

**5.112 Extra Problems**  
**d-orbitals, transition metals, etc.**

1. From chapter 3: 3.54, 3.56, 3.72, 3.80, 3.92.
2. Molecular orbitals for the metal complex  $[\text{Tc}(\text{CO})_3(\text{NH}_3)_3]^{1+}$ .
  - a. download the file “molecule.iv”
  - b. Open the file “molecule.iv” in ivview.
    - i. There are 2 possible geometries for the  $[\text{Tc}(\text{CO})_3(\text{NH}_3)_3]^{1+}$  molecule. Octahedral complexes of this sort are designated either *fac* or *mer* (facial or meridional) depending on whether three ligands of the same type lie all in the same plane (*mer*) or not (*fac*). Which type of  $[\text{Tc}(\text{CO})_3(\text{NH}_3)_3]^{1+}$  do you see? Rotate it around to be sure.
    - ii. Draw the other isomer of  $[\text{Tc}(\text{CO})_3(\text{NH}_3)_3]^{1+}$ . Use wedges to indicate bonds to Tc that are above the plane of the paper, dashed lines to indicate bonds below.
  - c. Download the file “homo.iv” and open it in ivview.
  - d. Your initial view of the HOMO is down the z axis. You can rotate the orbital on screen to get a feel for its nodal properties.
    - i. Does the d orbital that contributes to the HOMO look to be a member of the  $t_{2g}$  or of the  $e_g$  set? Specify which, and explain. (Hint: see Figure 16.39 of your text.)
    - ii. In the HOMO there are visible bonding interactions between the Tc atom and how many of the carbonyl C atoms?
    - iii. Which molecular orbital from CO steals electron density from Tc in the HOMO of  $[\text{Tc}(\text{CO})_3(\text{NH}_3)_3]^{1+}$ ?
    - iv. If you consider the interaction between Tc and a particular C atom, would it be best described as  $\sigma$  or as  $\pi$  in symmetry?
    - v. Is there a nodal surface in the HOMO that is midway between C and O ?
    - vi. Is there bonding between any of the ammonia molecules and Tc in the HOMO?
  - e. Download the file “homo\_1.iv” and open it in ivview.
    - i. Is HOMO\_1 similar to the HOMO in appearance and nodal properties?

- ii. To how many of the CO ligands is Tc simultaneously bonding with in the HOMO\_1?
- f. Download the file “homo\_2.iv” and open it in ivview.
- i. To how many of the CO ligands is Tc simultaneously bonding with in the HOMO\_2?
  - ii. There is a blue lobe of HOMO\_2 situated between the three ammonia ligands. Rotate the orbital around until you can see this lobe clearly. Which of the d orbitals participates in HOMO\_2? Hint: compare the appearance of HOMO\_2 with Figure 16.28 (page 632 of your textbook).
- g. Download the file “lumo.iv” and open it in ivview.
- i. To how many of the NH<sub>3</sub> ligands is Tc simultaneously *antibonding* with in the LUMO?
  - ii. Is the LUMO more likely to be a member of the t<sub>2g</sub> or of the e<sub>g</sub> set?
  - iii. Is the NH<sub>3</sub> interaction in the LUMO of a  $\sigma$  or is it of a  $\pi$  type?
- h. Download the file “lumo1.iv” and open it in ivview.
- i. Is the LUMO1 similar to the LUMO with regard to the number and type of interactions with NH<sub>3</sub> ligands? Explain.
  - ii. Putting electrons into the LUMO or LUMO1 (as by treatment with a reducing agent) should lead to weakening of (a) the Tc-C or (b) the Tc-N bonds. Pick one and explain.
- i. The term  $\Delta_o$  (see Figure 16.29 and accompanying text) corresponds to the gap between which orbitals of  $[\text{Tc}(\text{CO})_3(\text{NH}_3)_3]^{1+}$ ? Please refer to the orbitals by their file names.
- j. How many electrons populate the five orbitals we have inspected? Show how to calculate this.
3. Draw a completely labeled set of d orbitals using shading to represent negative lobes. For each of the orbitals, indicate the orientation relative to the Cartesian coordinate axes.
4. From chapter 16: 16.26, 16.30, 16.32, 16.38, 16.40, 16.48, 16.50, 16.58.