

Bonding in coordination compounds

Nobel prize 1913

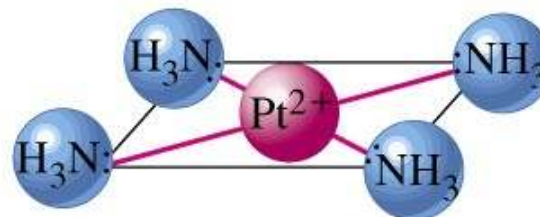
- Alfred Werner - 1893
- VBT
- Crystal Field Theory (CFT)
- Modified CFT, known as Ligand Field Theory
- MOT



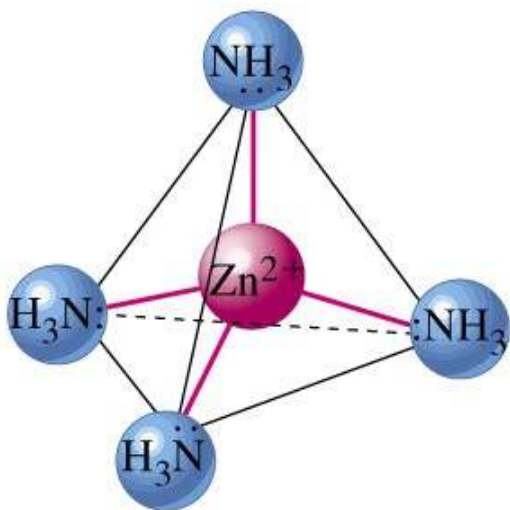
How & Why?



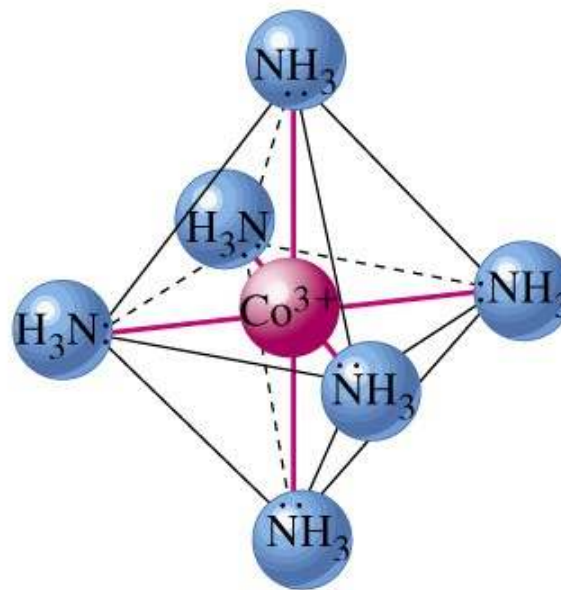
Linear



Square planar



Tetrahedral

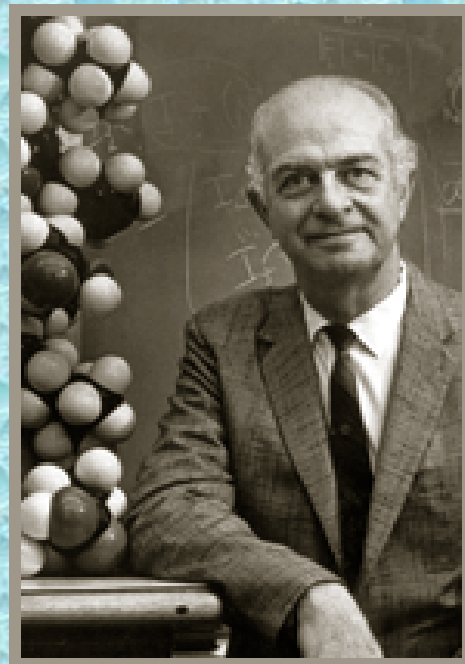


Octahedral

Valance Bond Theory

Basic Principle

A covalent bond forms when the orbitals 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

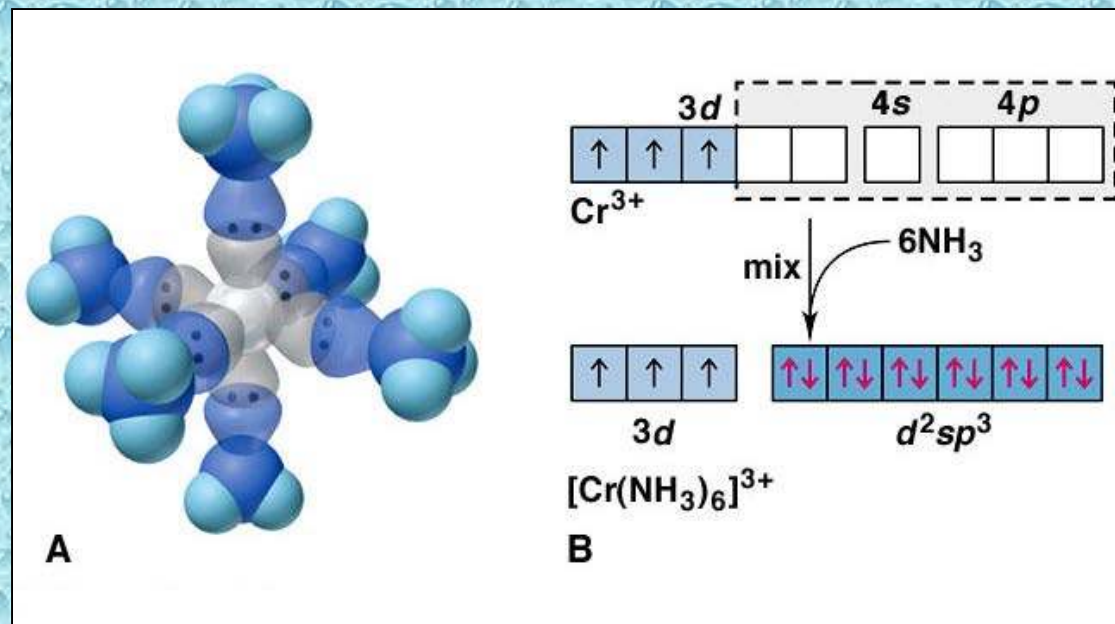
Metal = Lewis acid

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

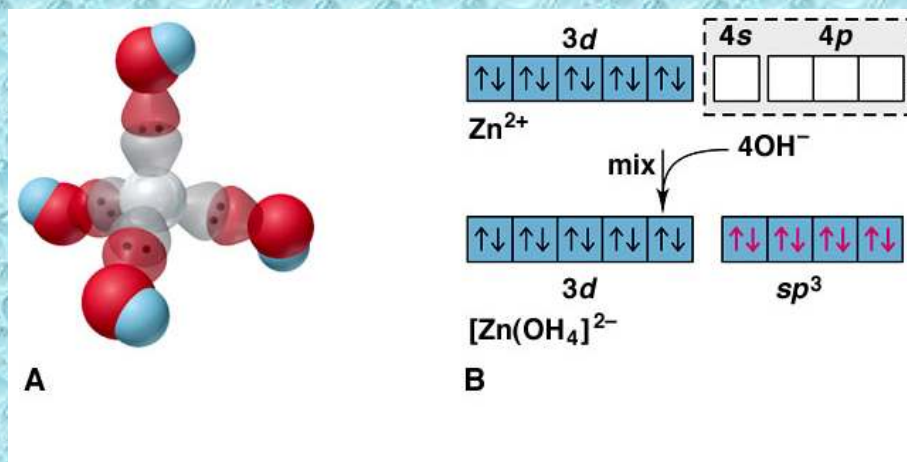
Number and type of M-L hybrid orbitals determines geometry of the complex

Octahedral Complex

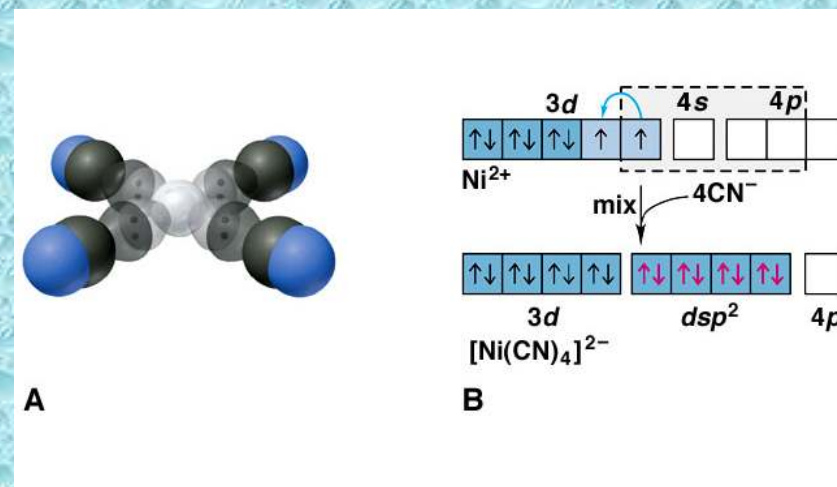
e.g. $[\text{Cr}(\text{NH}_3)_6]^{3+}$



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



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



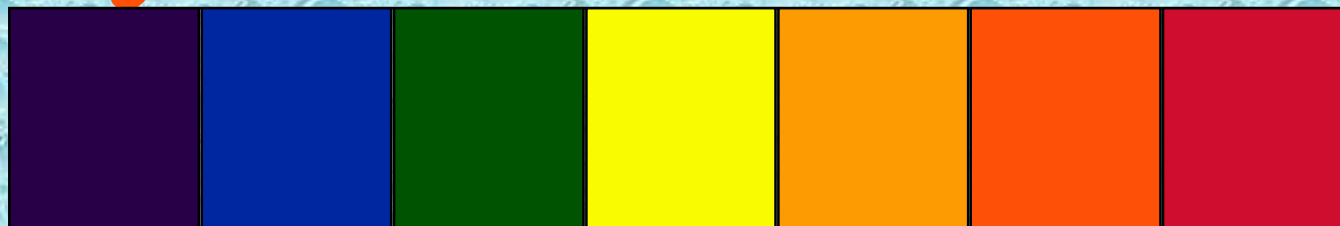
Limitations of VB theory

Cannot account for colour of complexes

May predict magnetism wrongly

Cannot account for spectrochemical series

Crystal Field Theory



400

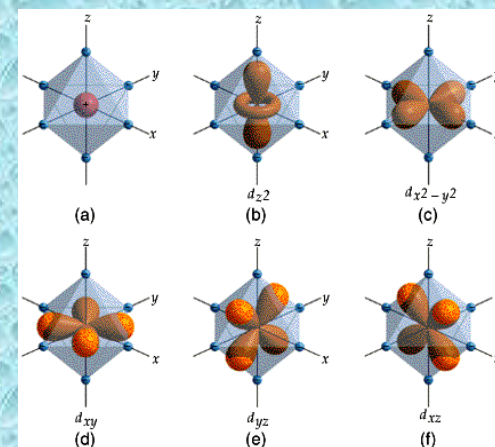


500

600

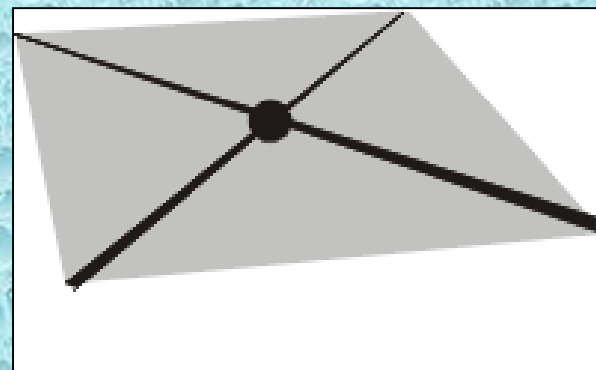
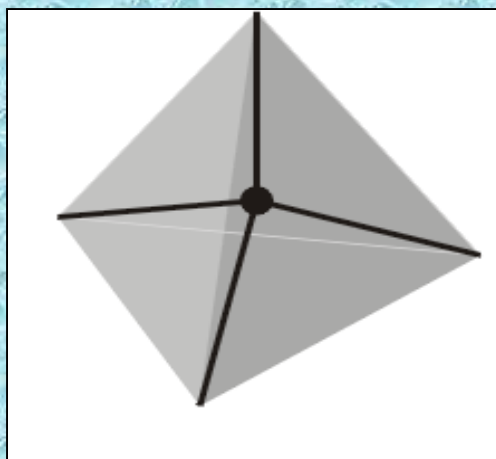
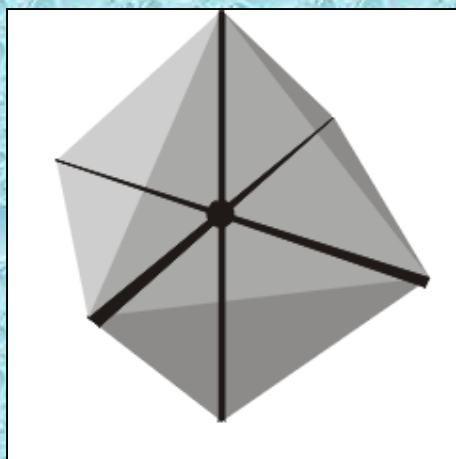
800

- The relationship between colors and complex metal ions

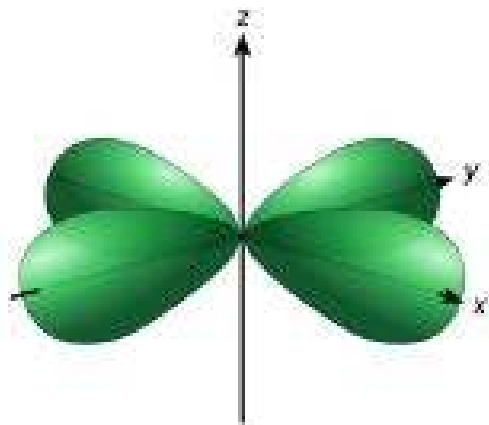


Crystal Field Model

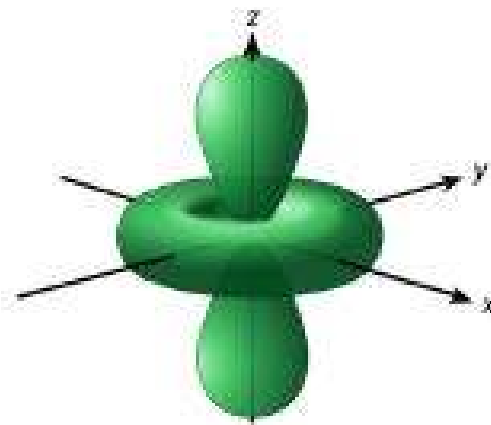
- A purely *ionic* model for transition metal complexes.
- Ligands are considered as point charge.
- Predicts the pattern of splitting of d-orbitals.
- Used to rationalize spectroscopic and magnetic properties.



