Chem 633 Final Exam, December 16, 1996

Name:______.

Some potentially useful information:

Spectrochemical series (ligands):

$$I < Br' < Cl' < F' < OH' < C_2O_4^{2'} < H_2O < -NCS' < py$$

< $NH_3 < en < bpy < o-phen < NO_2^{-1} < CN' < CO$

Trans effect series (ranked by increasing ability to labilize trans ligands):

$$H_2O, OH^-, NH_3, py < Br^-, Cl^- < l^-, C_6H_5^-, NO_2^-, -SCN^- < CH_3^- < PR_3, H^- < CN^- < C_2H_4, CO^-$$

Trans influence series (ranked by increasing ability to weaken bonds to trans ligands):

 $OH^{-} < NH_{3} < Cl^{-} < Br^{-}, < l^{-}, CH_{3}^{-}, CN^{-}, CO < -SCN^{-} < PR_{3} < H^{-}$

- (1) Reactions: Give the principal product(s) and/or missing reactant(s) and balance the following when possible:
 - (a) $BCl_3 + EtOH \rightarrow$
 - (b) Na + excess NH₃(anhydrous) \rightarrow
 - (c) $Al_2S_3 + H_2O \rightarrow$

(d) +
$$\xrightarrow{\text{THF}} \text{Mo}(\text{CO})_6 + \text{MgCl}_2$$

(e) $Al_2Cl_6 + P(CH_3)_3 \rightarrow$

(f)
$$B_2O_3(l) + NH_3(g) \xrightarrow{1200 \ ^\circ C}$$

(g) +
$$\rightarrow H \xrightarrow{H} H \xrightarrow{H}$$

(h) +
$$\rightarrow$$
 Ni(CO)₄

(i) +
$$\rightarrow$$
 Fe(η^5 -C₅H₅)₂ +

(j) K + O₂ (air)
$$\xrightarrow{25 \circ C}$$

(2) Which of the ions below has the <u>longest</u> Mo—Mo bond? (Explain.) $[Mo_2(SO_4)_4]^{4-}$ $[Mo_2(SO_4)_4]^{3-}$ $[Mo_2(SO_4)_4]^{2-}$ (3) If $CrCl_2$ is dissolved in warm aqueous HCl, chromium(II) reacts with water to give H₂ gas. In contrast, if either MoCl₂ or WCl₂ are dissolved in warm aqueous HCl, no hydrogen is evolved. Silver trifluoroacetate, Ag(CF₃COO), is successful in removing all the chloride ion from the chromium solution as AgCl, but can not remove all of the chloride from the molybdenum or tungsten solutions — $1^1/_3$ moles of chloride remain in solution for every mole of dissolved molybdenum (or tungsten).

Explain the principal difference between $CrCl_2$ and either $MoCl_2$ or WCl_2 that accounts for these observations.

(4) Bauxite is typically a mixture of AlO(OH) (boehmite and diaspore), Al_2O_3 , Fe_2O_3 , and some silica (SiO₂). Show how alumina (Al_2O_3) is industrially extracted from this mixture using simple acid-base chemistry (i.e., using <u>cheap</u> acids and/or bases).

(5) The stable boron hydride shown below has a particular charge that is in accord with Wade's rules (which govern the systematics of various clusters). Classify this species as *closo-, nido-,* or *arachno-* and give the charge on this ion.



(b) The structure of a class of metal borides is shown below. One unit cell is indicated by the dashed lines, metal atoms (M) are shown as large hatched spheres and boron atoms are the small open spheres. What is the chemical formula $(M_x B_y)$ for this compound?



(c) For which of the <u>sp-block</u> metals, M, would you expect a compound of this type to exhibit <u>semiconducting</u> behavior? (Explain your answer.)

- (6) Suppose that an aqueous solution of $[Co(NH_3)_5(H_2O)]^{3+}$ is divided into two equal volume portions. A NaCl solution is quickly added to one portion and a solution of NaNO₂ is quickly added to the other. The two reactions below occur, but the first proceeds at a rate much faster than the second. <u>Give a mechanistic explanation for the observed difference in rate</u>. (*Hint*: What is the difference in the pH of NaCl and NaNO₂ solutions?)
 - (i) $[Co(NH_3)_5(H_2O)]^{3+} + NO_2^- \rightarrow [Co(NH_3)_5(NO_2)]^{2+} + H_2O$
 - (ii) $[Co(NH_3)_5(H_2O)]^{3+} + Cl^- \rightarrow [Co(NH_3)_5(Cl)]^{2+} + H_2O^-$

(7) (a) For which transition metals (M) would you expect to find stable, monomeric, complexes with the formula $M(\eta^5-C_5H_5)(CO)_3$?

(b - e) For each of the following metals, draw the structure of simplest stable compounds consisting entirely the metal and carbonyl ligands *and* indicate the point group of each.

(b) Mo (c) Fe (d) Ir (e) Ni

(8) (a) How many isomers, optical and geometric, are there with the formula [PtPMe₃ClNH₃NO₂] (you may assume that nitrite binds to platinum only through the nitrogen atom).

- (b) What is the platinum oxidation state in these molecules?
- (c) Give methods of selectively synthesizing two of the isomers you gave in part (a), starting with either $PtCl_4^{2-}$ or $Pt(NO_2)_4^{2-}$.

(9) Consider the isomerization reaction shown below.



(a) What is the oxidation state of cobalt in these complexes.

(b) In the presence of a trace of the pentacyanocobalt(II) ion, $[Co(CN)_5]^3$, the rate of this isomerization reaction can be significantly accelerated. By means of appropriate equations, show why the rate enhancement occurs.

(10) The water exchange rates for some of the first-row divalent transition metal ions are given below.

$$[M(H_2O)_6]^{2+} + H_2O^* \rightarrow [M(H_2O)_5(H_2O^*)]^{2+} + H_2O$$

rate constants:

ie constants: $V^{2+}: 8 \times 10^{1}$ Ni²⁺: 5×10^{4} Co²⁺: 4×10^{6} Fe^{2+} : 5×10^{6} Mn²⁺: 3×10^7 Cu²⁺, Cr²⁺: 1×10^9

- (a) Give the ligand field stabilization energies (LFSEs) for each these aquo ions (note the position of water in the spectrochemical series).
- (b) Which two metals are most clearly "in the wrong order" if LFSEs alone are used to rationalize the relative rates of exchange? How is this explained?

(c) What *trivalent* aquo ions have the slowest water exchange rates? Why?

(11) In the complex, $[RuCl(NH_3)_4(SO_2)]^+$, the ruthenium atom lies in the same plane as the SO₂ unit:



Like virtually all other ligands, SO₂ is a σ donor.

Using symmetry adapted combinations of the two oxygen $p\pi$ orbitals and the sulfur $p\pi$ orbital, <u>construct a diagram for the π molecular orbitals (only)</u> of SO₂ in the space below. Be as accurate as possible — take into account the electronegativity difference between oxygen and sulfur in the relative energies used and in your drawings of the MOs. Show which π orbitals are occupied.

<u>Does SO₂ behave as a π -acceptor or a π -donor in this complex?</u> Specifically, indicate whether the highest occupied SO₂ π orbital can function as a π -donor to Ru or whether the lowest unoccupied π orbital on SO₂ can function as a π -acceptor from Ru (take into account the d electron configuration in this octahedral complex).