Chemistry 6011 (Fall 2016) Advanced Inorganic Chemistry I: From Atoms to Coordination Compounds Problem Set #3

## Chapter 6-

1. Define the equations for the Latimer diagram of iron (Appendix B). Assume the conditions are acidic. Which steps are spontaneous?

## Chapter 9 and 10-

1. Name the following compounds:

a. [Cu(NH<sub>3</sub>)<sub>4</sub>][PtBr<sub>4</sub>]

b. [Co(en)<sub>2</sub>Cl(NO<sub>2</sub>)]Cl

c. Na<sub>3</sub>[Al(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub>]

d. W(CO)<sub>5</sub>PMe<sub>3</sub>



- 2. Write structural formulas for the following:
- a. diamminetriaquahydroxochromium(III) nitrate
- b. tetrakis(pyridine)platinum(II) tetraphenylborate
- c. dibromotetracarbonyliron(II)

 $d.\ tetraammine cobalt (III)-\mu-amido-\mu-hydroxobis (ethylene diamine) cobalt (III)$ 

3. How might Werner have been able to distinguish between the following two formulations for a compound:  $[Co(NH_3)_5]Cl_3$  and  $[Co(NH_3)_5Cl]Cl_2$ ? The cation would be trigonal bipyramidal in the former and octahedral in the latter.

4. To show your understanding of basic bonding models, describe the bonding in  $[NiF_4]^{2-}$  with each of the following:

a. Valence bond theory

b. Crystal field theory

c. Molecular orbital theory

5. What bond angle would you expect for M-O-R

a. if there is no metal-oxygen  $\pi$  bonding?

b. if the alkoxide donates two  $\pi$  electrons?

c. if the alkoxide donates four  $\pi$  electrons?

6. If one  $[CuL_6]^{2+}$  solution is blue and another is green, which would be expected to have the higher value of  $\Delta_0$ ?

7. Write K and  $\beta$  expressions for the proton affinity of a tetraprotic ligand.

8. Write K and  $\beta$  expressions for the metal affinity of a tetraprotic ligand, which binds in a ratio of 1:1 metal:ligand.

9. A complex of nickel(II),  $[NiCl_2(PPh_3)_2]$ , is paramagnetic. The analogous complex of palladium(II) is diamagnetic. Predict the number of isomers that will exist for each of these formulations.

10. Determine the equilibrium constant for the following chemical reaction.

 $Ni(H_2O)_6^{2+}$  + 6 NH<sub>3</sub>  $\leftrightarrow$   $Ni(NH_3)_6^{2+}$  + 6 H<sub>2</sub>O  $\Delta G^\circ = -51.8 \text{ kJ/mol}$ 

Would you expect a major change in entropy?

11. Draw out all the isomers, geometric and optical, of the following:  $[Co(en)_2Cl_2]^+$  and  $[Co(en)_2(NH_3)Cl]^{2+}$ 

12. Draw the molecular structure of the following complexes:

- a. cis-dichlorotetracyanochromate(III)
- b. mer-triamminetrichlorocobalt(III)
- c. *trans*-dichlorobis(trimethylphosphine)palladium(II)
- d. *fac*-triaquatrinitrocobalt(III)

13. The macrocycle ligand enterobactin has an extremely high affinity for Fe(III) with a stability constant of  $10^{52}$  (the largest known stability constant for Fe(III) with a naturally occurring substance).



Harris, W.R.; Carrano, C. J.; Cooper, S.R.; Soften, S. R.; Aydeef, A.E.; McArdle, J.V.; Raymond, K.N. *J. Am. Chem. Soc.* **1979**, *101*, 6097-6104.

a. Suggest a structure for the Fe(III) enterobactin complex that explains its high stability.

b. If the concentration of the Fe(III)-enterobactin complex within the microorganism is  $10^{-7}$  mol/L, how many liters of bacteria would have to be searched to find a single free Fe(III) ion?