Chemistry 6011
Advanced Inorganic Chemistry I: From Atoms to Coordination Compounds
Exam 4
Name:

Show your work for maximum credit.

1. (26 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.
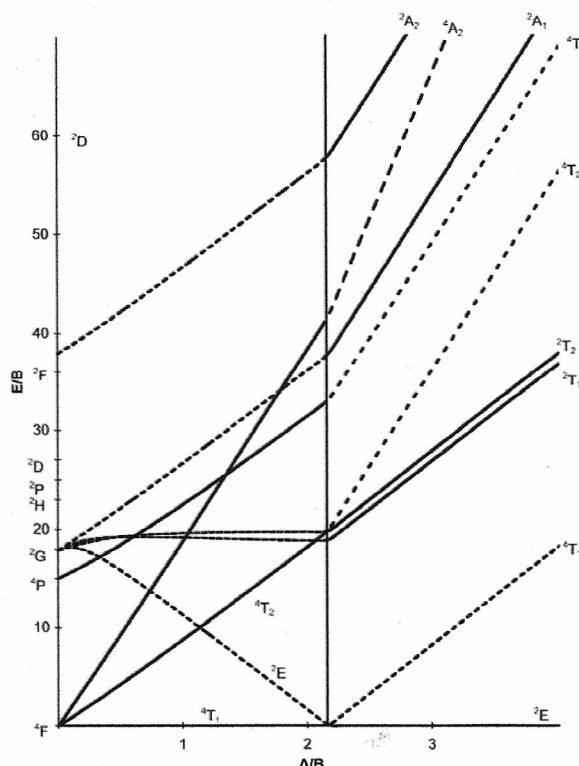
a. What is the ground state Term Symbol for the metal ion center in the absence of the octahedral arrangement of ligands? ^4F

b. What is the number of microstates possible in the absence of an octahedral arrangement of ligands? d^7

$$\# \text{ of microstates} = \frac{10!}{7!\,(10-7)!} = \frac{10\cdot9\cdot8\cdot7!}{7!\;3\cdot2\cdot1} = 120$$

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

weak Field   Strong Field
↑ ↑   ↑ —

Free metal ion

E

↑↓ ↑↓ ↑ — ↑ — ↑ ....   ↑ ↑
$S = \frac{3}{2}$ ↑↓ ↑↓ ↑

Mult. $= 2S+1 = 2(\frac{3}{2})+1 = \boxed{4}$ Mult. $= 4$

↑↓ ↑↓ ↑↓
Mult. $= 2$
$S = \frac{1}{2}$
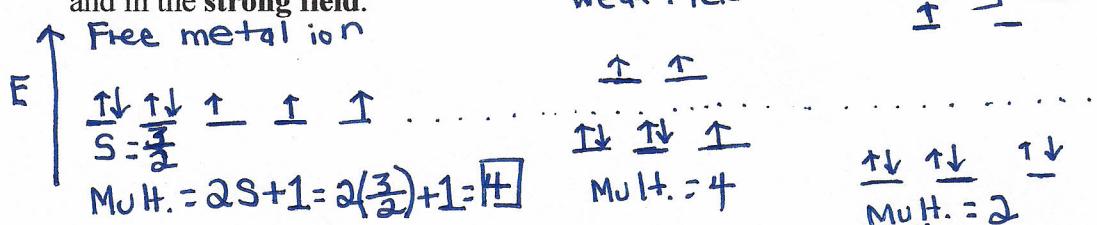
d. **Explain** the Term Symbol degeneracy of the metal ion in the **weak** and **strong field**. (Ground state

$4T_1$ Triple degeneracy $2E$ Double degeneracy
                                        ↑
                                  d_{z^2} $d_{x^2-y^2}$ ↑
                                                           d_{z^2} $d_{x^2-y^2}$

