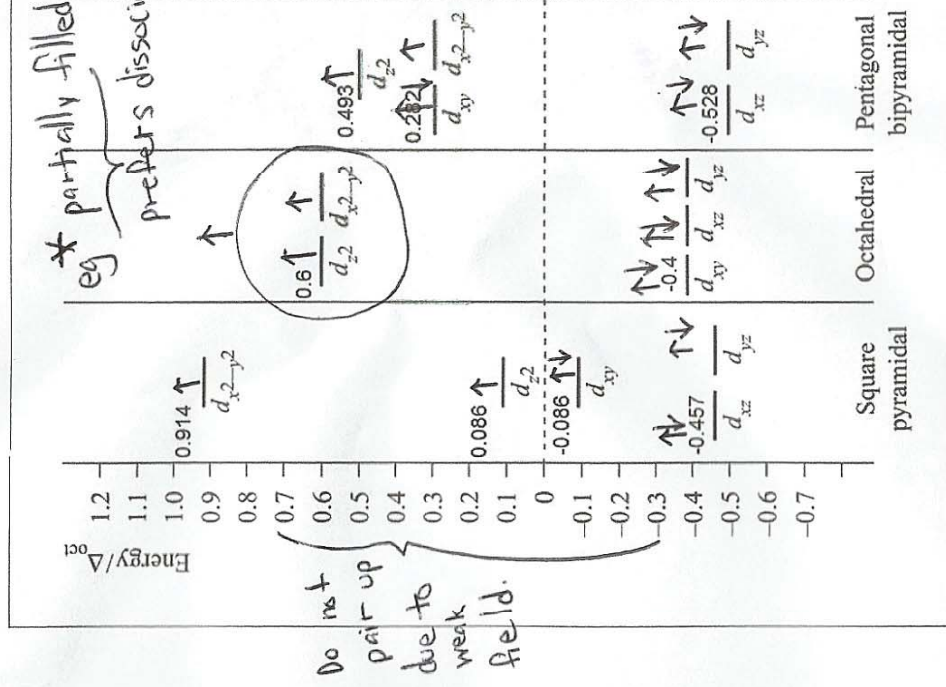


Show your work for maximum credit.

1. Will the following reaction go through an association or dissociation mechanism? Explain using the crystal field splitting diagrams below. (40 points)

High Spin



Octahedral field:

$$\text{CFSE} = [6 \times (-0.4) + 2(0.6)] \Delta_0 = [-2.4 + 1.2] \Delta_0 = -1.2 \Delta_0$$

If dissociation:



Square pyramidal intermediate

Square pyramidal field:

$$\text{CFSE} = [4 \times (-0.45)] + (2 \times 0.086) + (1 \times 0.086) + (1 \times 0.086) = -1.814 \Delta_0$$

$$= -1 \Delta_0$$

Octahedral	→	Square pyramidal
-1.2 Δ ₀		-1.0 Δ ₀
Loss of octahedral		0.2 Δ ₀ CFSE
-1.2 Δ ₀	→	Pentagonal bipyramidal
Loss of intermediate		0.773 Δ ₀
		0.43 Δ ₀ CFSE

If Association:
 $[\text{NiCl}_6]^{4-} + \text{F}^- \rightarrow [\text{NiCl}_6\text{F}]^{5-}$



Pentagonal bipyramidal

$$\text{CFSE} = [4 \times (-0.528) + (3 \times 0.388) + (1 \times 0.388)] = -0.773 \Delta_0$$