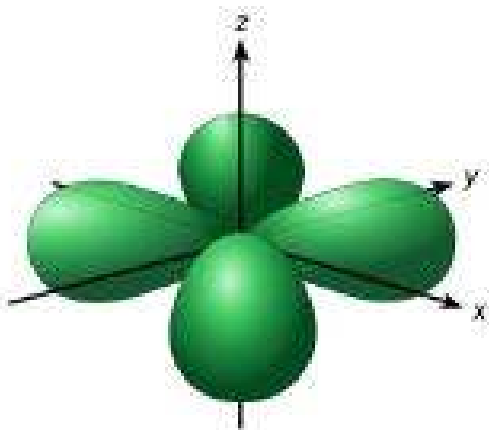
d-orbitals: look attentively along the axis



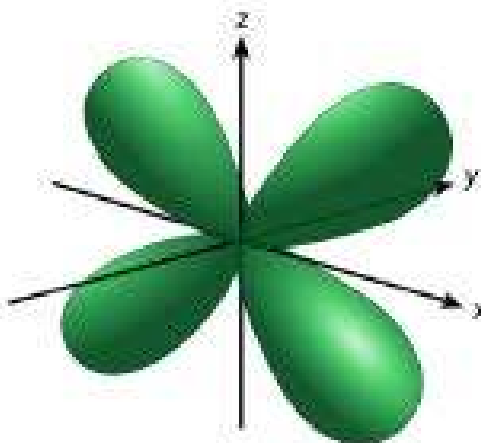
$d_{x^2-y^2}$



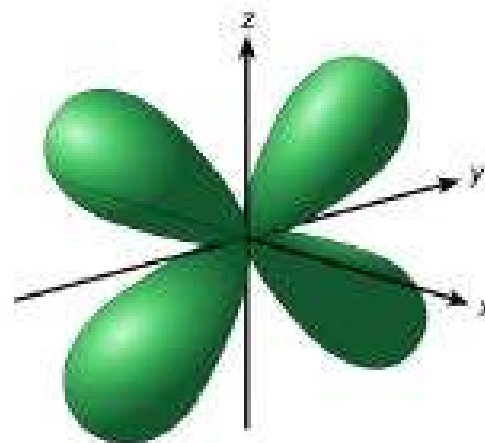
d_{z^2}



d_{xy}

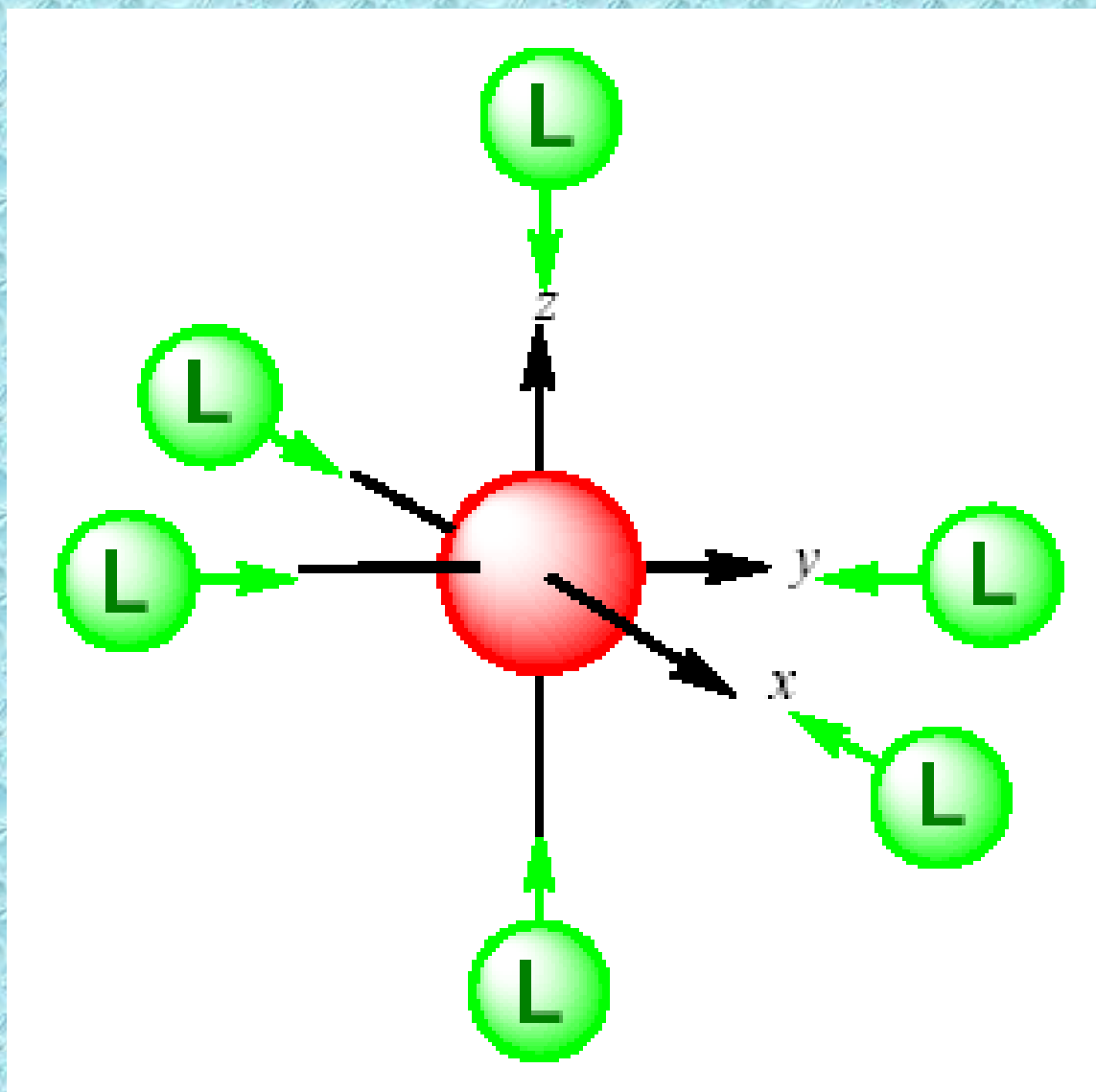


d_{xz}

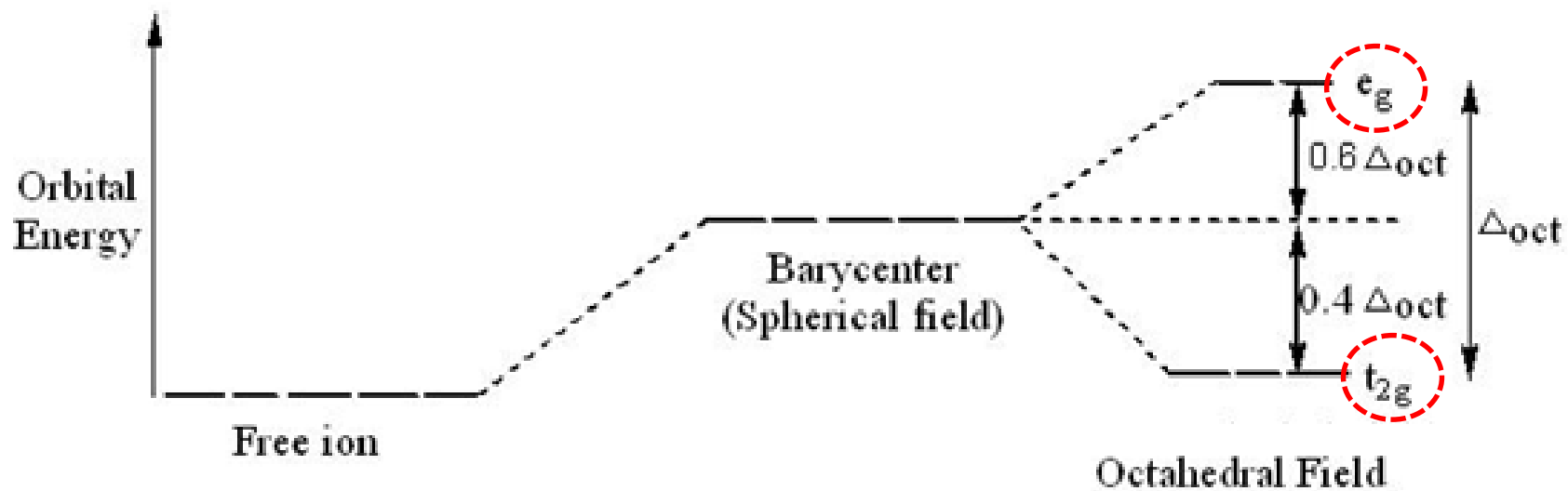


d_{yz}

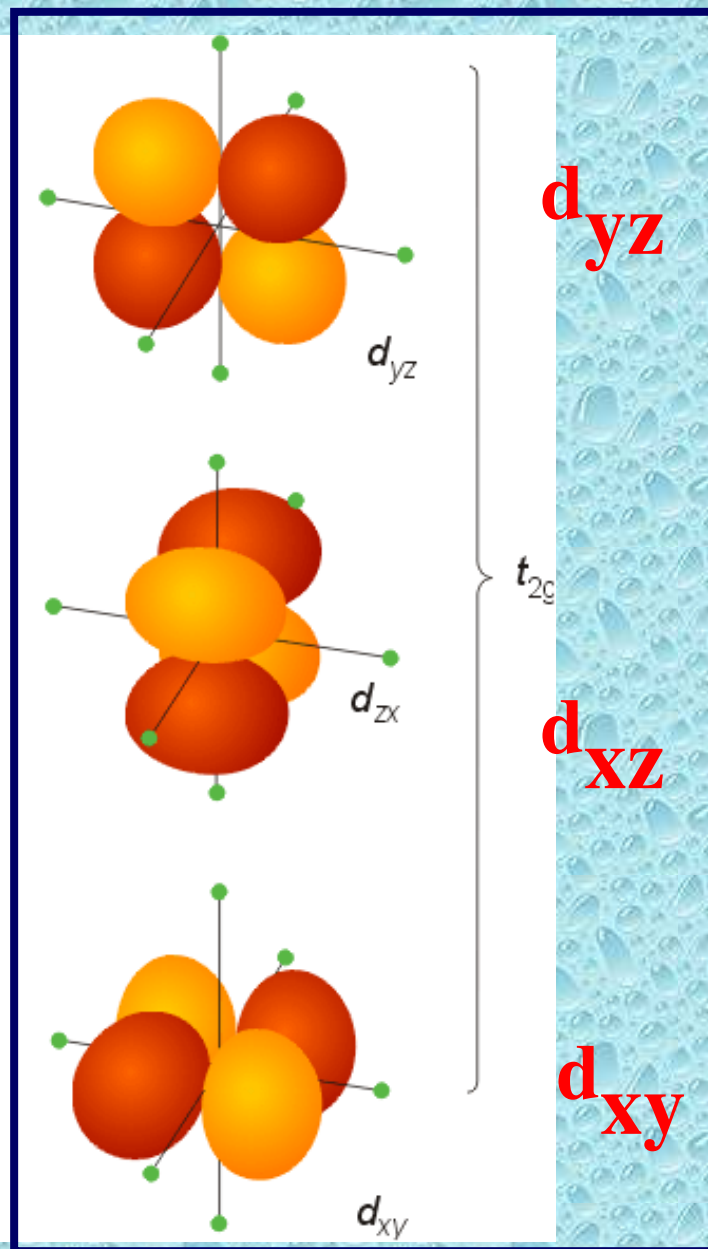
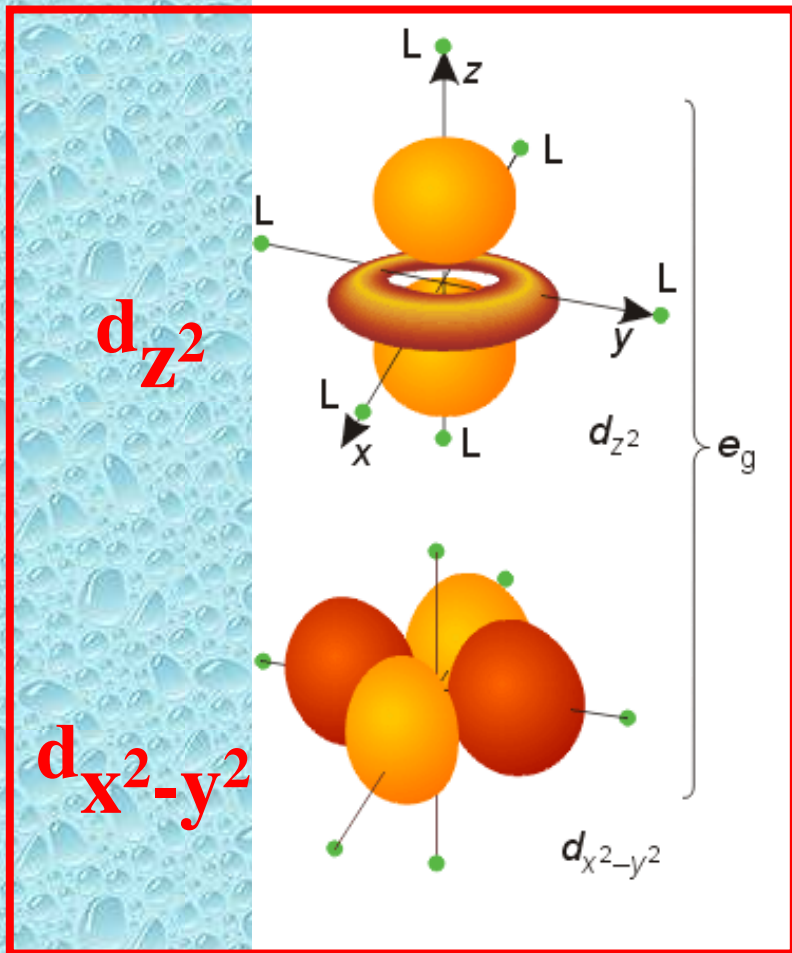
Octahedral Field



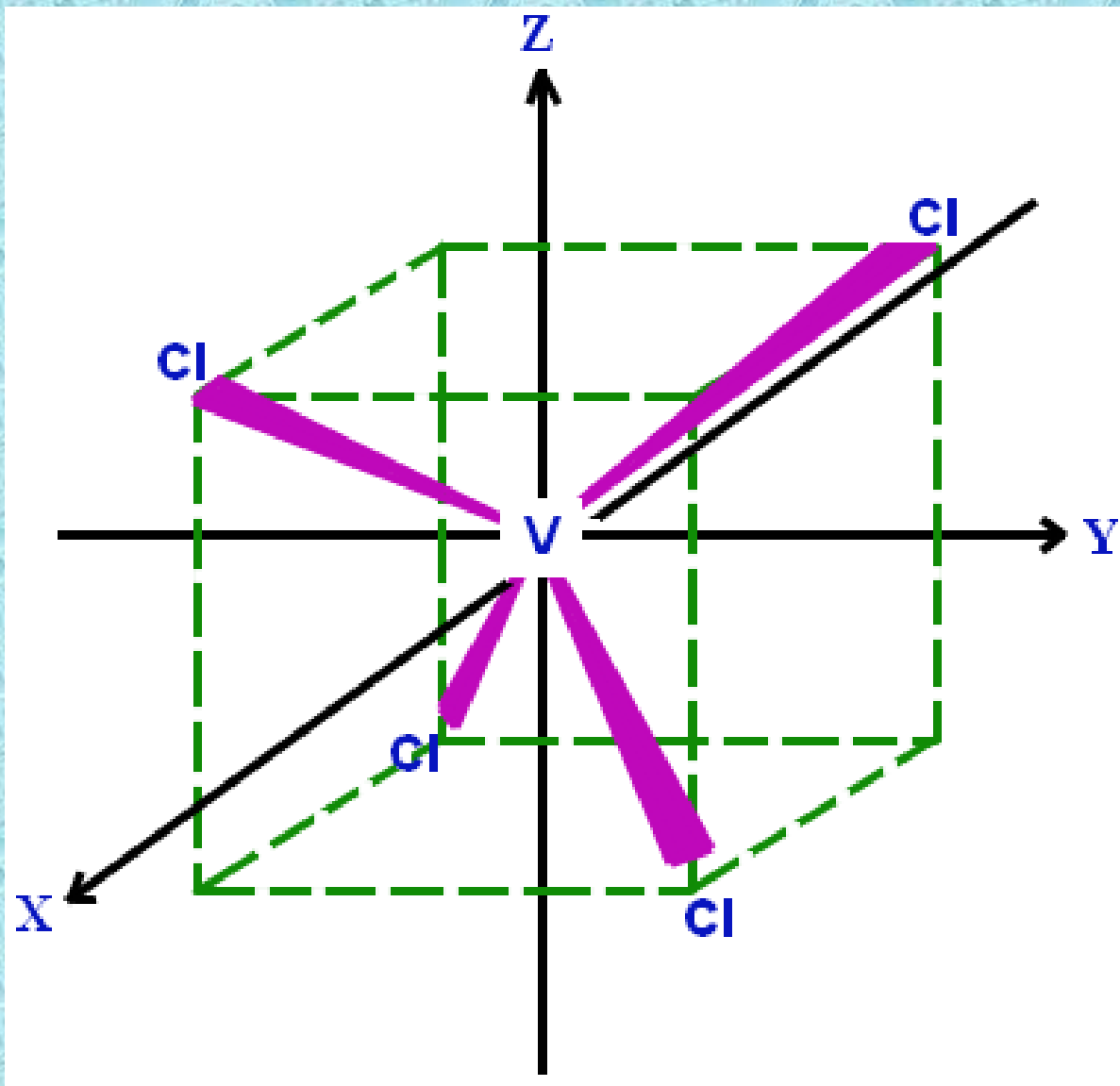
- We assume an octahedral array of negative charges placed around the metal ion (which is positive).
- The ligand orbitals lie on the same axes as negative charges.
 - Therefore, there is a large, unfavorable interaction between ligand and these orbitals (d_{z^2} and $d_{x^2-y^2}$).
 - These orbitals 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

