(20 points) Multiple choice. Circle the correct answer.

a)	blue color	$Zn(NH_3)_4^{2+}$	$Cu(H_2O)_6^{2+}$	TiF_6^{2-}
b)	pentaaquachlorocobalt(III) chloride	$[Co(H_2O)_5Cl]Cl$	$[Co(H_2O)_5Cl_2]Cl$	$[Co(H_2O)_5Cl]Cl_2$
c)	largest spin	$CoCl_4^{2-}$	$Co(CN)_6^{3-}$	$Co(H_2O)_6^{3+}$
d)	does not exist	FeO_4	OsO_4	CrO_3
e)	most negative CFSE	$Mn(H_2O)_6^{2+}$	$Cr(H_2O)_6^{2+}$	$Mn(CN)_6^{4-}$

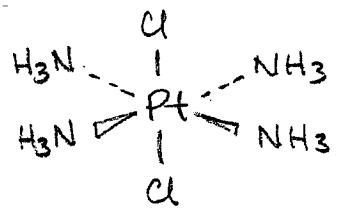
2. (10 points) A compound consists of Pd, Cl, and NH_3 in the ratio of 1 : 4 : 4.

a) When $AgNO_3$ is added to an aqueous solution of the compound, 2 moles of Cl^- per mole of Pd are precipitated as AgCl. Write the chemical formula for the compound.

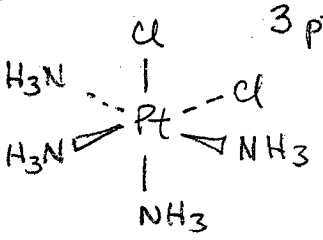
4 pts $[Pd(NH_3)_4Cl_2]Cl_2$

b) Draw all of the unique isomers of this compound. Be specific about the structure and the positions of the ligands.

3 pts



3 pts



-3 pt for each "extra" complex

3. (8 points) Consider the reaction between Fe and CO.

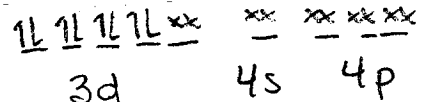
a) Use the 18 electron rule to predict the stoichiometry of the compound that forms.

Fe $[Ar]3d^6 4s^2$

need $10e^- = 5$ CO

$Fe(CO)_5$ 4 pts

b) What orbitals on the metal are used to form hybrid orbitals?



dsp^3 4

4. (9 points) Consider the following ligand exchange reaction of the tetrahedral complex $ZnCl_4^{2-}$.

$$ZnCl_4^{2-}(aq) + NH_3(aq) \leftrightarrows ZnCl_3NH_3^{-}(aq) + Cl^{-}(aq)$$

a) The entropy of activation is negative. What does this imply about the rate-determining step in the mechanism for the reaction?

2 pts. associative

b) Suggest a plausible rate-determining step with a negative entropy change.

2 pts. $ZnCl_4^{2-} + NH_3 \rightleftharpoons [ZnCl_4NH_3$

1 pt:

c) Is $ZnCl_4^{2-}$ labile or inert? Use crystal field stabilization energy to explain your thinking.

Zn^{2+} $[Ar]\,3d^{10}$ $\underline{\uparrow\downarrow}\ \underline{\uparrow\downarrow}\ \underline{\uparrow\downarrow}\ \underline{\uparrow\downarrow}\ \underline{\uparrow\downarrow}$

CFSE = 0 for $ZnCl_4^{2-}$ 4 pts and for the 5-coordinate intermediate

5. (9 points) Consider the square planar $PtCl_4^{2-}$ complex.

a) Use the ionic model to determine the energy of the Pt-Cl bond in $PtCl_4^{2-}$. The distance between the Pt nucleus and the Cl nucleus is 2.55×10^{-10} m.