↑ ↑   ↑ ↑   ↑ ↑
    or   or
↑↓ ↑↓ ↑   ↑↓ ↑ ↑↓   ↑↓ ↑↓ ↑↓   ↑↓ ↑↓ ↑↓   ↑↓ ↑↓ ↑↓
xy xz yz   xy xz yz xy xz yz
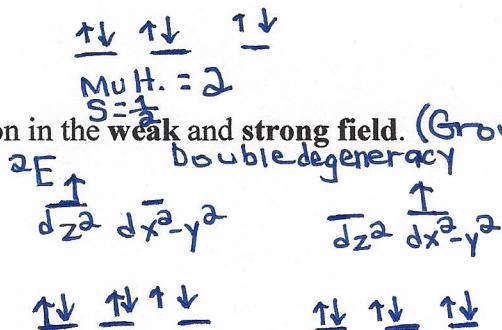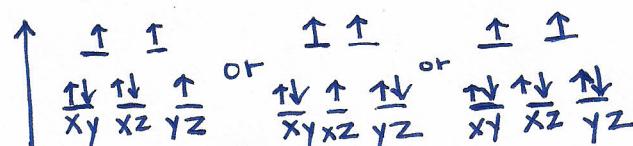
e. What are the **spin-allowed transitions** in the **weak and strong field** sections of the diagram? Why are these **Laporte forbidden**?

weak field
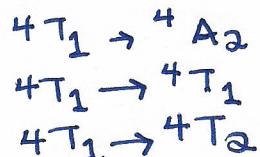
$4T_1 \rightarrow {}^4A_2$

$4T_1 \rightarrow {}^4T_1$

$4T_1 \rightarrow {}^4T_2$

Strong field   Laporte forbidden
$2E \rightarrow {}^2A_2$ because we have
$2E \rightarrow {}^2A_1$ a gerade to gerade
$2E \rightarrow {}^2T_2$ transition.
$2E \rightarrow {}^2T_1$

f. What would be the theoretical UV-Vis spectra for the transitions in the **weak and strong field**? How would these spectra more realistically look like?

Reality

weak Field
Theory
$4T_1 \rightarrow {}^4A_2$ $4T_1 \rightarrow {}^4T_1$ $4T_1 \rightarrow {}^4T_2$

Abs.

λ (nm)

Reality

Strong Field $2E \rightarrow {}^2T_2$ $2E \rightarrow {}^2T_1$
              $2E \rightarrow {}^2A_2$ $2E \rightarrow {}^2A_1$
Abs.

λ (nm)

Reality

λ(nm)
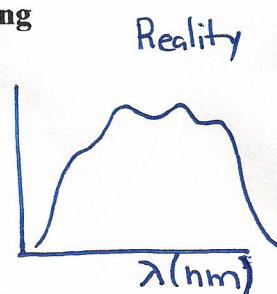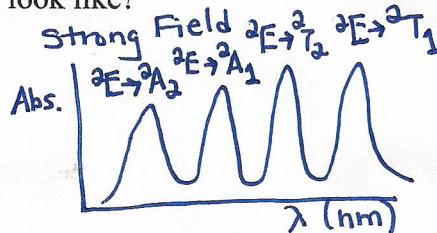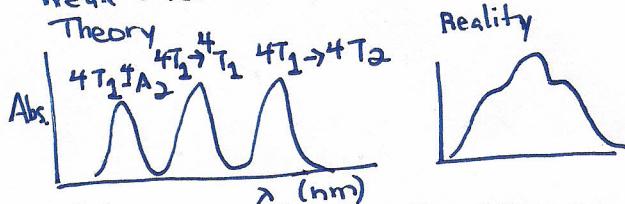
g. Is it easy to predict what type of distortion an octahedral complex of a d^7 metal ion will undergo? If not, what experimental data will you need? Be specific.

