Ch153a
Winter 2020
Due 31 January, 2020

Problem Set 4

1. Low-spin d^6 metal hexacarbonyl compounds exhibit two intense ($\varepsilon > 10^4$ M^{-1} cm^{-1}) absorption bands in the ultraviolet region of the spectrum; peak positions are listed in the following table.

Compound	$Cr(CO)_6$	$Mo(CO)_6$	$W(CO)_6$	$V(CO)_6^-$	$Mn(CO)_6^+$	$Re(CO)_6^+$
$\nu_{1,max}$ (cm^{-1})	35,700	34,600	34,650	28,400	44,500	44,500
$\nu_{2,max}$ (cm^{-1})	43,600	42,800	43,750	37,550	49,900	51,200

   a. Construct an MO diagram for d^6 metal hexacarbonyl compounds assuming O_h symmetry using: five metal *nd* orbitals; one metal (*n*+1)*s* orbital; three (*n*+1)*p* orbitals; six CO σ orbitals; twelve CO π orbitals; and twelve CO π^* orbitals. Give the electronic configuration and term symbol for the ground electronic state.

   b. Propose assignments for the two intense ultraviolet absorption bands in each compound. Identify the one-electron transitions giving rise to the bands and the term symbols for the resulting excited states.

2. John Ellis and coworkers have synthesized and partially characterized $Na_3[Nb(CO)_5]$ and $Cs_3[Nb(CO)_5]$ (*Inorg. Chem.*, **1998**, *37*, 6518-6527).

   a. What is the oxidation state of Nb in these compounds? Give references for any examples that you can find of complexes with metals in even lower oxidation states.

   b. Based on the IR spectrum of $Cs_3[Nb(CO)_5]$ shown in Figure 2 of the Ellis paper, propose and discuss the geometrical structure of $Nb(CO)_5^{3-}$.

   c. Based on the symmetry of your proposed structure, construct an MO diagram for the Nb anions using: five metal *nd* orbitals; one metal (*n*+1)*s* orbital; three (*n*+1)*p* orbitals; five CO σ orbitals; ten CO π orbitals; and ten CO π^* orbitals. Give the electronic configuration and term symbol for the ground electronic state.

   d. Ellis also reports $Nb(PF_3)_6^-$ and compares it to $Nb(CO)_6^-$. Do you think PF_3 is a better π-acceptor than CO? Why or why not?