1 pt for equation

$$PE = 1.37\times10^{-7}\left[\frac{4(+2)(-1)}{2.55\times10^{-10}} + \frac{4(-1)(-1)}{\sqrt{2}(2.55\times10^{-10})} + \frac{2(-1)(-1)}{2(2.55\times10^{-10})}\right]$$

Cl^- 1 pt 1 pt 1 pt

$Cl^- - Pt^{2+} - Cl^-$

Cl^- $\sqrt{2}$ r

correct answer

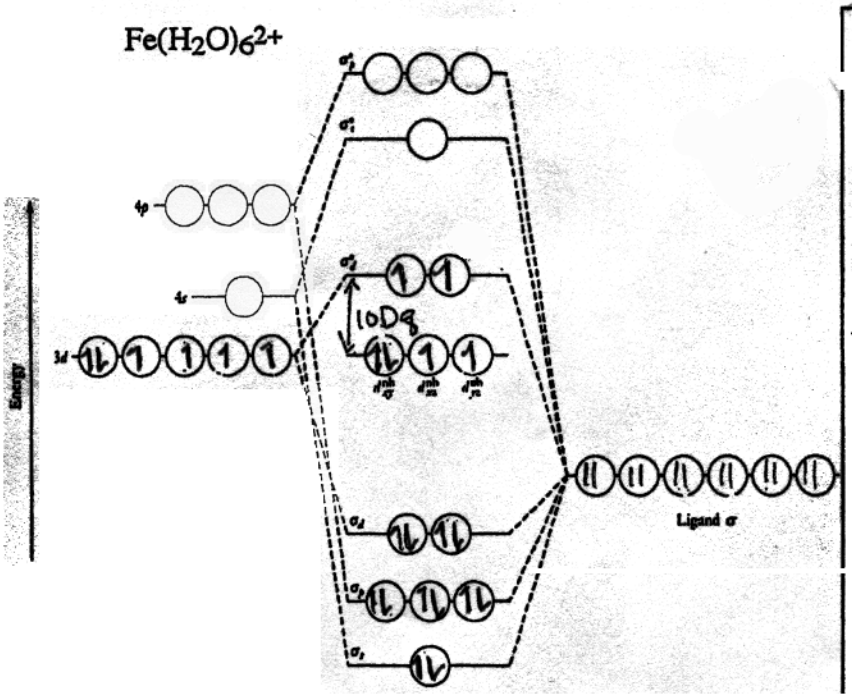
-2241 kJ/mol 1 pt

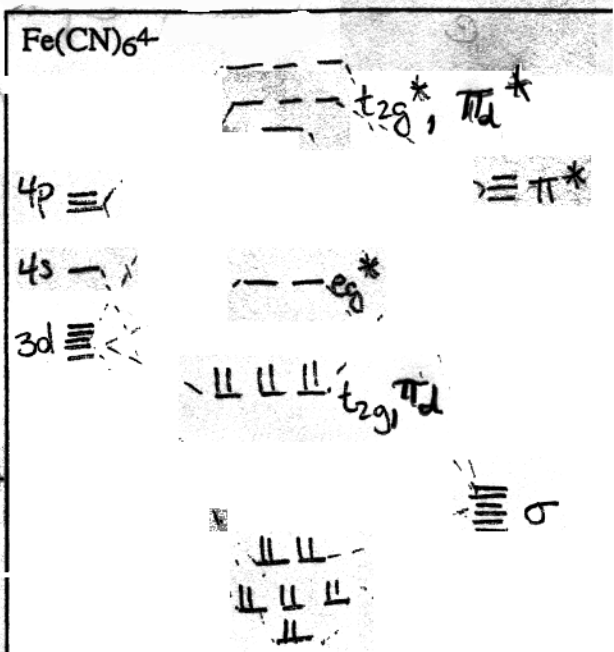
b) Do you expect the Au-Cl bond in $AuCl_4^-$ to be stronger or weaker? Explain your thinking. 1 pt.

Au^{3+} has a higher charge and a smaller size compare with Pt^{2+}

3 pts

6. (24 points) The molecular orbital diagram for $Fe(H_2O)_6^{2+}$ is shown below.





2 pts a) Label 10Dq.

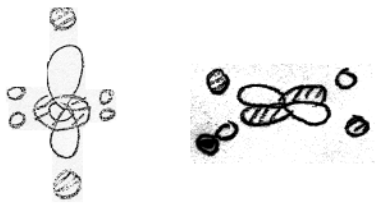
2 pts b) Show the electron filling. (The complex is paramagnetic.)

c) What is the bond order for each of the 6 bonds between Fe^{2+} and H_2O? Show your work.

