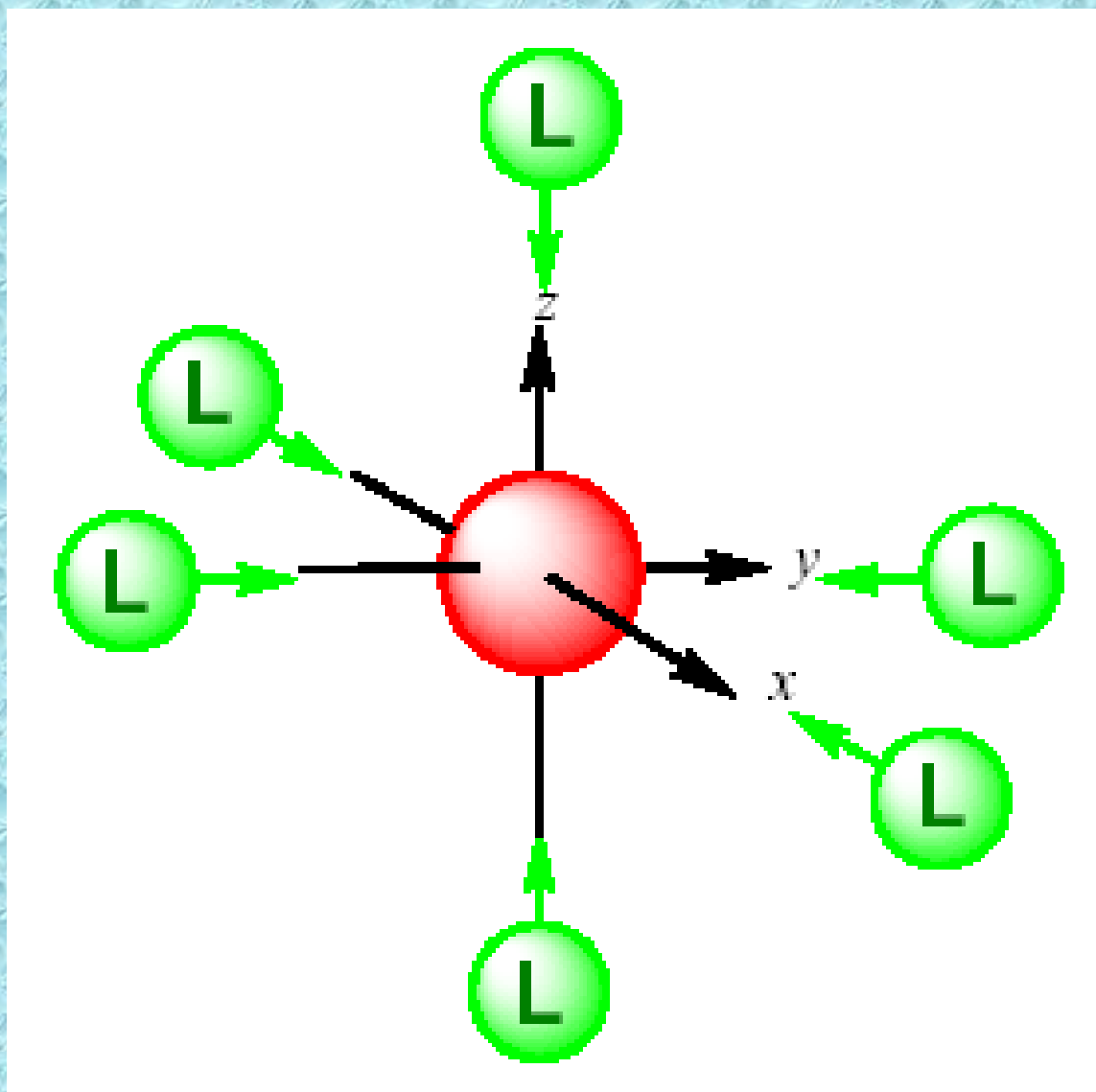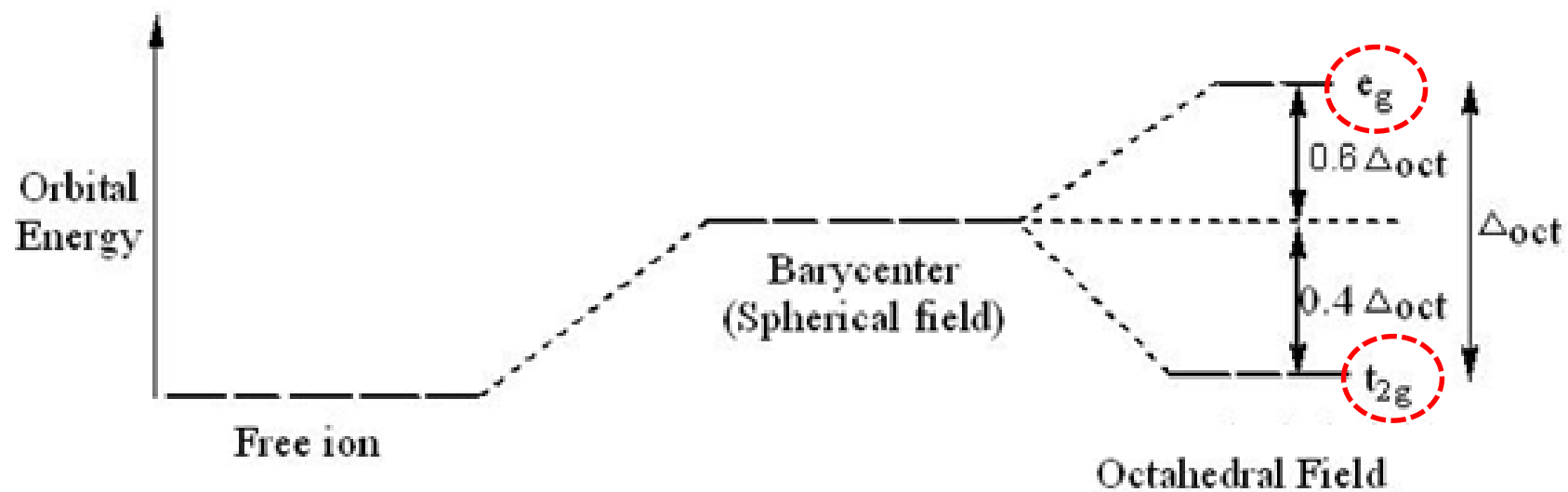# In Octahedral Field

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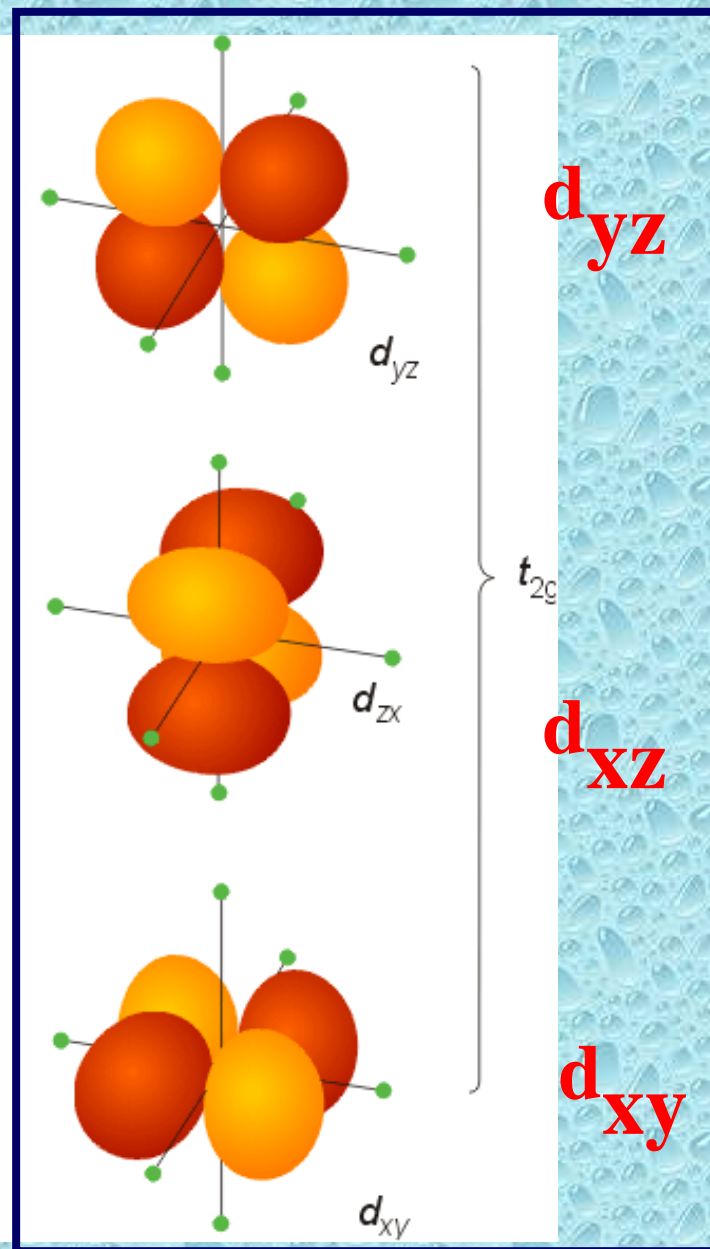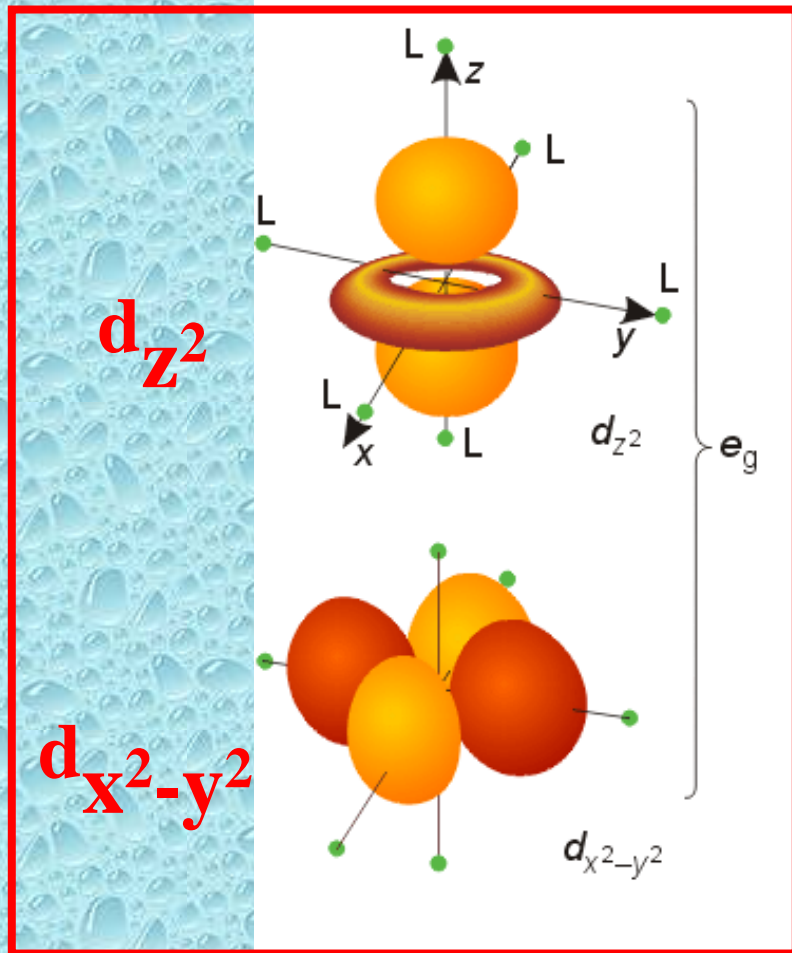
$d_{x^2-y^2}$

d_{yz}

d_{xz}

d_{xy}

Tetrahedral Field

- We assume an tetrahedral array of negative charges placed around the metal ion (which is positive).

- The ligand and orbitals lie in between the axes of the negative charges.

  – Therefore, there is a large, unfavorable interaction between ligand and these orbitals, d_{xy}, d_{yz}, and d_{xz} .

  – These orbitals form the degenerate high energy pair of energy levels.

- The orbitals along the axes (d_{z^2} and $d_{x^2-y^2}$)

  – Feels a smaller repulsion between ligand and metal for these orbitals.

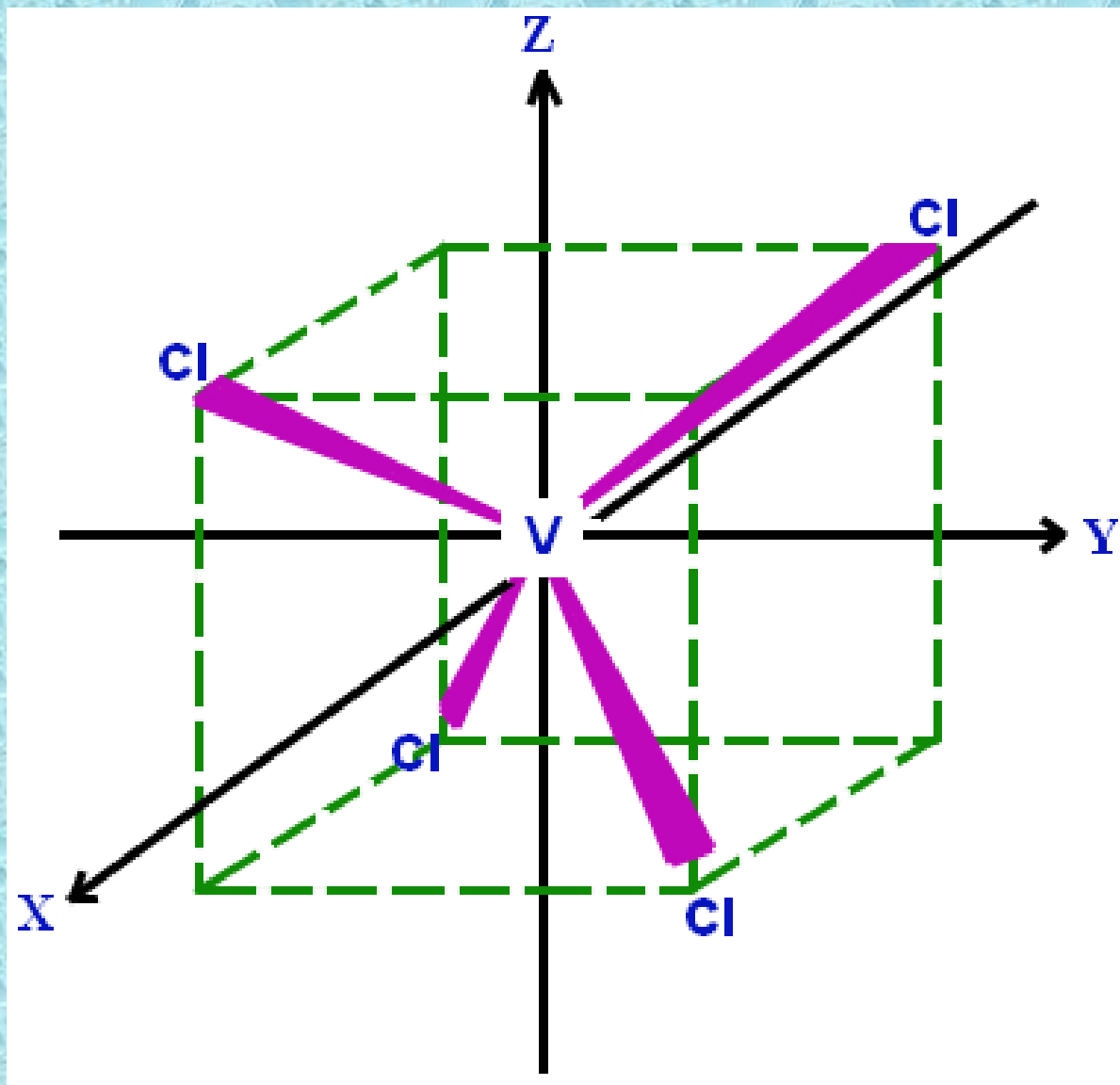 – These orbitals form the degenerate low energy set of energy levels.
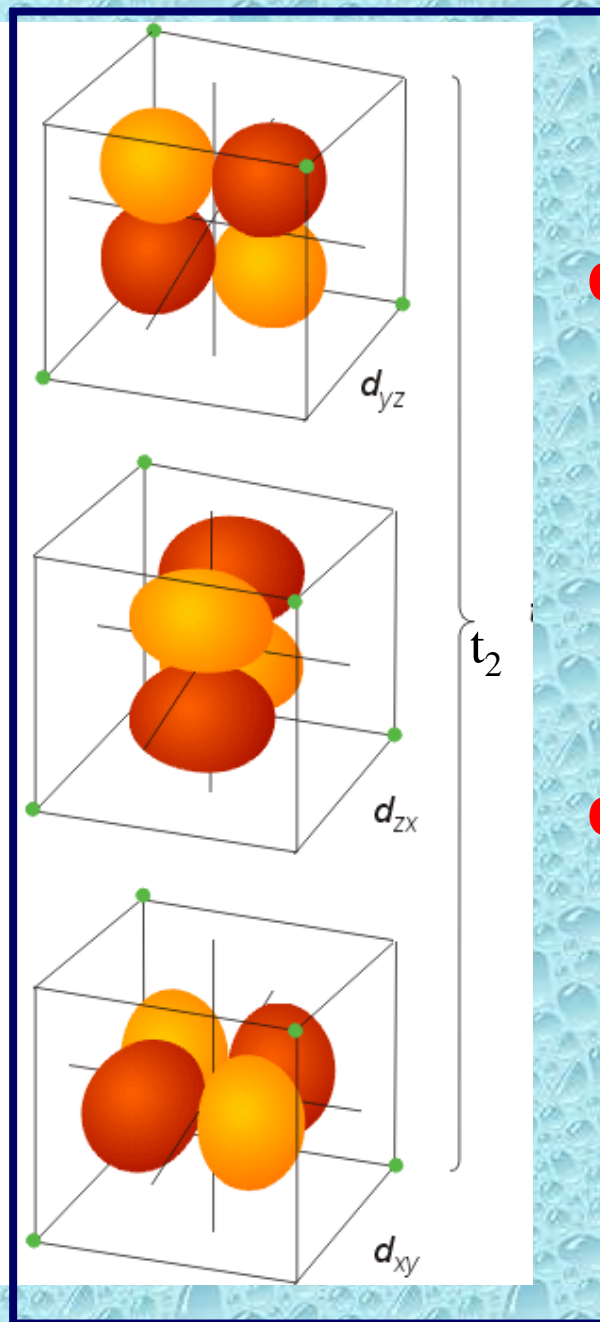
In Tetrahedral Field

