HW 6
CHEM 362

Due: October 29, 2019

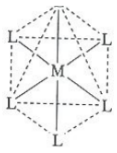
1. Define the terms *lability*, *labile*, and *inert*. Are these thermodynamic issues or kinetic issues?

Labile – ligands that are easily substituted
Lability – refers to the ability of a coordination complex to lose one or more of it's ligands with others in solution
Inert – refers to the lack of ability of a coordination complex to lose one or more of its ligands with others in solution

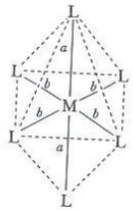
Kinetic issues.

2.

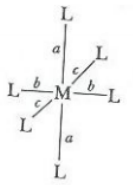
a. Draw a regular octahedron



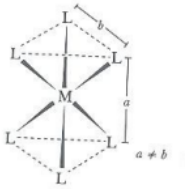
b. Draw all the ways a regular octahedron can be distorted, and explain in words how each distortion is achieved.



Axial distortion: a ≠ b
Stretch (or compress) along the axial direction



Rhombic distortion a ≠ b ≠ c
Three distinct M-L distances



Trigonal distortion
Compression or elongation along the axis containing two opposite faces

c. What is the rarest distorted geometry? Why?

Trigonal distortion
L-L distances are not maximized

3. What are the differences between the **trans influence** and the **trans effect**? How can the presence of the trans influence be determined? *Hint: which one is a thermodynamic effect? Which one is a kinetic effect? And why does that matter?*

Trans effect - the ligand promotes faster substitution rates for ligands trans to itself than ligands cis to itself. *Kinetic effect*

Trans influence- The ligands that are trans to strong ligands have longer (therefore weaker) bonds so they are substituted more easily. *Thermodynamic effect*

Can be determined by studying bond lengths observed in the crystal structure, also coupling constants, stretching frequencies, etc. there can be vatied answers to why does it matter..

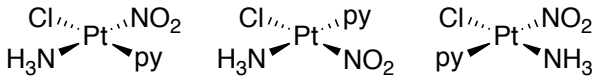
4. Draw the reactions and give the products (and include the proper IUPAC name) for the following reactions. Explain how you arrived at the product.
   a. $[Rh(Cl)_3(CO)]^{2-}$ with one equivalent of PPh_3

Product: *trans*-$[Rh(Cl)_2(CO)(PPh_3)]^-$ + Cl^-
Substitution occurs trans to the strongest trans effect ligand CO > Cl

   b. $[AuI_4]$ - with first one equivalent of PPh_3 followed by one equivalent of py.

***trans*-$[Au(I)_2(py)(PPh_3)]^+$ + 2 I**
The first substitution occurs can only give $[Au(I)_3(PPh_3)]$ and the second substitutes trans to the stronger trans effect ligand, PPh_3 > I-

5. Consider the compound $Pt(py)NH_3NO_2Cl$.
   i. Draw the three isomers of this compound



   ii. Using the trans effect sequence given in the text, devise rational procedures for selectively synthesizing each of the three isomers

Many correct answers. No credit if reaction to get to the product is incorrect.

6. What are the 6 types of reactions that octahedral complexes can undergo? Describe each and be sure to write the chemical reactions for any relevant or important steps in the reaction mechanism.

solvent interactions – solvent molecule can be involved in formation of final product
ion pair formation – form ion par [+][-] by electrostatic interactions
conjugate base formation – base reacts with coordinated ligand, leading to other reactivity. Note base catalysis
anation – addition of an anion and substitution of a neutral ligand
aquation – replacement of ligand with water

ligand assisted reactions – breaking of bonds within coordinating ligands, leads to other reactivity

7. Square planar complexes can undergo substitution reactions
   a. Write the general formula for this type of reaction

      $ML_3X + Y \rightarrow ML_3Y + X$

   b. What is the overall rate law?

      Rate = $k_1[ML_3X] + k_2[ML_3X][Y]$

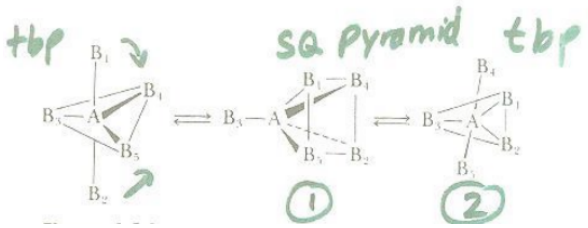
   c. What does this rate law tell you about the available reaction path(s)? Describe these path(s) in detail.

      The rate law indicates that there are two available paths

      A first order path with k1 rate constant This path involves a two-step process (one slow and one fast) in which X is first replaced by water in the rate-determining step and then the water is replaced by Y in the second (fast step)

      A second order path with k2 rate constant which involves direct replacement of X by Y

8. Square pyramidal complexes can be considered fluxional
   a. Show with drawings how axial-equatorial exchange in a square pyramidal complex AB_5 could occur through a trigonal bipyramidal intermediate.



   b. For the compound PCl_2F_3,, how many ^{19}F-NMR signals would you expect to see at room temperature? How signals many would you expect to see if the experiment was performed at a temperature that prevented a fluxional process? Explain

      One at room temperature, and two at low temperatures.

      Would be able to see both axial and equatorial fluorine signals if no fluxionality due to the pseudorotation process being stopped.