Jahn-Teller Distortion
z-in   z-in   z-out   z-out
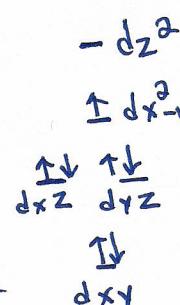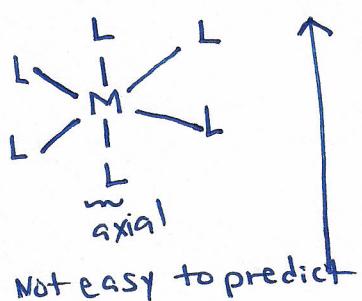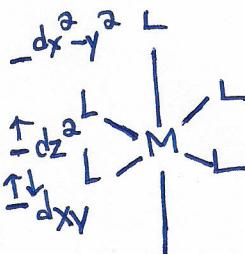
L   L $- d_{z^2}$ $- d_{x^2-y^2}$ L
 \ /   L
L—M—L   ↑ $d_{x^2-y^2}$ d_{z^2} $d_{x^2-y^2}$ ↑d_{z^2} \ | / L
 / | \   M
L   L   ↑↓ ↑↓   ↑↓   / | \
    | d_{xz} d_{yz} d_{xy} ↑↓ d_{xy} L L
  axial |
                           ↑↓   — — —   L
                           d_{xy} d_{xy} d_{xz} d_{yz} axial
Not easy to predict   ↑↓ ↑↓
                                                  d_{xz} d_{yz} the unequal e^-
Both a z-in + z-out distortion   resolves   need an x-ray structure to
occupancy; Therefore we would
know what distortion occured.

2. (24 points) Predict (and explain) the extinction coefficient for the d-d transitions of the following iron compounds.

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

Fe^{3+}
d^5

π acceptor
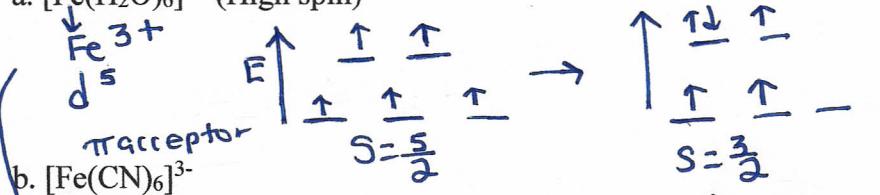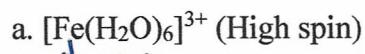
Spin-forbidden
Laporte-forbidden
$E \sim 1\ M^{-1}cm^{-1}$
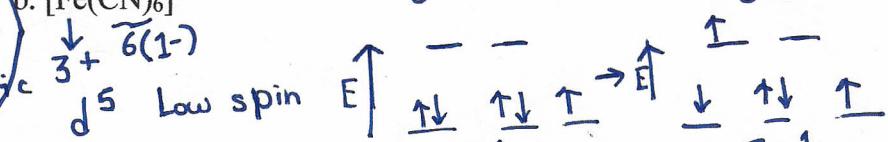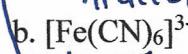
$S = \frac{5}{2}$ → $S = \frac{3}{2}$