d_{z^2}

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

d_{yz}

d_{xz}

d_{xy}
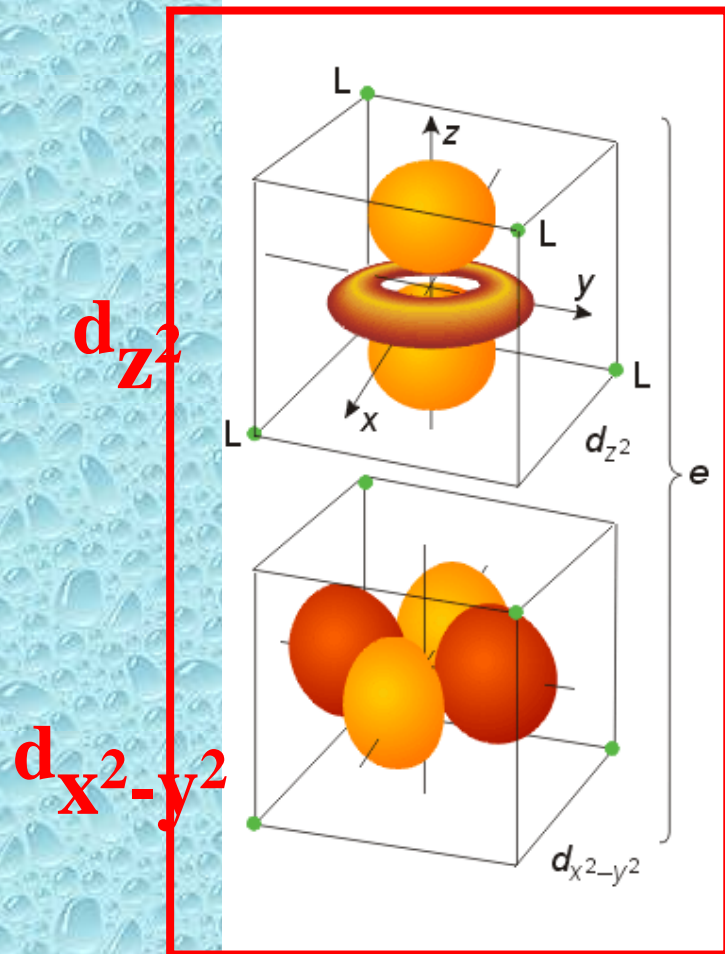
tetrahedral (T_d) crystal field splitting

$d_{x^2-y^2}$ d_{z^2} **e$_g$**

$\frac{3}{5}$ $_o$

E

$_o$

$\frac{2}{5}$ $_o$

d_{xy} d_{xz} d_{yz} **t$_{2g}$**

Octahedral

d_{xy} d_{xz} d_{yz} **t$_2$**

$\frac{3}{5}$ $_t$

$\frac{2}{5}$ $_t$

$_t$

$d_{x^2-y^2}$ d_{z^2} **e**

Tetrahedral
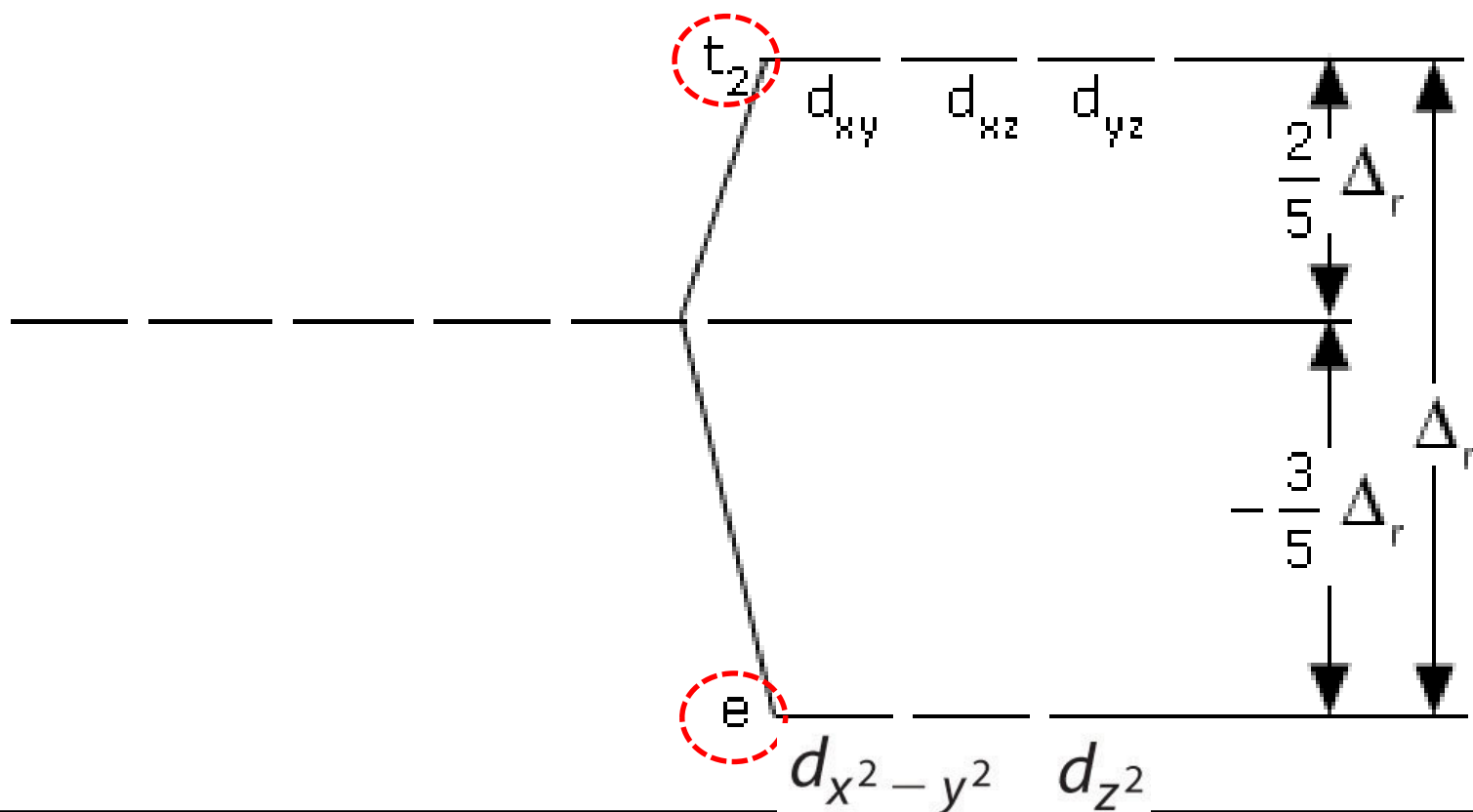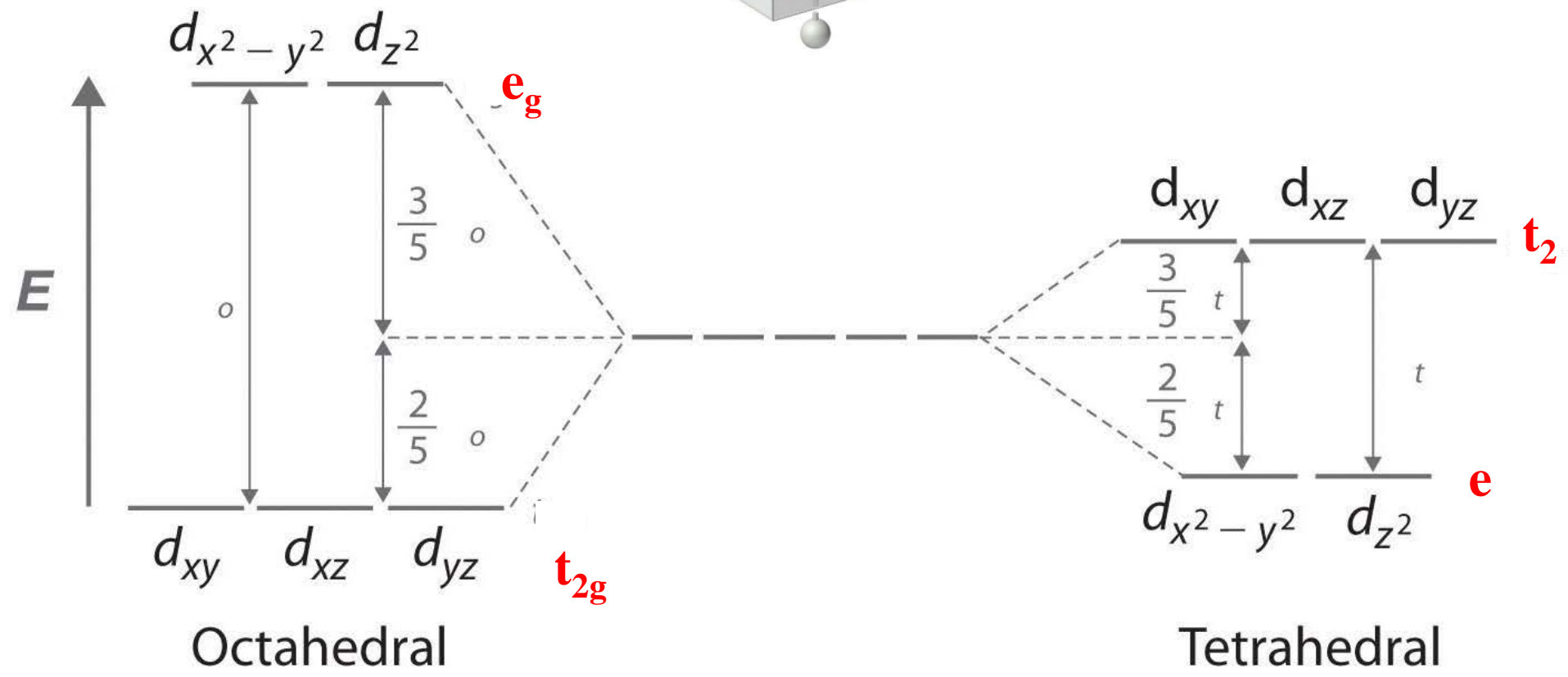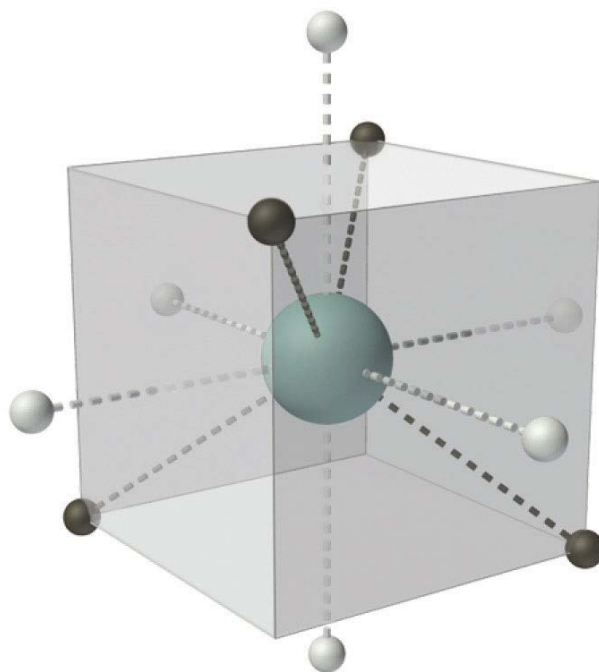
Magnitude of Δ

Oxidation state of the metal ion

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

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

Number of ligands and geometry

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

Nature of the ligand

$I^- < Br^- < S^{2-} < SCN^- < Cl^- < NO_3^- < N_3^- < F^- < urea < OH^- < C_2O_4^{2-} < O^{2-} < H_2O < NCS^- < py < NH_3 < en < bpy, phen < NO_2^- < CH_3^- < C6H5^- < CN^- < CO$
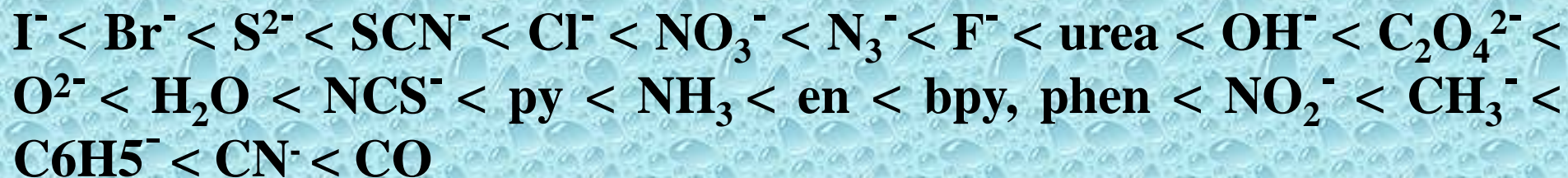
Crystal Field Stabilization Energy (CFSE)

- **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: $\Delta_O < P, \Rightarrow t_{2g}^{3} e_{g}^{1}$