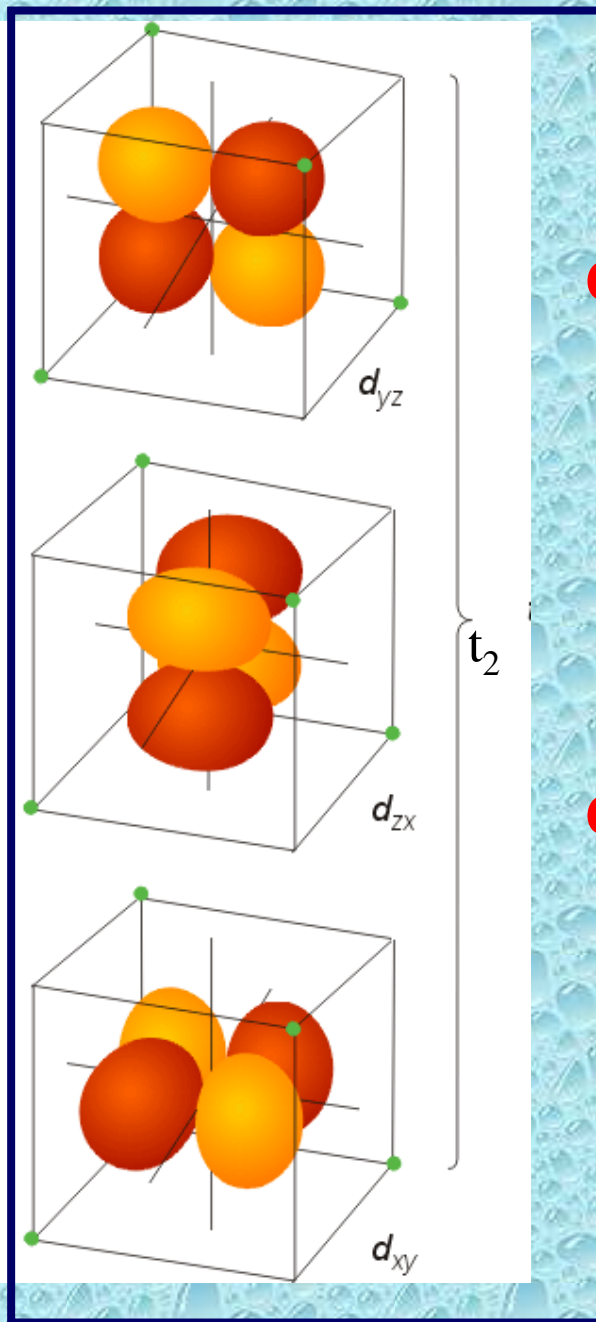
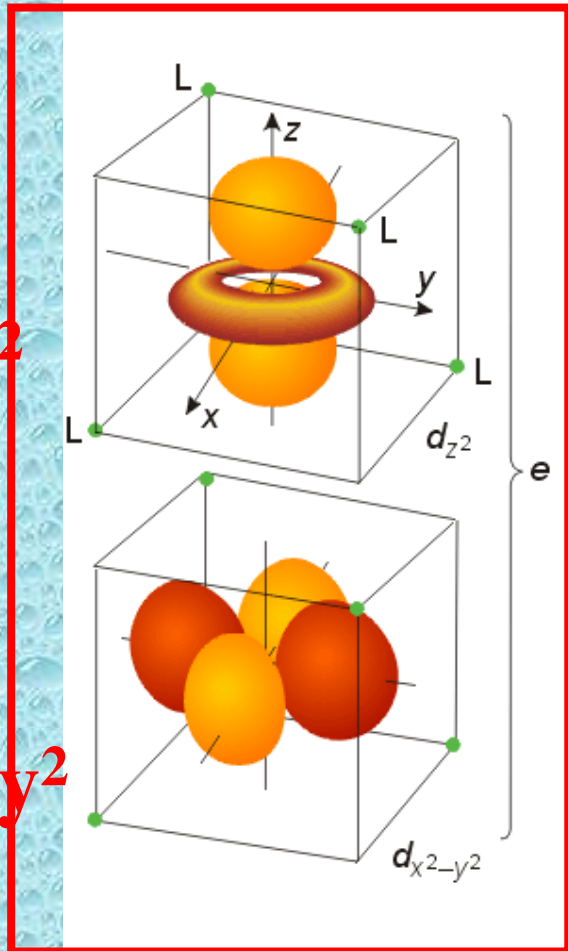


Tetrahedral Field

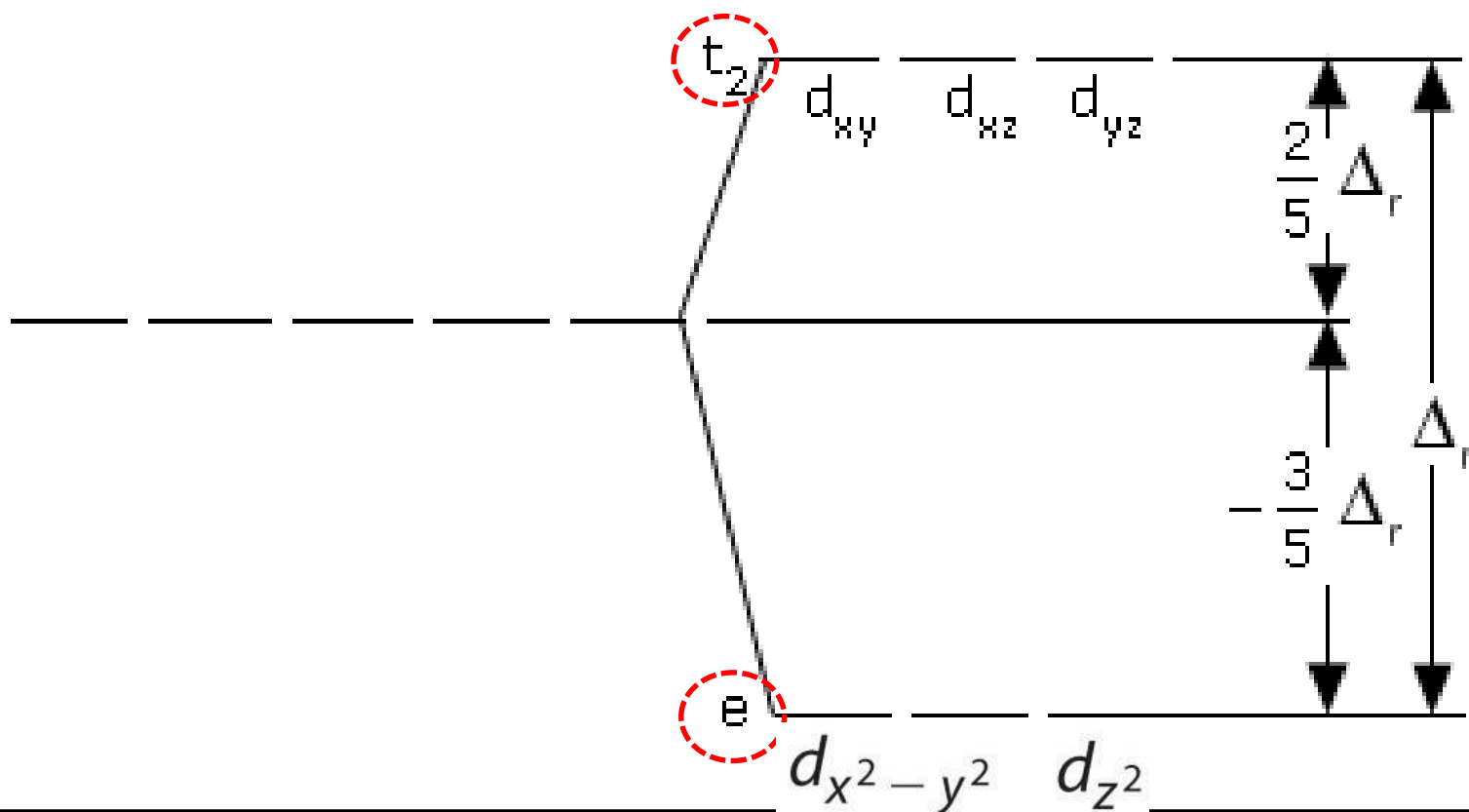


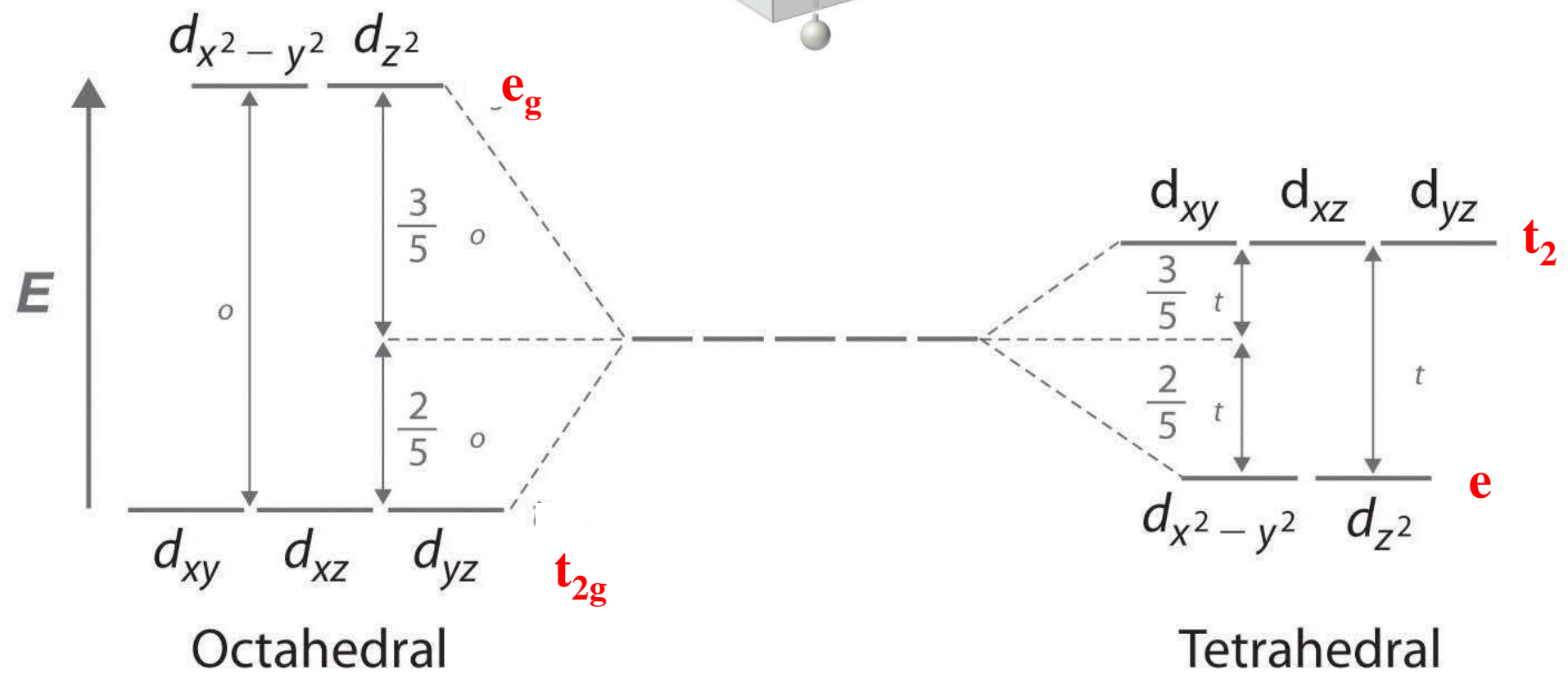
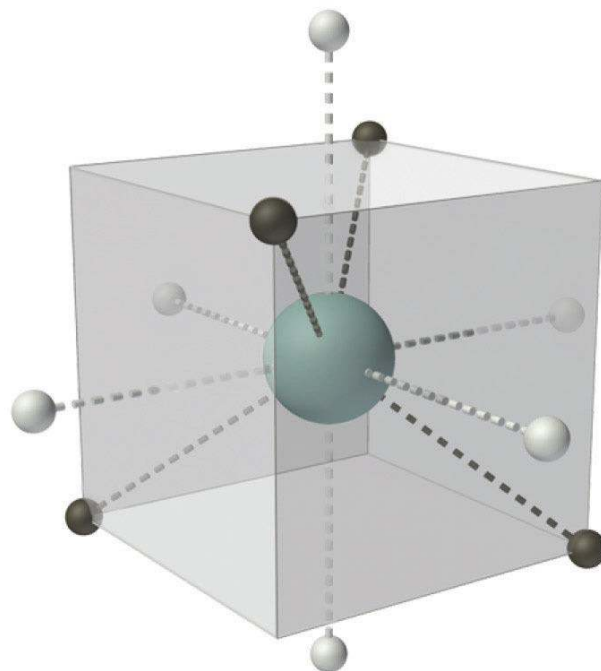
- We assume an tetrahedral array of negative charges placed around the metal ion (which is positive).
- The ligand and orbitals lie in between the axes of the negative charges.
 - Therefore, there is a large, unfavorable interaction between ligand and these orbitals, d_{xy} , d_{yz} , and d_{xz} .
 - 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



tetrahedral (T_d) crystal field splitting





Magnitude of Δ

Oxidation state of the metal ion

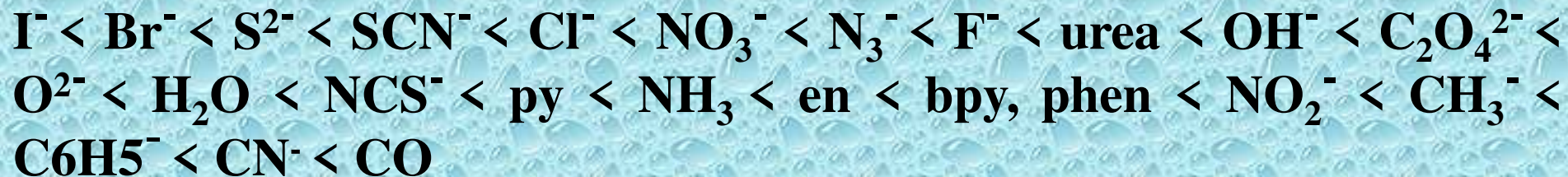


Number of ligands and geometry

$$\Delta_o > \Delta_t$$

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

Nature of the ligand



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 - pairing energy

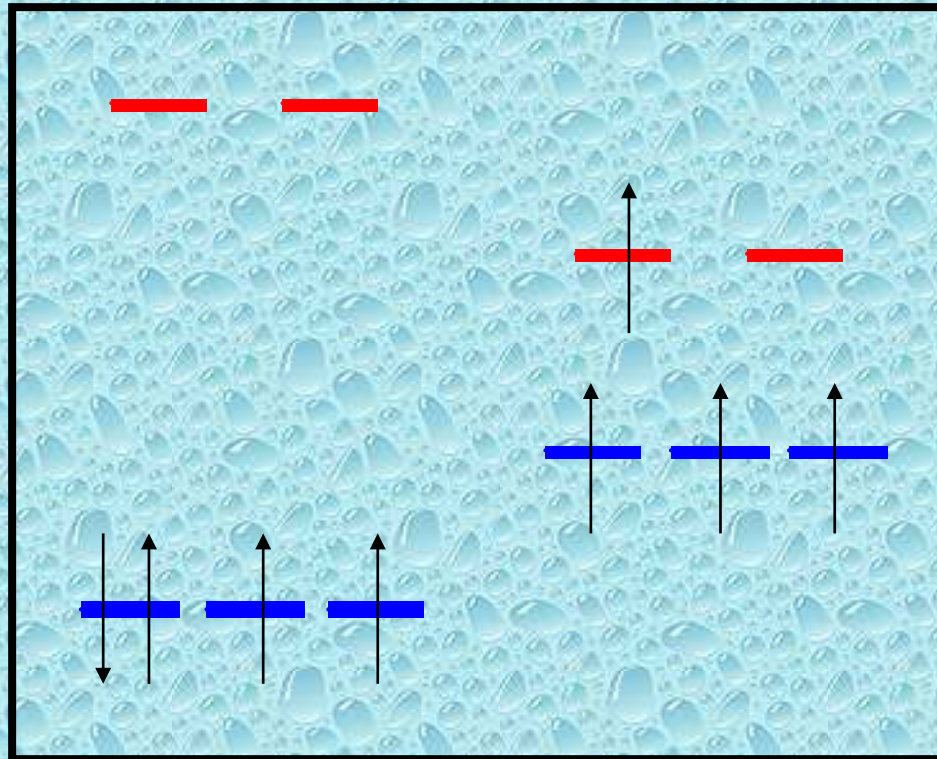
Ground-state Electronic Configuration, Magnetic Properties and Colour

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.

