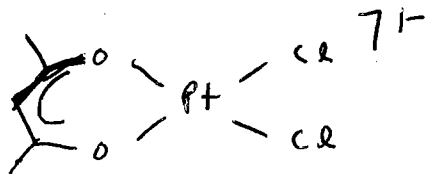


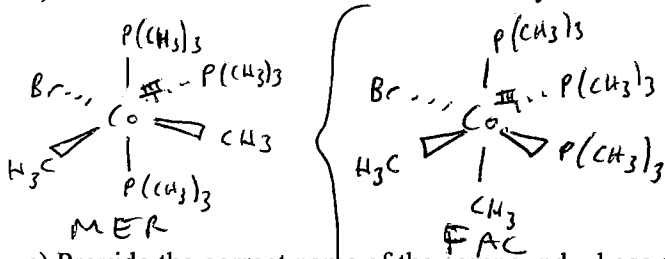
PART A. (52 points) BASIC QUESTIONS. Answer **QUESTION #1** and **THREE** of the next four questions, e.g. 1/2/3/4, 1/2/3/5, 1/3/4/5, etc. Write your answer in the space provided. SHOW YOUR WORK & WRITE EXPLANATIONS IN COMPLETE SENTENCES.

1. Answer the following questions that involve drawing structures, naming, or determining isomers of various transition metal complexes.

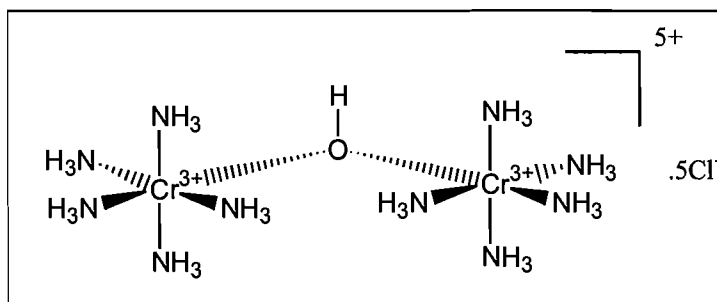
a) Draw the structure of the complex ion *cis*-acetylacetonatodichloroplatinate(II).



b) Draw the structure of bromo-*cis*-dimethyl-*mer*-tris(trimethylphosphine)cobalt(III).

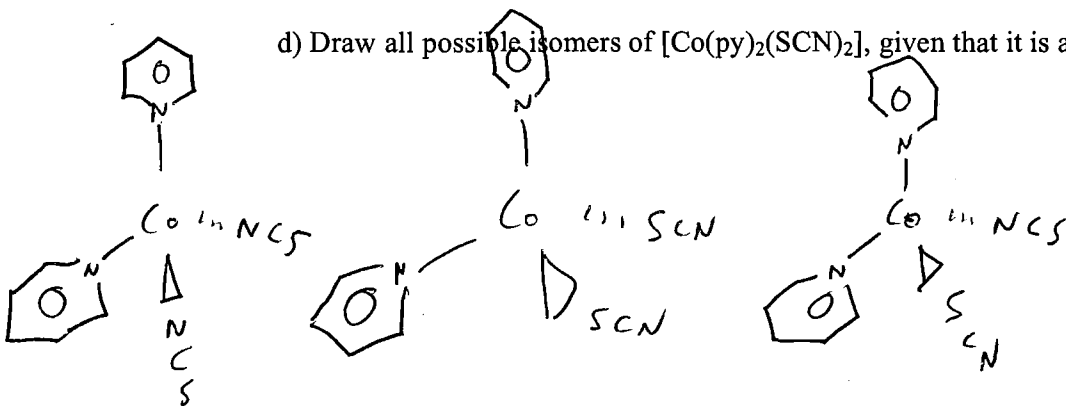


c) Provide the correct name of the compound whose structure is shown below.



NAME = μ -hydroxo bis(pentaamminechromium(III)) chloride

d) Draw all possible isomers of $[\text{Co}(\text{py})_2(\text{SCN})_2]$, given that it is a tetrahedral complex.