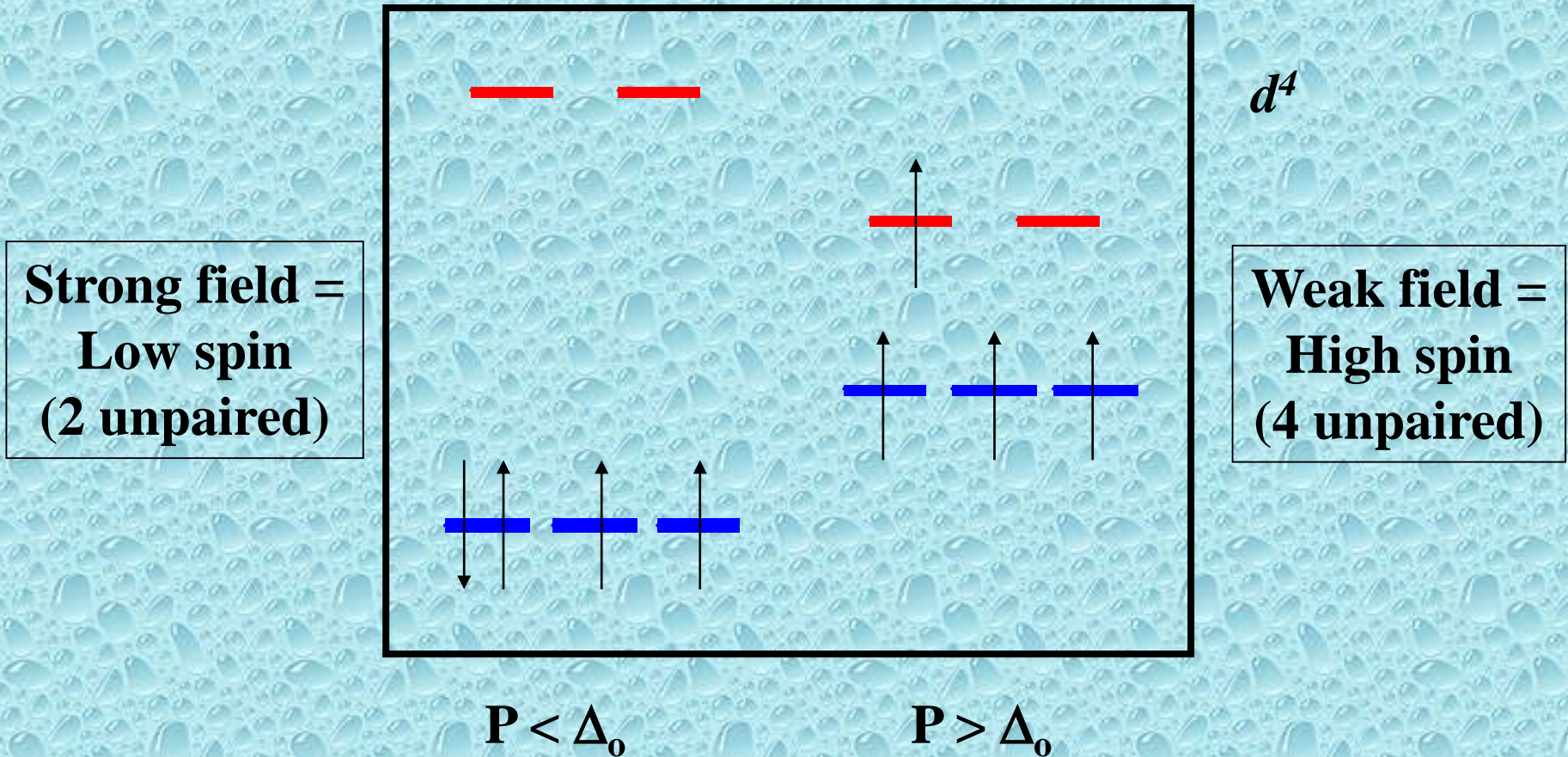- In strong field $\Delta_O > P, \Rightarrow t_{2g}^{4}$

- P - paring energy

Ground-state Electronic Configuration, Magnetic Properties and Colour

d^1-d^{10}
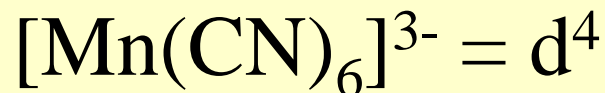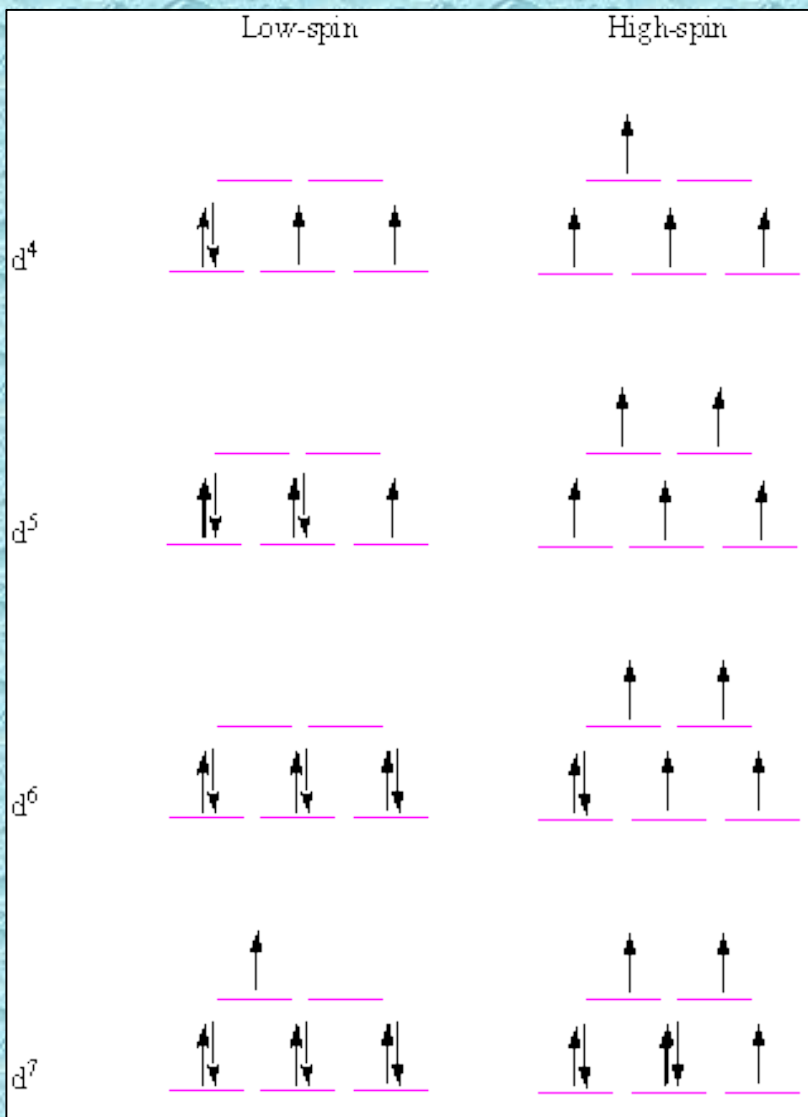## High spin and low spin complexes

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.

d^4

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

Low-spin   High-spin

d^4

d^5

d^6

d^7

$[Mn(CN)_6]^{3-} = d^4$

Strong field Complex

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

Low Spin Complex

$[Mn(H_2O)_6]^{3+} = d^4$
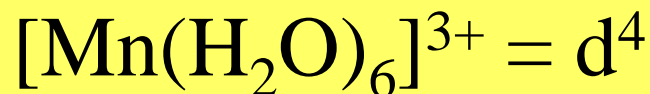
Weak Field Complex

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

High Spin Complex

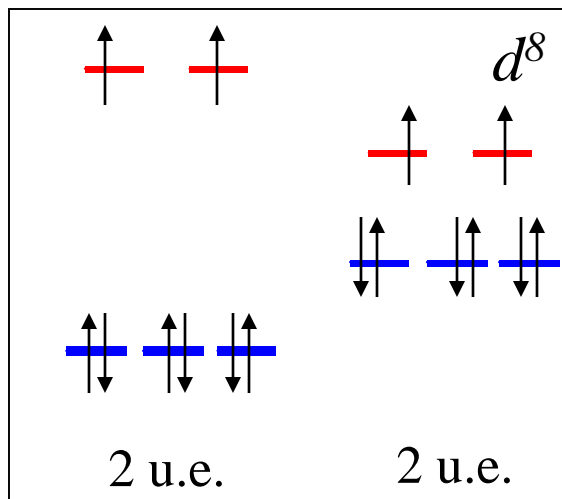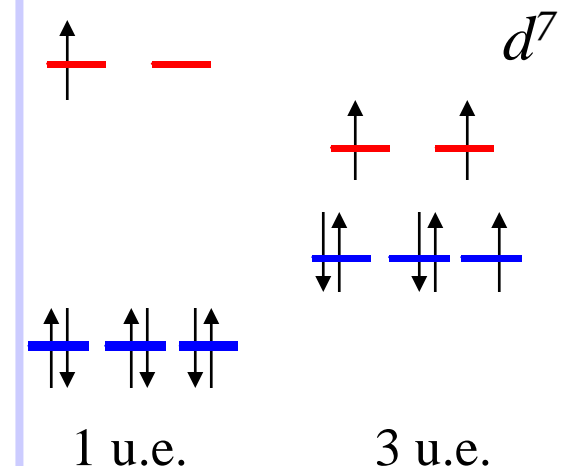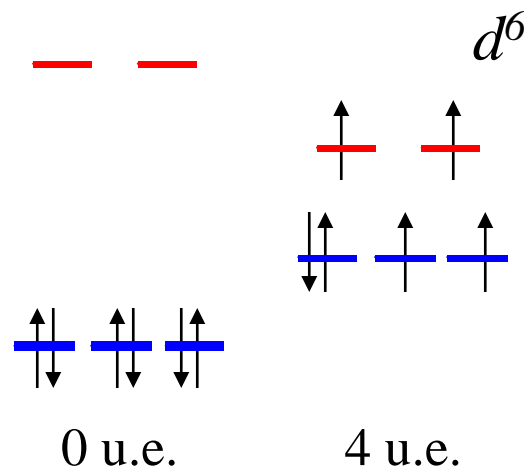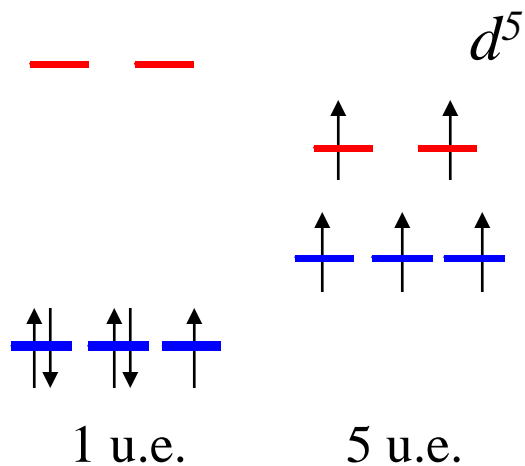# *Placing electrons in d orbitals*
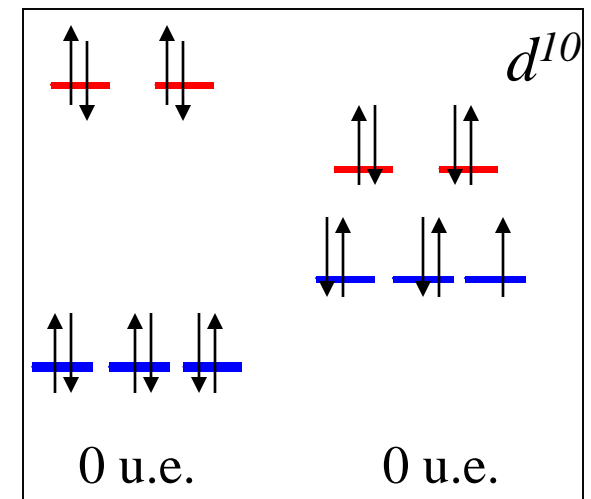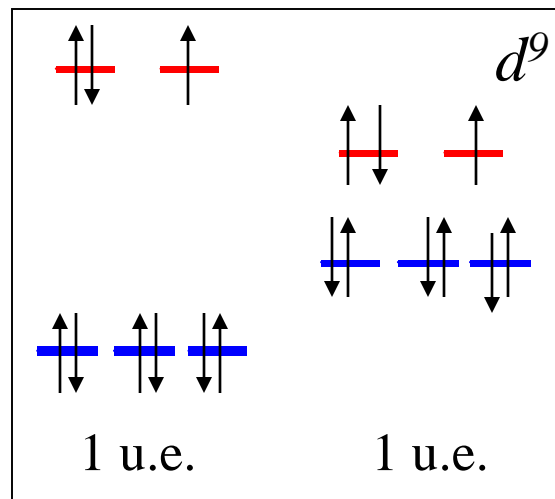
What is the CFSE of $[Fe(CN)_6]^{3-}$?

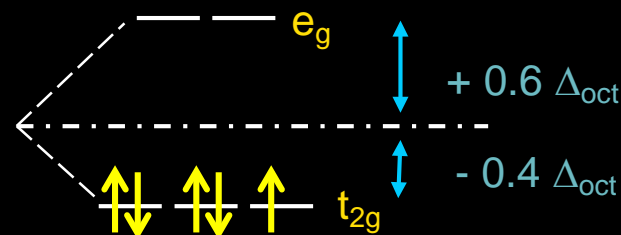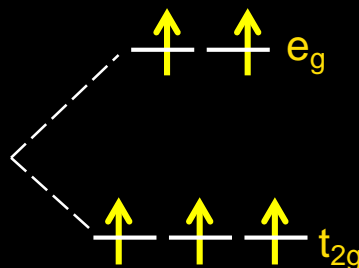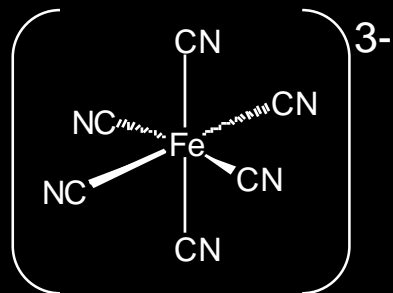C.N. = 6 ∴ O_h Fe(III) ∴ d^5 h.s.   l.s.