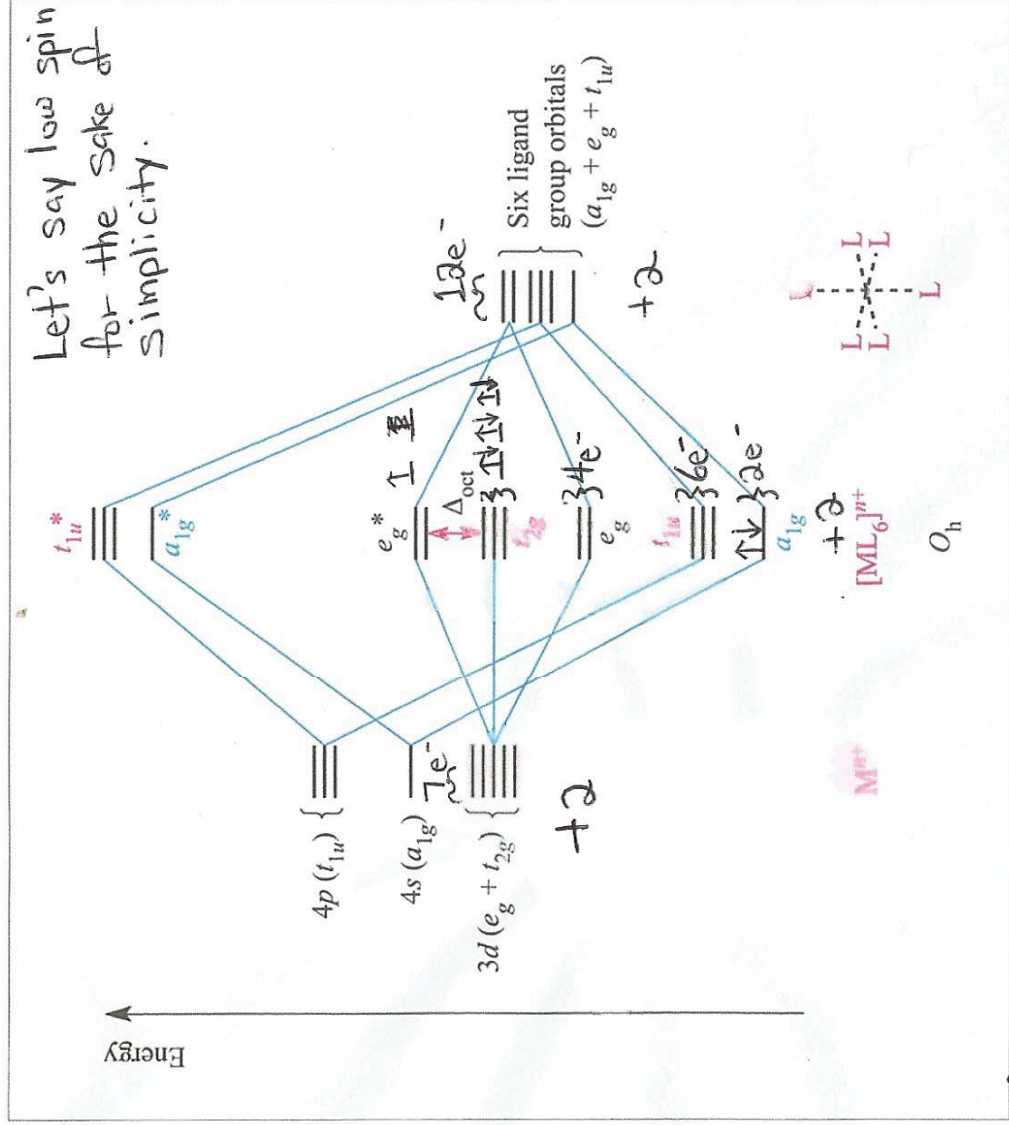
Both mechanisms lead to an intermediate with loss of CFSE but dissociation leads to less of a loss.

Intermediate

Loss of intermediate

Loss of intermediate

2a. The following molecular orbital diagram represents the ligand metal bonding interactions in the complex $[\text{Co}(\text{NH}_3)_6]^{2+}$. Paying attention to the oxidation state of the metal and using the diagram below calculate the bond order of this complex and explain what this bond order means. (10 points) $\text{Co}^{2+}: d^7$ NH_3 is a σ donor



If low spin Bond Order = $\frac{12 \text{ bonding } e^- - 1 \text{ antibonding } e^-}{2}$

$$= \frac{11}{2} = 5.5$$

If high spin

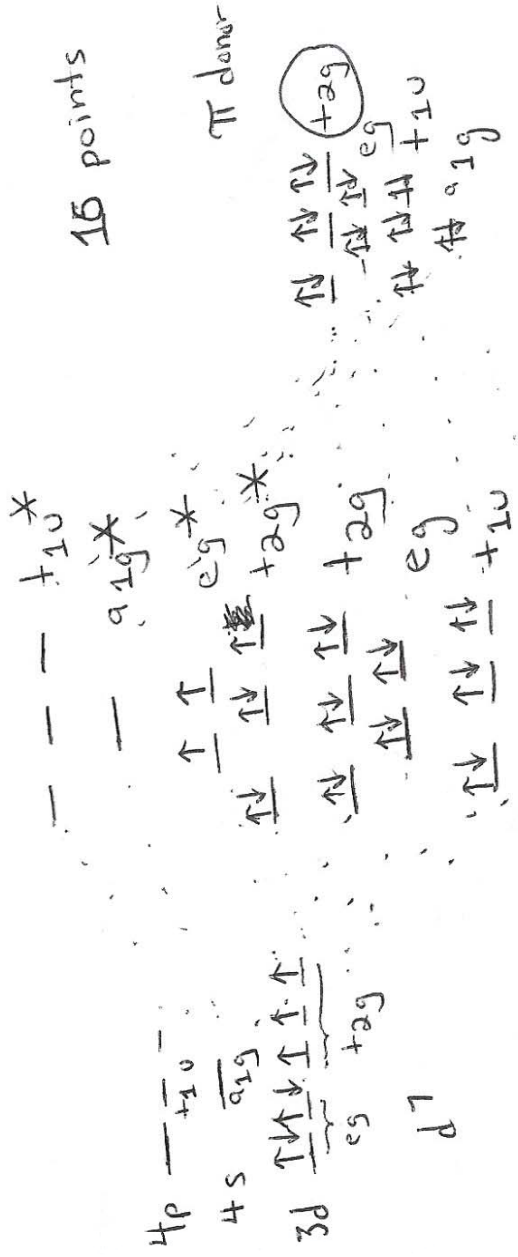
$$\text{Bond Order} = \frac{12 \text{ } be^- - 2 \text{ } ab \text{ } e^-}{2} = 5$$

