Chem 64 Problem Set 2: Molecular Symmetry and Group Theory

1. SA chapter 4: Exercises 4.1-4.6 and 4.11; Problems 4.1 and 4.2

[For exercise 4.3f (BF₄⁻) beware of a typo in the solutions manual: this ion is tetrahedral.]
[For Exercise 4.2, see Strauss page 54. The question asks if an S₄ axis is present, but the manual doesn't answer it for parts a and b. Since there is an S₀₀ axis in the D₀₀h point group appropriate for a and b, it includes an S₄ axis as well.]

2. Find the point groups for:
   (a) trans-PtCl₂(NH₃)₂ (square planar Pt; ignore the H's)
   (b) cis-[CrCl₂(H₂O)₄]⁺ (octahedral Cr; ignore the H's)
   (c) XeF₂
   (d) XeF₄

3. Give the symmetry designations of the s, p, and d metal orbitals for each molecule in problem 2, parts a-i. [Hint, look in the character tables!]

For e, f, and g, it will help to build the molecules; you may need to build two models of each one, so you can confirm that a symmetry operation doesn't change the structure. If you don't have enough atoms in your kit, do it with a classmate. Assume the ligand N~N has CH₂ linkers, as shown. To see the symmetry of (e) more conveniently, play with paper and scissors as on the next page.

(h) ferrocene (eclipsed conformation)
(i) ferrocene (staggered conformation) See the text pp. 124-125 for helpful pictures.
4. Give the point groups of these molecules, using VSEPR to find their structure if needed.
   i. benzene                      ii. chlorobenzene
   iii. 1,2-dichlorobenzene        iv. 1,4-dichlorobenzene
   v. 1,3,5-trichlorobenzene       vi. 1,3-dichlorobenzene
   vii. B\textsubscript{2}Cl\textsubscript{4} (planar, with a B-B bond)  viii. [InCl\textsubscript{6}]\textsuperscript{3-}
   ix. [SnCl\textsubscript{3}]\textsuperscript{-}
   x. cis and trans N\textsubscript{2}F\textsubscript{2} (planar, with N-N double bonds)
   xi. NSF                           xii. I\textsuperscript{3}\textsuperscript{+} and I\textsuperscript{3}\textsuperscript{-}

5. (a) Consider the square pyramidal complex [VOCl\textsubscript{4}]\textsuperscript{2-}. Using a vector placed along the V-O bond, determine the symmetry of the V-O stretching vibration.

   \[ \text{[VOCl}_4\text{]}^2\text{-} \]

6. Reduce the following representations to their corresponding irreducible representations.

   \[
   \begin{array}{ccccccc}
   \text{C}_{6\text{v}} & \text{E} & 2\text{C}_6 & 2\text{C}_3 & \text{C}_2 & 3\sigma_y & 3\sigma_d \\
   \Gamma & 7 & 1 & 1 & 1 & -1 & -3 \\
   \hline
   \text{D}_{2\text{d}} & \text{E} & 2S_4 & \text{C}_2 & 2C_2' & 2\sigma_d \\
   \Gamma & 5 & 1 & -3 & -1 & -1 \\
   \hline
   \text{T}_{\text{d}} & \text{E} & 8C_3 & 3C_2 & 6S_4 & 6\sigma_d \\
   \Gamma & 8 & -1 & 0 & -2 & 2 \\
   \end{array}
   \]

7. The octahedral anion [MnBr\textsubscript{2}(CO)\textsubscript{4}]\textsuperscript{-} exhibits 4 CO stretching bands in its IR spectrum. Are the Br ligands cis or trans to each other? Explain your answer.
Cut out the circle and make two half-circles by cutting on the solid line. Then make cuts along the dotted lines so you can put semicircles A and B together at a 90° angle to get the right symmetry for this problem. Final hint: compare to allene!