CN⁻ = s.f.l.

$$\left[\begin{array}{c} \text{CN} \\ \text{NC} \cdots \text{Fe} \cdots \text{CN} \\ \text{NC} \quad \text{CN} \\ \text{CN} \end{array}\right]^{3-}$$

h.s.:
↑ ↑ e_g
↑ ↑ ↑ t_{2g}

l.s.:
— — — e_g
+ 0.6 Δ_{oct}
- 0.4 Δ_{oct}
↑↓ ↑↓ ↑ t_{2g}

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

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.

$$\left[\begin{array}{c} \text{OH}_2 \\ \text{H}_2\text{O} \cdots \text{Co} \cdots \text{OH}_2 \\ \text{H}_2\text{O} \quad \text{OH}_2 \\ \text{OH}_2 \end{array}\right]^{2+}$$

h.s.:
↑ ↑ e_g
↑↓ ↑↓ ↑ t_{2g}

CFSE = (5 x - 0.4 Δ_{oct})
+ (2 x 0.6 Δ_{oct}) +2P = - 0.8 Δ_{oct}+2P

l.s.:
↑ — e_g
+ 0.6 Δ_{oct}
- 0.4 Δ_{oct}
↑↓ ↑↓ ↑↓ t_{2g}
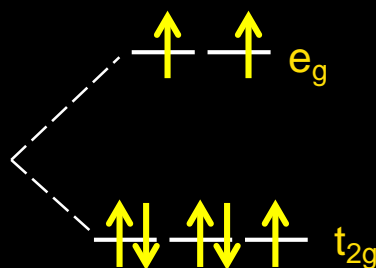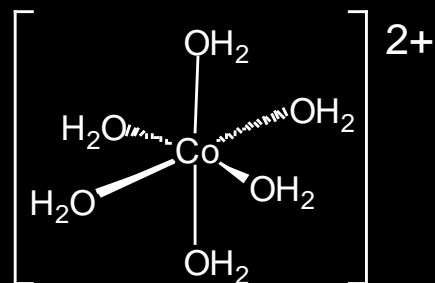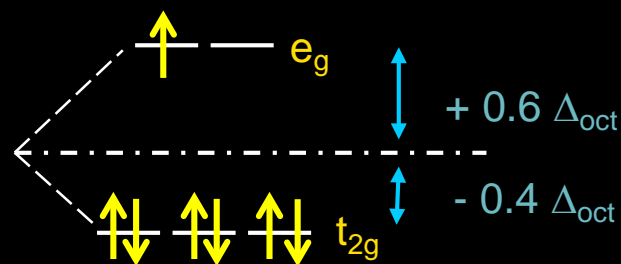
CFSE = (6 x - 0.4 Δ_{oct})
+ (0.6 Δ_{oct}) + 3P= - 1.8 Δ_{oct} + P

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}
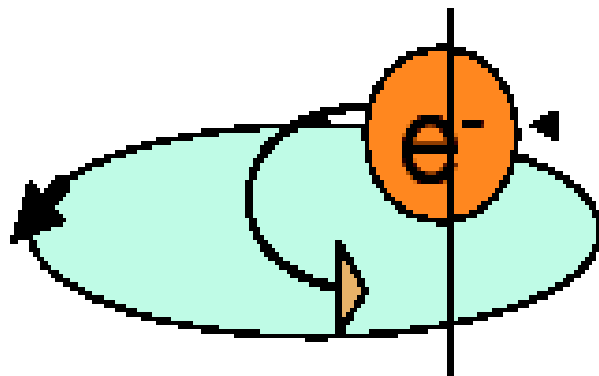- **Since each unpaired electron has a spin ½,**
- **$S = (½)n$, where n = no. of unpaired electrons**
- $\mu = \{n(n+2)\}^{1/2}\, \mu_B$
- **In d^4, d^5, d^6, and d^7 octahedral complexes, magnetic measurements can very easily predict weak versus strong field.**
- **Tetrahedral complexes - only high 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

Balance
Sample
Magnet
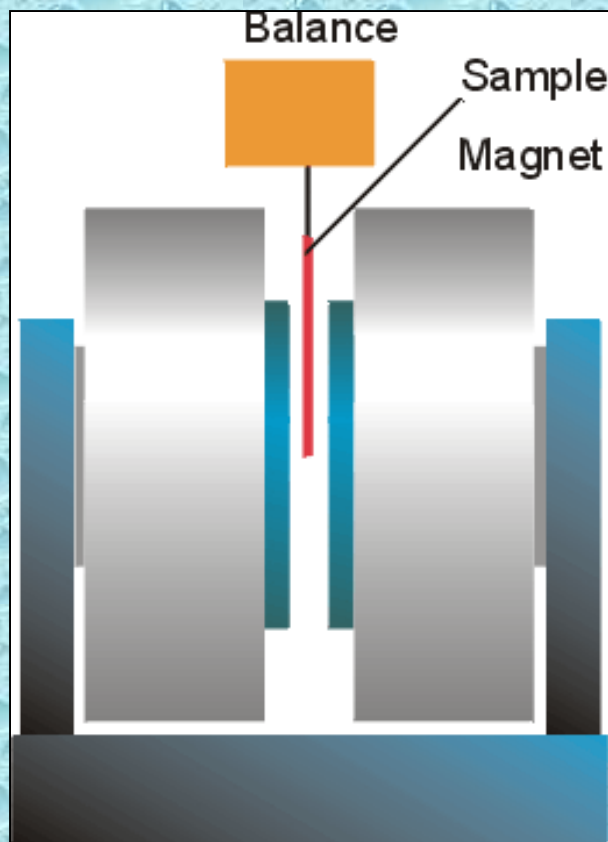
Gouy balance to measure the magnetic susceptibilities

- 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
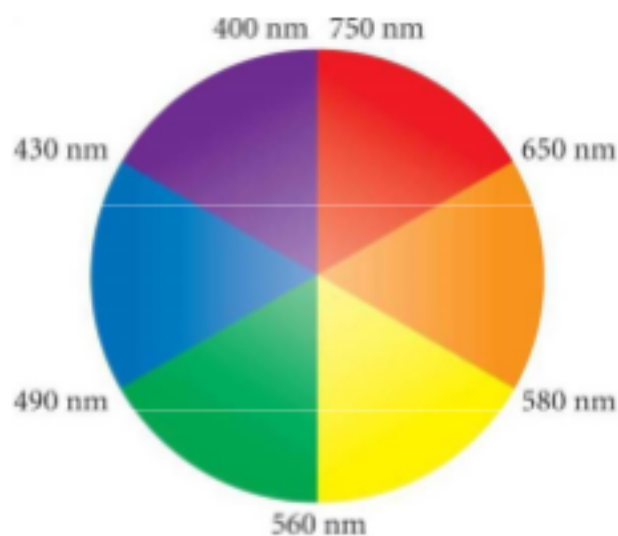
The origin of the color of the transition metal compounds
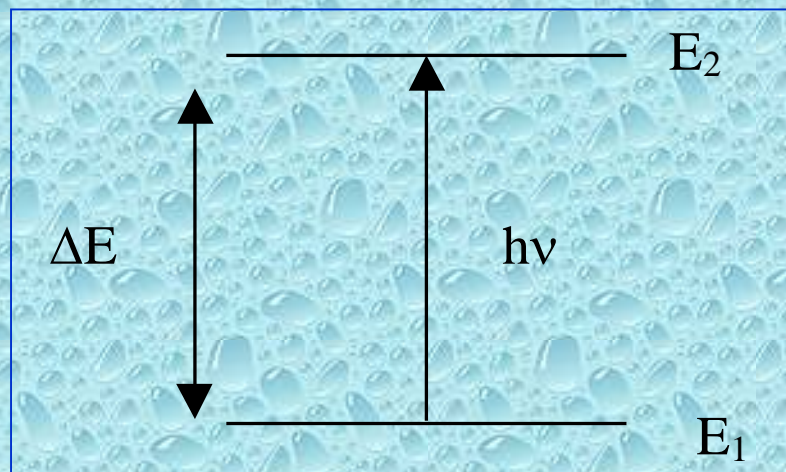
$$\Delta E = E_2 - E_1 = h\nu$$

Ligands influence Δ_O, therefore the colour

Origin of Color

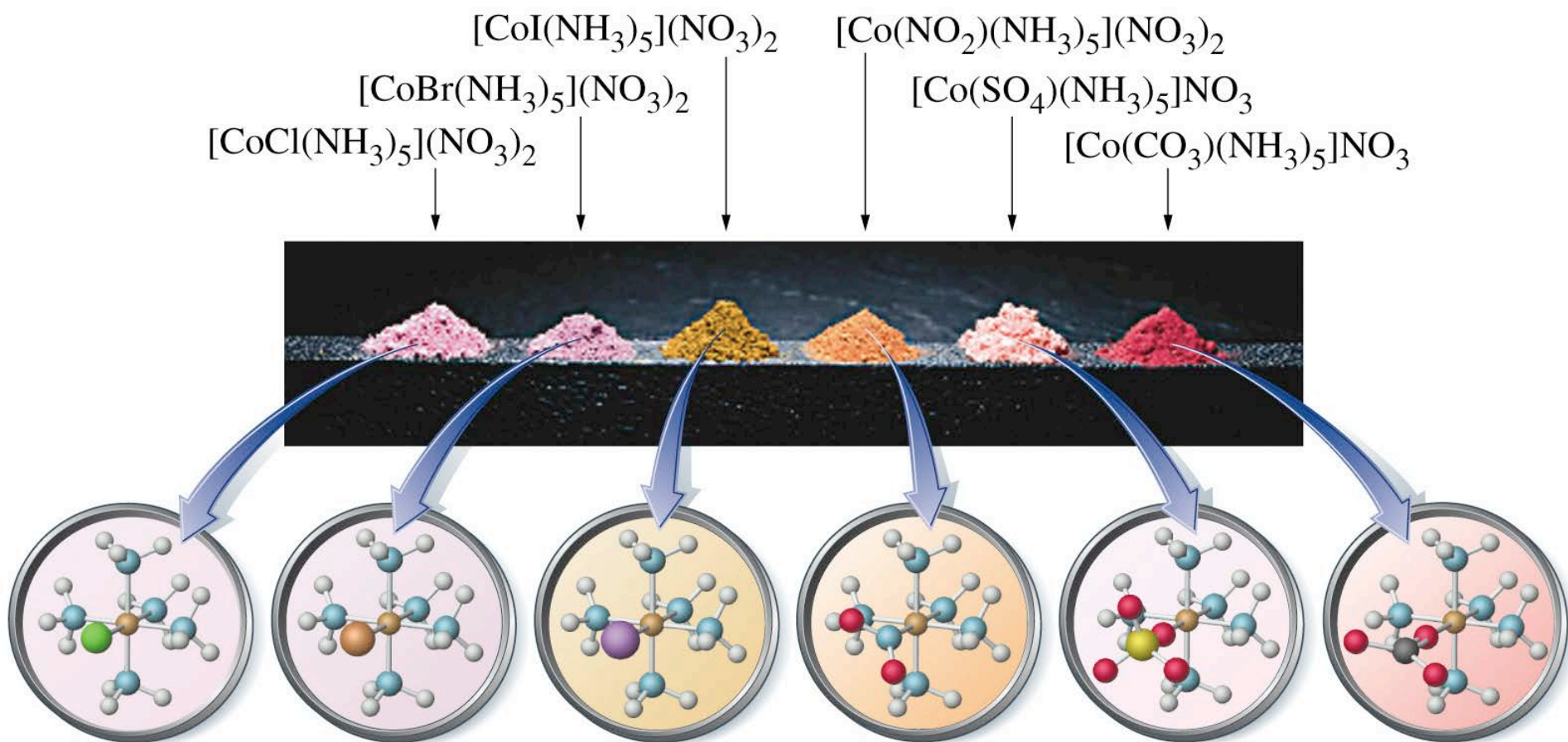| Absorbed Color	λ (nm)	Observed Color	λ (nm)
Violet	400	Green-yellow	560
Blue	450	Yellow	600
Blue-green	490	Red	620
Yellow-green	570	Violet	410
Yellow	580	Dark blue	430
Orange	600	Blue	450
Red	650	Green	520

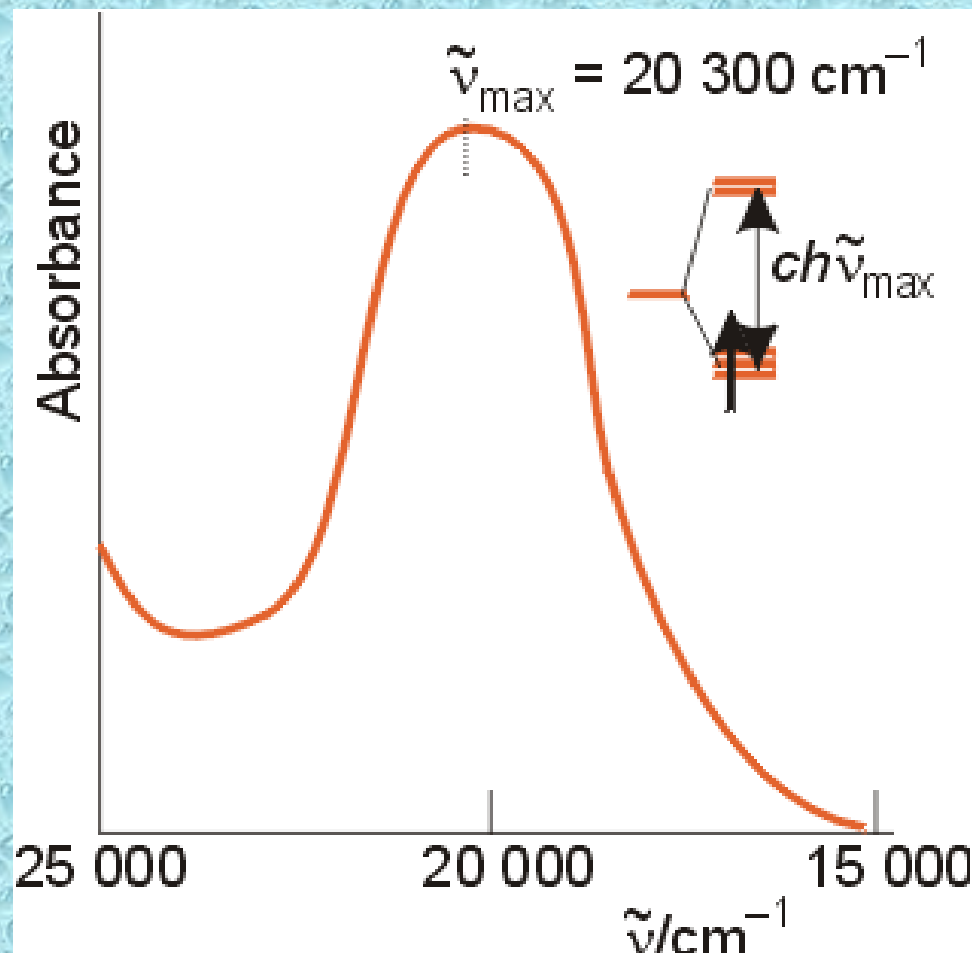## The Beer-Lambert Law

$$A = \log_{10}(Io/I) = \varepsilon cl$$

where ε is the molar extinction coefficient (in $L\ cm^{-1}\ mole^{-1}$), c is concentration in mole L^{-1} and l is the path length in cm. A is known as 'Absorbance' and it is dimensionless.