**Strong field =
Low spin
(2 unpaired)**



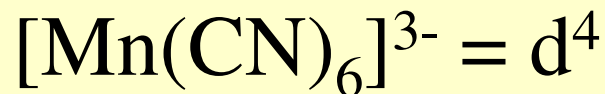
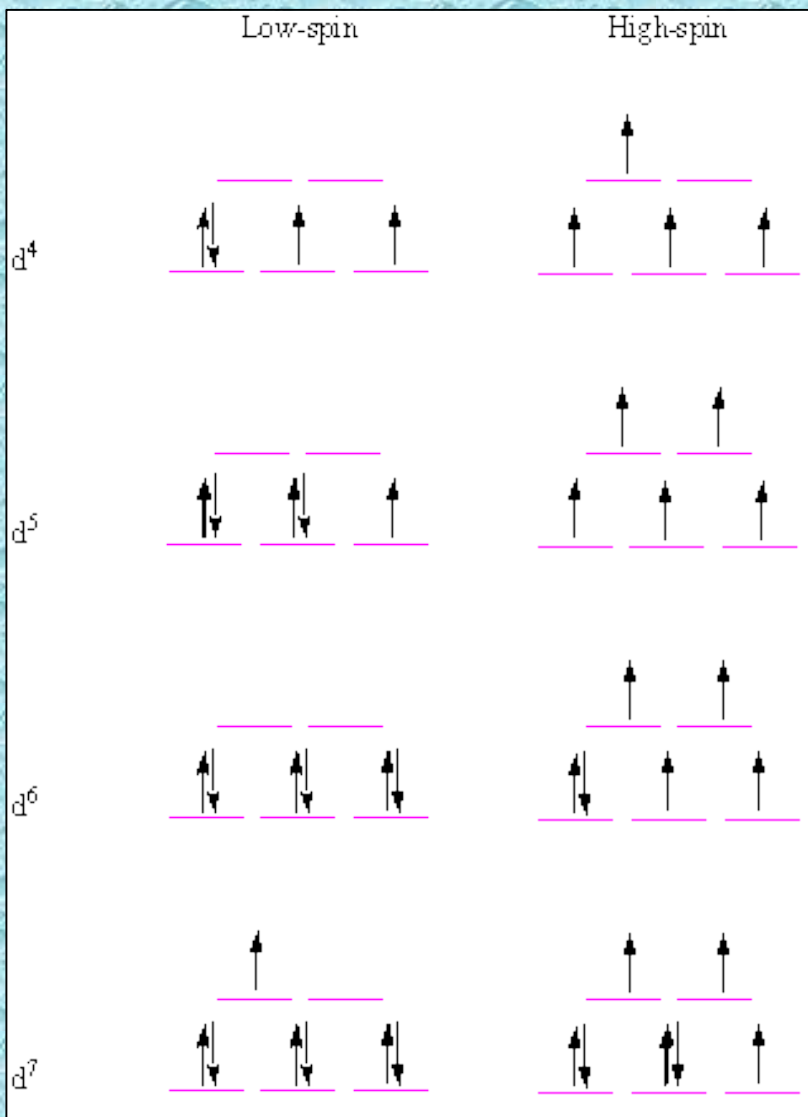
**Weak field =
High spin
(4 unpaired)**

$$P < \Delta_o$$

$$P > \Delta_o$$

Coulombic repulsion energy and exchange energy

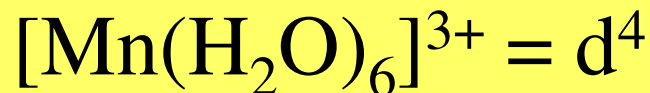
Ground-state Electronic Configuration, Magnetic Properties and Colour



Strong field Complex

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

Low Spin Complex

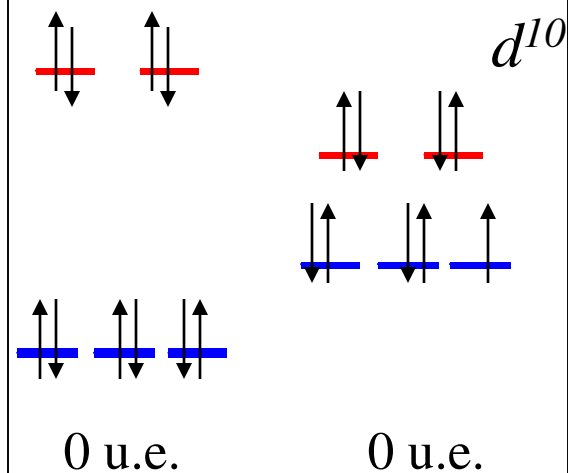
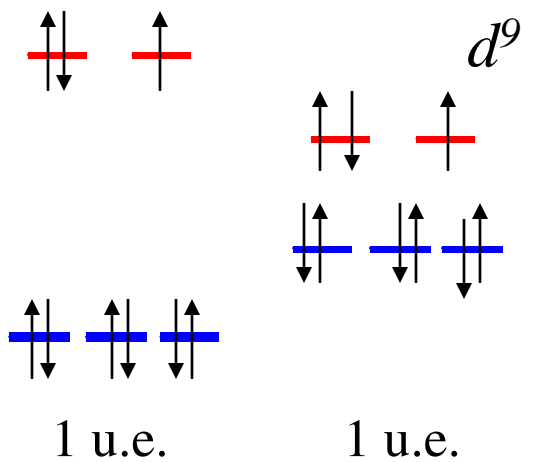
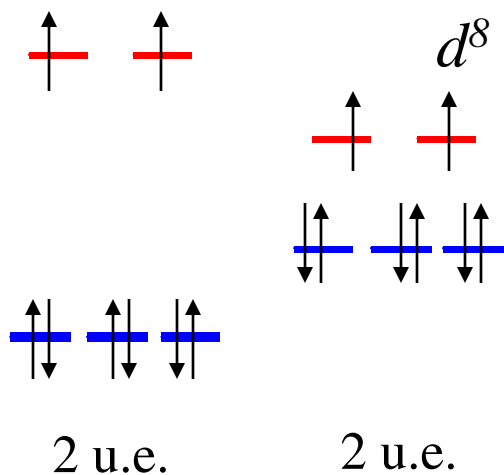
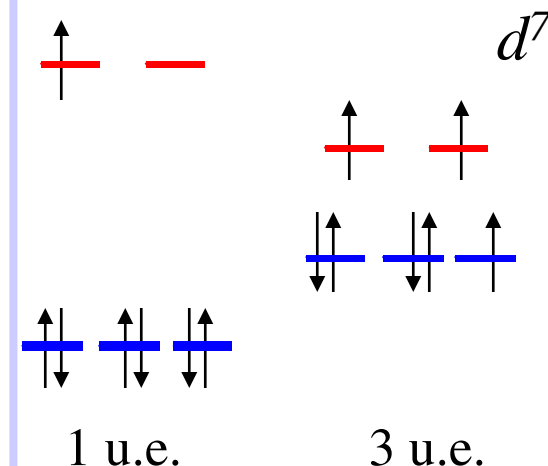
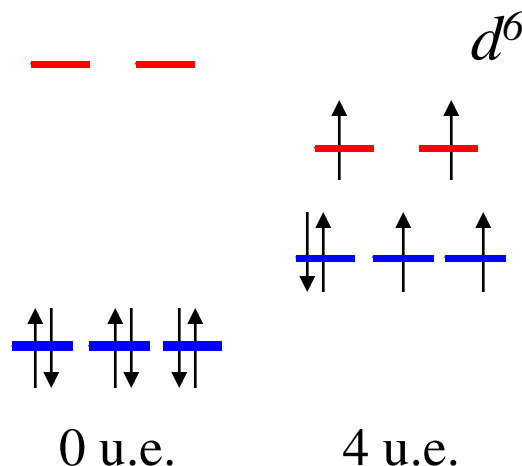
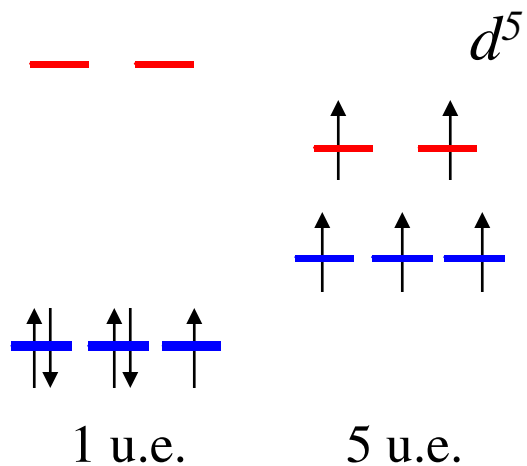


Weak Field Complex

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

High Spin Complex

Placing electrons in d orbitals



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

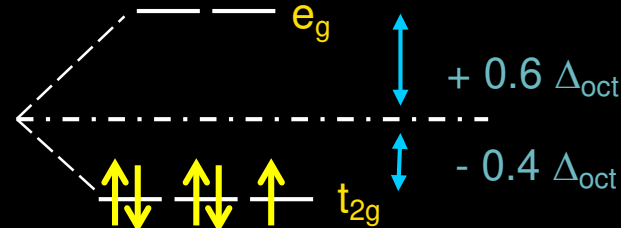
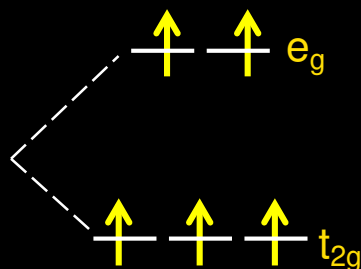
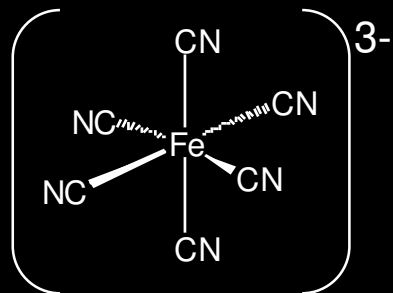
C.N. = 6 \therefore O_h

Fe(III) \therefore d^5

h.s.

l.s.

\swarrow $\text{CN}^- = \text{s.f.l.}$



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

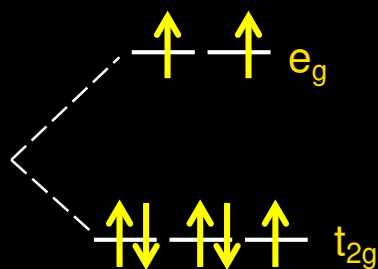
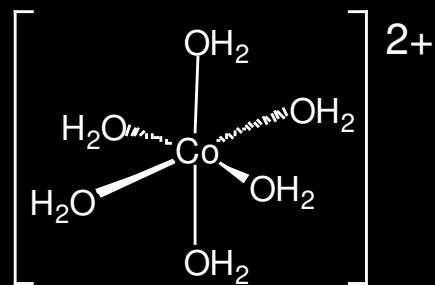
If the CFSE of $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ is $-0.8 \Delta_{\text{oct}}$, what spin state is it in?

C.N. = 6 \therefore O_h

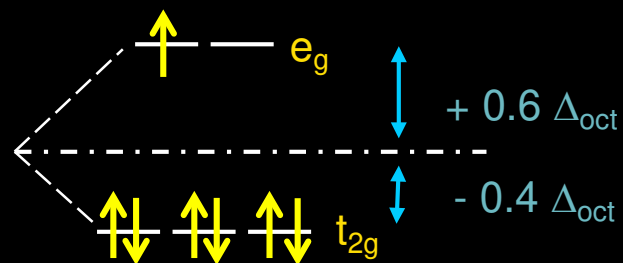
Co(II) \therefore d^7

h.s.

l.s.



$$\begin{aligned} \text{CFSE} &= (5 \times -0.4 \Delta_{\text{oct}}) \\ &+ (2 \times 0.6 \Delta_{\text{oct}}) + 2P = -0.8 \Delta_{\text{oct}} + 2P \end{aligned}$$



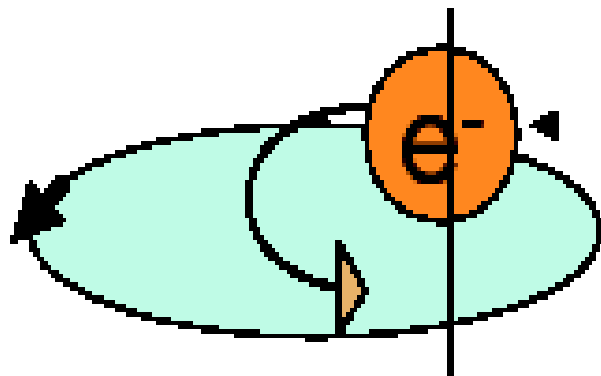
$$\begin{aligned} \text{CFSE} &= (6 \times -0.4 \Delta_{\text{oct}}) \\ &+ (0.6 \Delta_{\text{oct}}) + 3P = -1.8 \Delta_{\text{oct}} + P \end{aligned}$$

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

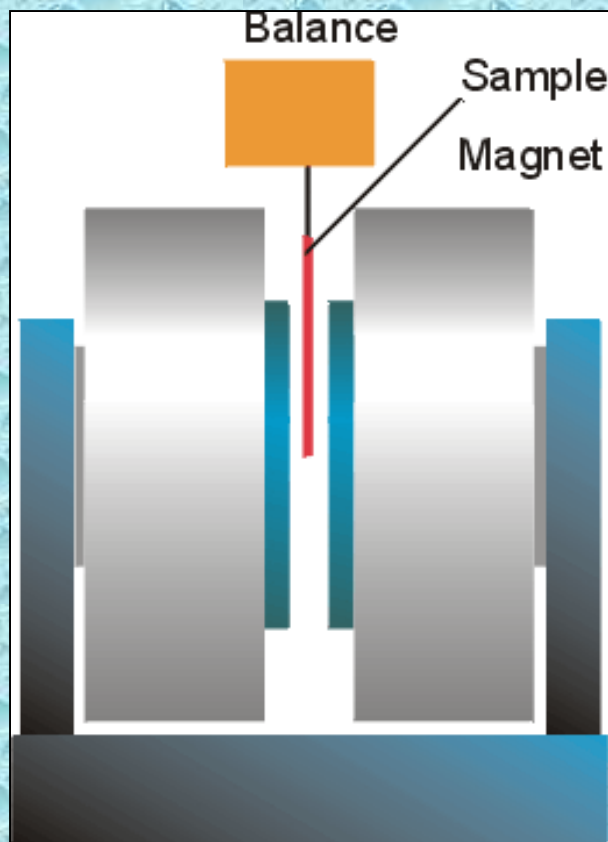
- The magnetic moment μ of a complex with total spin quantum number S is:
- $\mu = 2\{S(S+1)\}^{1/2} \mu_B$ (μ_B is the Bohr magneton)
- $\mu_B = eh/4\pi m_e = 9.274 \times 10^{-24} \text{ J T}^{-1}$
- Since each unpaired electron has a spin $1/2$,
- $S = (1/2)n$, where n = no. of unpaired electrons
- $\mu = \{n(n+2)\}^{1/2} \mu_B$
- 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 $\Delta_t \ll \Delta_o$.

n = no. of unpaired electrons

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

Ion	n	S	μ/μ_B Calculated	Experimental
Ti³⁺	1	1/2	1.73	1.7 – 1.8
V³⁺	2	1	2.83	2.7 – 2.9
Cr³⁺	3	3/2	3.87	3.8
Mn³⁺	4	2	4.90	4.8 – 4.9
Fe³⁺	5	5/2	5.92	5.3

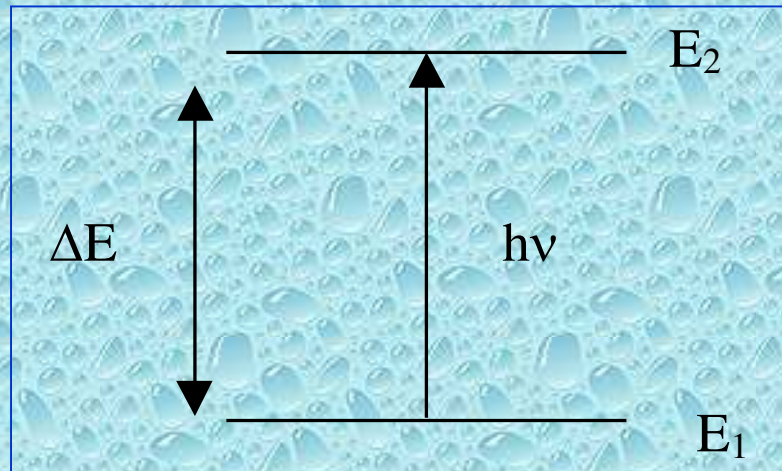
**Similar Calculation can be done
for Low-spin Complex**



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

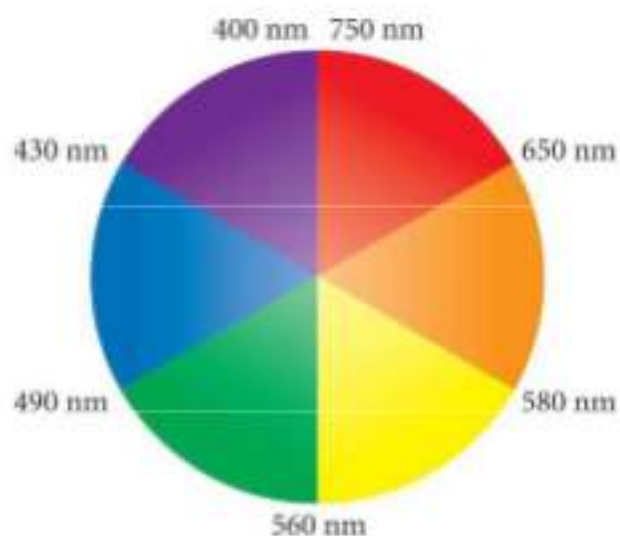
The origin of the color of the transition metal compounds