$BO = \frac{1}{2}[12-2] = 5$ 2 pts

each bond $= \frac{5}{6}$ 1 pt

d) Draw the molecular orbitals for the two e_g^* orbitals.



2 pts. 2 pts

5 pts. e) Draw the molecular orbital diagram for $Fe(CN)_6^{4-}$ in the space provided above.

2 pts. f) Show the electron filling for $Fe(CN)_6^{4-}$. (The complex is diamagnetic.)

g) Explain why the bond between Fe^{2+} and CN^- is stronger than the bond between Fe^{2+} and H_2O. Be specific about the bond order.

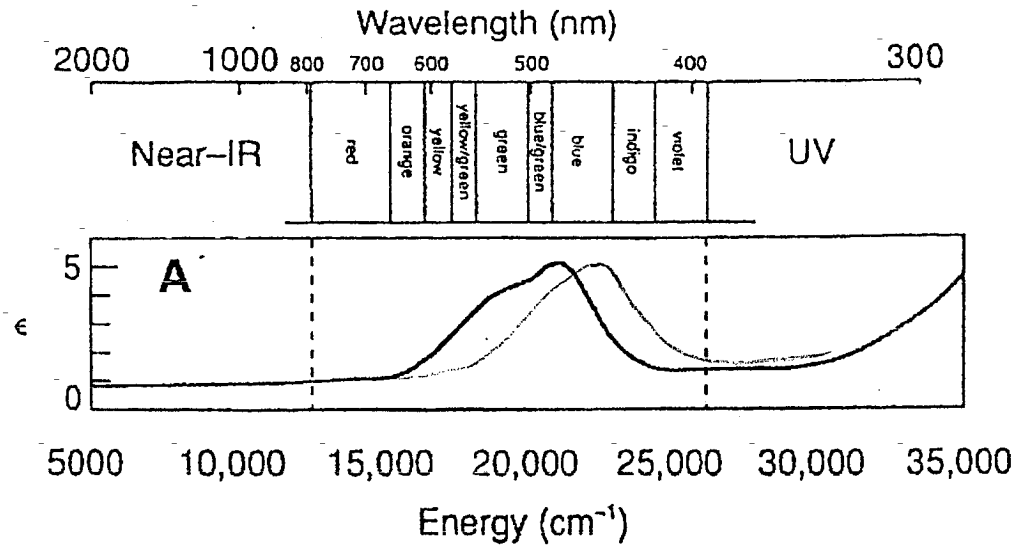
$BO = \frac{1}{2}[18-0] = 9$

3 pts each bond is $1\frac{1}{2}$

h) Do you expect the bond order for the bond between C and N in CN^- to increase, (decrease) or stay the same when CN^- coordinates to Fe^{2+}? Explain your thinking.

2 pts electrons are donated from the metal into the $C\equiv N^-$ π^* orbital, which lowers the bond order

7. (9 points) The absorption spectrum for $Ti(H_2O)_6^{3+}$ is shown below.



3 pts. a) What color is the complex?

purple

3 pts. b) What is the value of 10Dq?

$\sim 20{,}000\ cm^{-1}$ $\sim 4 \times 10^{-19}\ J$ $239\ kJ/m$

3 pts c) Sketch the spectrum for $Ti(NH_3)_6^{3+}$ on the graph.

8. (11 points) Consider the following ligand exchange reaction.

