5.111 Principles of Chemical Science
Fall 2008

5.111 Lecture Summary #30
Transition Metals
Topic: Crystal Field Theory and the Spectrochemical Series.
Chapter 16

A molecule's color can depend on oxidation state or liganded state. Example: oscillating clock. Consider the overall reaction:

$$\mathbf{IO_3^- + 2\,H_2O_2 + CH_2(CO_2H)_2 + H^+ \rightarrow ICH(CO_2H)_2 + 2\,O_2 + 3\,H_2O}$$

The overall reaction can be broken into two components (**1** and **2**), the second of which can be further divided into components (**a** and **b**):

(1) $\mathbf{IO_3^- + 2\,H_2O_2 + H^+ \rightarrow HOI + 2\,O_2 + 2\,H_2O}$ ***what is happening to "I"?***

(Note that the HOI produced in the first reaction is a reactant in the second reaction.)

(2) $\mathbf{HOI + CH_2(CO_2H)_2 \rightarrow ICH(CO_2H)_2 + H_2O}$

(a) $\mathbf{I^- + HOI + H^+ \rightarrow I_2 + H_2O}$ ***what is being oxidized and what is being reduced in this reaction?***

(*b*) $\mathbf{I_2CH_2(CO_2H)_2 \rightarrow ICH_2(CO_2H)_2 + H^+ + I^-}$

As this reaction proceeds, the color will oscillate from clear to amber to deep blue. Specifically, I^- is clear. The amber color is from I_2 formation. The deep blue color results from the I^- and I_2 binding to the starch present in the solution. Thus, the color of iodine depends on its oxidation state and its liganded state (whether or not it is bound to starch).

Transition metal coordination complexes can have beautiful colors. The color given off by a coordination complex depends on the nature of the transition metal and the nature of the ligands. Crystal field theory can be used to explain the observed colors of various coordination complexes.

Spectrochemical Series -relative abilities of common ligands to split the d-orbital energy levels.

Strong field ligands - produce large energy separations between d-orbitals

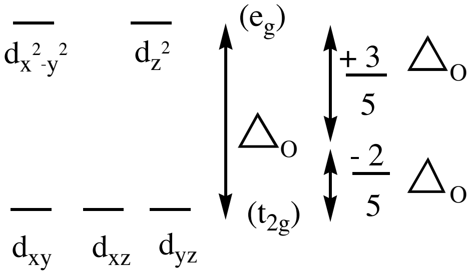
Weak field ligands - produce small energy separations between d-orbitals

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

Spectrochemical Series (Octahedral Example)

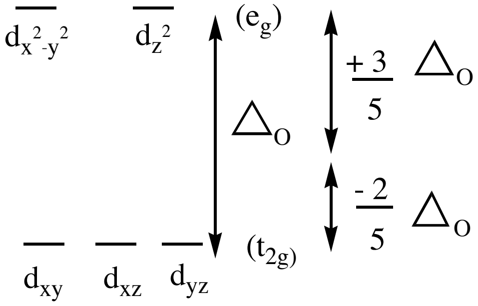
Consider Fe^{3+} in two different compounds: high spin $[Fe(H_2O)_6]^{3+}$ and low spin $[Fe(CN)_6]^{3-}$.

d count = ?



high spin

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



low spin

Fe^{3+} in $[Fe(CN)_6]^{3-}$

d^n electron configuration =	d^n electron configuration =
CFSE=	CFSE =

Light Absorbed by Octahedral Coordination Complexes

A substance absorbs photons of light if the energies of the photons match the energies required to excite the electrons to higher energy levels.

$E_{light} = hv = \Delta_o$

E = energy of light absorbed
h = planck's constant
v = frequency
Δ_o = octahedral crystal field splitting energy

If high frequency light is absorbed, the wavelength of the absorbed light is _________.

$c = \lambda v$

c = speed of light

λ = wavelength

v = frequency

<u>Going back to our example:</u> high spin $[Fe(H_2O)_6]^{3+}$ and low spin $[Fe(CN)_6]^{3-}$
High spin $[Fe(H_2O)_6]^{3+}$ has a crystal field splitting energy of 171 kJ/mol

Low spin $[Fe(CN)_6]^{3-}$ has a crystal field splitting energy of 392 kJ/mol

Calculate the wavelength of light absorbed by both complexes.