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

Ligands influence Δ_0 , 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

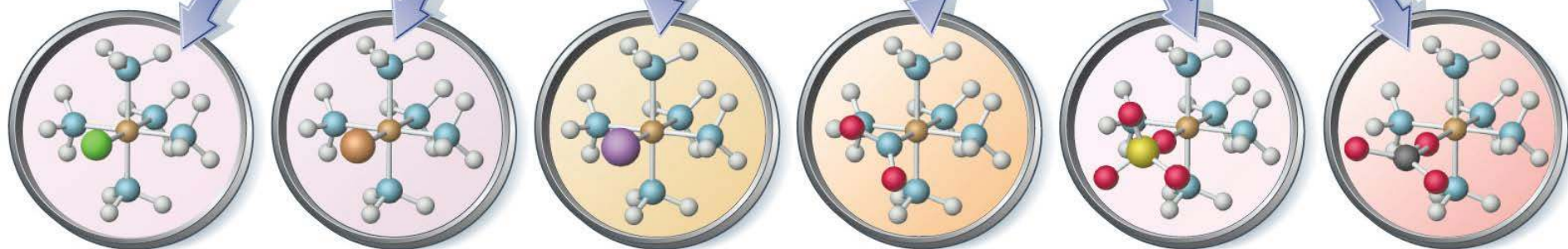
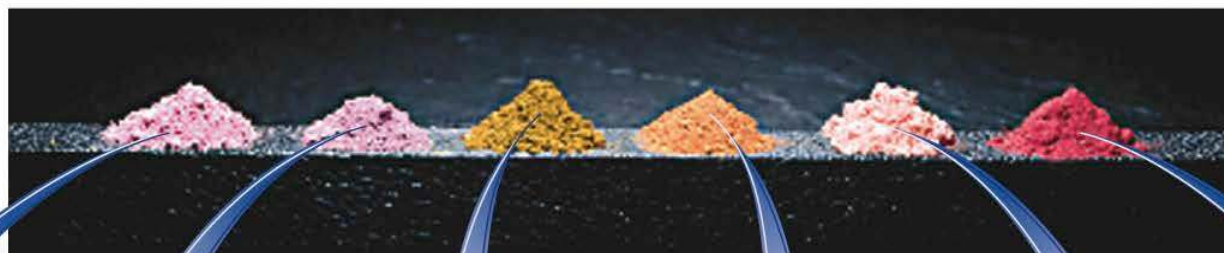
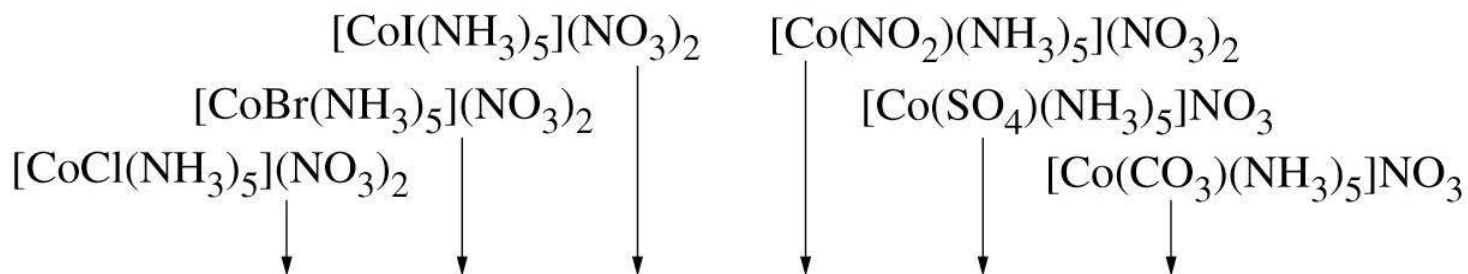
The Beer-Lambert Law

$$A = \log_{10}(I_0/I) = \epsilon c l$$

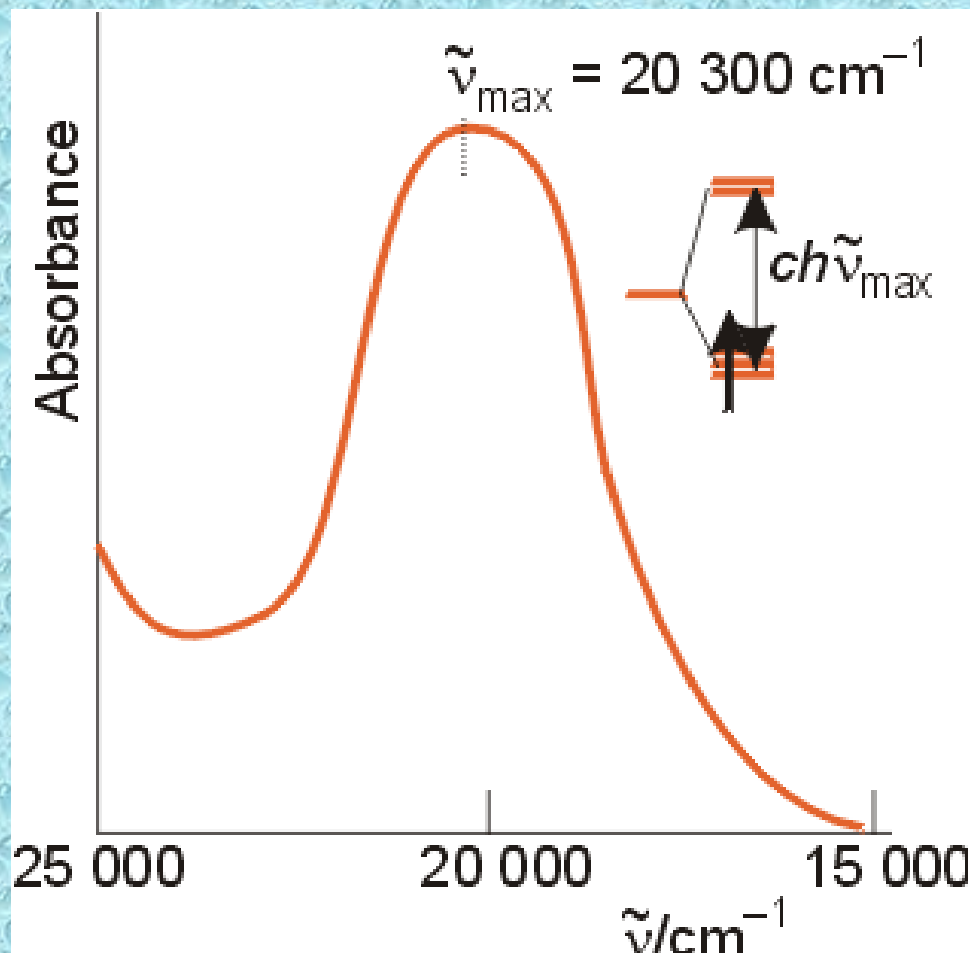
where ϵ is the molar extinction coefficient (in $L \text{ cm}^{-1} \text{ mole}^{-1}$), c is concentration in mole L^{-1} and l is the path length in cm. A is known as 'Absorbance' and it is dimensionless.

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

1. Metal charge
2. Ligand strength



The optical absorption spectrum of $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$



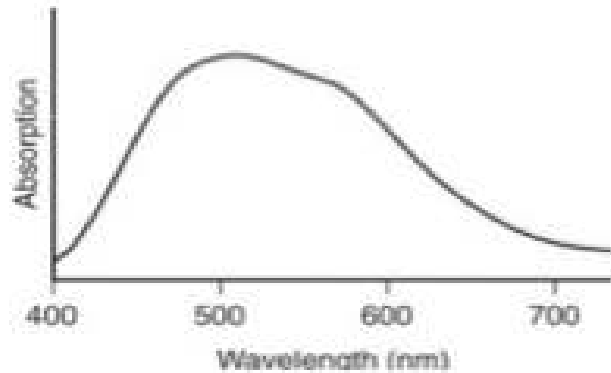
Assigned transition:



**This corresponds to
the energy gap**

$$\Delta_o = 243\text{ kJ mol}^{-1}$$

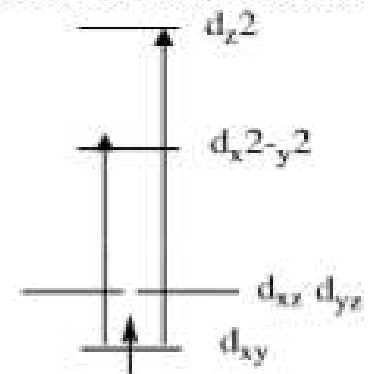
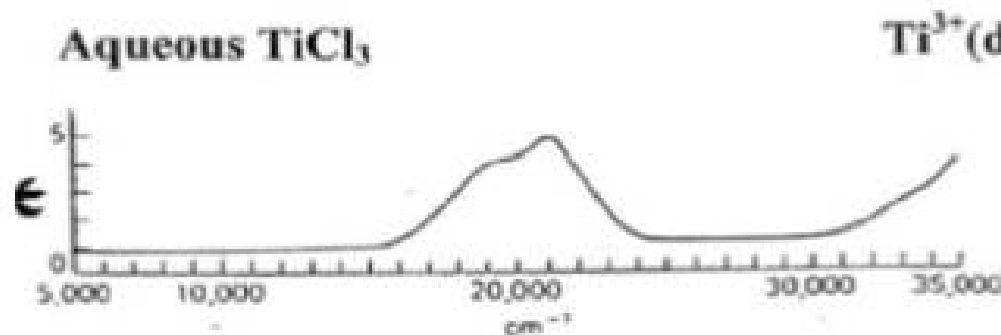
Color of $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$

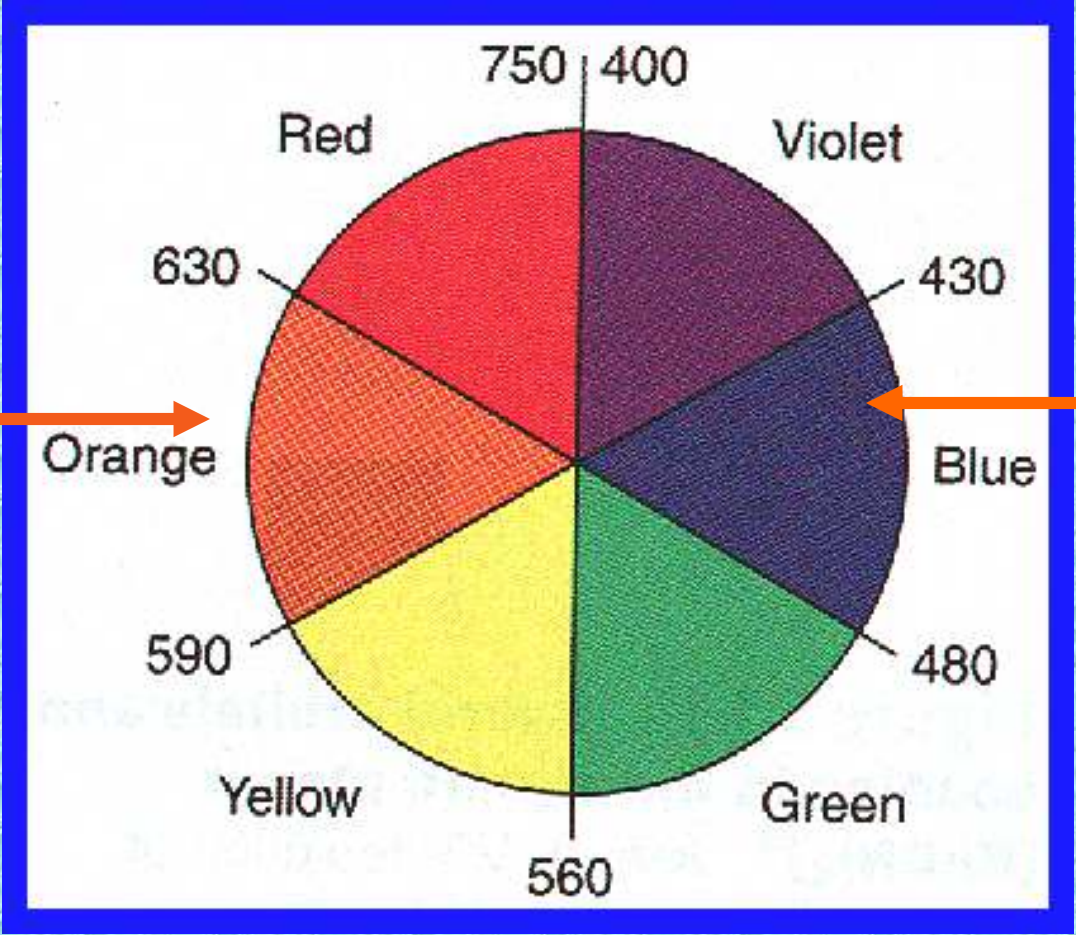


Absorption at 520 nm gives the complex its purple color



A more resolved absorption spectrum of the complex has a shoulder





**absorbed
color**

**observed
color**

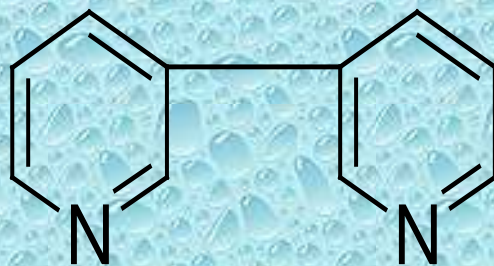
- **Spectrochemical Series: An order of ligand field strength based on experiment:**

Weak Field $I^- < Br^- < S^{2-} < SCN^- < Cl^- < NO_3^- < N_3^- < F^- < \text{urea} < OH^- < C_2O_4^{2-} < O^{2-} < H_2O < NCS^- < py < NH_3 < en < bipy, phen < NO_2^- < CH_3^- < C_6H_5^- < CN^- < CO$

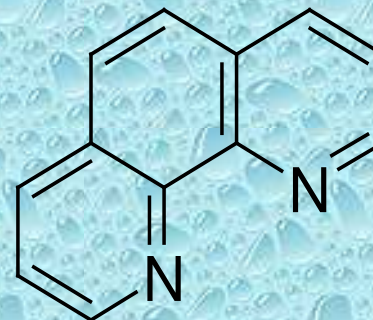
Strong Field



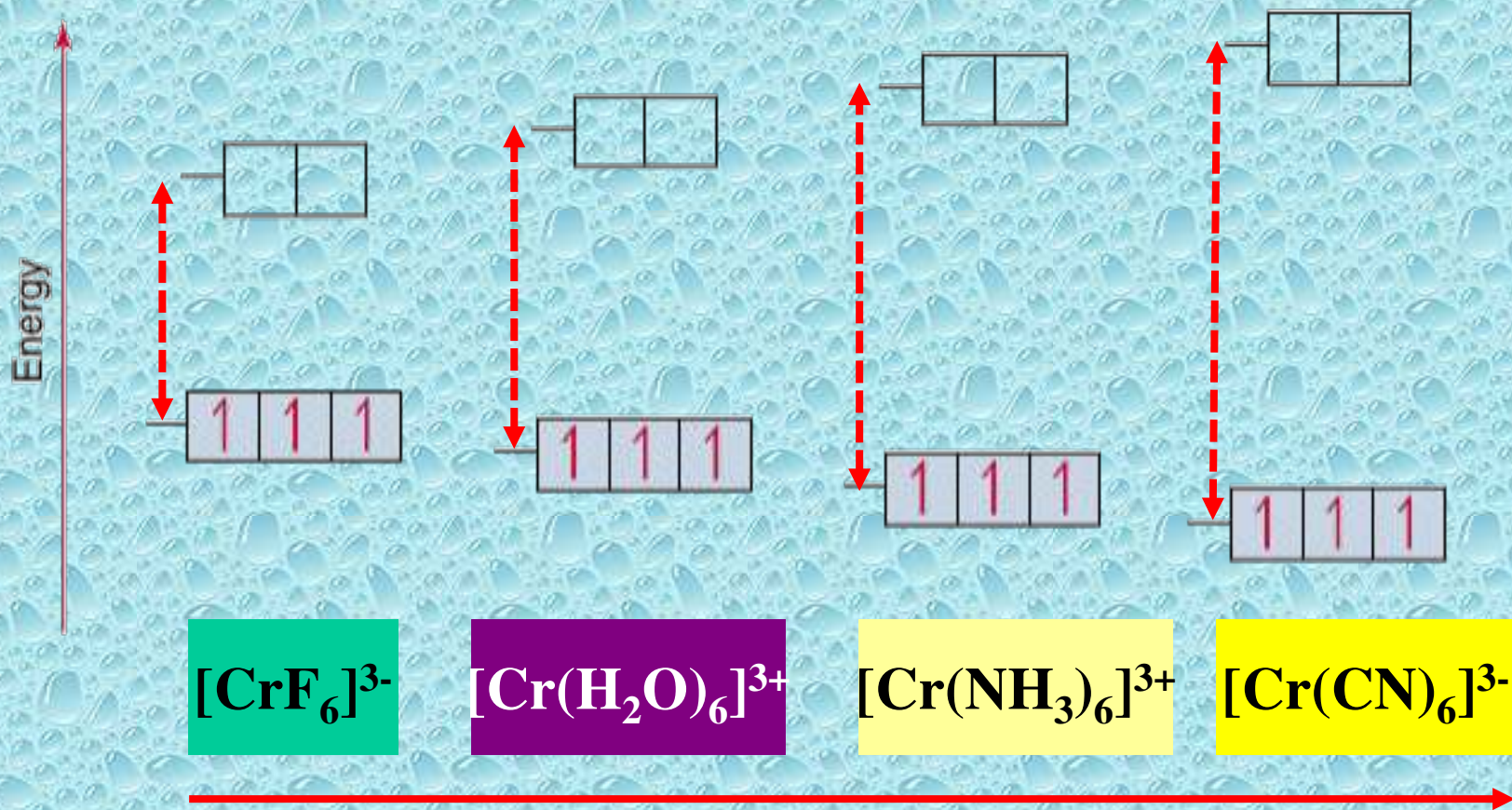
Ethylenediamine (en)



2,2'-bipyridine (bipy)

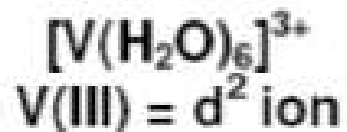


1,10-phenanthroline (phen)

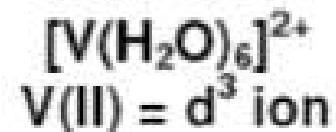
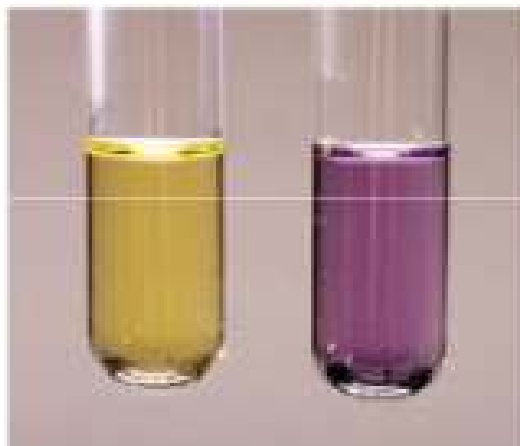
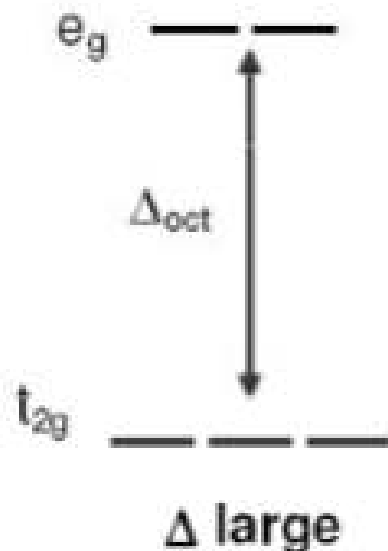


As Cr^{3+} goes from being attached to a weak field ligand to a strong field ligand, Δ increases and the color of the complex changes from green to yellow.