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

1. **Metal charge**
2. **Ligand strength**

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

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

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

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

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

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

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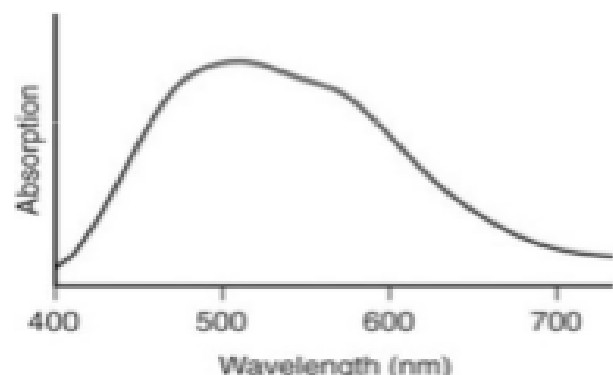

Assigned transition:

$e_g \longrightarrow t_{2g}$
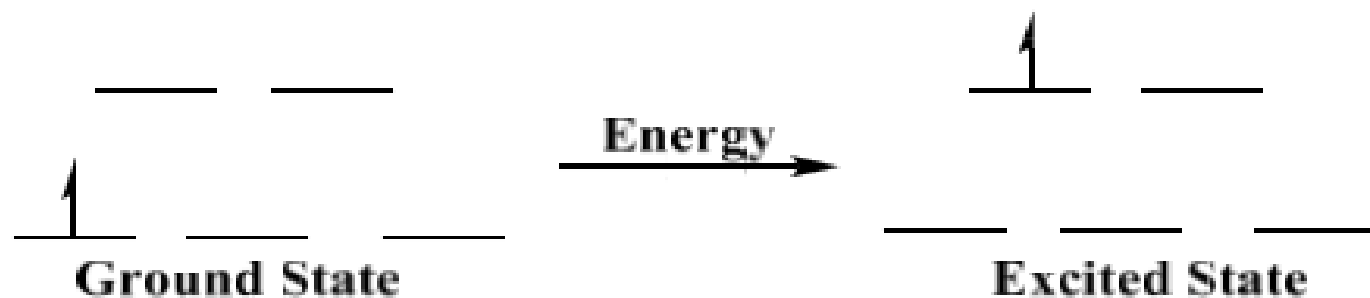
This corresponds to the energy gap

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

Color of $[Ti(H_2O)_6]^{3+}$

Energy →

Ground State

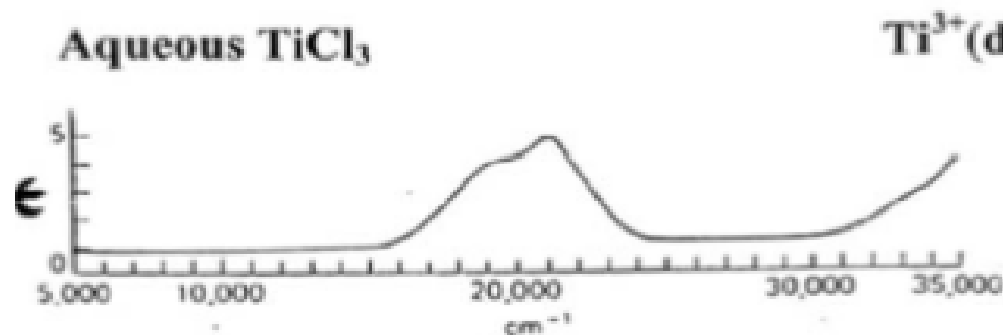**Excited State**
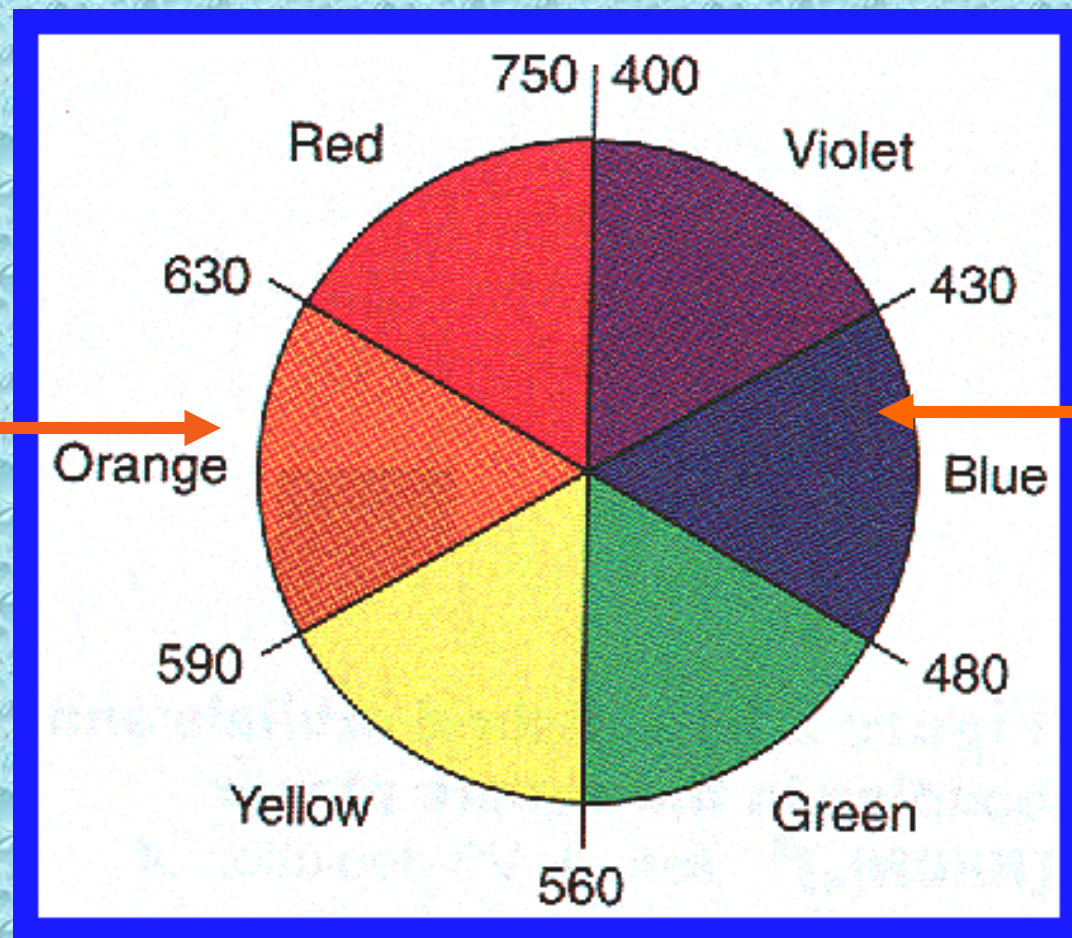
Absorption at 520 nm gives the complex its purple color

A more resolved absorption spectrum of the complex has a shoulder

Aqueous $TiCl_3$

$Ti^{3+}(d^1)$

d_{z^2}

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

$d_{xz}\ d_{yz}$

d_{xy}
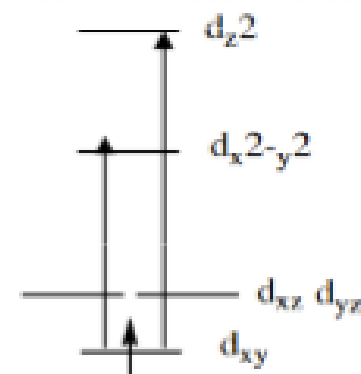
absorbed color

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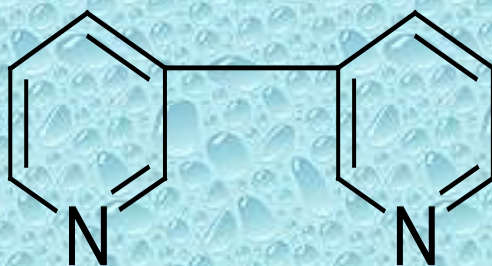
- **Spectrochemical Series: An order of ligand field strength based on experiment:**

Weak Field $I^- < Br^- < S^{2-} < SCN^- < Cl^- < NO_3^- < N_3^- < F^- < urea < OH^- < C_2O_4^{2-} < O^{2-} < H_2O < NCS^- < py < NH_3 < en < bipy, phen < NO_2^- < CH_3^- < C6H5^- < CN^- < CO$ **Strong Field**
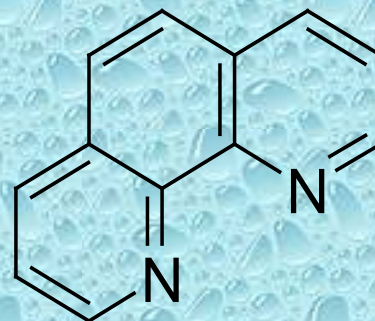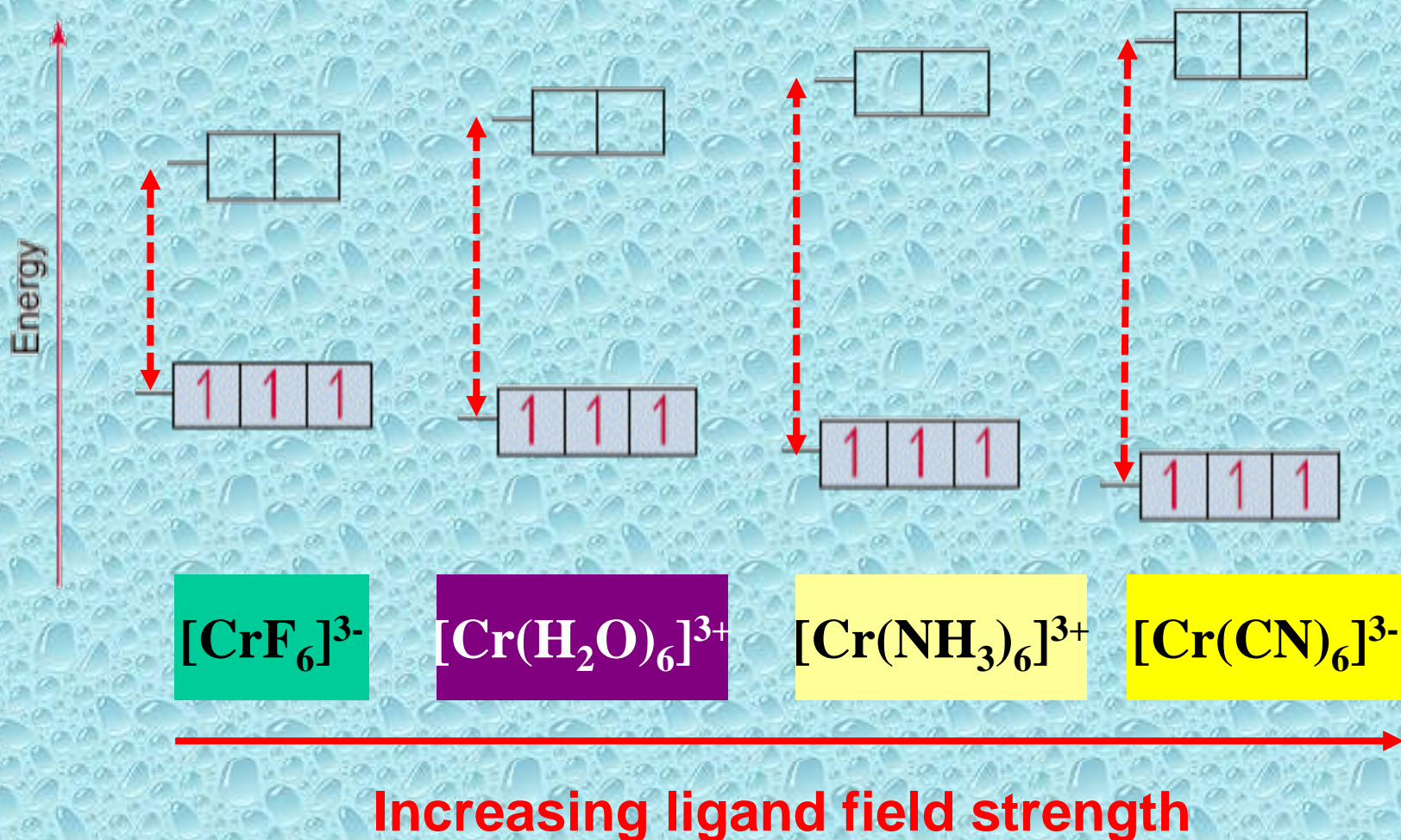

Ethylenediamine (en)

2,2'-bipyridine (bipy)

1.10 - penanthroline (phen)

Energy

[CrF$_6$]$^{3-}$ [Cr(H$_2$O)$_6$]$^{3+}$ [Cr(NH$_3$)$_6$]$^{3+}$ [Cr(CN)$_6$]$^{3-}$

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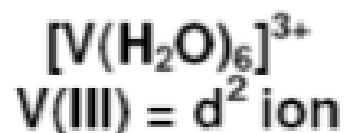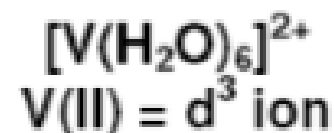
As Cr^{3+} goes from being attached to a weak field ligand to a strong field ligand, Δ increases and the color of the complex changes from green to yellow.

Color and CFT

.

$[V(H_2O)_6]^{3+}$
V(III) = d^2 ion

violet light absorbed
complex appears yellow

$[V(H_2O)_6]^{2+}$
V(II) = d^3 ion
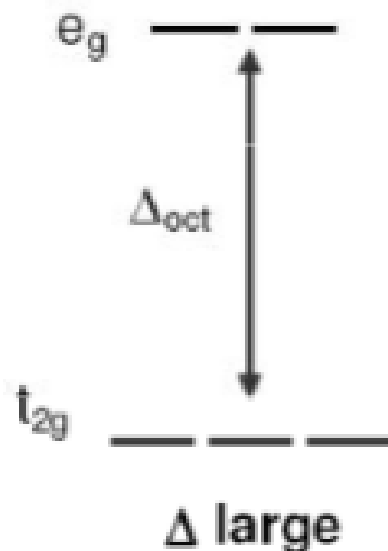
yellow light absorbed
complex appears violet

e_g ___ ___

Δ_{oct}

t_{2g} ___ ___ ___

Δ large

___ ___ e_g

Δ_{oct}

___ ___ ___ t_{2g}

Δ small

Color and CFT

$[Cr(NH_3)_6]^{3+}$
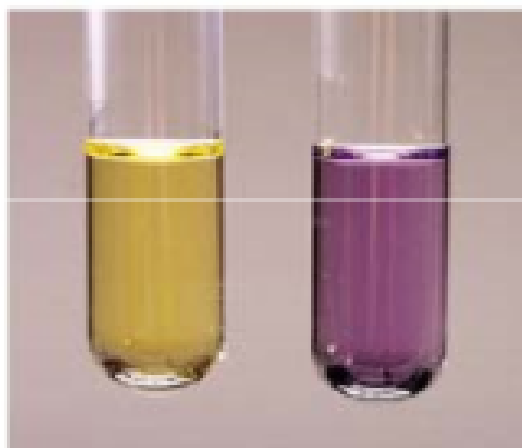
$[Cr(NH_3)_5Cl]^{2+}$

NH₃

H₃N⸳⸳⸳Cr⸳⸳⸳NH₃
H₃N — NH₃

NH₃
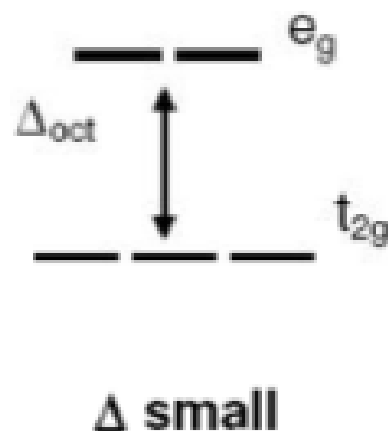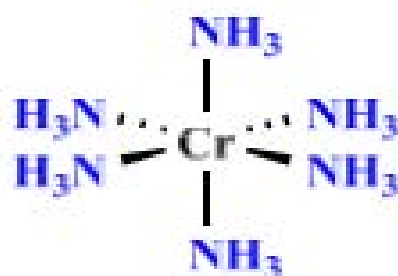
Strong ligands, leading to high Δ_o. Absorbs violet and appears yellow.

Cl

H₃N⸳⸳⸳Cr⸳⸳⸳NH₃
H₃N — NH₃

NH₃
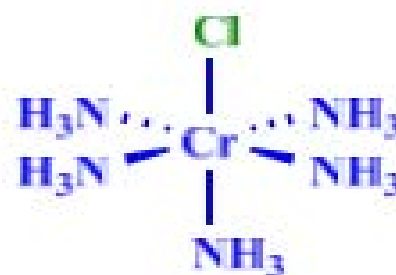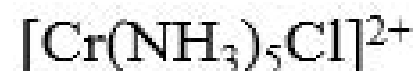
Relatively weak set of ligands, leading to reduced Δ_o. Absorbs yellow and appears magenta.

Laporte Rule

In a molecule or ion possessing center of symmetry, transitions are not allowed between orbitals of same parity. Transitions are only possible between orbitals that differ by $\Delta l = \pm 1$; 'l' is the orbital quantum number.

Examples of forbidden transitions are: s to s, d to d, p to f etc.

Tetrahedral geometry is not affected by this rule as it does not have a center of symmetry.
As a consequence, ε for tetrahedral complexes are 100 times more than the ε for octahedral complexes.

Even octahedral complexes lose their center of symmetry transiently due to unsymmetrical vibrations. This leads to color in octahedral and square planar complexes

Spin-forbidden and Spin-allowed Transitions

Any transition for which $\Delta S^1 \neq 0$ is *strongly forbidden;* that is, in order to be allowed, a transition must involve no change in spin state.

