5.111 Lecture #28 Wednesday, November 19, 2014

Reading For Today: 16.8-16.11 in 4th and 5th editions
Reading for Lecture #29: same as above

Topic: I. Introduction to Crystal Field Theory
II. Crystal Field Theory: Octahedral Case
III. Spectrochemical Series

I. Introduction to Crystal Field Theory

Crystal field and ligand field theories were developed to explain the special features of transition metal coordination complexes, including their beautiful colors and their magnetic properties. Coordination complexes are often used as contrast agents for magnetic resonance imaging (MRI) and other types of imaging.

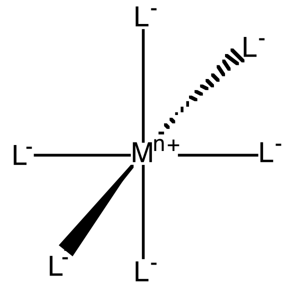
Basic idea behind theories:

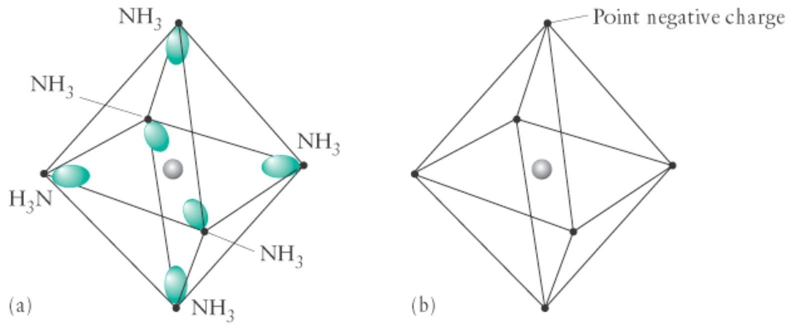
When a metal ion with a given oxidation number (M^{n+}, where M is a metal and n+ is its oxidation number) is placed at the center of a coordination sphere defined by a set of ligands, the energy levels of the d orbitals housing the metal electrons are ____________________ from those in the free metal ion.

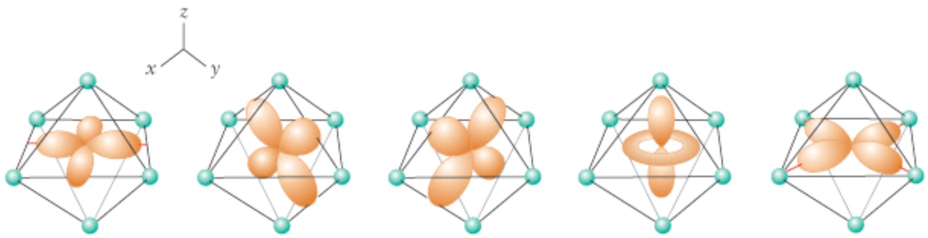
Crystal field theory is based on an **ionic** description of the metal-ligand bond.

Ligand field theory includes **covalent** and **ionic** aspects of coordination. It is a more powerful description of transition metal complexes. It is, however, beyond the scope of this course. (Take 5.03 if you are interested in this topic).

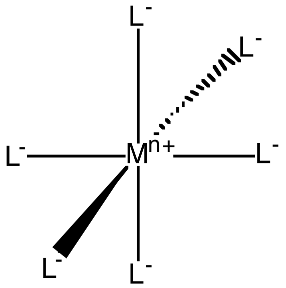
Crystal Field Theory considers ligands as ___________ point charges and considers the **repulsion** between the negative point charges and the d-orbitals, and even though this theory is simple, a number of properties of transition metals can be explained.