Centro-symmetric {

b. $[Fe(CN)_6]^{3-}$

$3+\ \widetilde{6(1-)}$
d^5 Low spin

$S = \frac{1}{2}$ → $S = \frac{1}{2}$

Laporte-forbidden
$E \doteq 10-200\ M^{-1}cm^{-1}$

c. $[Fe(H_2O)_6]^{2+}$ High spin

$Fe^{2+}\ d^6$

$S = 2$ → $S = 2$

Laporte-forbidden
$E = 10-200\ M^{-1}cm^{-1}$

d. $[Fe(CN)_6]^{4-}$

$2+\ d^6$ Low spin

$S = 0$ → $S = 0$
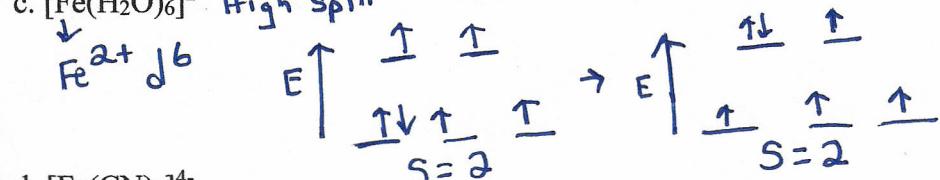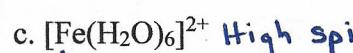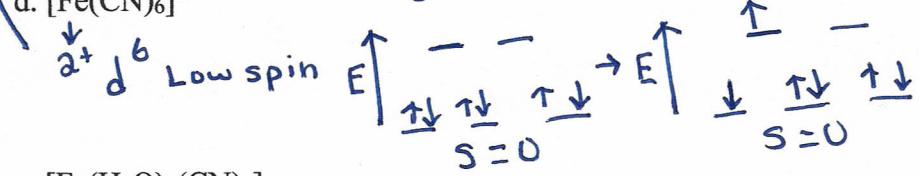
Laporte-forbidden
$E = 10-200\ M^{-1}cm^{-1}$
Less Laporte-forbidden
$E = 100-1000\ M^{-1}cm^{-1}$

e. $[Fe(H_2O)_3(CN)_3]$ → $Fe^{3+}\ d^5$ Low spin

Regardless of the isomer, is not centrosymmetric.
The molecular orbitals will not have parity symbols.

$S = 0$ $S = 0$
Laporte-forbidden
$E = 10-200\ M^{-1}cm^{-1}$

Centro-symmetric f. $[FeF_6]^{4-}$ π donor

Fe^{2+} High spin
d^6

$S = 2$ → $S = 2$

Laporte-forbidden
$E = 10-200\ M^{-1}cm^{-1}$

g. $[Fe(CN)_6]^{6-}$
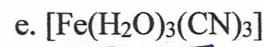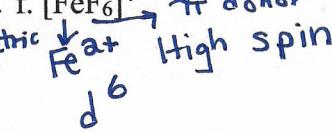
$6(-1)$
$Fe(0) \to 3s^2 4d^6$
High spin because of low metal oxidation state.
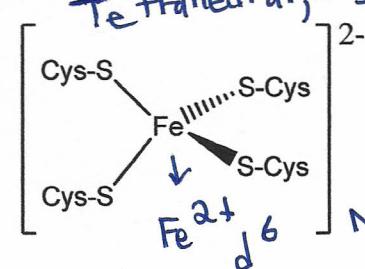
$S = 2$ $S = 2$
Laporte-forbidden
$E = 10-200\ M^{-1}cm^{-1}$

h.

Tetrahedral; High spin usually; The molecular orbitals will not have parity symbols.

$\begin{bmatrix} \text{Cys-S} \quad \text{S-Cys} \\ \quad Fe \\ \text{Cys-S} \quad \text{S-Cys} \end{bmatrix}^{2-}$

$Fe^{2+}\ d^6$ Not centrosymmetric

$S = 2$ → $S = 2$

Less Laporte-forbidden
$E = 100-1000\ M^{-1}cm^{-1}$

3. (5 points) Distinguish between ligand to metal charge transfer and metal to ligand charge transfer electronic transitions.

Charge transfers are an electronic transition in which electrons more from ligands to metals or vice versa. Ligand to metal charge transfers (LMCT) are movement of e^- from molecular orbitals with ligand character to molecular orbitals with metal character. These transitions can occurs with complexes of all ligand types. Metal to ligand CT (MLCT) are movement of e^- from M.O. of metal character to M.O. of ligand character. These transitions occur with complexes of ligands that are π acceptor.

4. (5 points) Use Hard Soft Acid Base theory to distinguish between an organometallic compound and a coordination compound.

Organometallic compounds: Soft metal + soft ligand interactions

Coordination compounds: Hard metal + hard ligand interactions

5. (10 points) Which would be a more stable compound $[Ti(CO)_4]^{2+}$ and $[Ti(CO)_4]^{4+}$? Explain.

CO ligands are π acceptor and would have a stronger interaction with metals that have d electrons at least a d^2 configuration to allow for back bonding.

$[Ti(CO)_4]^{2+}$
$\rightarrow Ti^{2+} \quad d^2$

$[Ti(CO)_4]^{4+}$
$\rightarrow Ti^{4+} \quad d^0$
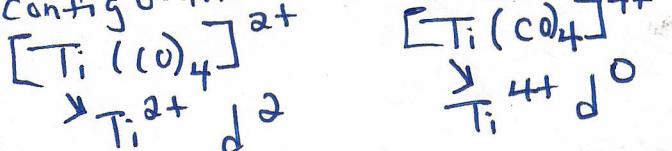
would be a more stable compound.