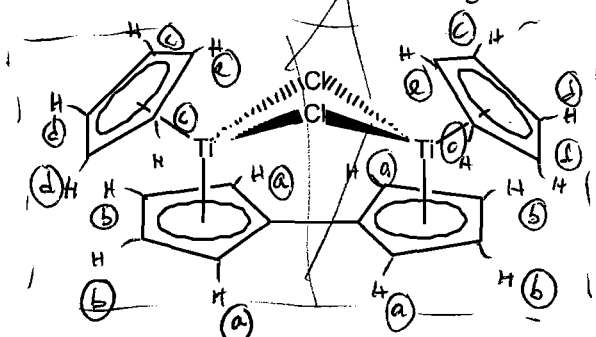


2. Fill in each blank below with the formula of a *related* compound with the property given (as in the example):

Example: Stronger acid than HCl: HBr

- a) Stronger Lewis base than PF_3 : PH_3
- b) Stronger Arrhenius acid than HNO_2 : HNO_3
- c) Harder Lewis acid than Fe^{2+} : Fe^{3+}
- d) Weaker Bronsted-Lowry base than $\text{N}(\text{CH}_3)_3$: NH_3
- e) Softer Lewis base than AsH_3 : SbH_3
- f) Stronger Arrhenius acid than $\text{CH}_3\text{SO}_3\text{H}$: $\text{CF}_3\text{SO}_3\text{H}$

3. The following questions refer to the compound shown below. Assume for the purposes of this question that the cyclopentadienyl rings do not rotate and that there are no other chemical processes that can interconvert the two rings.



- a) Is this molecule chiral? Explain your answer using point group symmetry.

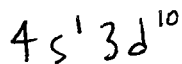
no, b/c it contains mirror planes

- b) How many different proton NMR peaks will be observed for this complex? Explain on the basis of symmetry, indicating which symmetry operations, if any, interconvert the protons.

5 NMR peaks ; ~~the~~ symmetry-equiv. H's are related to each other by mirror planes

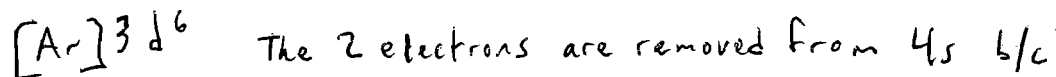
4. In the transition metals of the 4th period, the 4s & 3d orbitals are close in energy.

a) What is the electron configuration of a neutral copper atom? Rationalize the observed configuration in terms of total pairing energy (i.e. $\Pi = \pi_c + \pi_e$) and orbital energy considerations.



B/c the orbital energy differences between 4s & 3d are small, the cost of promoting electrons to a higher energy orbital is less than that of pairing electrons. There is also a net stabilization obtained from exchange interactions.

b) What is the electron configuration of Fe^{2+} ? Rationalize the observed configuration in terms of effective nuclear charge (Z_{eff}) and the relative energies of the 4s and 3d orbitals.

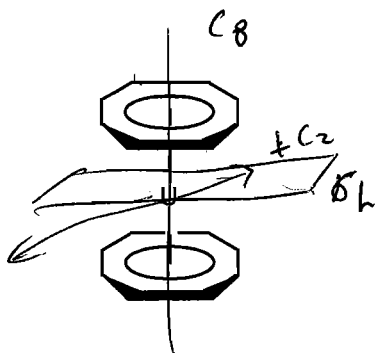


Z_{eff} experienced by a 4s electron is always less than that experienced by a 3d electron:

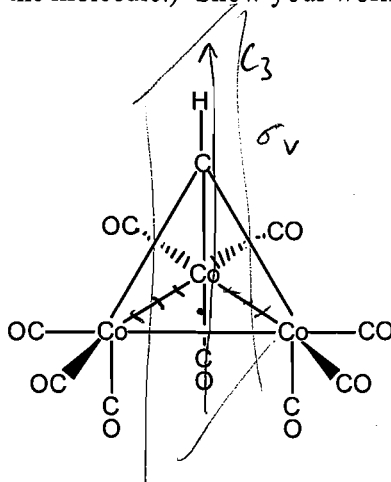
for Fe^0

$$\begin{cases} Z_{eff} \text{ (of a } 4s e^-) = Z - \sigma = 26 - ((1)(0.35) + (14)(0.85) + (10)(1.00)) = 3.75 \\ Z_{eff} \text{ (of a } 3d e^-) = Z - \sigma = 26 - ((5)(0.35) + 18) = 6.25 \end{cases}$$

5. Assign the point group symmetry of the following molecules or objects. (Write the point group in the space below the molecule.) Show your work so that I know how you arrived at your conclusion.