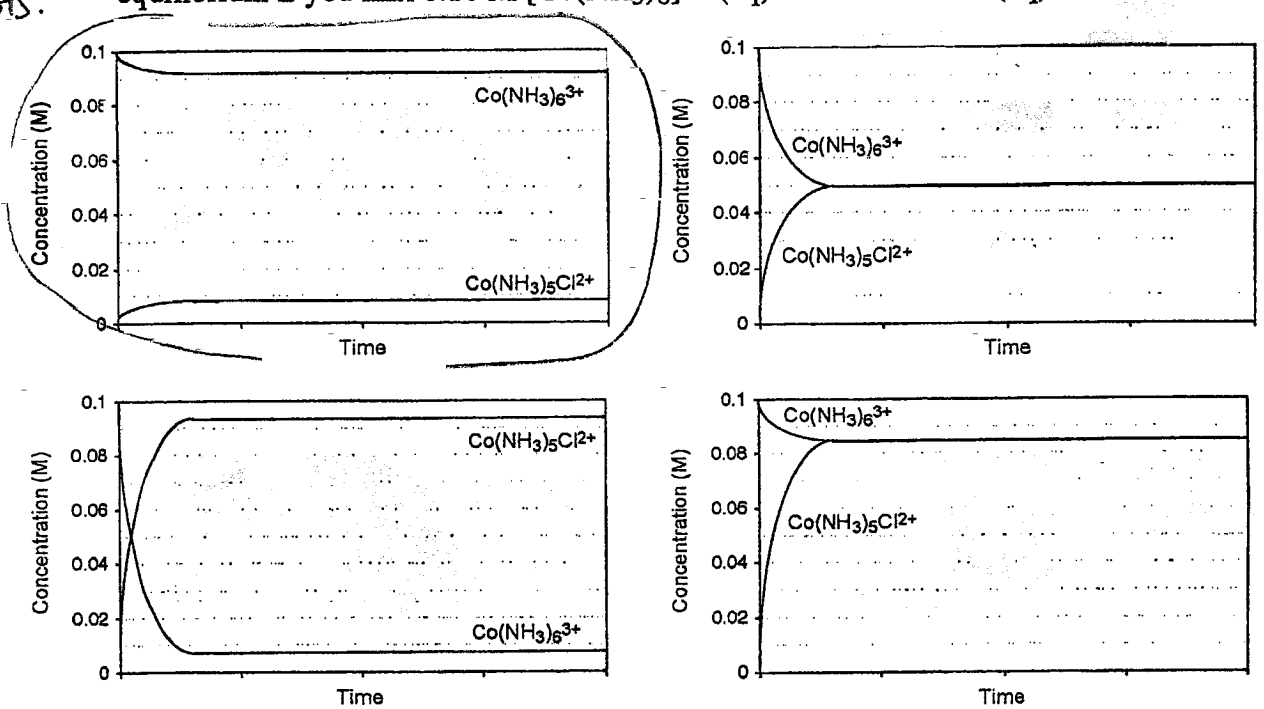
$[Co(NH_3)_6]^{3+}(aq) + Cl^-(aq) \leftrightarrows [Co(NH_3)_5Cl]^{2+}(aq) + NH_3(aq)$

a) Is the equilibrium constant greater than or less than one? Explain your thinking.

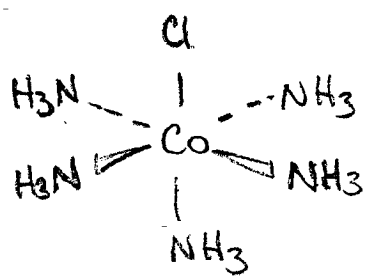
$K = \frac{[Co(NH_3)_5Cl^{2+}][NH_3]}{[Co(NH_3)_6^{3+}][Cl^-]} < 1$ 1 pt.

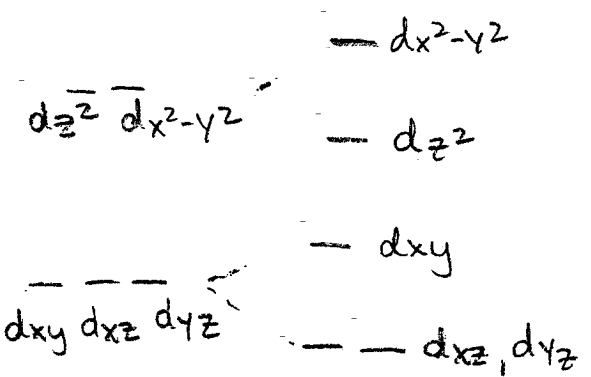
Cl^- is a weaker field ligand 2 pts.

b) Which graph best represents the relative amounts of the two cobalt complexes at equilibrium if you mix 0.10 M $[Co(NH_3)_6]^{3+}(aq)$ with 0.10 M $Cl^-(aq)$? 3 pts.



c) The $[Co(NH_3)_5Cl]^{2+}$ is not a perfect octahedron because NH_3 and Cl^- do not have the same strength. Draw the d orbital splitting pattern taking this into account. Orient the Cl^- on the z axis.





5 pts.