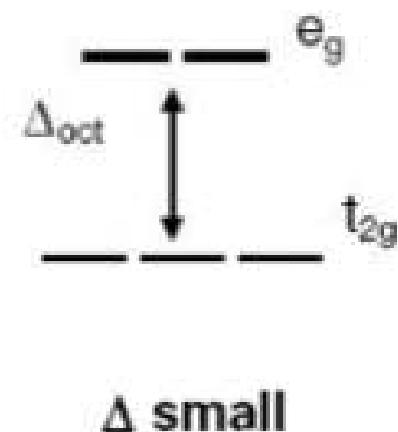
Color and CFT



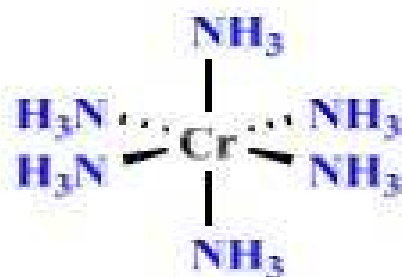
violet light absorbed
complex appears yellow



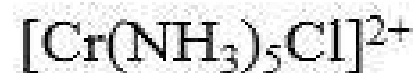
yellow light absorbed
complex appears violet



Color and CFT



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



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



$[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$ 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 MnO_4^- , CrO_4^{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

Zn²⁺ d^{10} ion white

TiF₄ d^0 ion white

TiCl₄ d^0 ion white

TiBr₄ d^0 ion **orange**

TiI₄ d^0 ion **dark brown**

[MnO₄]⁻ Mn(VII) d^0 ion **purple**

[Cr₂O₇]⁻ 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

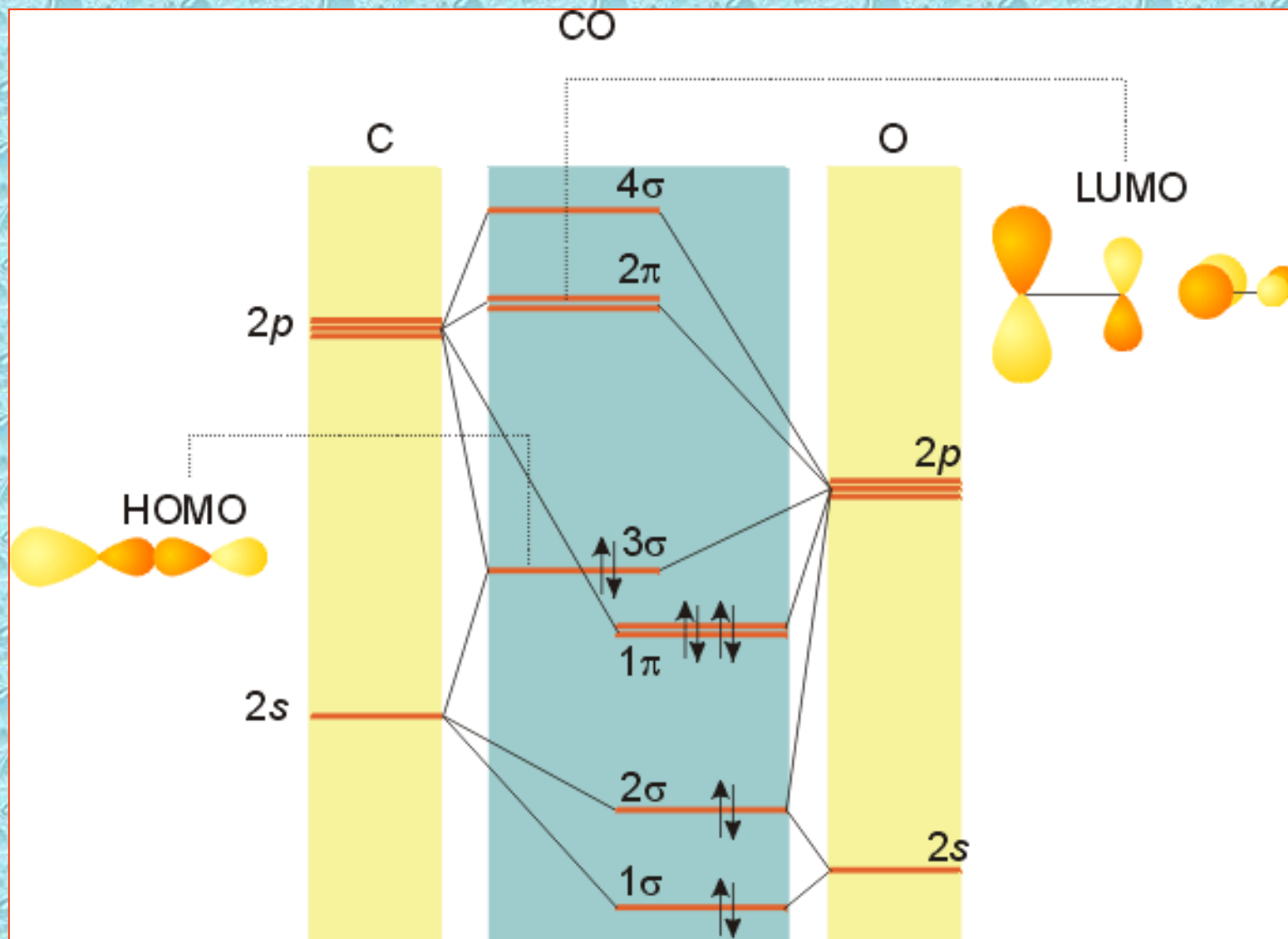
Consequence

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

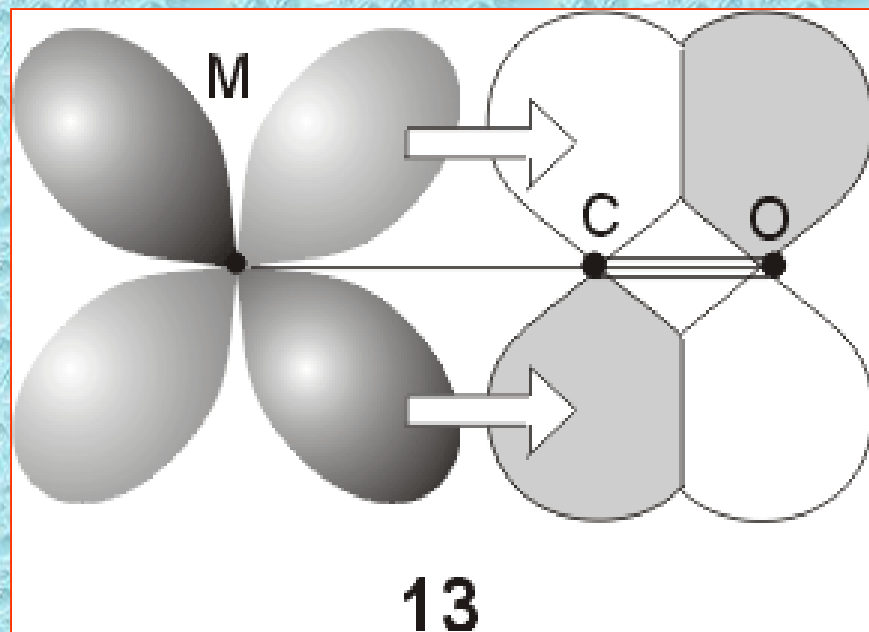
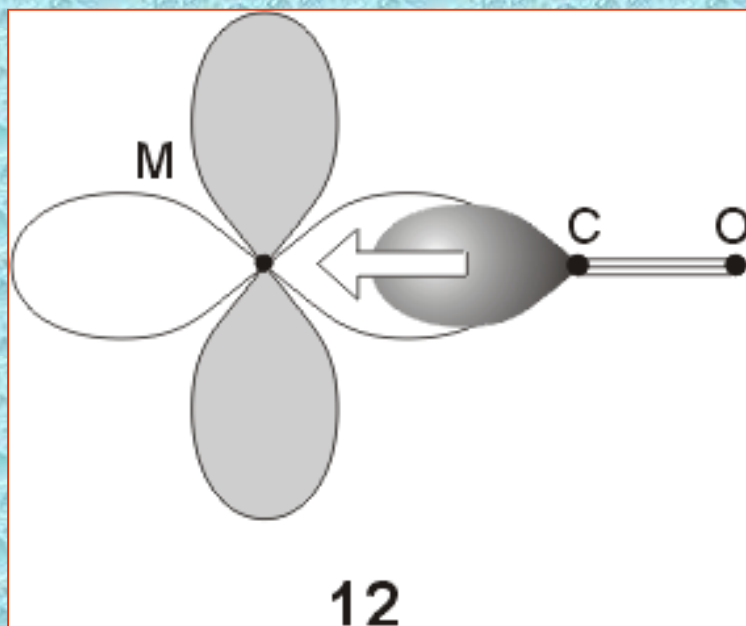
Metals in Low Oxidation States

- 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.

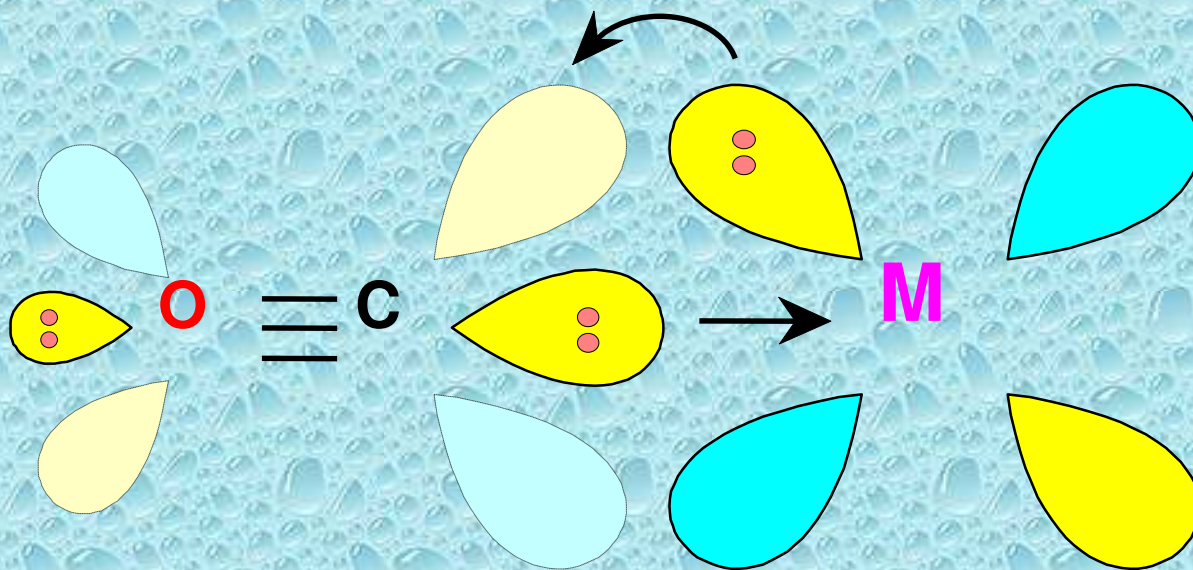
Stabilizing Low Oxidation State: CO Can Do the Job



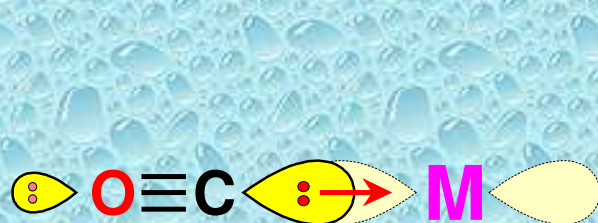
Stabilizing Low Oxidation State: CO Can Do the Job



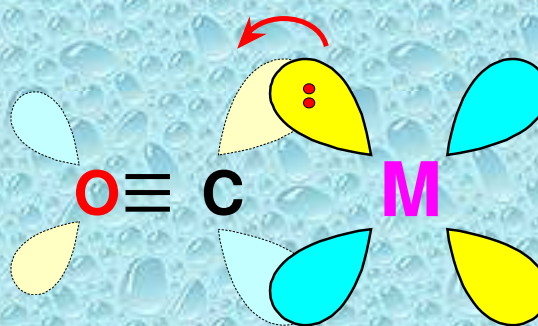
**$\text{Ni}(\text{CO})_4$, $[\text{Fe}(\text{CO})_5]$, $[\text{Cr}(\text{CO})_6]$, $[\text{Mn}_2(\text{CO})_{10}]$,
 $[\text{Co}_2(\text{CO})_8]$, $\text{Na}_2[\text{Fe}(\text{CO})_4]$, $\text{Na}[\text{Mn}(\text{CO})_5]$**



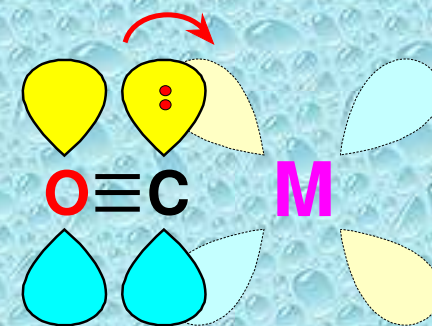
σ orbital serves as a very weak donor to a metal atom



CO-M sigma bond

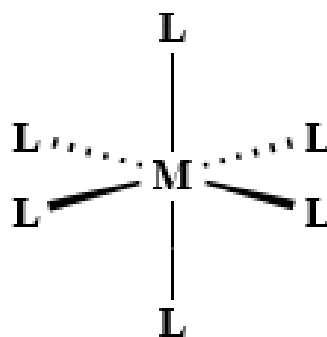


M to CO pi backbonding

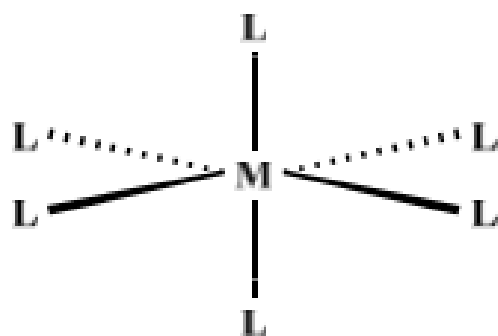


CO to M pi bonding
(rare)

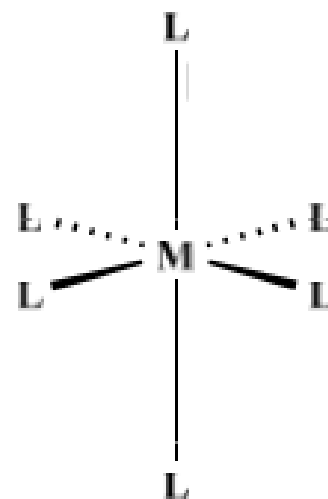
Distortions in Octahedral Geometry



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



Compressed

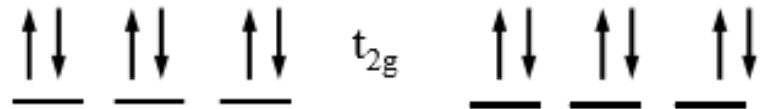
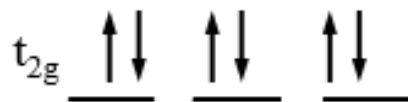
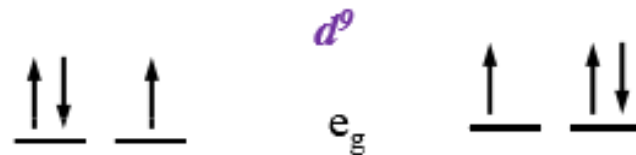
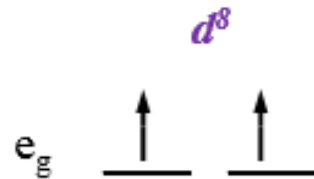