6. (10 points)
a. Explain the strength of binding to metals. Lone pair > π bond donors > σ bond donors

The strength of binding has to due with the availability of e^-s to engage in bonding with a metal. From left to right, there is less e^- density available for bonding.

b. If H_2 is the source of a σ bond donor pair of electrons, then under what condition(s) would its interaction with a metal result in an oxidative addition?
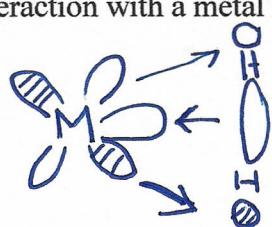
An oxidative addition would occur if the metal has d e^- in the $d\pi$ orbitals of sufficient energy to backbond into the H_2^* antibonding molecular orbital to cause the H-H to break.

$M + H_2 = M + \begin{array}{c} H \\ | \\ H \end{array} \rightarrow M \begin{array}{c} H \\ | \\ H \end{array} \rightarrow M \begin{array}{c} H \\ | \\ H \end{array}$
$\quad (0) \quad \quad (0) \quad \quad (II)$

$$[MX_aL_b]^{c+} \quad \text{# } e^- \text{ count} = N + a + 2b - c \quad \text{covalent model}$$
$$O.S. = C + a$$
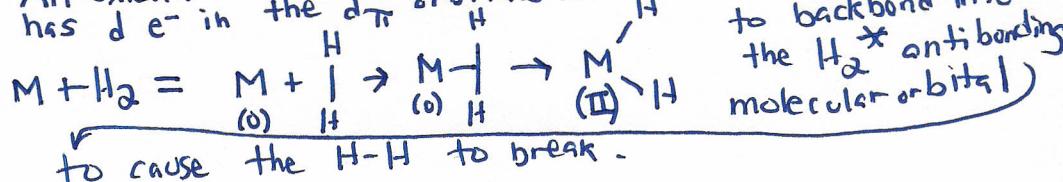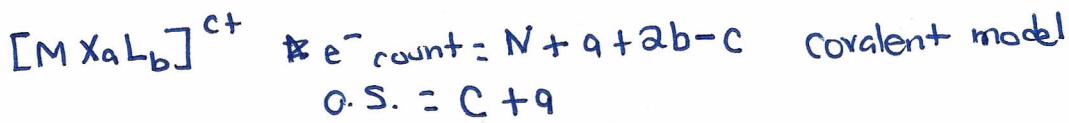
7. (20 points) What is the electron count of the following complexes? Identify the metal oxidation state.

a. Fe(CO)$_5$

$\widetilde{\overset{L}{}}$

e^- count $= 8 + 2(5) = 18e^-$

O.S. $= 0$

FeL$_5$

b. Ir(CO)Cl(PPh$_3$)$_2$

Ir L X L$_2$

Ir X L$_3$

e^- count $= 9 + 1 + 3(2) = 16e^-$

O.S. $= 1+$

c. (η^5-C$_5$H$_5$)Re(=O)$_3$

Re L$_2$X (X$_2$)$_3$

Re X$_7$L$_2$

e^- count $= 7 + \overset{7}{\cancel{6}} + 2(2) = 18e^-$

O.S. $= 7+$

d. [(η^3-C$_3$H$_3$)(η^5-C$_5$H$_5$)Mn(NH$_3$)]$^-$
Note: Picture η^3-C$_3$H$_3$ as a triangular ligand that binds via an anionic carbon and a π-bond donor pair.

$\overset{\widetilde{LX}}{[Mn\ LX\ L_2X\ L]^-}$

[Mn X$_2$L$_4$]$^-$

e^- count $= 7 + 2 + 4(2) + 1 =$
$\qquad 9 + 8 + 1 = 18e^-$

O.S. $= 2 - 1 = +1$

e. (η^3-C$_3$H$_5$)(η^5-C$_5$H$_5$)Cr(CH$_3$)(NO)
Note: NO is linearly coordinated. In the covalent model, it is a 3 e$^-$ ligand. In the ionic model, it is considered NO$^+$ and considered a 2 e$^-$ ligand.

