

Today

Ligand Field Theory Section 10.3

Section 10.1 Experimental Data Used in when
Describing Bonding in Coordination Compound

Section 10.2 Crystal Field Theory

Rework Test 3 and hand in on Wednesday, December 15

Thermodynamic Data and Formation Constants

Section 10.1.1

Are a way to measure how well ligands coordinate to our metals.

			K	Cu^{2+}	Ag^+
$[M(H_2O)_6]^{Z+}(aq) + NH_3(aq)$	\rightleftharpoons	$[M(NH_3)(H_2O)_5]^{Z+}(aq) + 1 H_2O(l)$		17,000	2,000
$[M(H_2O)_6]^{Z+}(aq) + F^-(aq)$	\rightleftharpoons	$[M(F)(H_2O)_5]^{(Z-1)}(aq) + 1 H_2O(l)$	8	0.68	
$[M(H_2O)_6]^{Z+}(aq) + Cl^-(aq)$	\rightleftharpoons	$[M(Cl)(H_2O)_5]^{(Z-1)}(aq) + 1 H_2O(l)$	1.2	1,200	
$[M(H_2O)_6]^{Z+}(aq) + Br^-(aq)$	\rightleftharpoons	$[M(Br)(H_2O)_5]^{(Z-1)}(aq) + 1 H_2O(l)$	0.9	20,000	

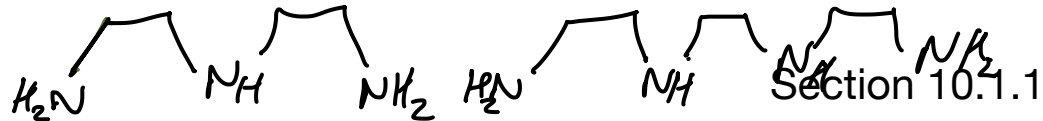
For Cu Z = 2, for Ag Z = 1

$$K = \frac{[Cu(F)(H_2O)_5]^+}{[Cu(H_2O)_6]^{2+} [F^-]}$$

what is happening here?
 Hard Cu^{2+} binds more strongly to F^- than the soft Ag^+
 Soft Ag^+ binds soft Br^- more strongly

Q is the reaction quotient that can be used to determine whether a rxn is at equilibrium by comparing it to K

Thermodynamic Data and the Chelate Effect



$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad \Delta G^\circ = -RT \ln K$$

$$\ominus \quad \ominus \quad (-\ominus)\oplus$$

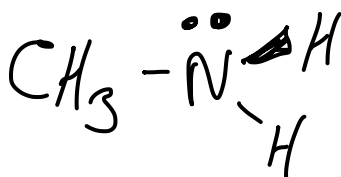
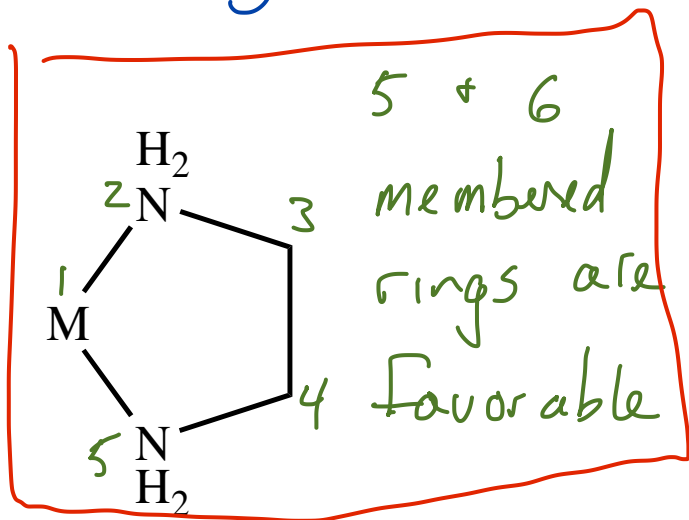


ΔH° (kJ/mol)	ΔS° (K kJ/mol)	K
-57.3	-67.3	3.3×10^6
-56.5	14.1	4.0×10^{10}

3

5

Lewis base will be



attractive to Lewis acids like Cd^{2+}

$\Delta G^\circ < 0$ are favorable

$\Delta H^\circ < 0$ are favorable

$\Delta S^\circ < 0$ is unfavorable ... it's a decrease in entropy (randomness)