Elongated

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

Distortions in Octahedral Geometry

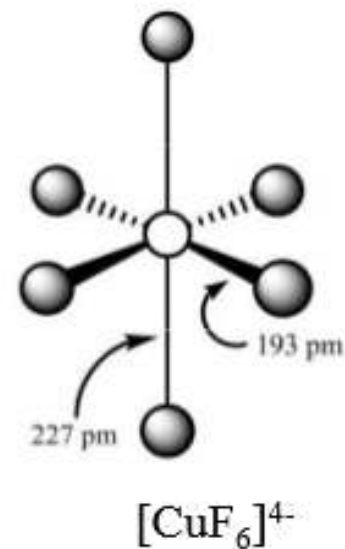
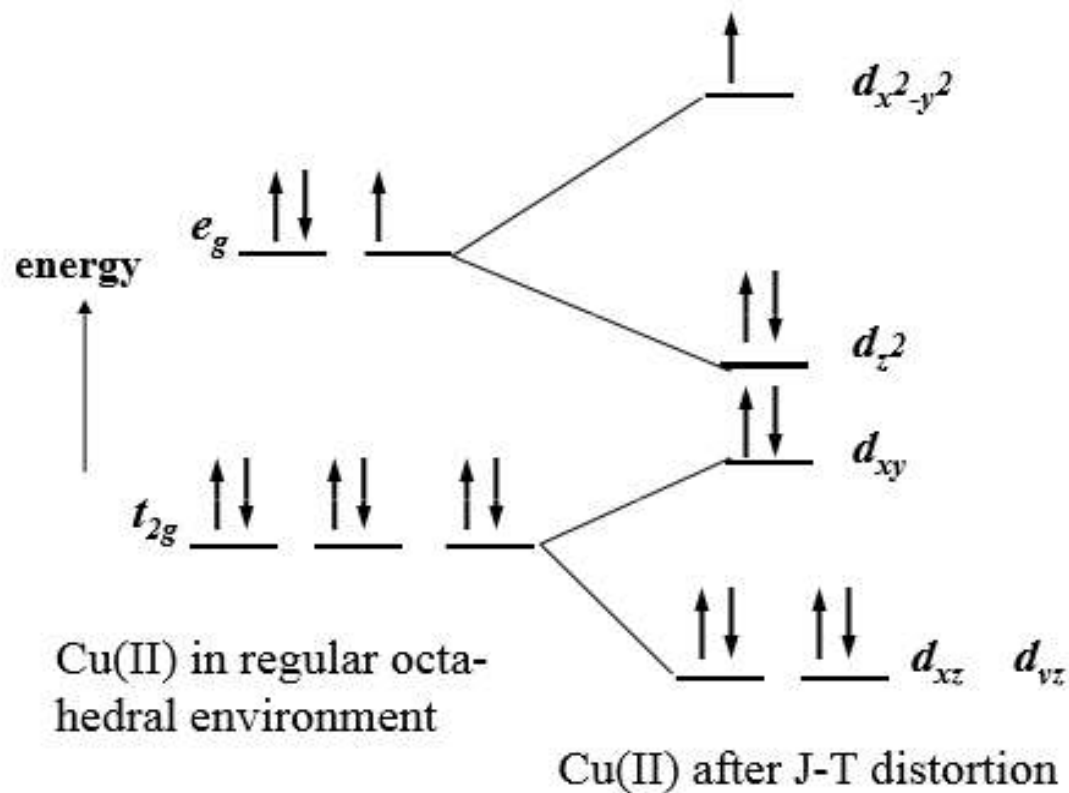
If the ground electronic configuration of a non-linear complex is orbitally degenerate, the complex will distort so as to remove the degeneracy and achieve a lower energy. This is called the **Jahn-Teller Effect**



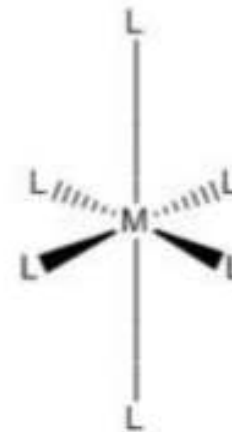
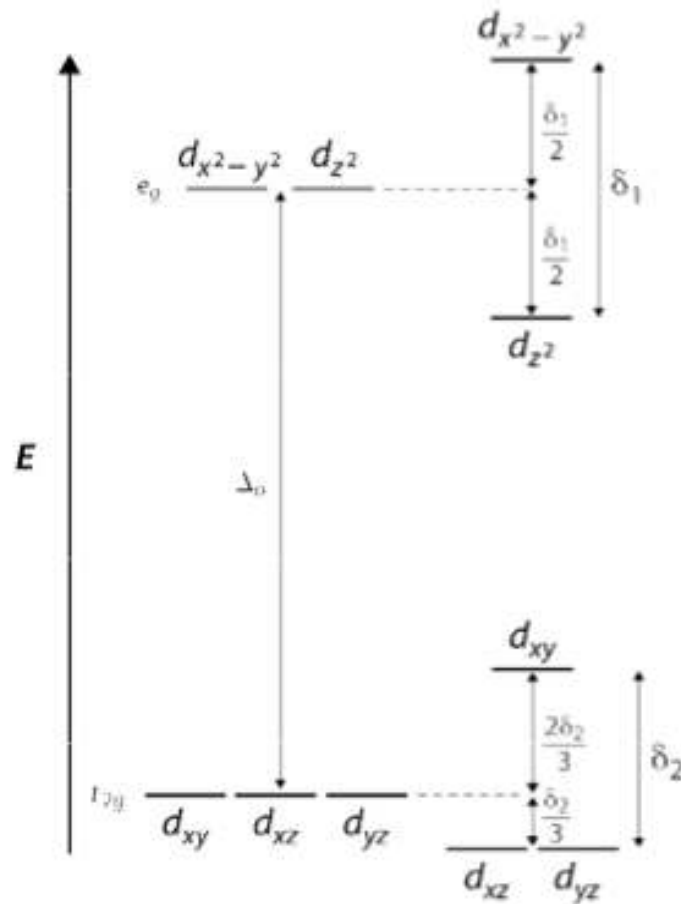
Ni^{2+} : Only one way of filling the orbitals; not degenerate and no Jahn-Teller Distortion

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



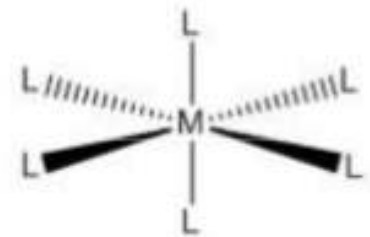
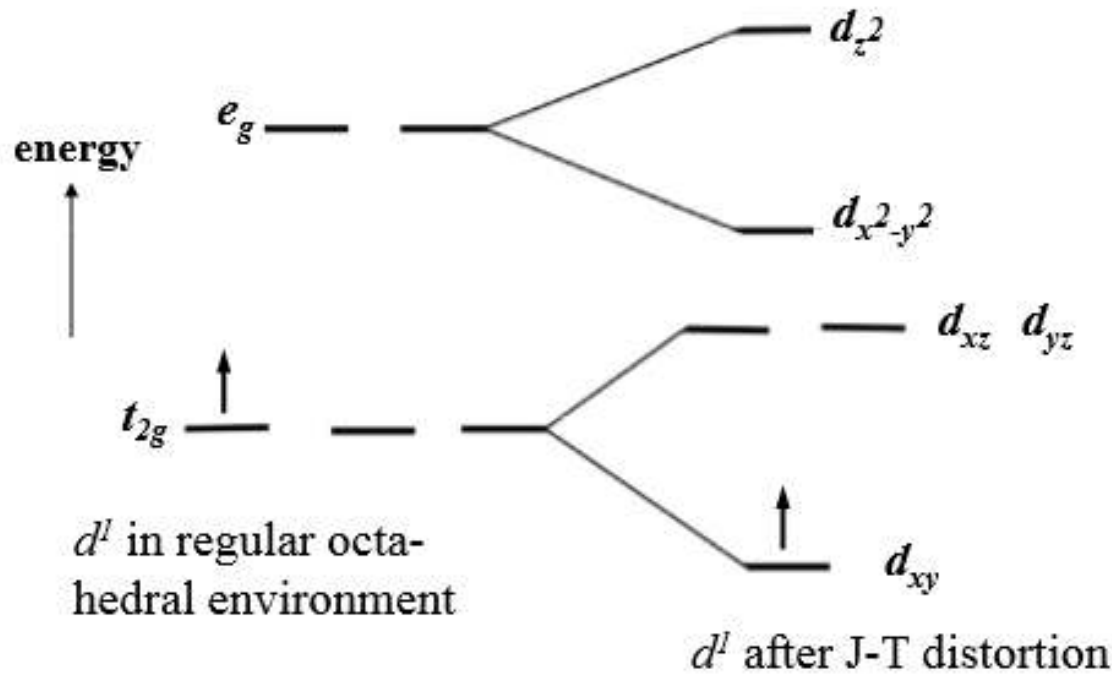
Jahn-Teller Distortion in d^9 Complexes



Elongated

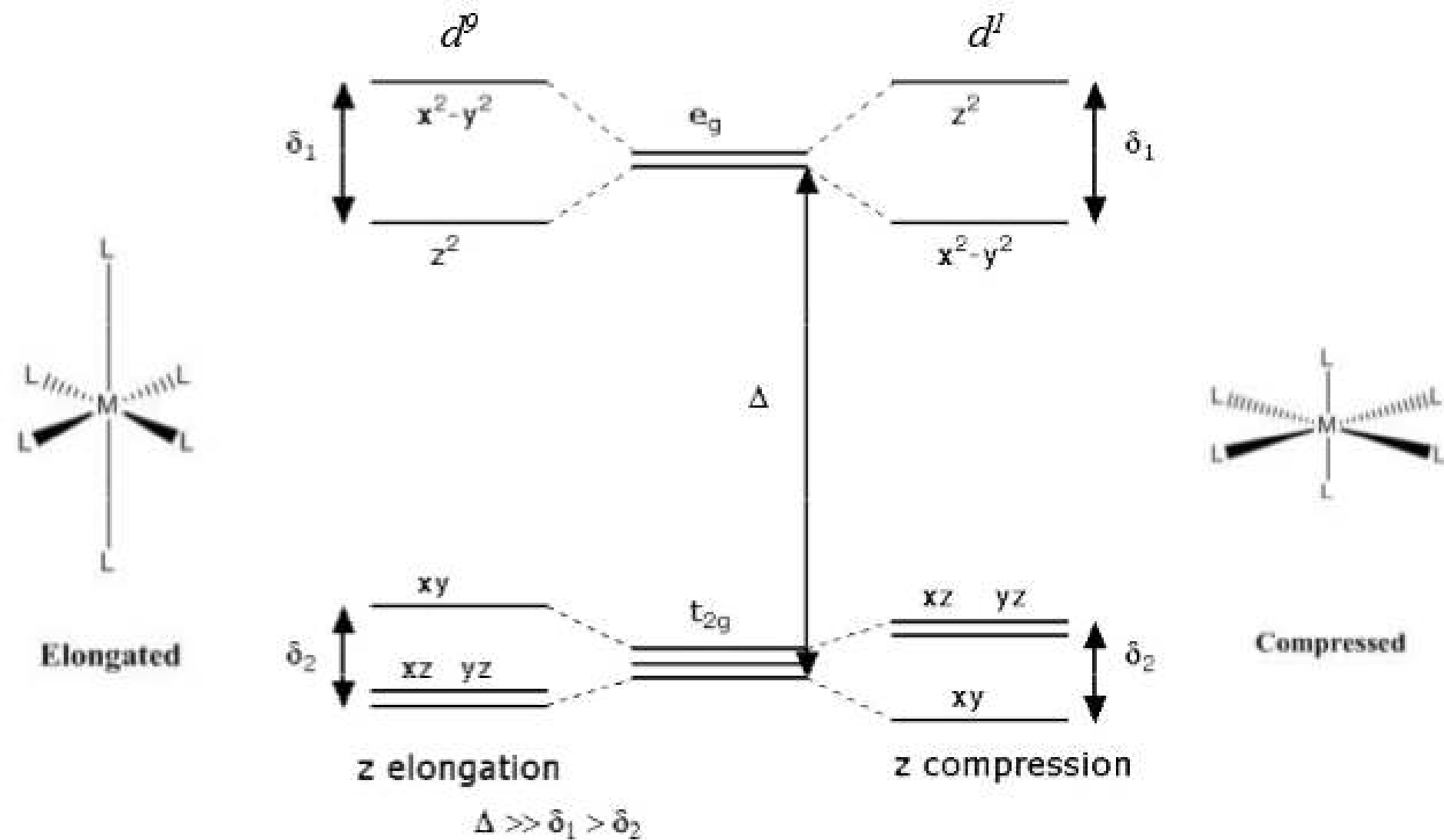
$$\Delta_0 \gg \delta_1 > \delta_2.$$

Jahn-Teller Distortion in d^1 Complexes



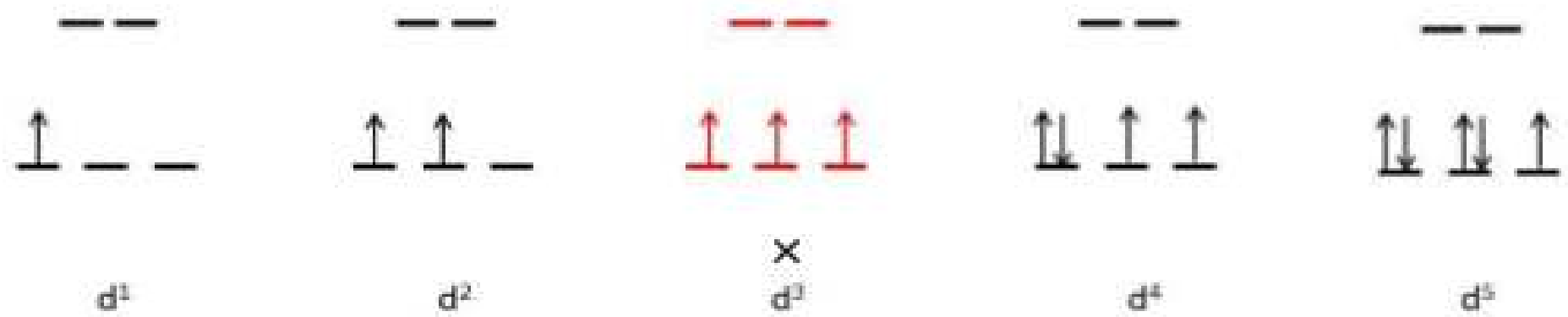
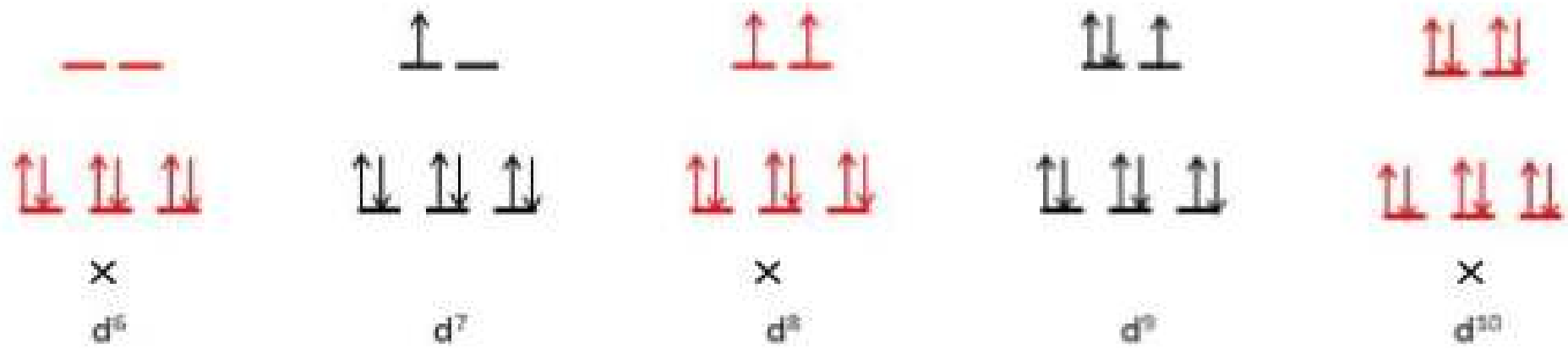
Compressed

