

Recommended Reading: 20, 21.2-21.4, 13 (3rd edition); 19, 20.2-20.4, 13 (4th edition)

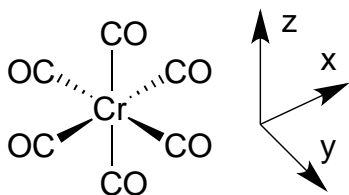
Ch 102 – Problem Set 5

Due: Thursday, May 12 – Before Class

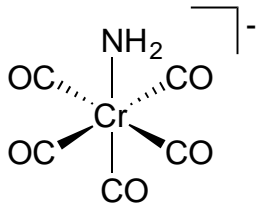
Problem 1 (2 points)

Part A

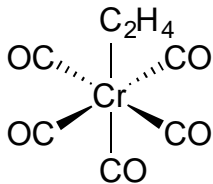
a) Sketch the MO d-splitting diagram for the metal carbonyl complex $\text{Cr}(\text{CO})_6$, as derived in class. Only show the five d orbitals and populate with electrons. What are the d and valence electron counts? Clearly label the d parentage of each MO and the HOMO and LUMO. Draw HOMO and LUMO (for degenerate sets draw only one example of MO). Make sure to represent backbonding to $\pi_{\text{C-O}}^*$ if appropriate.



b) Derive a new d splitting diagram for the chromium-amide complex below. First assume no π -interaction between N and Cr, and that the σ -interaction is similar to that of CO. Sketch this diagram. With the same axes as above, assume that the NH_2 fragment is planar and located in the xz plane. Now sketch a new MO diagram and provide the d and valence electron count assuming a strong π -donation interaction from the amide to the metal. Clearly label the d parentage of each MO. Label the HOMO and LUMO and sketch them. What is the nature of the HOMO in terms of the Cr-N interaction (bonding, non-bonding, vs anti-bonding and σ vs π). What is the bond order for the Cr-N bond? Based on the electron count and MO analysis derived above, discuss how a π -interaction from the amide to the metal might affect stability.



c) Derive a new d splitting diagram for the chromium-ethylene complex below. With the same axes as above, assume that the C-C vector is located in the xz plane. Clearly label the d parentage of each MO. Label the HOMO and LUMO. Sketch the molecular orbital corresponding to the Cr-ethylene interaction. What is the nature of this MO (bonding, non-bonding, vs anti-bonding and σ vs π). Provide the d and valence electron count. How do you expect the average CO stretching frequency to change in this compound compared to the one in question b) above?



Part B

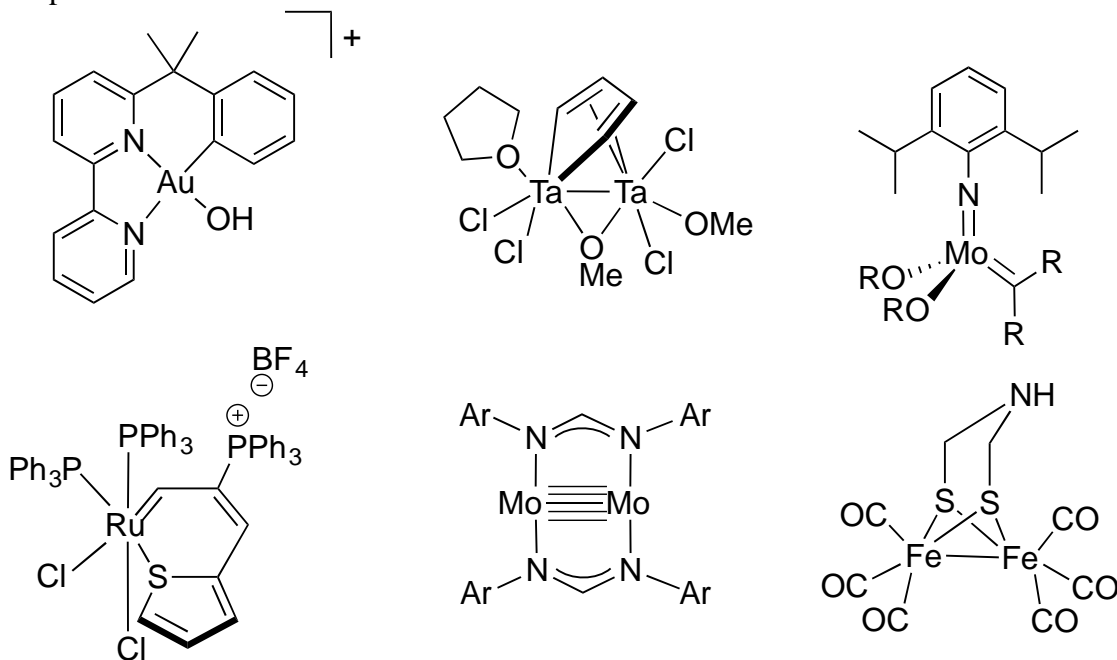
For each pair of complexes, predict which has the larger *d-d* splitting, and explain all the relevant factors in your reasoning (do not just cite trends; explain them).