Lewis base

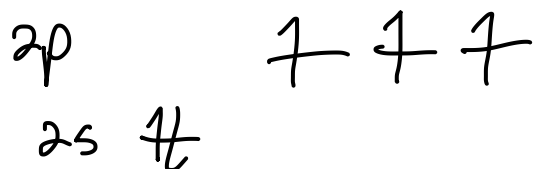


en = ethylenediamine

rxn has a favorable

ΔS due to increase in number of molecules chelate effect

Hunds rule says that e^- 's will singly occupy degenerate orbitals before pairing



Diamagnetic compounds are slightly repelled by magnetic fields

an N atom would be
paramagnetic
unpaired e^- 's

because of the
Paramagnetic compounds are
attracted to magnetic fields

all e^- 's are paired,
so they cannot
line up with the
applied magnetic
field

at least 1
 e^- is unpaired,
so the e^- can
line up with the
applied field + be
attracted to it

magnetic susceptibility constant 2.0003

Magnetic Susceptibility is related to magnetic moment

$$\mu = 2.828 (\chi T)^{1/2}$$

↑ magnetic moment

or with some approximating....

$$\mu_{S+L} = g[S(S+1) + [1/4 L(L+1)]]^{1/2}$$

$$\mu_S = (n(n+2))^{1/2} \text{ for 1st row transition metals } L \text{ is not significant}$$

and magnetic moment is related to the total spin magnetic moment (the spin quantum number S)

the sum of all the m_S 's

and the magnetic moment can tell you the # of unpaired e^- 's, n .

and the orbital angular momentum (L) is the maximum possible sum of the m_l values for an electron configuration

make $m_l + m_l + m_l$ be the largest # possible

m_l for $s = 0$ p 1, 0, -1 d 2, 1, 0, -1, -2

S and L

$$m_l \quad 1 \quad 0 \quad -1$$

$$M_S + M_S + M_S \quad \text{Section 10.1.2}$$

for N

$$2p \quad \uparrow \quad \uparrow \quad \uparrow$$

$$2s \quad \uparrow \quad m_l = 0$$

$$1s \quad \uparrow \quad m_l = 0$$

$$S = +\frac{1}{2} + \frac{1}{2} + \frac{1}{2} = \frac{3}{2}$$

$$L = 0 + 0 + 1 + 0 + -1 = 0$$

for ~~Fe~~ O

$$1 \quad 0 \quad -1$$

$$2p \quad \uparrow \quad \uparrow \quad \uparrow$$

$$2s \quad \uparrow$$

not

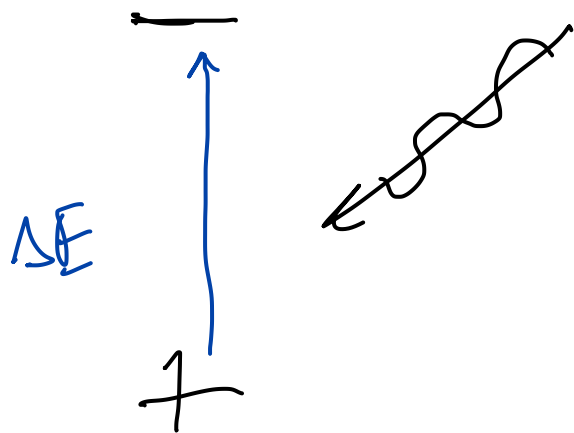
$$\uparrow \quad \uparrow \quad \uparrow$$

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

$$L = 1 + 1 + 0 \quad -1$$

$$= \underline{\underline{1}}$$

$$L \neq 1 + 0 - 1 - 1$$

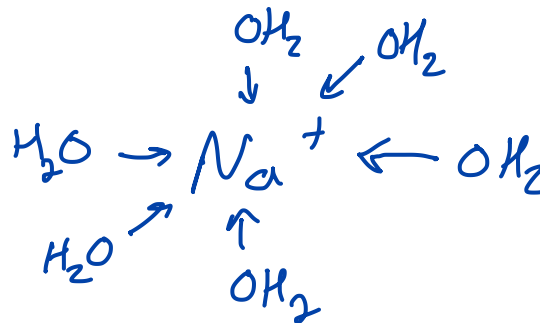


can tell us
about the
banding between
ligand + metal

photons with specific
frequencies can excite
 e^- from lower E
orbitals to higher energy
orbitals. Measuring the
frequency of those photons
tells us the energy gap
between the orbitals