Cr LX L$_2$X X (NO$^+$)

Cr X$_3$L$_3$ (NO$^+$)
$\qquad\quad \widetilde{}$
$\qquad\quad$ 3e$^-$

e^- count $= 6 + 3 + 3(2) + 3$
$\qquad\qquad = 9 + 6 + 3$
$\qquad\qquad = 18e^-$

O.S. $= 3 \cancel{\ominus} 1+$
$\qquad = \cancel{} 2+$

Cr $= \cancel{} 2+$

Extra Credit (10 points):

1. The following perovskite contains Pb^{2+}, Ti^{4+}, and O^{2-} ions. Shown below is one unit cell of the perovskite.

(blue circle)	Pb^{2+}
(green circle)	Ti^{4+}
(red circle)	O^{2-}
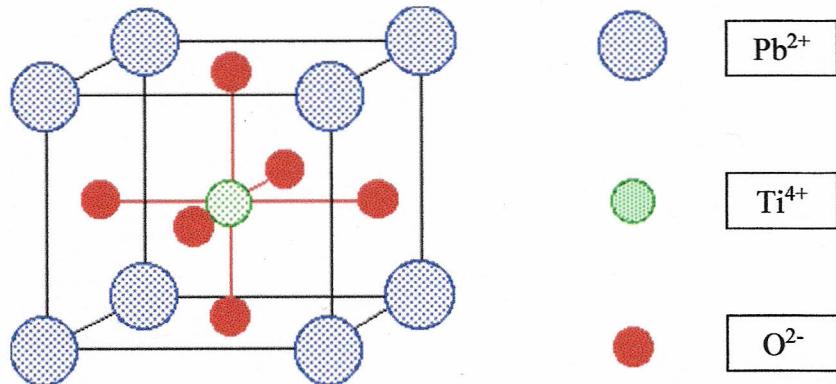
a. How many Pb^{2+} ions lie within one unit cell?

Corner atoms/ions $8 \times \frac{1}{8} = 1$

b. How many Ti^{4+} ions lie within one unit cell?

1

c. How many O^{2-} ions lie within one unit cell?

Face atoms/ions $6 \times \frac{1}{2} = 3$

d. What is the empirical formula for perovskite?

$PbTiO_3$

e. With respect to the O^{2-} ions, in what type of hole is Ti^{4+} located?

Octahedral

f. With respect to the Pb^{2+} ions, in what type of hole is Ti^{4+} located?

cubic

2. Methylation is used by certain species of fungi and bacteria to methylate inorganic arsenic species to form methylarsenicals, an organic arsenic species. These methylarsenicals are volatile. How might one use this information for a bioremediation proposal?

Team Arsenic explained that organic forms of arsenic are less toxic than inorganic ones. Perhaps one could design a sort of filtering device that contains these organisms such that inorganic arsenic contaminated water could be converted into the volatile methylarsenicals. Then some material could be used to capture the volatile methylarsenicals to allow for appropriate disposal.

3. Draw a feasible structure for Sb_2O_3 and Sb_2O_5 that follows the geometric guidelines described by team Antimony.
elemental formula

Team Antimony stated that Sb (III) adopted pyramidal structures and Sb(V) adopted octahedral structures. Here is my best attempt.

ox. state = 3

Sb_2O_3

Sb : $5s^2 5p^3$
O : $2s^2 2p^4$

$(2 \times 5e) + (3 \times 6e) =$
$10e^- + 18e^- = 28e^-$

→ pyramidal

28e⁻ used

→ pyramidal

$Sb_2O_5 \Rightarrow Sb_4O_{10}$ Easier for me to visualize.

$(4 \times 5e^-) + (10 \times 6e^-) = 80e^-$

octahedral

octahedral

octahedral