- $[\text{Cr}(\text{OH}_2)_6]^{3+}$ vs. $[\text{Cr}(\text{NH}_3)_6]^{3+}$
- $[\text{Fe}(\text{CN})_6]^{4-}$ vs. $[\text{Ru}(\text{CN})_6]^{4-}$
- $[\text{NiCl}_4]^{2-}$ vs. $[\text{Fe}(\text{oxalate})_3]^{3-}$
- $[\text{Co}(\text{phen})_3]^{3+}$ vs. $[\text{Co}(\text{NH}_3)_6]^{3+}$
- $[\text{Fe}(\text{OH}_2)_6]^{3+}$ vs. $[\text{Fe}(\text{OH}_2)_6]^{2+}$
- $[\text{PdCl}_4]^{2-}$ vs. $[\text{PtCl}_4]^{2-}$

Problem 2 (2 points)

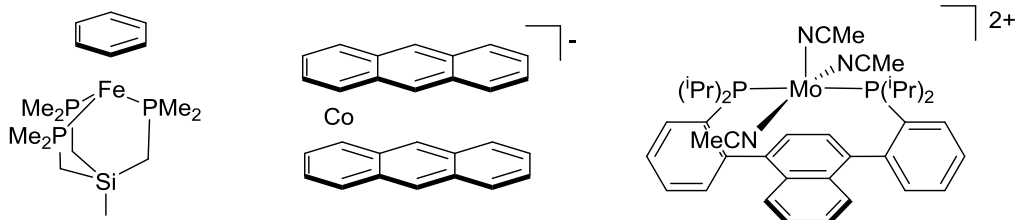
Part A

Give the oxidation state, d-electron count, and valence electron count for the following compounds:



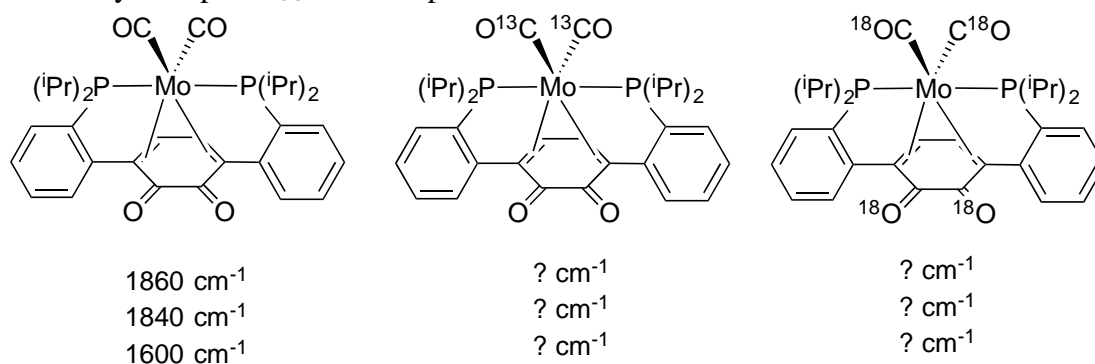
Part B

The following are all 18-electron compounds that exhibit a metal-arene interaction (with the central arene). Redraw each compound showing the metal-arene interaction and specify the hapticity (i.e. η^2 , η^3 , η^4 , η^5 , or η^6). Give the oxidation state and the d-electron count.