Should be 6 Co-N bond but less than one bond order between each Co-N bond.

+2

b. How would the molecular orbital diagram in part 2a change if the complex were $[\text{CoF}_6]^{4-}$? Note that the metal's oxidation state has not changed. What would be the bond order of this complex and what does it mean? (20 points)

High spin d^7



Bond order = $\frac{18 \text{ bonding } e^- - 7 \text{ antibonding } e^-}{2} = \frac{11}{2} = 5.5$ + 2

L.G.O

Means the same as +2 in part a

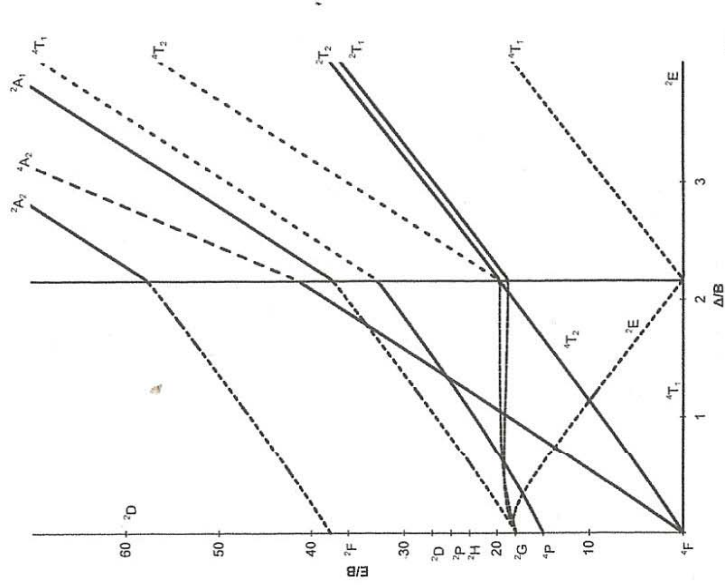
c. Do you predict a higher stability constant for $[\text{Co}(\text{NH}_3)_6]^{2+}$ or $[\text{CoF}_6]^{4-}$? Why? (3 points)

Intermediate acid \rightarrow Intermediate \rightarrow Hard base

$[\text{Co}(\text{NH}_3)_6]^{2+}$ should have a ^{base} higher affinity constant.

50

3. (45 points) Use the Tanabe-Sugano diagram shown below for a d^7 metal ion in an octahedral field, to answer the following set of questions.



a. What is the ground state Term Symbol for the metal ion center in the absence of the octahedral arrangement of ligands? $4F$

b. What is the number of microstates possible in the absence of an octahedral arrangement of ligands?

$\uparrow \uparrow \uparrow \uparrow \uparrow$
 $\underbrace{\hspace{1.5cm}}_{5 \text{ d orbitals (degenerate)}}$
 Max. occupancy is $10 e^-$

$$\# \text{ of microstates} = \frac{10!}{7! 3!} = \frac{10 \cdot 9 \cdot 8 \cdot 7 \cdot 6 \cdot 5 \cdot 4 \cdot 3 \cdot 2 \cdot 1}{7 \cdot 6 \cdot 5 \cdot 4 \cdot 3 \cdot 2 \cdot 1 \cdot 3 \cdot 2 \cdot 1} = 120 \text{ microstates}$$

c. Explain the ground state multiplicity of the free metal ion, the metal ion in the weak field, and in the strong field.