D_{2h}



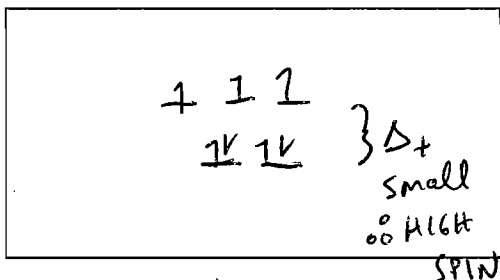
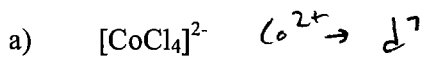
D_{3h}

Hope College
Safety Glasses

C_s

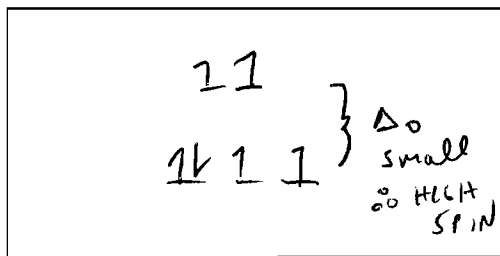
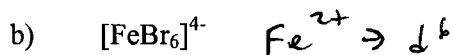
Part B. (48 points) COMPETENCY QUESTIONS. Answer THREE of the next four questions. SHOW ALL WORK & WRITE EXPLANATIONS IN COMPLETE SENTENCES.

6. For each of the compounds below, (i) draw a d orbital splitting diagram in the box on the left, (ii) determine the d orbital electron occupancies, and (iii) compute the total spin S & spin-only magnetic moment μ_s . Rationalize your choice by making specific reference to the relative magnitude of Δ_o or Δ_t for each complex.



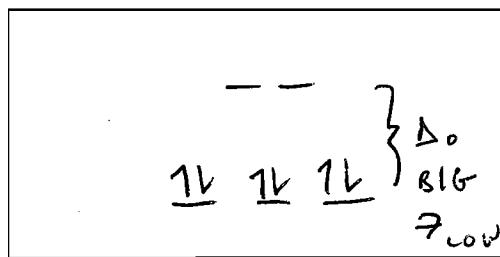
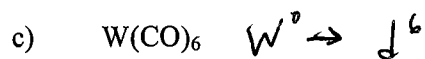
$$S = \underline{3/2} \quad \mu = \sqrt{n(n+2)}$$

$$\mu_s = \underline{3.87} \text{ Bohr magnetons}$$



$$S = \underline{2} \quad \mu = \sqrt{n(n+2)}$$

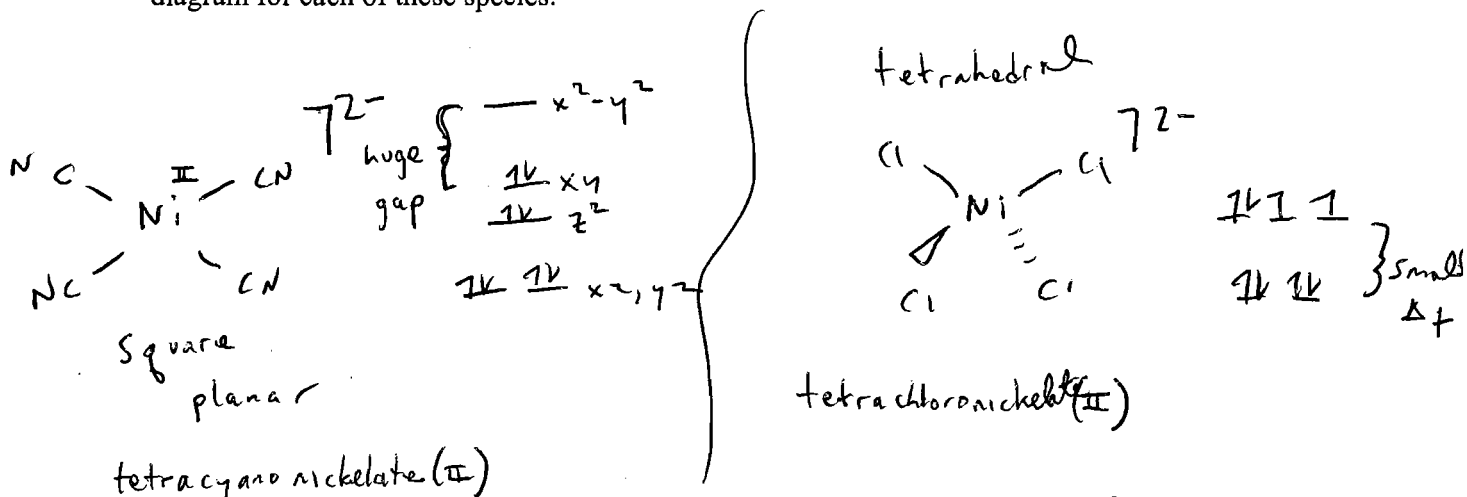
$$\mu_s = \underline{4.90} \text{ Bohr magnetons}$$