Bonding Models

Section 10.1.4



Crystal Field Theory

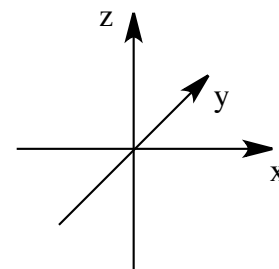
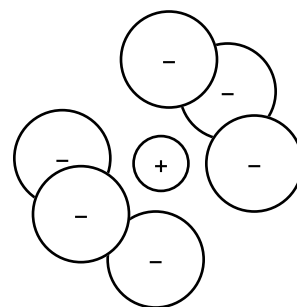
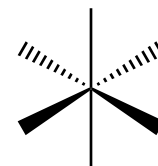
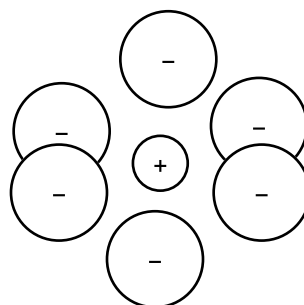
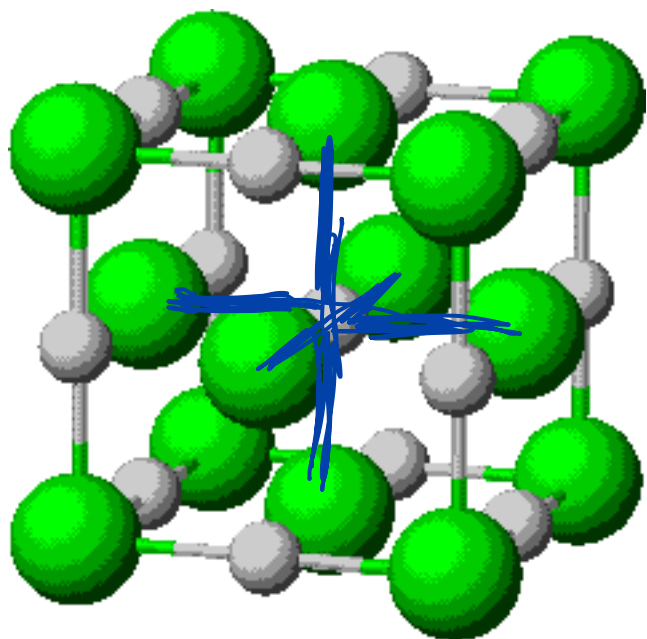
Electrostatic approach where d orbital splitting is explained using an ionic model

Ligand Field Theory

MO approach that describes bonding in terms of ligand HOMO/LUMO interactions with metal orbitals

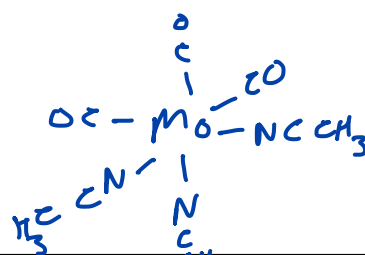
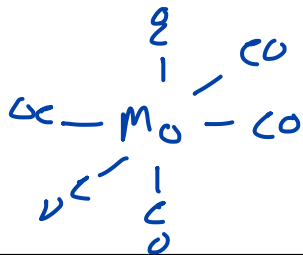
Angular Overlap Method

A method for estimating the energies of the the orbitals



the metal is in the middle of an octahedral field of e^- density supplied by the Cl^- ions. How does this O_h field effect the d orbitals of the metal

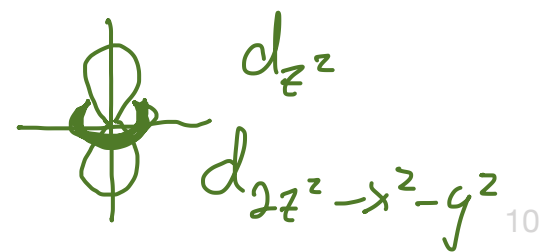
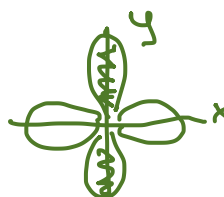
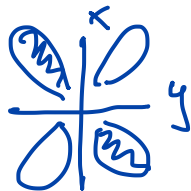
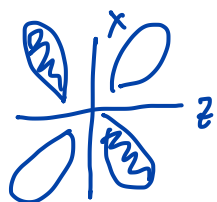
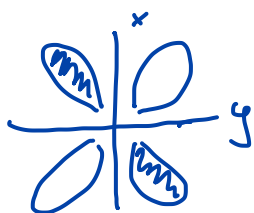
O_h Point Group



