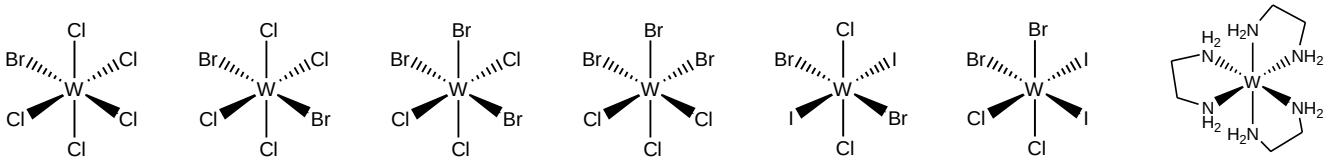
# Chemistry 529
# Problem Set #1 – Symmetry and Group Theory

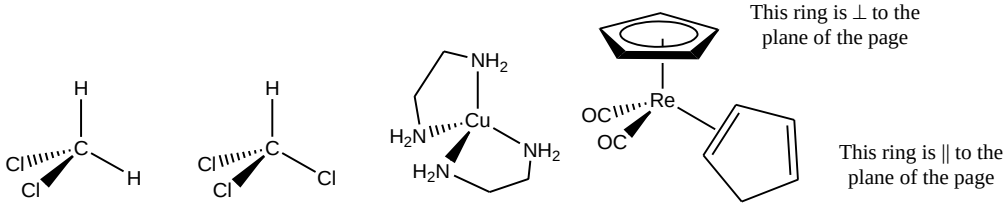
1. Assign each of the following species to their proper point group.

   a) In the following, all L-M-L angles are 90° (ignore all protons):



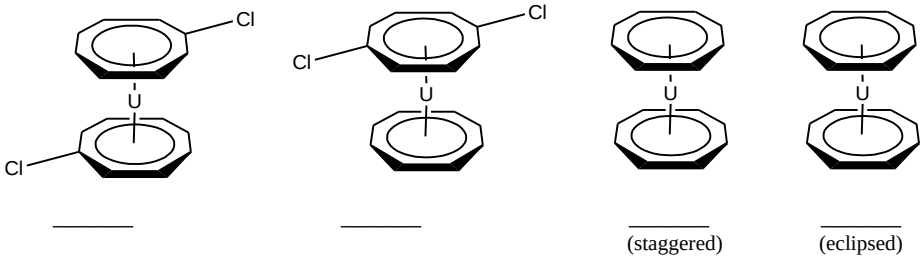
_____ _____ _____ _____ _____ _____ _____

   b) In the following, all L-M-L angles are 109.5°:

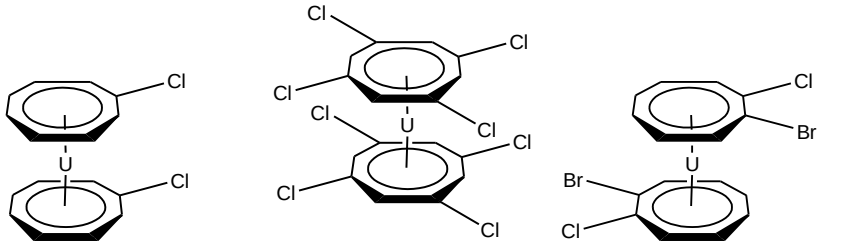



_____ _____ _____ _____

   c) Rings, rings, and more rings…

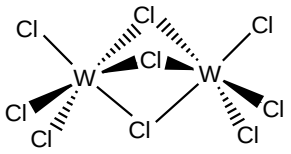


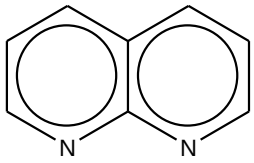
_____ _____ _____ (staggered) _____ (eclipsed)

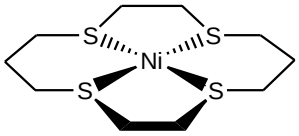


_____ _____ _____

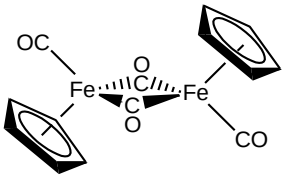
d) And now for a few more difficult examples

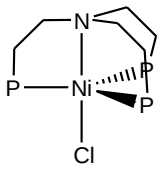


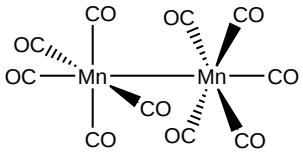




(planar)




2. In the $O$ point group, show that the functions $(x, y, z)$ and $(xy, yz, xz)$ correspond to the $T_1$ and $T_2$ irreducible representations, respectively.

3. Determine the symmetry of vibrations that can be excited using electric dipole selection rules for molecules of $C_{4v}$ and $D_{3d}$ symmetry. *Hint:* you will need to evaluate the transition moment integral for vibration absorption transitions, *i.e.*, $\left\langle \Psi^{\Gamma_i}_{\nu=0} \middle| \hat{\mu} \middle| \Psi^{\Gamma_i}_{\nu=1} \right\rangle$.

4. Consider $PF_5$.

   a) What are the SALCs constructed from σ orbitals on F atoms that can be employed to form the P-F bonds in $PF_5$?

   b) What are the symmetries of the valence orbitals available on P?

   c) Which of the orbitals in (b) will be involved in forming P-F bonds? From this, how many bonds are holding the molecule together?

5. Consider an octahedral first-row transition metal complex ($ML_6$). In such complexes, the metal orbitals involved in bonding are generally the 3*d*, 4*s*, and 4*p* orbitals. If one of the ligands is removed, a square pyramidal $ML_5$ complex is formed and if the ligand that is *trans* to the open coordination position is removed, we finally obtain a square planar complex, $ML_4$.

   a) Determine the symmetry of the metal orbitals that might be involved in bonding for each of the three species described above.

   b) Based on part (a), what is the effect of lowering the symmetry on the nature of the metal 3d orbitals? ("nature" = the orbital wavefunction, not energies)

6. Briefly describe (in your own words) the similarities and differences between valence bond theory and molecular orbital theory. How does symmetry and group theory fit into each of these?