$$S = \underline{0}$$

$$\mu_s = \underline{0} \text{ Bohr magnetons}$$

7. The complex $[\text{Ni}(\text{CN})_4]^{2-}$ is diamagnetic, but $[\text{NiCl}_4]^{2-}$ is paramagnetic with two unpaired electrons. Use the magnetic behavior of these complexes to deduce the geometric structures, i.e. molecular geometry, of each of these species. In recording your answer, be sure to also provide the name of each molecule and include a well-articulated explanation of the origin of the observed magnetism by showing a d orbital splitting diagram for each of these species.



8. $[\text{Co}(\text{H}_2\text{O})_6]^{3+}$ is a strong oxidizing agent that will oxidize water, but $[\text{Co}(\text{NH}_3)_6]^{3+}$ is stable in aqueous solution. Explain the differing reactivity of these two cobalt complexes using ligand-field stabilization energies (e.g. $\text{LFSE}_{[\text{Co}(\text{NH}_3)_6]^{3+}} = ? \cdot \Delta_o$) and the following helpful information.

(i) Both Co(III) complexes are low-spin; both Co(II) complexes are high-spin.

(ii) $\Delta_o [\text{Co}(\text{NH}_3)_6]^{3+} = 24,000 \text{ cm}^{-1}$

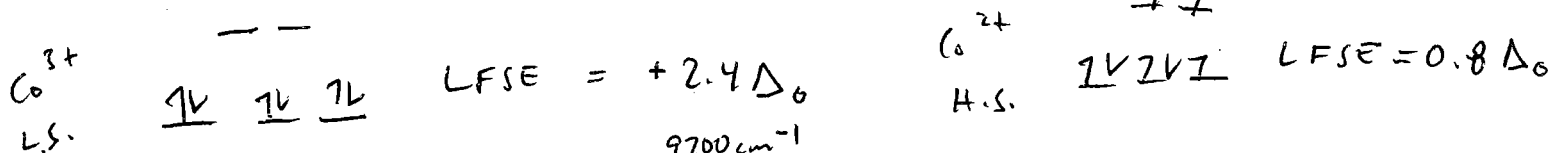
(iii) $\Delta_o [\text{Co}(\text{NH}_3)_6]^{2+} = 13,000 \text{ cm}^{-1}$

(iv) $\Delta_o [\text{Co}(\text{H}_2\text{O})_6]^{3+} = 18,000 \text{ cm}^{-1}$

(v) $\Delta_o [\text{Co}(\text{H}_2\text{O})_6]^{2+} = 9,700 \text{ cm}^{-1}$

means $[\text{Co}(\text{H}_2\text{O})_6]^{3+}$ has an earlier time gaining electrons

requires smaller Δ_o .



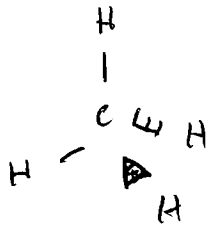
$$\Delta E_{\text{Co}^{3+} \rightarrow \text{Co}^{2+}(\text{H}_2\text{O})} = (0.8)(9700 \text{ cm}^{-1}) - (2.4)(18000 \text{ cm}^{-1}) = 35440 \text{ cm}^{-1} \text{ required}$$

$$\Delta E_{\text{Co}^{3+} \rightarrow \text{Co}^{2+}(\text{NH}_3)} = (0.8)(13000 \text{ cm}^{-1}) - (2.4)(24000 \text{ cm}^{-1}) = 47200 \text{ cm}^{-1} \text{ required}$$

Since $35440 \text{ cm}^{-1} < 47200 \text{ cm}^{-1}$, $[\text{Co}(\text{H}_2\text{O})_6]^{3+}$ must be the stronger oxidizing agent!