Free metal ion. $S = \frac{1}{2}$ Multiplicity = $2S + 1 = 2(\frac{1}{2}) + 1 = 4$
 $4F$

Weak field. $\uparrow \uparrow \uparrow \uparrow \uparrow$ $S = \frac{3}{2}$ Multiplicity = 4
 $\uparrow \uparrow \uparrow \uparrow \uparrow$ t_{2g}

$4T_1$

Strong field. $\uparrow - \uparrow \uparrow$ $S = \frac{1}{2}$ Multiplicity = 2
 $\uparrow \uparrow \uparrow \uparrow \uparrow$ e_g

$\uparrow \uparrow \uparrow \uparrow \uparrow$ t_{2g}

d. What are the spin-allowed transitions in the weak field section of the diagram?



e. What are the spin-allowed transitions in the strong field section of the diagram?



f. Estimate the molar absorptivity for the electronic transitions described in parts 3d and 3e? Laporte forbidden, spin-allowed d-d e⁻ transitions in octahedral field. $\epsilon \approx 1 - 100 \text{ M}^{-1} \text{ cm}^{-1}$

g. How concentrated should your solution be to observe the electronic transitions in parts 3d and 3e?

m M

h. What is the magnetic moment and molar magnetic susceptibility (298 K) for a d⁷ metal ion coordinated in a weak octahedral field?

$$n = 3$$

$$\mu_0 = \sqrt{n(n+2)}$$

$$= \sqrt{3(3+2)}$$

$$= \sqrt{15} \mu_B$$

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

$$\mu^2 = 7.998 \chi_m T$$

$$\frac{\mu^2}{7.998 T} = \chi_m = \frac{(\sqrt{15} \mu_B)^2}{7.998 (298K)} = \frac{0.00629}{K}$$

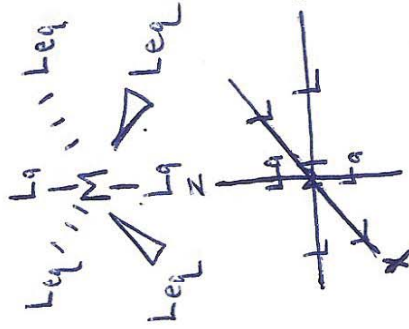
Fig. Simplicity

i. How would the magnetic susceptibility of the complexes described in part 3h depend on temperature?

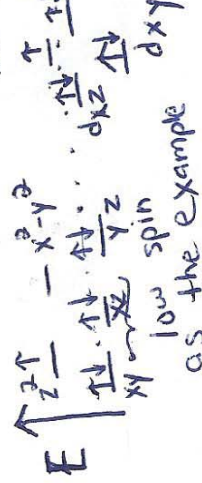


j. If you obtain the x-ray structure for an octahedral complex of a d⁷ metal ion and it shows that the bond lengths of the M-L bonds in the axial positions are shorter than the M-L bonds in the equatorial positions, would this represent a Z-out or Z-in Jahn Teller distortion? Explain.

For the axial ligands to be shorter than the equatorial ligands implies that a Z-in Jahn Teller distortion occurred. The Z-in distortion means that the ligands along the Z-axis are closer in to the metal.



Helps to remove unequal distribution of e⁻ in degenerate orbitals.



Extra Credit (11 points)-

Match the leader in Inorganic Chemistry with the description.

Jacqueline K. Barton	Richard Schrock	Vincent Pecoraro	Gary Brudvig
Daniel Nocera	Katherine Franz	Stephen Lippard	Kenneth D. Karlin
Robert Crabtree	Alison Butler	Kenneth Raymond	

1. This professor has worked in the development of Cp*Ir metal-oxo complexes, which have an immense variety of uses including hydrogenation, water oxidation catalysis, C-H oxidation, and anchoring in DSSC. **Robert Crabtree**
2. This professor works in the search for energy alternatives through water oxidation by an artificial photosynthetic system. **Gary Brudvig**
3. In order to effectively inhibit the formation of cell damaging free radicals, this professor focuses on the synthesis of pro-chelators that would selectively unmask in areas of high oxidative stress, thus releasing chelators that would bind with excess of iron ions without affecting the body's metal homeostasis. **Katherine Franz**
4. This professor works with solar to energy conversion and is the founder of Sun Catalyx and the artificial leaf. ~~Robert Crabtree~~ **Daniel Nocera**
5. This professor focuses on studying platinum complexes as potential anti-cancer drugs as well as other metal complexes that could promote apoptosis in cancer cells. **Stephen Lippard**
6. This professor studies the synthesis via ROMP and characterization of many polymers using organometallic catalysts. **Richard Schrock**
7. This professor focuses on the bioinorganic chemistry of copper-iron complexes involved in O₂ transportation and nitrogen oxide redox chemistry. **Kenneth D. Karlin**
8. This professor focuses on the chemical and physical properties of DNA and the biological impact of these properties to develop a new approach to novel chemotherapeutic design. **Jacqueline K. Barton**
9. This professor's research interests in bioinorganic chemistry focus on the characterization of amphiphilic siderophores and the elucidation of their biosynthetic pathways. **Alison Butler**
~~This professor~~
10. ~~Robert Crabtree~~ focuses on de novo protein design, a computational method where based on a primary amino acid sequence we can determine its tertiary structure. **Vincent Pecoraro**
11. This professor's research focuses on the various applications of HOPO ligands which include actinide and lanthanide chemistry, iron transport, and MRI contrasting agents. **Kenneth Raymond**