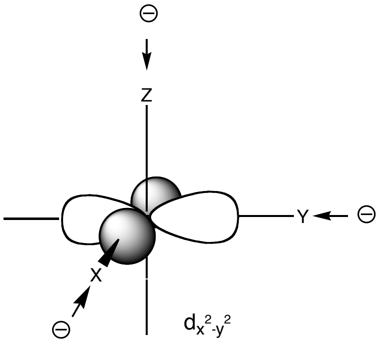


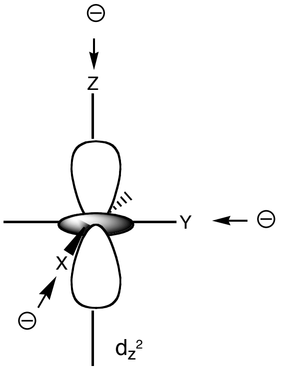




II. Crystal Field Theory: Octahedral Case



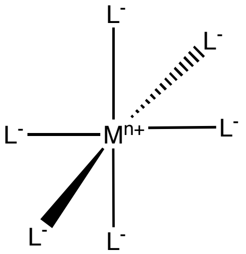


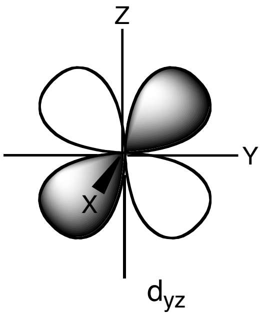


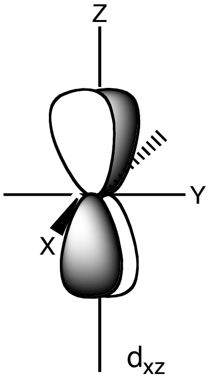
- Ligand (L) point charges are directed right toward the d_{z^2} and $d_{x^2-y^2}$ orbitals of metal (M^{n+}), resulting in a **large** repulsion.

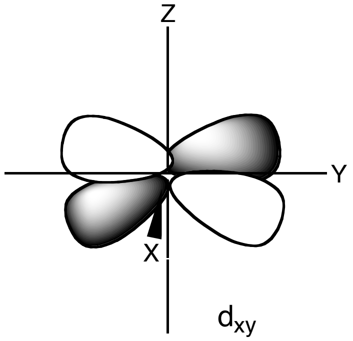
- The d_{z^2} and $d_{x^2-y^2}$ orbitals are **destabilized**, and they are destabilized by the same amount. d_{z^2} and $d_{x^2-y^2}$ are ___________.

- The d_{z^2} and $d_{x^2-y^2}$ orbitals are destabilized relative to d_{xy}, d_{yz}, and d_{xz}.