9. Consider a molecule of methane, CH₄.

a) Using group theoretical methods, identify all the vibrations of methane.



T _d	E	BC ₃	3C ₂	6S ₄	6σ _d
Γ _{vib}	5	2	1	1	3
Γ _{xyz}	3	0	-1	-1	1
Γ _{TOTAL MOTION}	15	0	-1	-1	3
-Γ _{xyz}	3	0	-1	-1	1
-Γ _{Rz, Ry, Rx}	12	0	0	0	2
Γ _{vib}	9	0	1	-1	3

→ reduce $\Gamma_{vib} = 1A_1 + 1E + 2T_2$

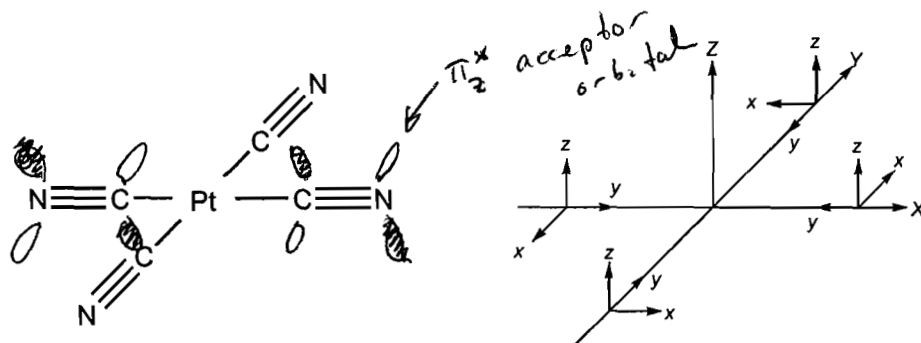
b) Based on your results from part a), determine which motions are IR active and which are Raman active, and briefly explain how you made this choice.

— T₂ transforms as x, y, z ∴ the T₂ modes are IR active

— Raman active modes transform as quadratic Fxn of x, y, z ∴ all modes are Raman Active

Part C. (25 points) MASTERY QUESTIONS. Answer ONE of the next two questions.
SHOW ALL YOUR WORK AND WRITE EXPLANATIONS IN COMPLETE SENTENCES.

10. $\text{Pt}(\text{CN})_4^{2-}$ is a diamagnetic complex with square planar geometry. CN^- is a π -acceptor ligand; this problem will explore π bonding in this complex. The complex, and an axis system to which you should refer, is shown below.



a) Using the group theoretical approach to bonding, find the irreducible representations of the symmetry adapted linear combinations of CN^- acceptor orbitals that will form π bonds to the central Pt atom. The acceptor orbital on CN^- is the π^* orbital.

• there are 2 π^* orbitals on each CN^- , one π_x^* and one π_z^* ; they must be treated separately

D_{4h}	E	$2C_4$	C_2	$2C_2'$	$2C_2''$	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$
$\Gamma_{\pi_x^*}$	4	0	0	-2	0	0	0	4	-2	0
$\Gamma_{\pi_z^*}$	4	0	0	-2	0	0	0	-4	2	0