pseudo O_h

Review

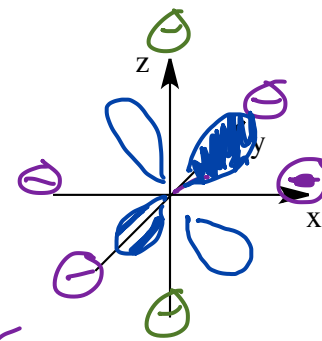
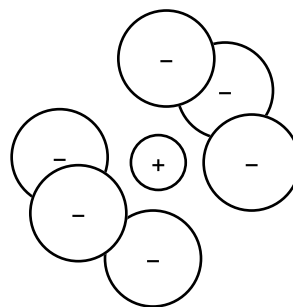
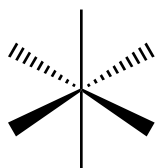
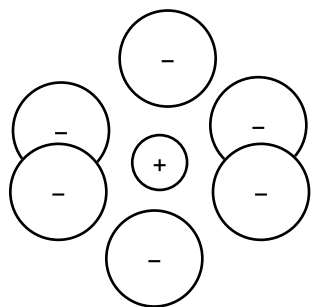
O _h	E	8 C ₃	6 C ₂	6 C ₄	3 C ₂ (C ₄ ²)	i	6 S ₄	8 S ₆	3 σ _h	6 σ _d		
A _{1g}	1	1	1	1	1	1	1	1	1	1		x ² + y ² + z ²
A _{2g}	1	1	-1	-1	1	1	-1	1	1	-1		
E _g	2	-1	0	0	2	2	0	-1	2	0		(2z ² - x ² - y ² , x ² - y ²)
T _{1g}	3	0	-1	1	-1	3	1	0	-1	-1	(R _x , R _y , R _z)	
T _{2g}	3	0	1	-1	-1	3	-1	0	-1	1		(xy, yz, xz)
A _{1u}	1	1	1	1	1	-1	-1	-1	-1	-1		
A _{2u}	1	1	-1	-1	1	-1	1	-1	-1	1		
E _u	2	-1	0	0	2	-2	0	1	-2	0		
T _{1u}	3	0	-1	1	-1	-3	-1	0	1	1	(x, y, z)	
T _{2u}	3	0	1	-1	-1	-3	1	0	1	-1		



Crystal Field Theory

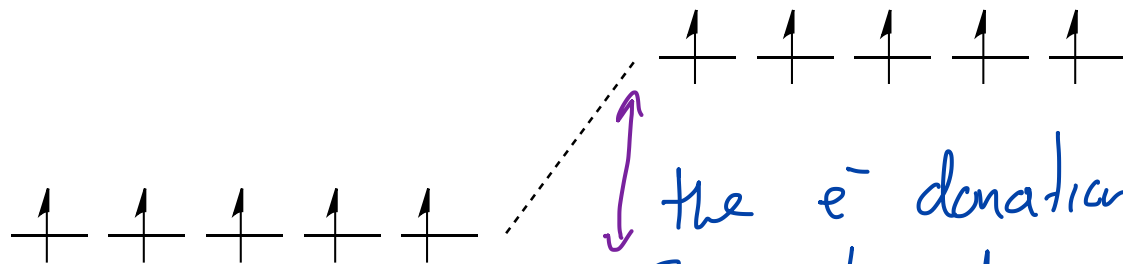
E_g set of d orbitals lie on the x, y, + z axes interacts w/ d_{z^2}

Section 10.2.1



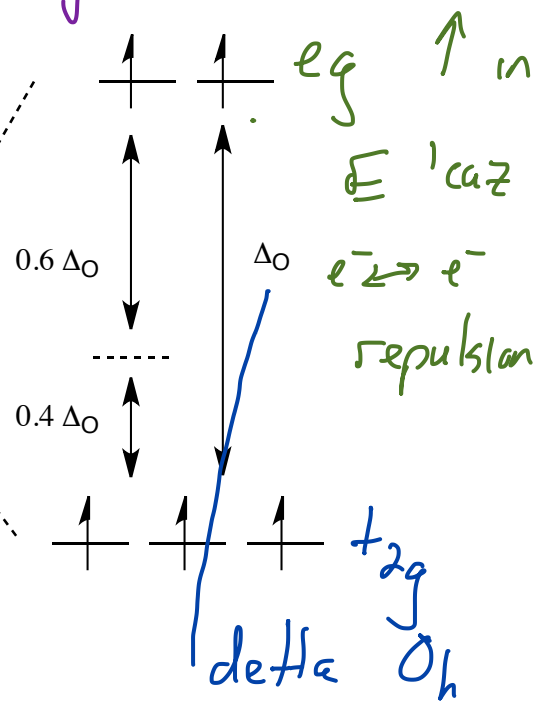
T_{2g} set of d orbitals lie in between the x, y, + z axes and since they do not point at the ligands they are not effected by the ligands