High spin $[Fe(H_2O)_6]^{3+}$

$\lambda = c/v$ and $v = \Delta_o/h$

$$\text{so } \lambda = hc/\Delta_o = \frac{(6.626 \times 10^{-34}\ \text{J s})\ (2.997 \times 10^{8}\ \text{m/s})}{(171\ \text{kJ/mol})(1000\ \text{J/kJ})(1\ \text{mol}/6.022 \times 10^{23})} = 7.00 \times 10^{-7}\ \text{m or 700. nm}$$

$[Fe(H_2O)_6]^{3+}$ absorbs red light

Low spin $[Fe(CN)_6]^{3-}$

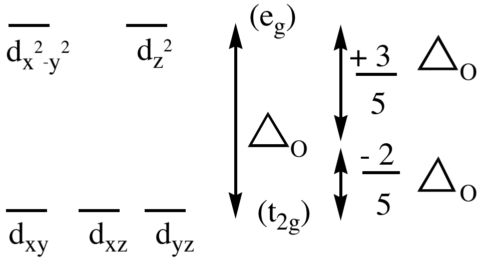
$$\lambda = hc/\Delta_o = \frac{(6.626 \times 10^{-34}\ \text{J s})\ (2.997 \times 10^{8}\ \text{m/s})}{(392\ \text{kJ/mol})(1000\ \text{J/kJ})(1\ \text{mol}/6.022 \times 10^{23})} = 3.05 \times 10^{-7}\ \text{m or 305. nm}$$

$[Fe(CN)_6]^{3-}$ absorbs violet light

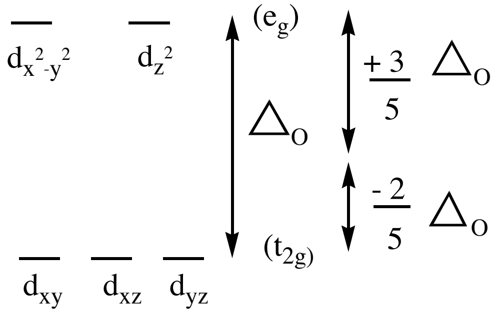
<u>Example: Explain the different colors of $[Cr(H_2O)_6]^{3+}$ and $[Cr(NH_3)_6]^{3+}$?</u>

	$[Cr(H_2O)_6]^{3+}$	$[Cr(NH_3)_6]^{3+}$
oxidation number of Cr?		
d count?		
CN?		
Type of Ligand?		

Octahedral Crystal Field Splitting Diagrams:



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



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

H_2O is a weak to intermediate field ligand (Δ_o is smaller)			NH_3 is a stronger field ligand (Δ_o is larger)		
Δ_o =	E =	hv	Δ_o =	E	= hv
smaller Δ_o	lower E	________ frequency absorbed	larger Δ_o	higher E	________ frequency absorbed
c/v =	λ		c/v =	λ	
lower frequency absorbed	________ wavelength absorbed		higher frequency absorbed	_________ wavelength absorbed	

violet blue green yellow orange red__________

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

Color of transmitted light is complementary to the color of absorbed light. Violet is complementary to yellow; blue is complementary to orange; green is complementary to red.

Transmitted light has a _______wavelength $[Cr(H_2O)_6]^{3+}$ is violet (400-430nm)	Transmitted light has a ________wavelength $[Cr(NH_3)_6]^{3+}$ is yellow (560-580nm)

Estimate crystal field splitting energy in kJ/mol

Example $[CrCl_6]^{3-}$ wavelength of most intensely absorbed light is 740 nm

predicted color:

frequency of light absorbed is $c/\lambda = (2.997 \times 10^8\ m/s)/(740 \times 10^{-9}\ m) = 4.05 \times 10^{14}\ s^{-1}$

crystal field splitting energy Δ_o is $hv = (6.626 \times 10^{-34}\ J\ s)(4.05 \times 10^{14}\ s^{-1}) = 2.68 \times 10^{-19}\ J$

$$(2.68 \times 10^{-19}\ J) \times (1\ kJ/1000\ J) \times (6.022 \times 10^{23}\ mol^{-1}) = 160\ kJ/mol$$

Which coordination complexes are colorless?

All d-orbitals are ________. No d-d transitions in the visible range possible.

Examples. Zn^{2+} and Cd^{2+}

Color in Octahedral Coordination Complexes Summary

Ligands	$I^- < Br^- < Cl^-$	$<F^- < OH^- < H_2O$	$<NH_3 < CO < CN^-$
	weak field ligands		strong field ligands
	Δ_o small		Δ_o is large
	High spin		Low spin
Complexes Absorb	low energy photons		high energy photons
	low frequency (v)		high frequency (v)
	long wavelength (λ)		short wavelength (λ)
	(yellow/orange/red end of spectra)		(violet/blue/green end of spectra)
Complexes Transmit	Complementary to absorbed		Complementary to absorbed
	(violet/blue/green end of spectra)		(yellow/orange/red end of spectra)

Violet is complementary to yellow; orange is complementary to blue; red is complementary to green.

Cobalt containing coordination complexes display a wide variety of colors
Which vitamin contains cobalt?