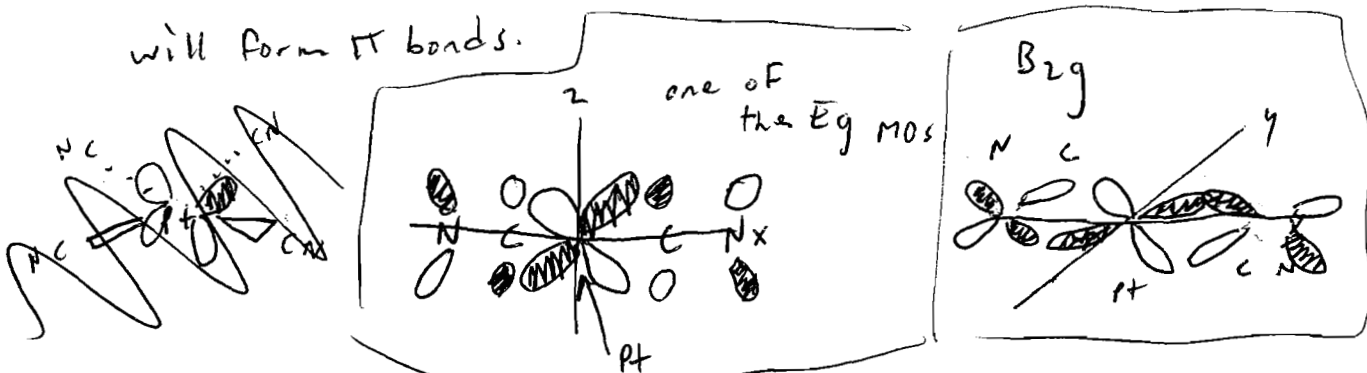
) unmoved orbitals

\Rightarrow reduce... $\Gamma_{\pi_x^*} = E_u + A_{2g} + B_{2g}$

$\Gamma_{\pi_z^*} = E_g + A_{2u} + B_{2u}$

b) Using your character tables, deduce which metal orbitals will be used to form the π bonds, and draw pictures of the π bonding interactions between the Pt(II) and the CN^- ligands. (For your pictures, simply show diagrams that illustrate the π bonding between the d orbitals and ligand orbitals of correct symmetry.)

Potential π symmetry orbitals on the metal are
 d_{xz}, d_{yz}, d_{xy} . In D_{4h} symmetry, these orbitals transform
 as E_g and B_{2g} . Therefore only E_g and B_{2g} SALCS
 will form π bonds.

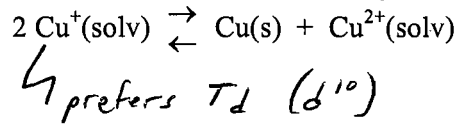


c) The CN^- ligand can act as a σ donor and a π acceptor. The σ donor orbital is antibonding with respect to the C-N bond. Given that the C-N vibrational frequency in the IR spectrum of $\text{Pt}(\text{CN})_4^{2-}$ is 2170 cm^{-1} while free CN^- exhibits a C-N stretch at 2080 cm^{-1} , which property, σ donation or π acceptance dominates in this complex? Provide a clear explanation of your reasoning.

Since ν_{CN} is higher in complex than in free CN^- ,
 CN^- bond in complex must be stronger. Backbonding
 from filled metal $d\pi$ orbitals would increase e^- density
 in the π^* MO of CN^- , weakening the bond. In contrast,
 σ donation from the CN^- to the metal will lower e^-
 density in an orbital that is σ^* and will strengthen
 the C-N bond.

$\rightarrow \sigma$ donation must dominate.

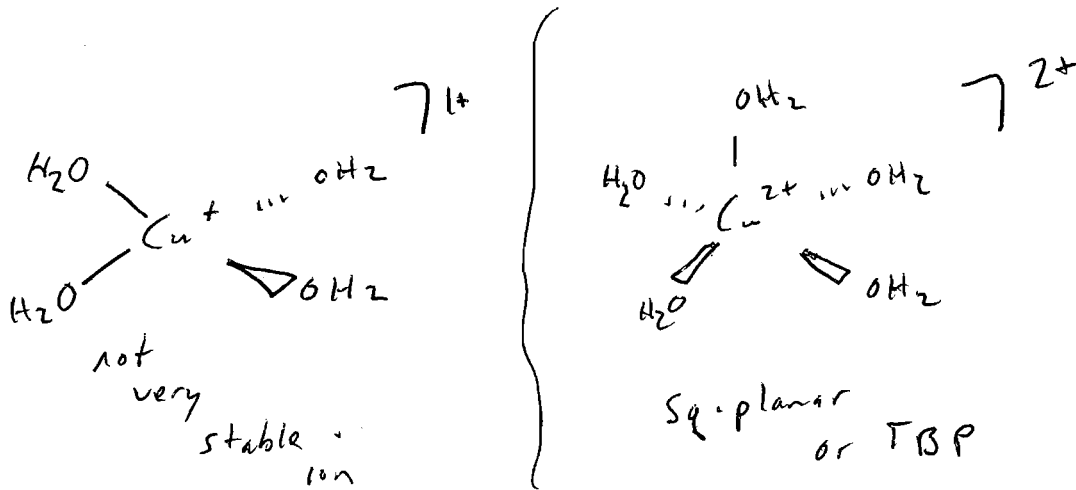
11. Cu(I) and Cu(II) may equilibrate according to the reaction below, where the designation (solv) implies that the metal ions are solvated by a number of solvent molecules. (Hint: Before answering any part of this question, it would be worthwhile for you to read the entire question first!)