Allowed $\longrightarrow$ $\longrightarrow$ Forbidden

$S = +\frac{1}{2}$ $S = +\frac{1}{2}$ $S = 1$ $S = 0$

$[Mn(H_2O)_6]^{2+}$ has a d^5 metal ion and is a high-spin complex. Electronic transitions are not only Laporte-forbidden, but also spin-forbidden. The dilute solutions of Mn^{2+} complexes are therefore colorless.

However, certain complexes such as $MnO4^-$, $CrO4^{2-}$ etc are intensely colored even though they have metal ions without electrons in the d orbitals. The color of these complexes are not from d-d transitions, but from charge-transfer from ligand to metal orbitals.

d^0 and d^{10} ions have no d-d transitions

Zn^{2+} d^{10} ion   white

TiF_4 d^0 ion   white

$TiCl_4$ d^0 ion   white

$TiBr_4$ d^0 ion   orange

TiI_4 d^0 ion   dark brown

$[MnO_4]^-$ Mn(VII) d^0 ion   purple

$[Cr_2O_7]^-$ Cr(VI) d^0 ion   bright orange

$[Cu(MeCN)_4]^+$ Cu(I) d^{10} ion   colourless

$[Cu(phen)_2]^+$ Cu(I) d^{10} ion   dark orange

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.**

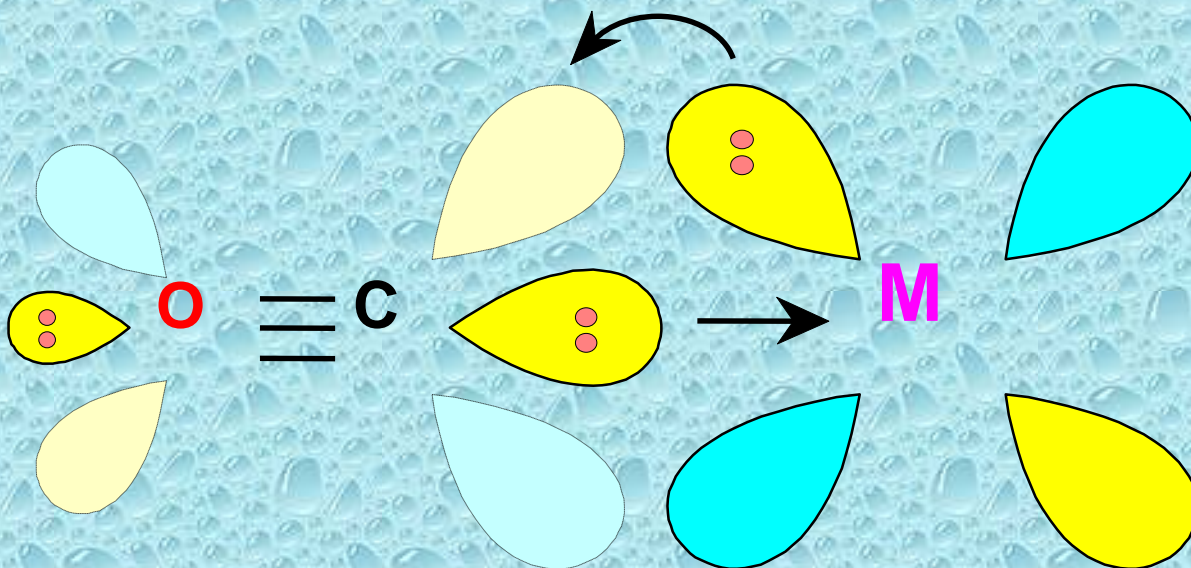# Stabilizing Low Oxidation State: CO Can Do the Job
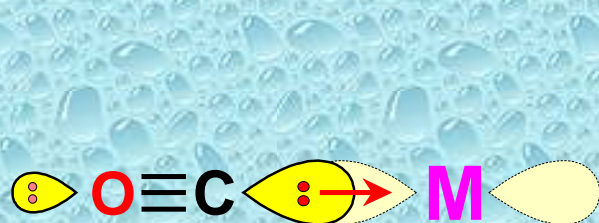
Stabilizing Low Oxidation State: CO Can Do the Job

12

13
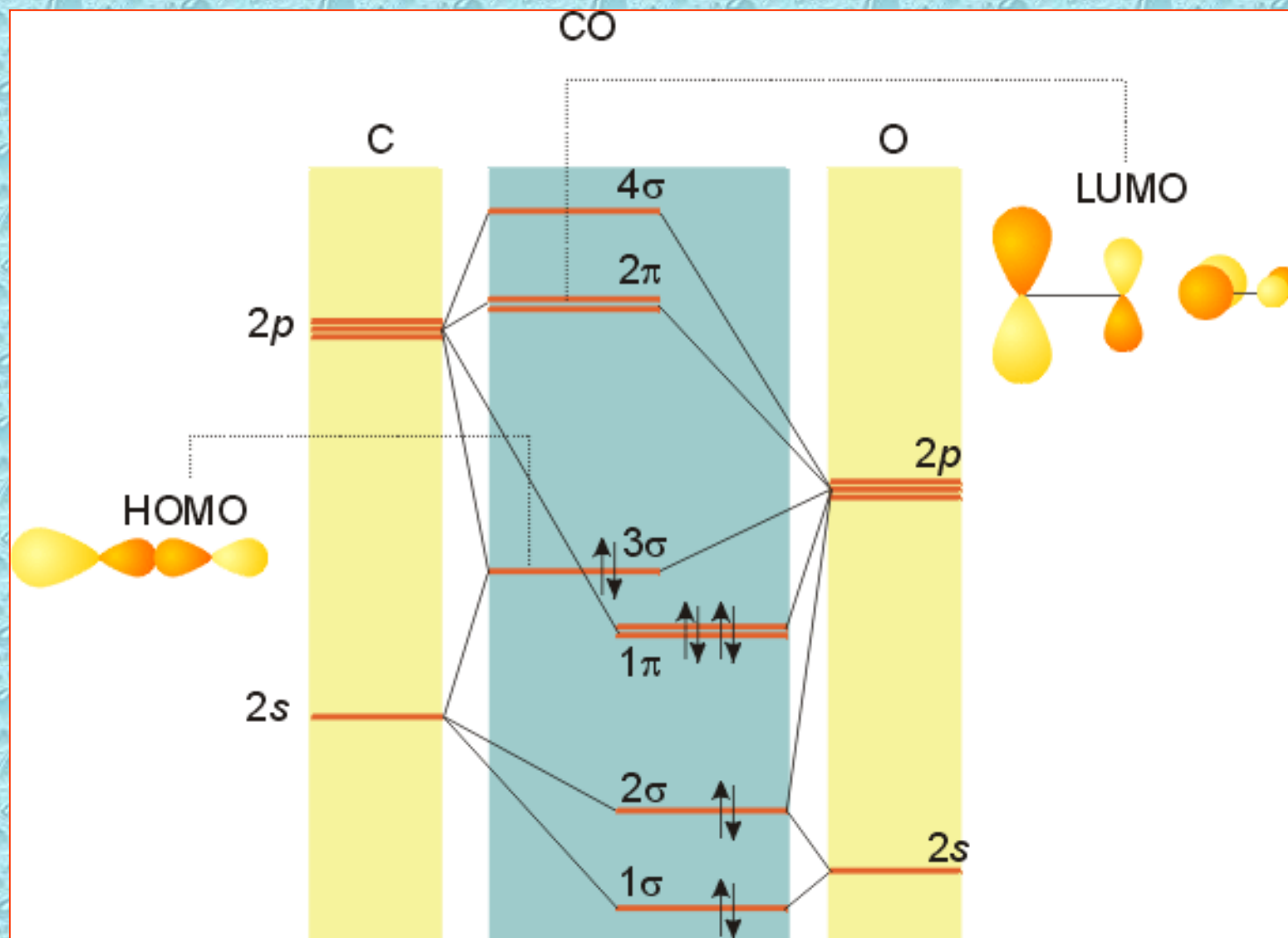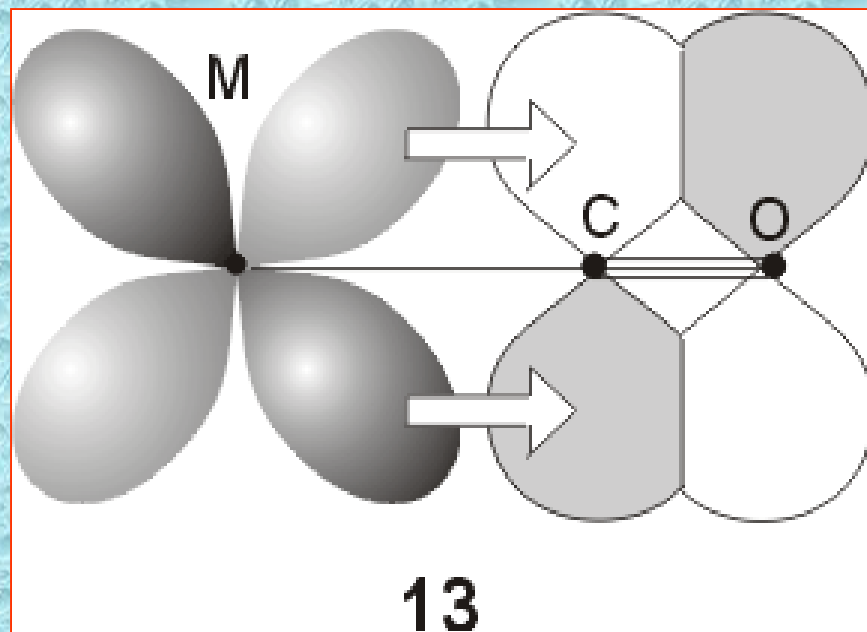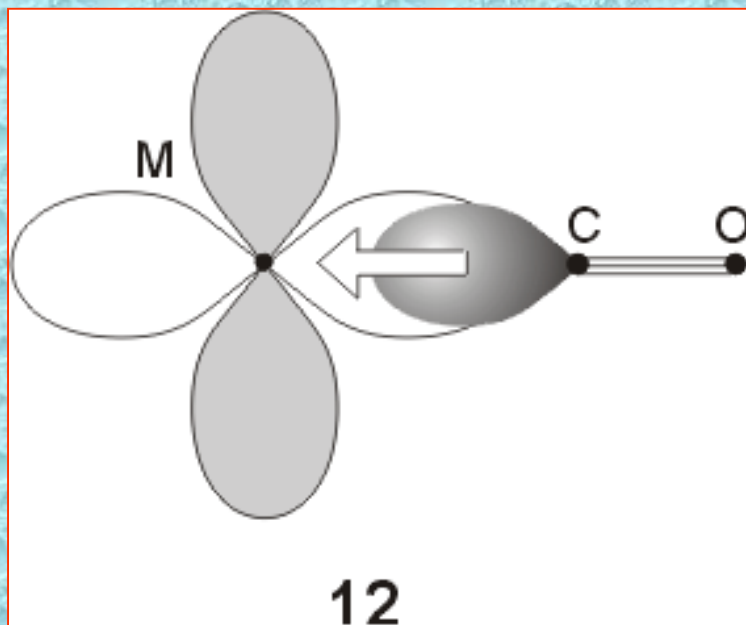
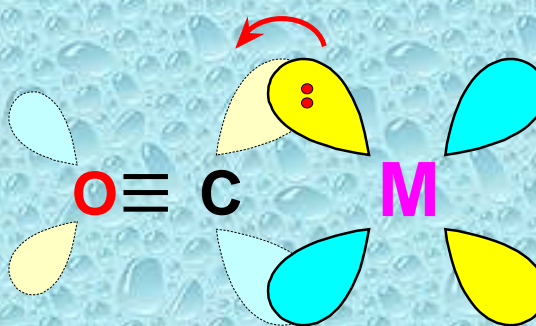$Ni(CO)_4$, $[Fe(CO)_5]$, $[Cr(CO)_6]$, $[Mn_2(CO)_{10}]$, $[Co_2(CO)_8]$, $Na_2[Fe(CO)_4]$, $Na[Mn(CO)_5]$
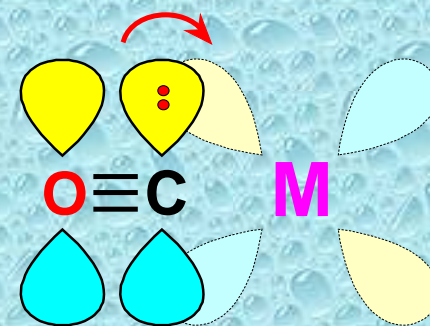
σ orbital serves as a very weak donor to a metal atom
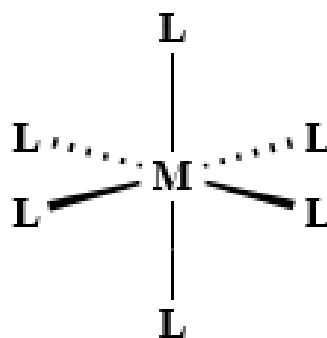
CO-M sigma bond
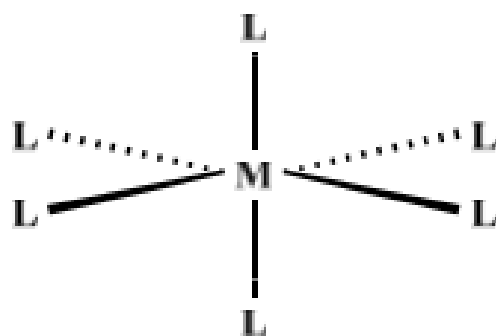
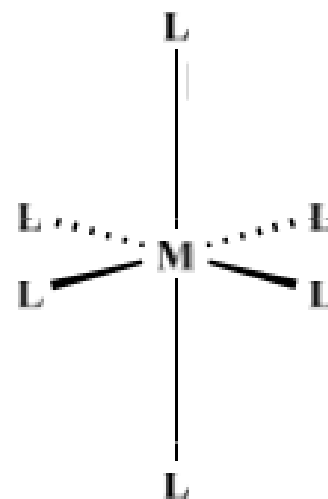**M to CO pi backbonding**

CO to M pi bonding
(rare)

Distortions in Octahedral Geometry

Regular Octahedron: Complexes with regular octahedral geometry are expected to form, when all of the ligands are of the same kind
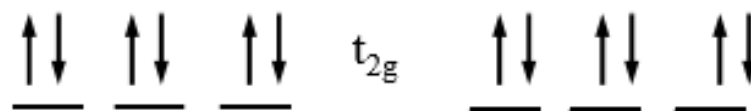

Compressed

Elongated

Distorted Octahedron: Complexes with distorted octahedral geometry are expected to form, when the ligands are of different kinds