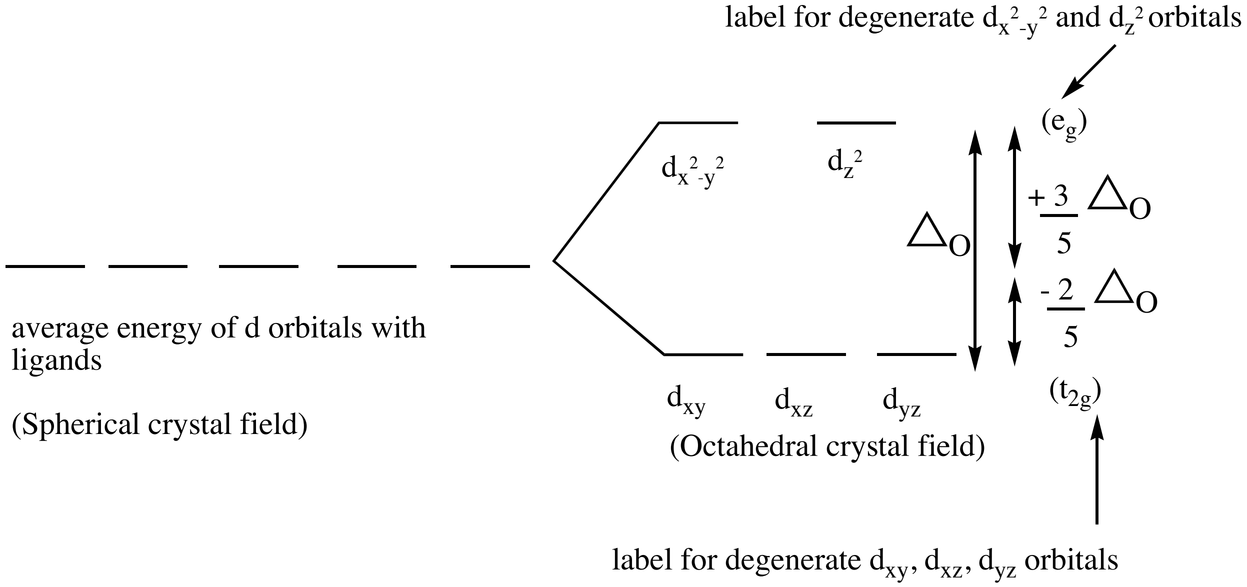


- Ligand point charges are directed in between d_{xy}, d_{xz}, and d_{yz} orbitals (not directly toward them), resulting in __________repulsion.

- The d_{xy}, d_{xz}, and d_{yz} orbitals are **stabilized** relative to d_{z^2} and $d_{x^2-y^2}$ orbitals, and they are stabilized by the same amount.

- d_{xy}, d_{xz}, and d_{yz} orbitals are degenerate with respect to each other.

Octahedral Crystal Field Splitting Diagram



Δ_o is the overall splitting between e_g and t_{2g} orbitals = octahedral field splitting energy ("o" in Δ_o is for octahedral)

Because the overall energy is maintained, the energy of the three t_{2g} orbitals are lowered by (2/5) Δ_o and the energy of the two e_g orbitals are raised by (3/5) Δ_o relative to the spherical crystal field.

What determines the magnitude of Δ_o ? Answer: the _____________of the ligand.

III. Spectrochemical Series

The relative abilities of common ligands to split the d-orbital energy levels generate what is known as the spectrochemical series.

Strong field ligands - produce __________energy separations between d-orbitals (big Δ_o)

Weak field ligands - produce **small** energy separations between d-orbitals (small Δ_o)

$I^- < Br^- < Cl^- \quad < F^- < OH^- < H_2O$	$< NH_3 < CO < CN^-$
weak field ligands	strong field ligands
Δ_o is small	Δ_o is large

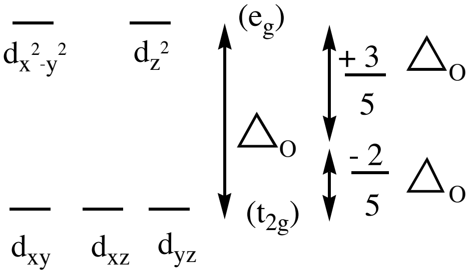
Example 1. Consider two different iron compounds: $[Fe(H_2O)_6]^{3+}$ and $[Fe(CN)_6]^{3-}$.

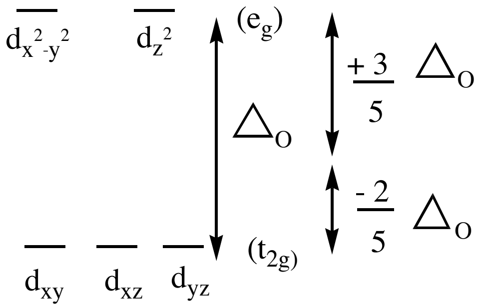
(a) Figure out the oxidation number of Fe

(b) Figure out d count

(c) Draw octahedral crystal field splitting diagrams

Small Δ_o(______________field) Large Δ_o(______________field)





Compound is _________________ **Compound is** ________________

(d) Place electrons. There are two ways to place electrons: (1) singly to the fullest extent possible before pairing (i.e. using both t_{2g} and e_g orbitals) or (2) only fill t_{2g} before pairing.

The decision is made based on whether Δ_o is greater or less than the pairing energy (PE): energy of electron-electron repulsion.

When Δ_o is small, $\Delta_o < PE$
Electrons are placed singly with parallel spins to the fullest possible extent in t_{2g} and e_g orbitals.

This arrangement of electrons gives the maximum number of unpaired electrons (**high** spin).