N prefers S-coord (d⁹)

↳ prefers T_d (d¹⁰)

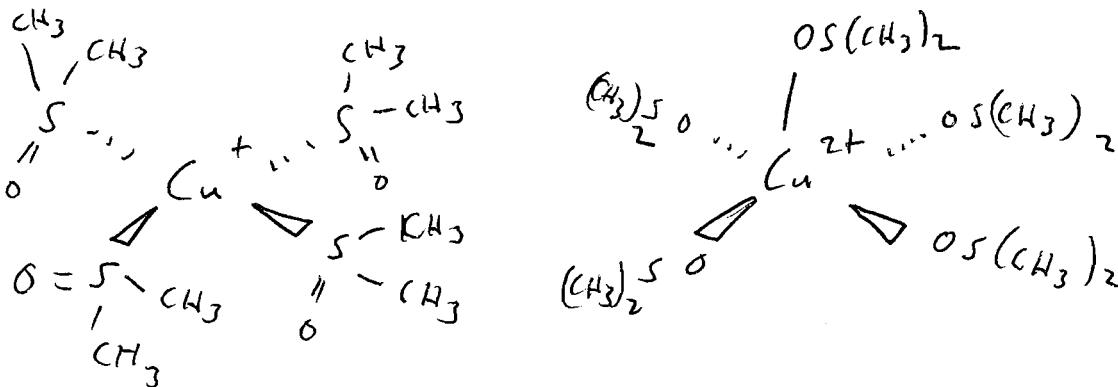
- a) If the solvent molecules in the above reaction are water ligands, the equilibrium constant for this process is very large ($K_{\text{eq}} = 1 \times 10^6$). Using your knowledge of metal coordination chemistry, including metal-ion d electron counts and structural preferences, draw probable structures for the solvated ions. Briefly explain your reasoning.



- b) If the solvent molecules in the above reaction are dimethylsulfoxide $[(\text{CH}_3)_2\text{SO}]$, ligands, the equilibrium constant is small ($K_{\text{eq}} = 2$). Draw probable structures for the solvated ions and rationalize the small magnitude of the equilibrium constant.

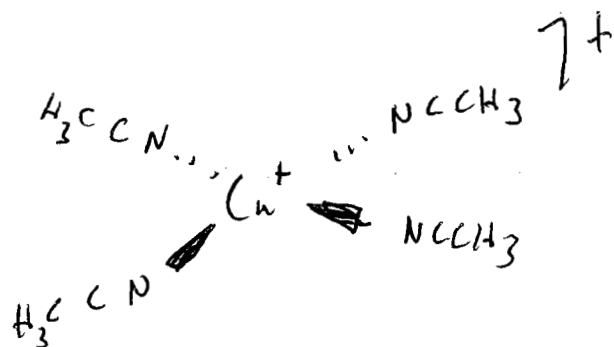
Cu⁺ → d¹⁰ soft acid ⇒ prefers S over O

Cu²⁺ → d⁹ borderline " ⇒ " O over S



*Both ions are of approximately equal E based on HSAB
→ K is near 1.*

c) If the solvent molecules in the above reaction are acetonitrile (CH_3CN) ligands, the equilibrium constant is very small, $K_{\text{eq}} < 1 \times 10^{-3}$. What solvated complex ion is most stable in CH_3CN solution and what property of CH_3CN do you think is important in contributing to this stability?



acetonitrile is a σ donor and a π -acceptor. Its π acceptor property makes it a soft base, ~~is~~ and hence a good ligand for the soft acid Cu^+

d) Synthesis of Cu(I) complexes often begins with Cu(s) and Cu(II)X salts, where X may be a poorly basic anion like BF_4^- . Which of the three solvents would you use to prepare a Cu(I) complex by this method and why?

MUST USE ACETONITRILE B/C IT IS THE ONLY SOLVENT THAT STABILIZES Cu^+ SUFFICIENTLY