Distortions in Octahedral Geometry

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. This is called the **Jahn-Teller Effect**
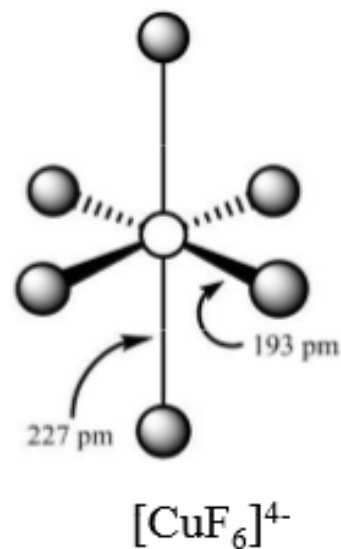

d^8

e_g ↑ ↑

t_{2g} ↑↓ ↑↓ ↑↓
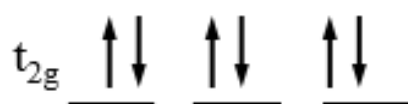
Ni^{2+}: Only one way of filling the orbitals; not degenerate and no Jahn-Teller Distortion

d^9

e_g ↑↓ ↑   ·   ↑ ↑↓
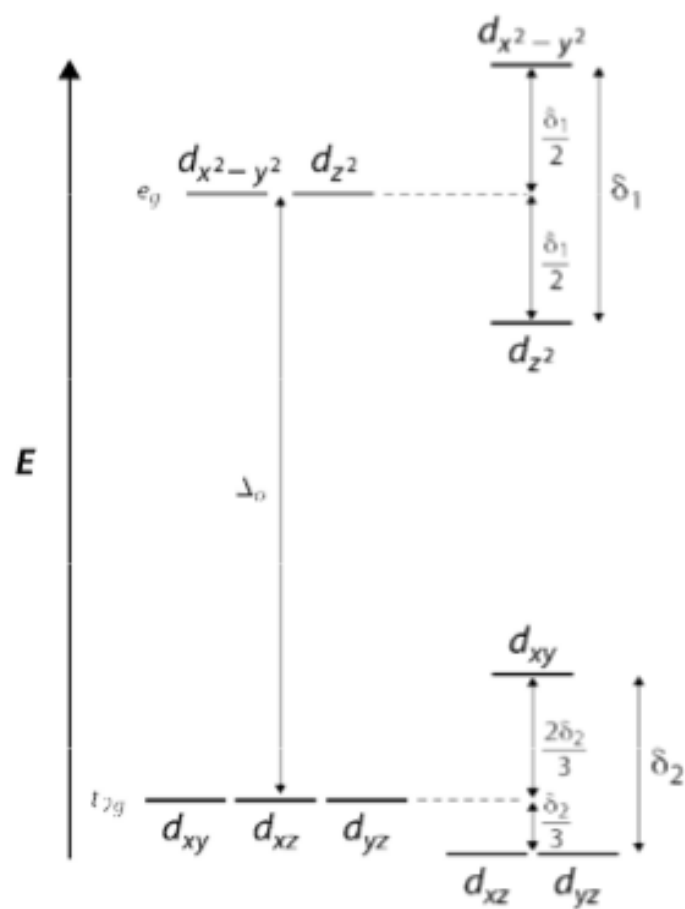
t_{2g} ↑↓ ↑↓ ↑↓   ·   ↑↓ ↑↓ ↑↓

Cu^{2+}: Two ways of filling the e_g orbitals; there is degeneracy and Jahn-Teller Distortion is observed

Jahn-Teller Distortion in Cu(II) Complexes

energy

e_g

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

d_{z^2}

d_{xy}

t_{2g}

d_{xz} d_{yz}

Cu(II) in regular octa-
hedral environment

Cu(II) after J-T distortion

193 pm

227 pm

$[CuF_6]^{4-}$
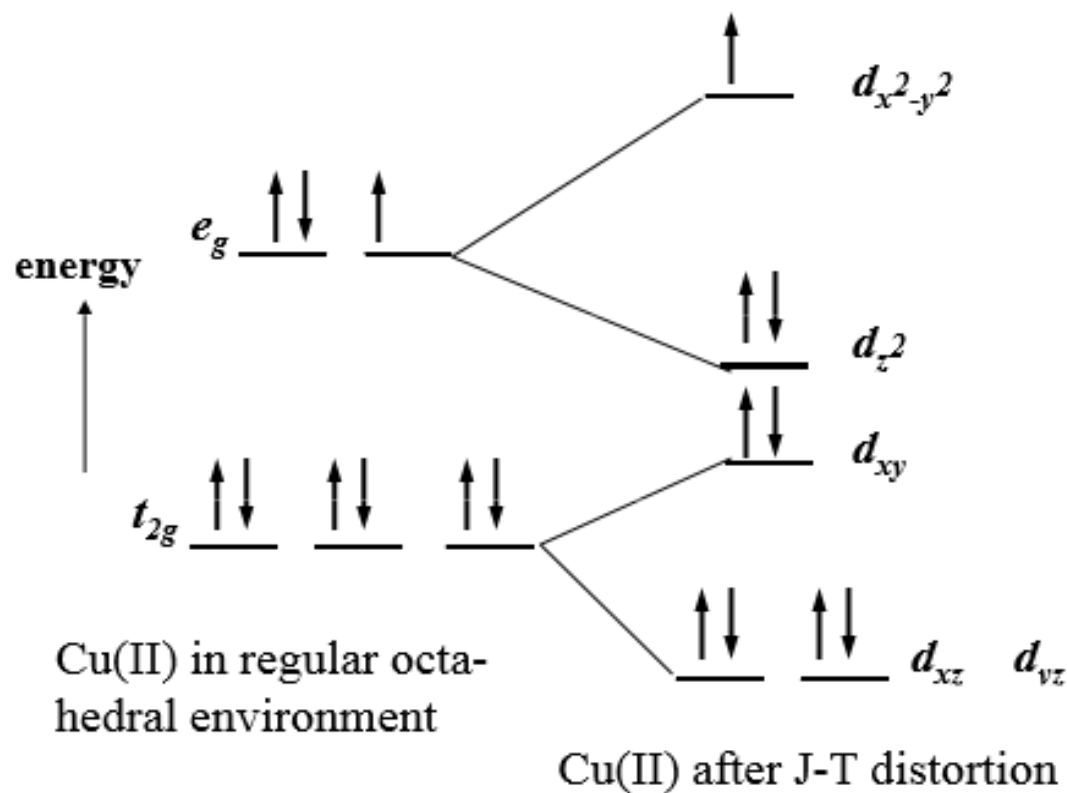
Jahn-Teller Distortion in d^9 Complexes

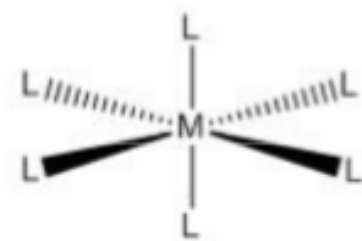
$\Delta o \gg \delta 1 > \delta 2.$
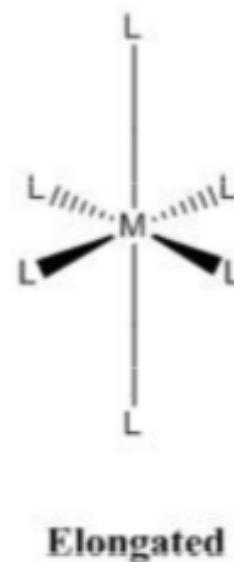
Jahn-Teller Distortion in d^1 Complexes

energy

e_g

d_{z^2}

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

d_{xz} d_{yz}

t_{2g}

d_{xy}

d^1 in regular octa-
hedral environment

d^1 after J-T distortion
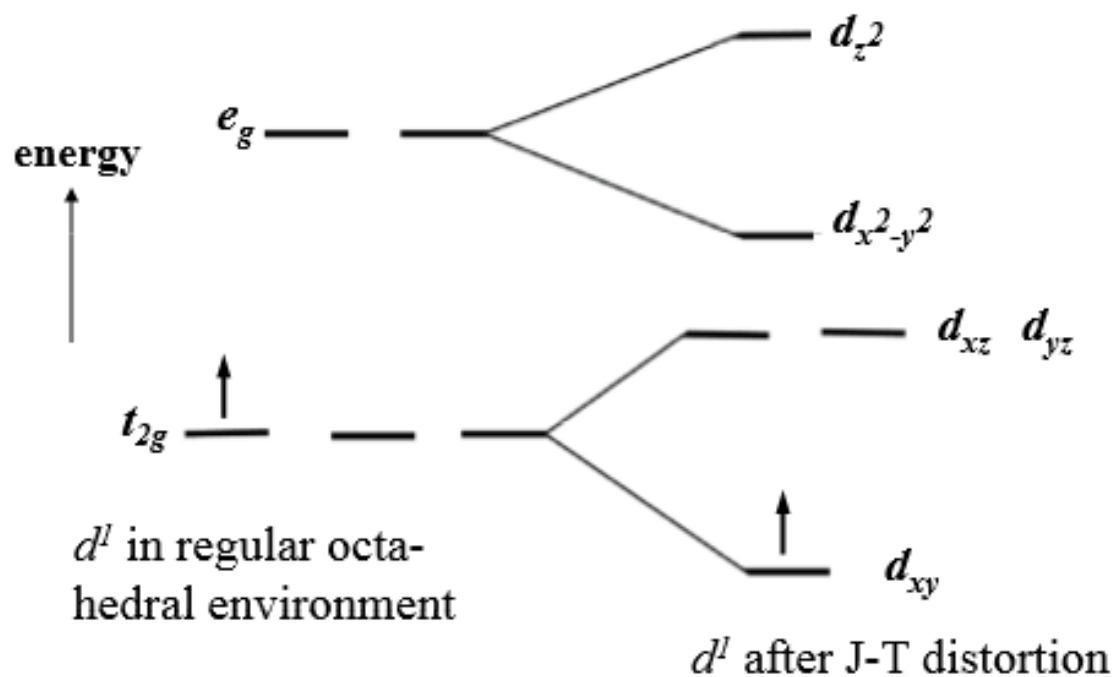
Compressed

d¹ Vs *d⁹*
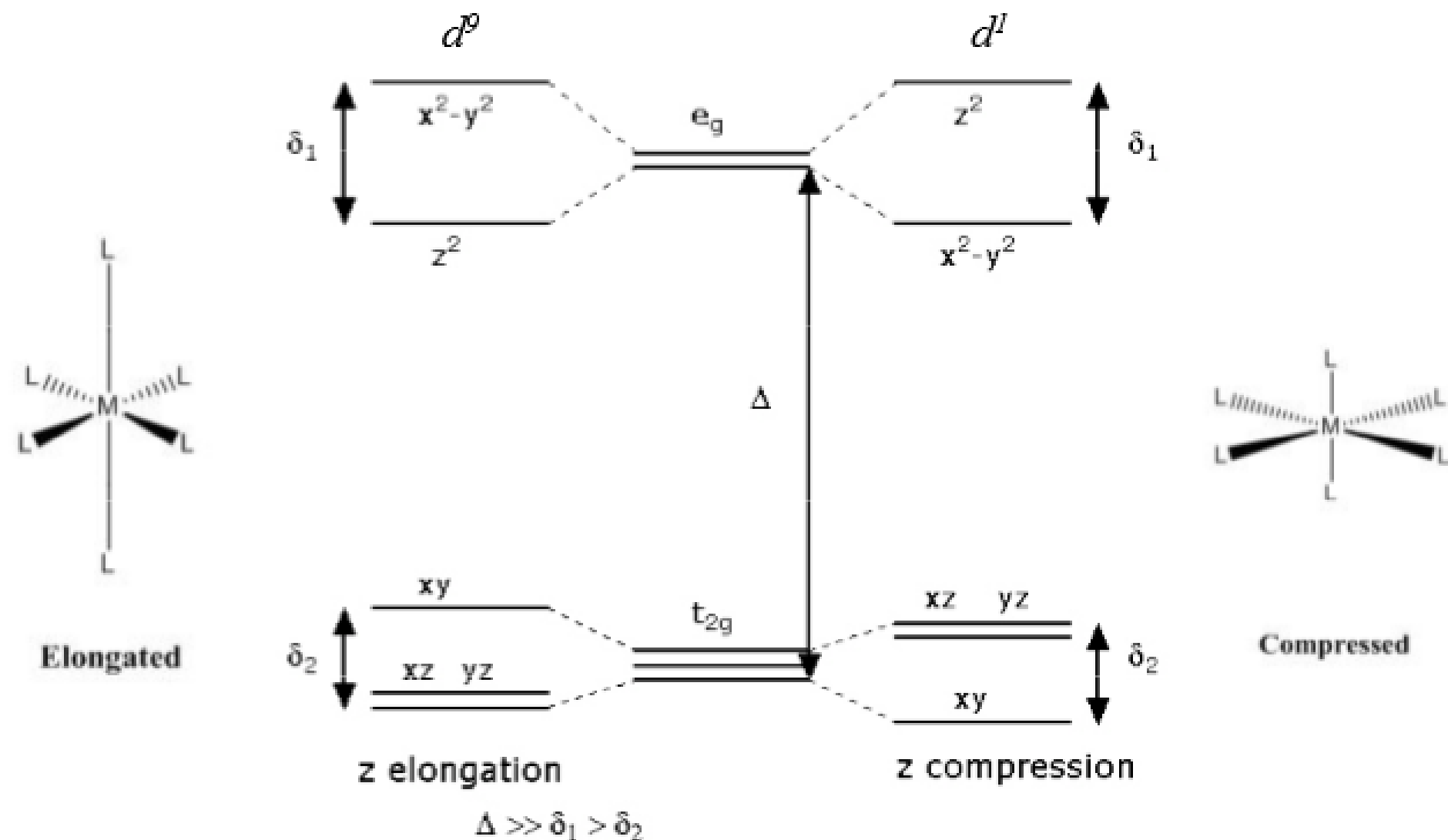
Distortions are more pronounced if the degeneracy occurs in an e_g orbital

Distortions in Low-Spin Complexes
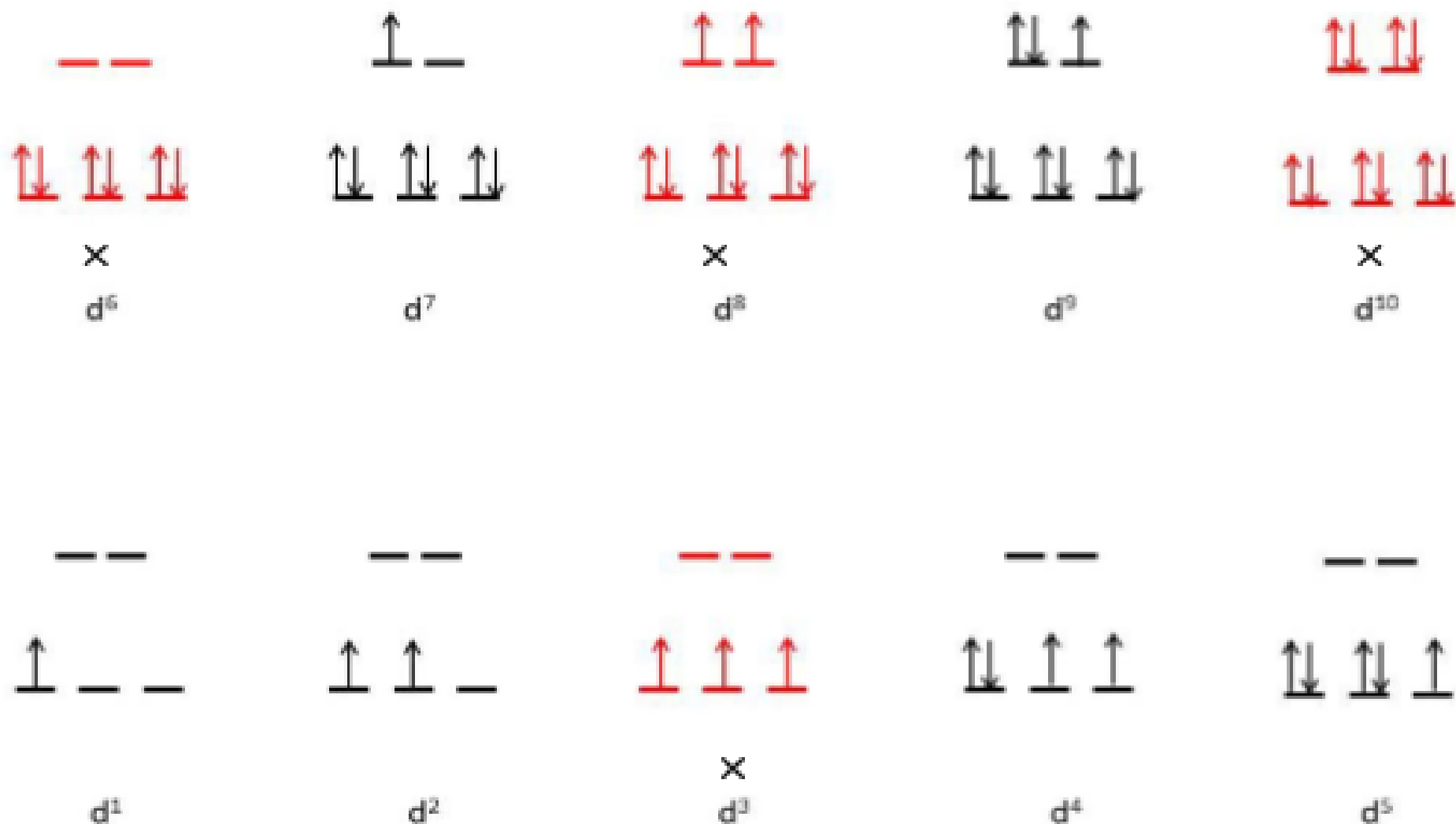
Distortions in High-Spin Complexes