these interact with $d_{x^2-y^2}$

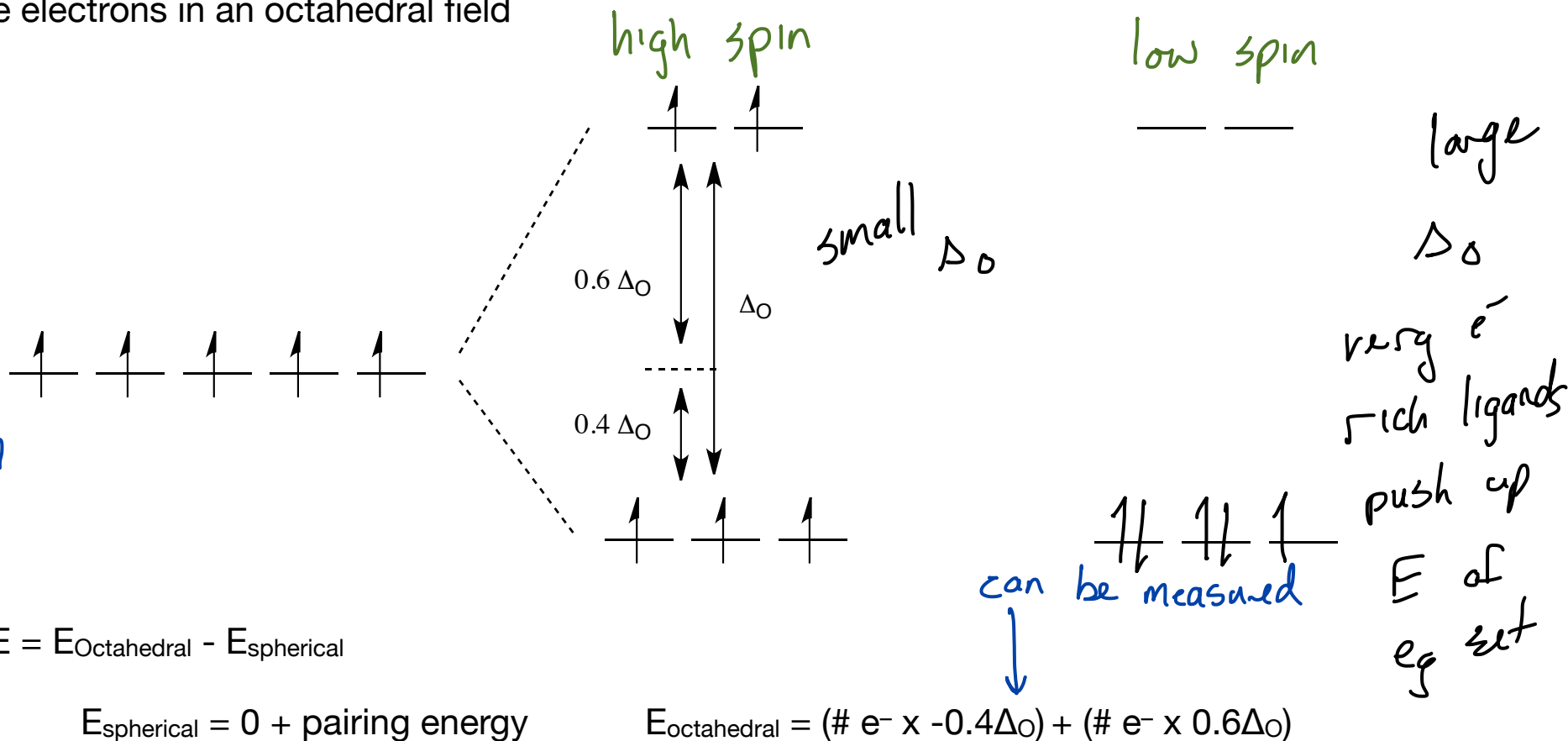


Free metal ion

the e^- donation from ligands repels metal e^- and raises energy



Crystal Field Stabilization Energy compares the energy of the electrons in a spherical field to the energy of the electrons in an octahedral field



In this example there is no pairing energy and pairing energy is determined by the identity of the metal

CFSE tells us about the e^- donation from the ligands and we can compare

Compares the energy of the metal ion in a spherical field of electron density to the energy of the metal ion in an octahedral field (or the appropriate field for the geometry of the complex)

Δ_o can be determined using spectroscopic techniques

Number of unpaired spins can be determined by using magnetic spectrometry

Finding the Δ_o and electronic structure of the metal allows us to compare the relative effect that ligands have on a metal

Does not account for stabilization due to bonding