When Δ_o is large, $\Delta_o > PE$
Electrons are paired in lower energy t_{2g} orbitals. e_g orbitals are not both occupied until t_{2g} orbitals are filled.

This arrangement of electrons gives the minimum number of unpaired electrons (**low** spin).

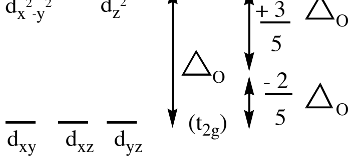
(e) Write d^n electron configuration:

(f) Predict Crystal Field Stabilization Energy (CFSE) - ______________________ relative to that of the hypothetical spherical crystal.

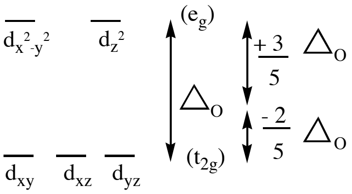
CFSE =

Practice Questions

1. Place electrons correctly for an octahedral Co^{2+} (d^7) weak field complex.



2. Predict the CFSE of a high spin octahedral Mn^{3+} (d^4) complex ________________



***Back to* $[Fe(H_2O)_6]^{3+}$ and $[Fe(CN)_6]^{3-}$**

Predict whether these compounds are paramagnetic (attracted by a magnetic field) or diamagnetic (repelled by a magnetic field).

Based on the above diagrams, they are likely to be____________________(i.e. have _____________electrons).

Predict the colors of these two iron complexes

Light Absorbed and Emitted by Octahedral Coordination Complexes
A substance absorbs photons of light if the energies of the photons ________________ the energies required to excite the electrons to higher energy levels.

$E_{light} = h\nu = \Delta_o$ E = energy of light absorbed; h = planck's constant
ν = frequency; Δ_o = octahedral crystal field splitting energy

If **low** frequency light is absorbed, the wavelength of the absorbed light is__________.
(yellow/orange/red end of spectrum)

If **high** frequency light is absorbed, the wavelength of the absorbed light is__________.
(violet/blue/green end of spectrum)

$c=\lambda\nu$ c = speed of light
λ = wavelength
ν = frequency

violet blue green yellow orange red

λ 400nm 430nm 490nm 560nm 580nm 620nm 800nm

Color of transmitted light is ________________________to the color of absorbed light.

Going back to our example: high spin $[Fe(H_2O)_6]^{3+}$ and low spin $[Fe(CN)_6]^{3-}$

High spin $[Fe(H_2O)_6]^{3+}$ **absorbs** low frequency/long wavelength light and **transmits** _________ wavelength light. It can appear pale violet to yellow brown.

Low spin $[Fe(CN)_6]^{3-}$ **absorbs** high frequency/short wavelength light and **transmits** ___________wavelength light. It is bright red-orange.

Which coordination complexes are colorless?

All d-orbitals are ___________ . __________d-d transitions in the visible range possible.

Examples:

Will Co^{3+} be colorless?

Which vitamin contains cobalt?

Cobalt Flower Demonstration
Predict the color of $[Co(H_2O)_6]^{2+}$ ($\Delta_o = 239$ kJ/mol)

(a) Calculate the wavelength of absorbed light

$$\lambda = hc/\Delta_o = \frac{(6.626 \times 10^{-34}\ \text{J s})\ (2.997 \times 10^{8}\ \text{m/s})}{(239\ \text{kJ/mol})(1000\ \text{J/kJ})(1\ \text{mol}/6.022 \times 10^{23})} =$$

$[Co(H_2O)_6]^{2+}$absorbs ______________ light.

(b) Predict the color of the transmitted light__________.

In solution, $CoCl_2 + H_2O \rightarrow [Co(H_2O)_6]^{2+}$ color =
In the solid state, $CoCl_2 + H_2O \rightarrow$ *trans*-$[CoCl_2(H_2O)_4]$ color = blue

So we can go between______and blue by adding water (hydrating) or removing water (dehydrating).

5.111 Principles of Chemical Science
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