d⁶

d⁷

d⁸

d⁹

d¹⁰

d¹

d²

d³

d⁴

d⁵
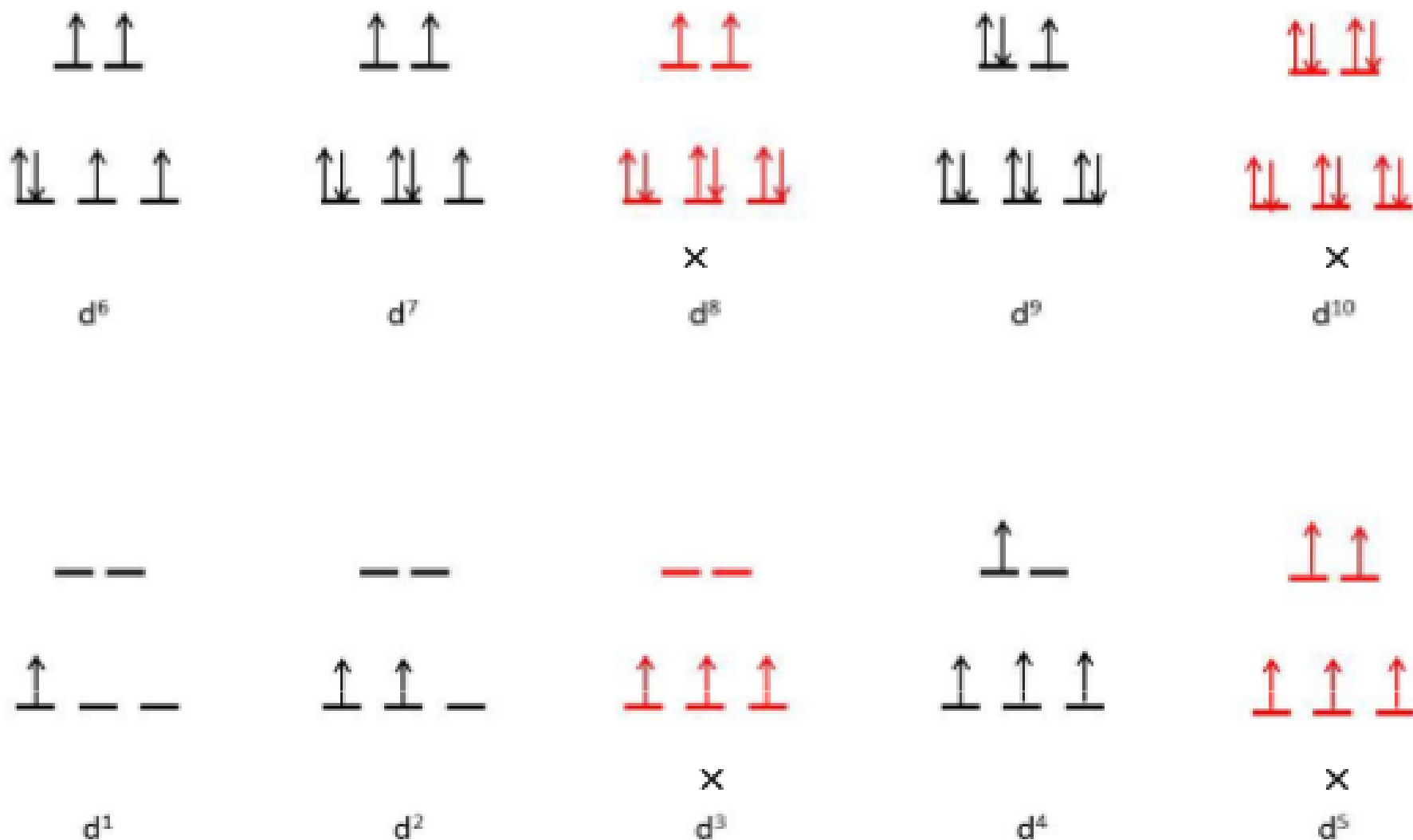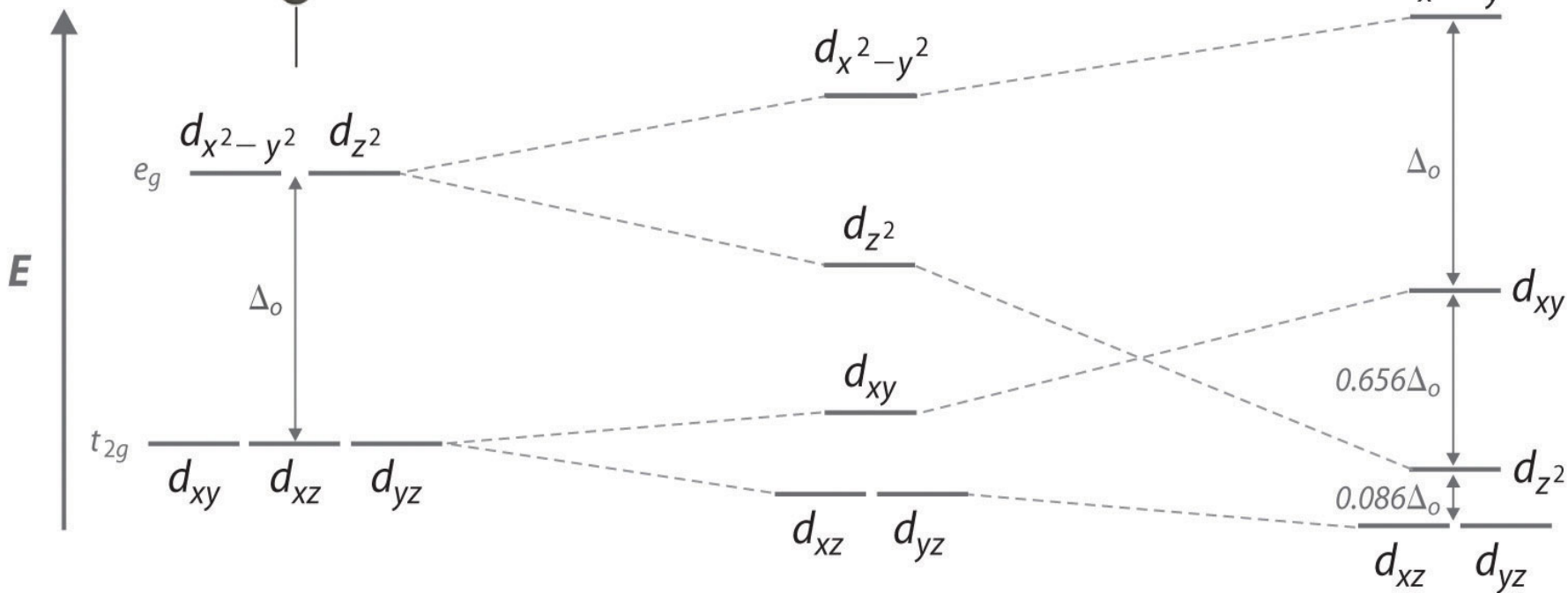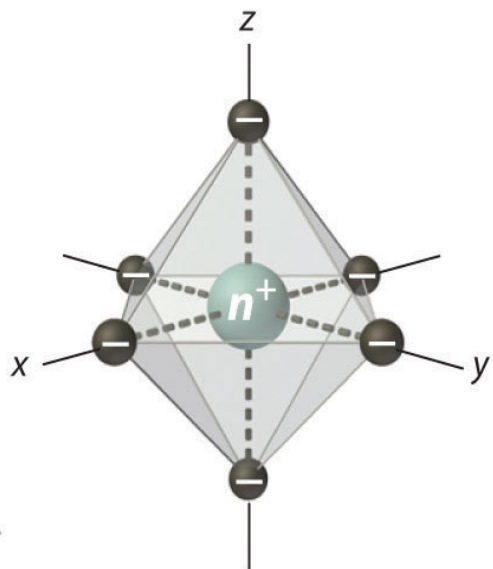
Crystal field splitting of linear complexes

➢ **Ligands approach along the z axis**

 ∴ **Orbitals containing z component go higher in energy and others get stabilized.**

d_{z^2}

d_{xz}, d_{yz}

$d_{xy}, d_{x^2-y^2}$
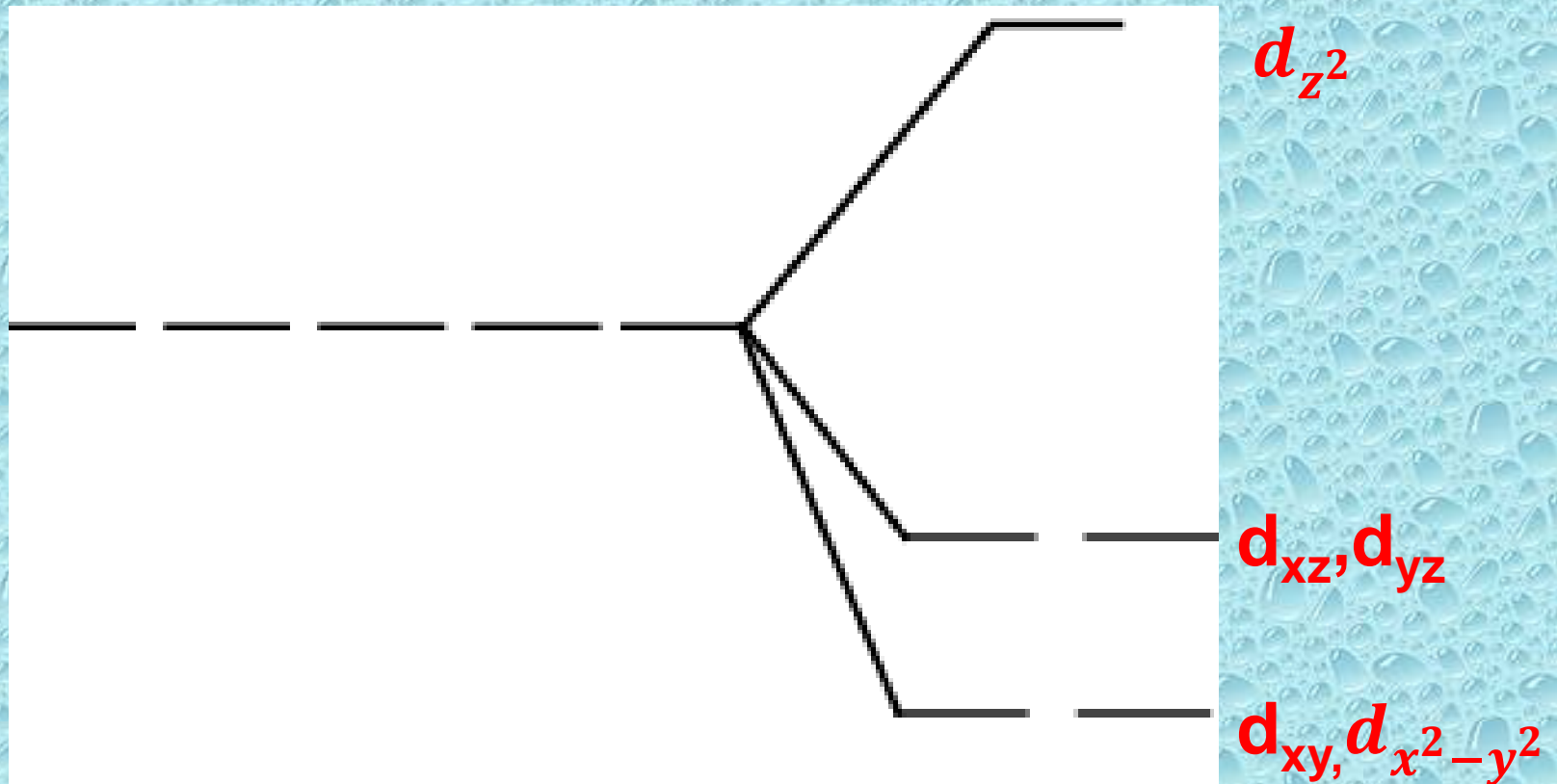
Crystal field splitting of TBP complexes
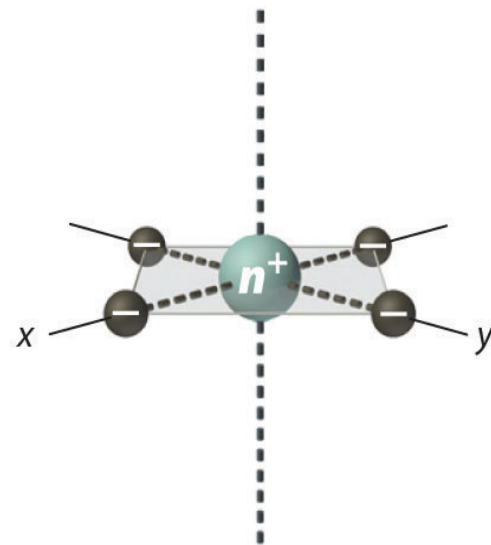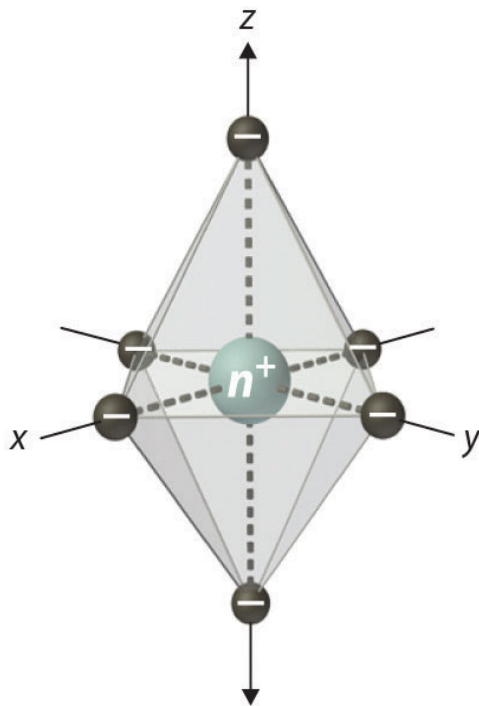
➤ **Ligands approach along the z axis and in between the axis in the XY plane**

∴ **Orbital along z go higher in energy, orbitals in the XY plane have intermediate energy and orbitals in XZ and YZ plane experience lowest repulsion and hence gets stabilized**

Energy

d_z^2

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

d_{xz} d_{yz}

Trigonal bipyramidal

To summarize

Spherical	Trigonal Bipyramidal	Linear	Square Planar	Tetrahedral	Octahedral

x^2-y^2 (Square Planar, top)

z^2 (Trigonal Bipyramidal) z^2 (Linear)

z^2 x^2-y^2 (Octahedral, upper)

xy x^2-y^2 (Trigonal Bipyramidal) xz yz (Linear) xy (Square Planar)

xy xz yz (Tetrahedral, upper) Δ_t

z^2 (Square Planar)

Δ_o (Octahedral)

xz yz (Trigonal Bipyramidal, lower) xy x^2-y^2 (Linear, lower) xz yz (Square Planar, lower)

z^2 x^2-y^2 (Tetrahedral, lower)

xy xz yz (Octahedral, lower)