d^1 Vs d^9

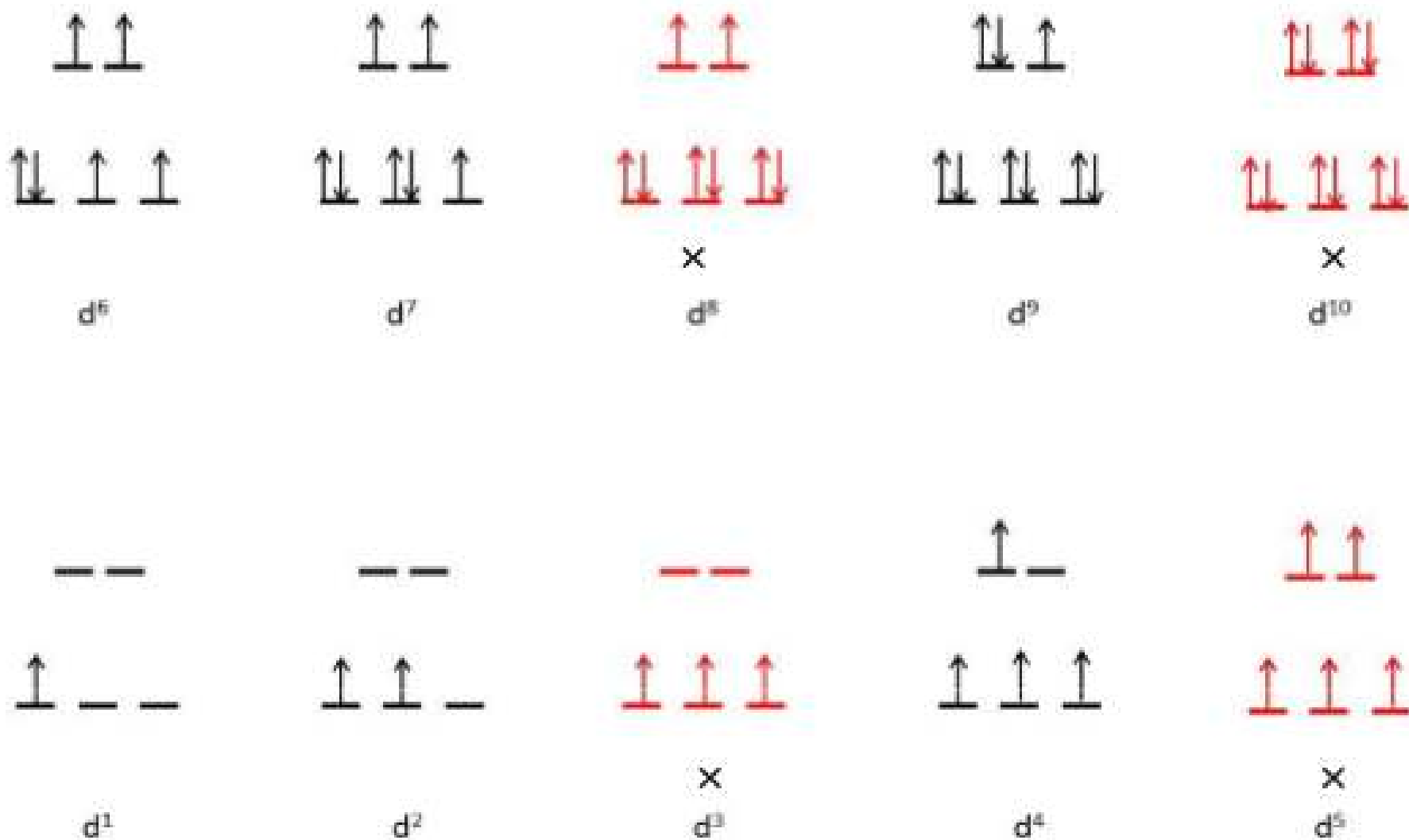


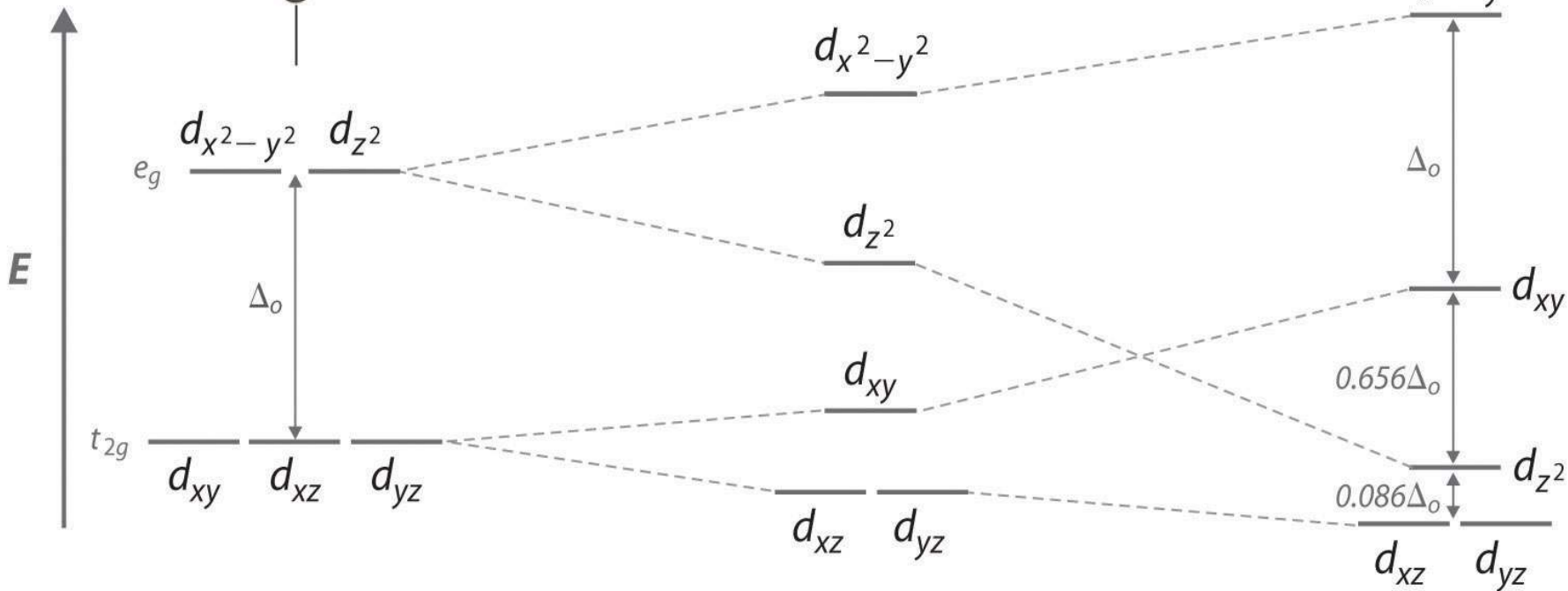
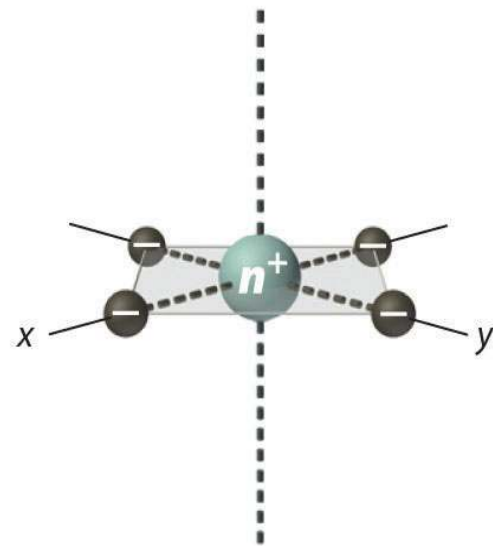
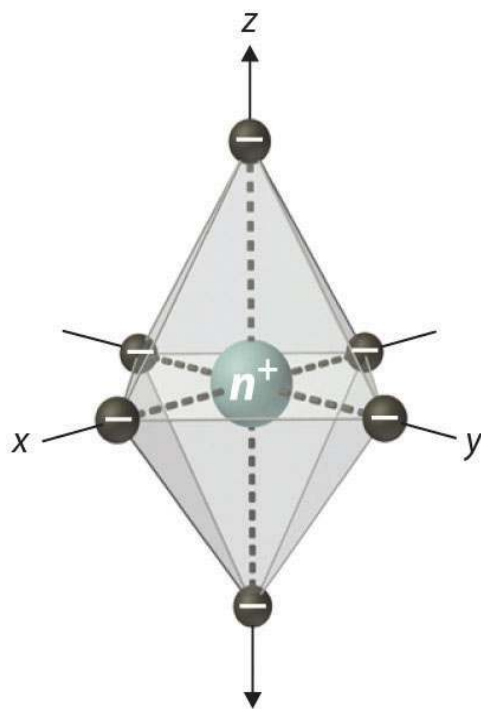
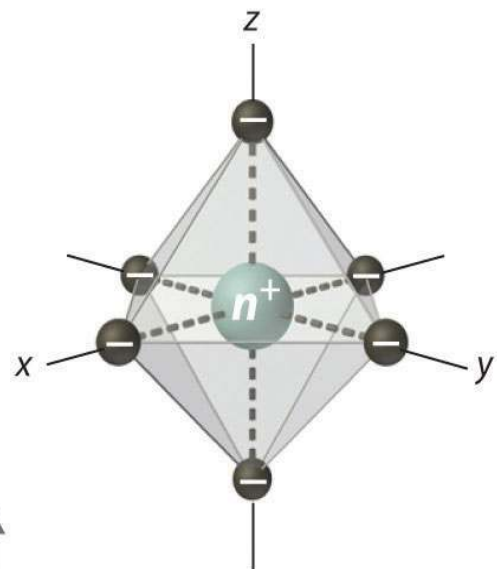
Distortions are more pronounced if the degeneracy occurs in an e_g orbital

Distortions in Low-Spin Complexes



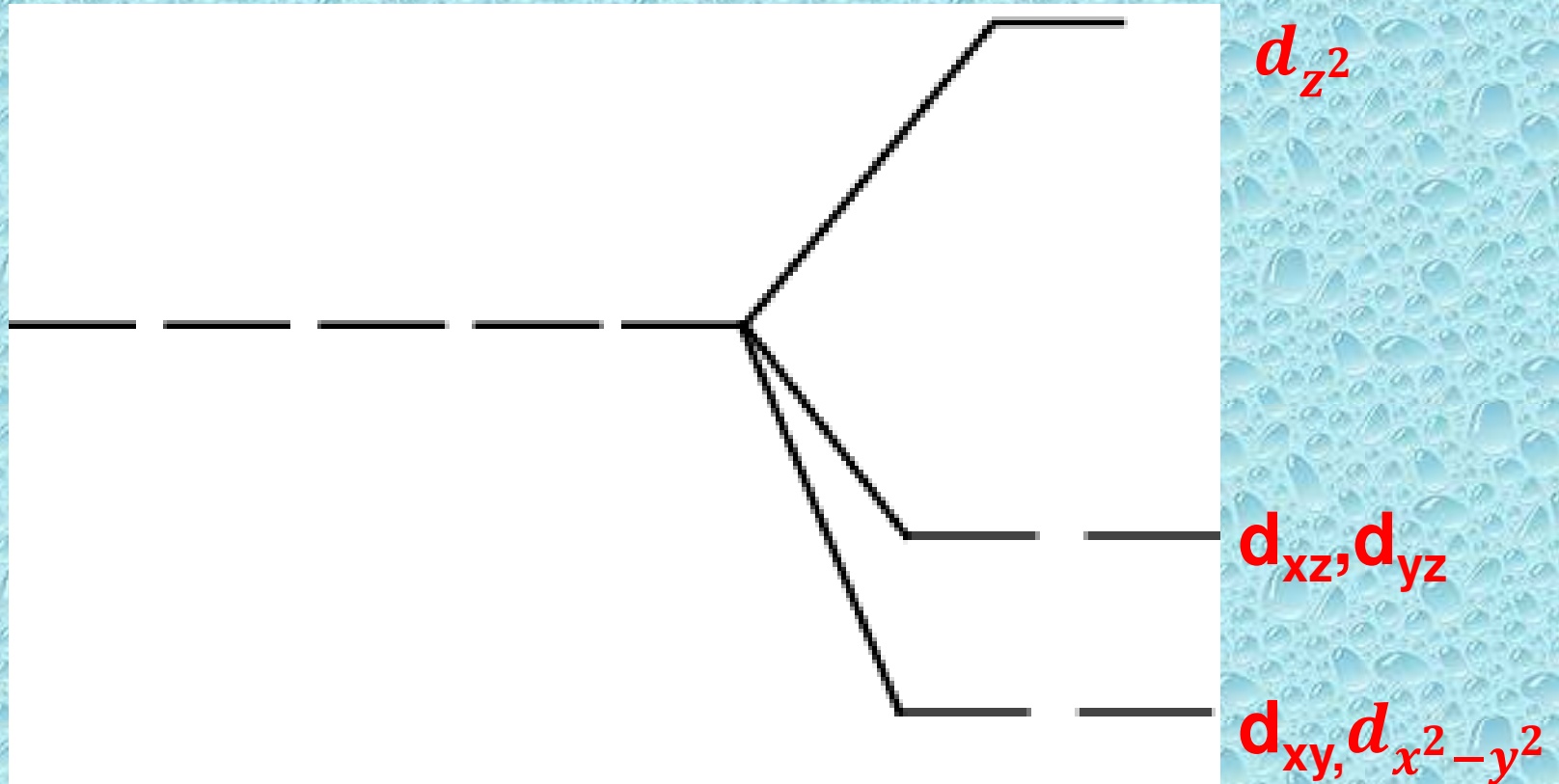
Distortions in High-Spin Complexes





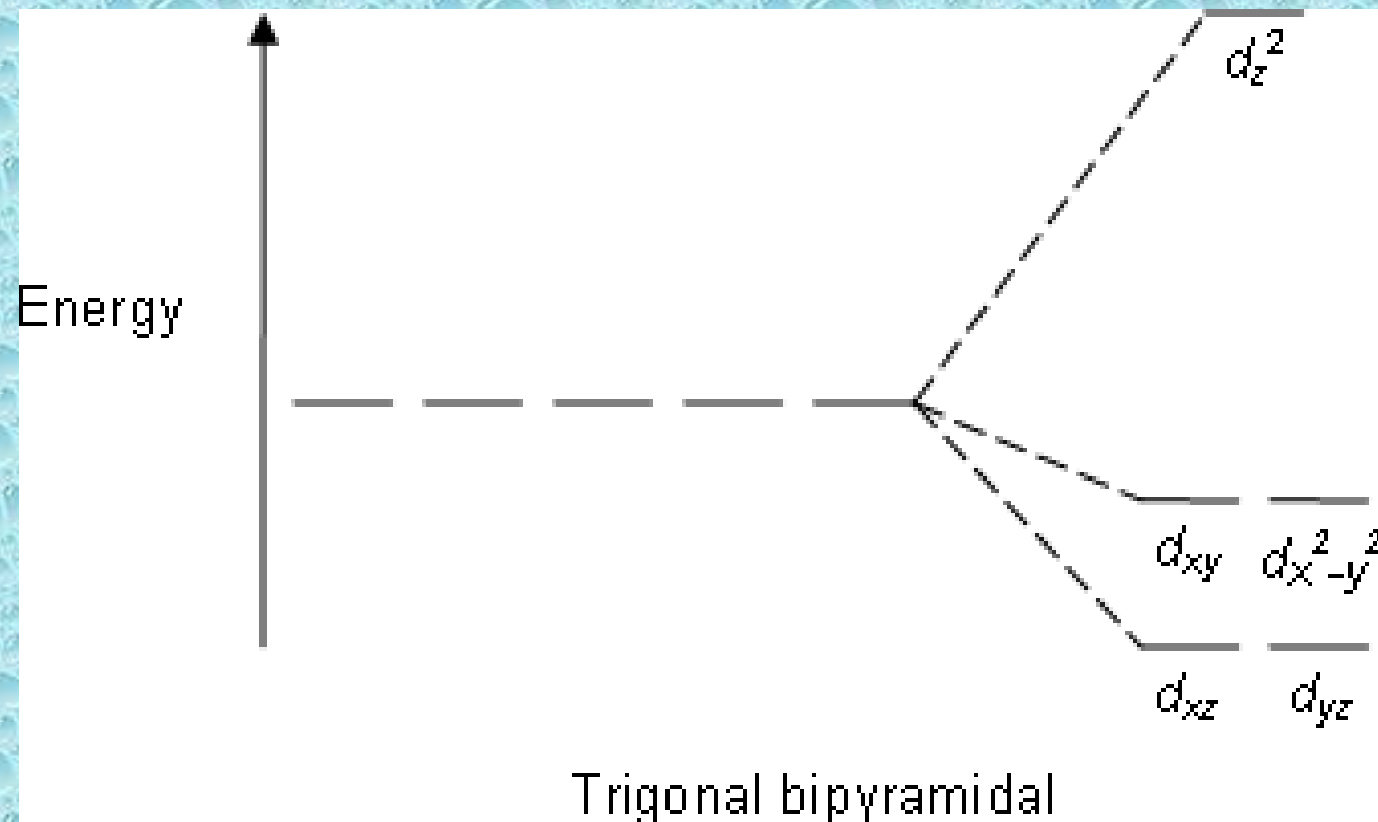
Crystal field splitting of linear complexes

- Ligands approach along the z axis
∴ Orbitals containing z component go higher in energy and others get stabilized.



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



To summarize