Part C

Some IR data is given for the first compound below. Note that, for this system, bands between $1800\text{-}2000\text{ cm}^{-1}$ are assigned to ν_{CO} of metal carbonyl moieties and bands between $1600\text{-}1700\text{ cm}^{-1}$ are assigned to ν_{CO} of organic (quinone) moieties. For each isotopologue, give the expected C–O stretching frequency of the metal carbonyl and C=O of the central arene. Show your work. How do you expect ν_{CO} to shift upon reduction?



Problem 3 (2 point)

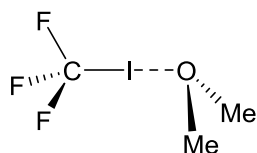
Part A

Hydrogen bonding is common interaction observed in both natural and synthetic chemical systems. Shown below are two examples of hydrogen bonding between hydrogen bond donor methanol and acceptors dimethyl ether (DME) and dimethyl sulfide (DMS). The enthalpies of association (ΔH) were experimentally determined via temperature dependent vibrational spectroscopy.

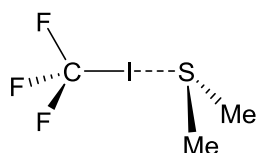


Halogen atoms may form analogous interactions in which a halogen bond donor interacts with a halogen bond acceptor. Halogen bonding has been found to play significant roles in nature,

including the enzymatic recognition of thyroid hormones, which contain iodine. Below are examples of halogen bonding interactions between trifluoromethyl iodide (CF_3I) and DME and DMS. The enthalpies of association were determined via temperature dependent vibrational spectroscopy.



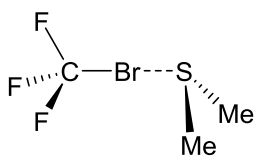
$$\Delta H = -15.5 \text{ kJ}\cdot\text{mol}^{-1}$$



$$\Delta H = -17.4 \text{ kJ}\cdot\text{mol}^{-1}$$

a) For all four interactions above ($\text{MeOH}\cdot\text{DME}$, $\text{MeOH}\cdot\text{DMS}$, $\text{CF}_3\text{I}\cdot\text{DME}$, and $\text{CF}_3\text{I}\cdot\text{DMS}$) determine which molecule is acting as the Lewis acid and which as the Lewis base. Then, using hard and soft acid and base (HSAB) theory, explain the experimentally observed trend in ΔH for MeOH versus CF_3I .

Trifluoromethyl bromide (CF_3Br) also complexes with DMS and the enthalpy of association is shown below.



$$\Delta H = -9.5 \text{ kJ}\cdot\text{mol}^{-1}$$

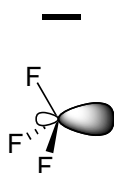
This value can be compared with the enthalpy of association for $\text{CF}_3\text{I}\cdot\text{DMS}$ ($-17.4 \text{ kJ}\cdot\text{mol}^{-1}$), showing that the iodine forms a stronger halogen bonding interaction than bromine. Derive a simplified molecular orbital diagram to provide insight into this observation.

b) Consider the interaction between a trifluoromethyl sp^3 -hybridized orbital and the p_z orbital of bromine and iodine, respectively. On the diagram provided, place the p_z orbital of bromine (on the left) and iodine (on the right), keeping in mind the relative energies of these two atomic orbitals. Show the interaction of the Br_{p_z} and I_{p_z} generating the σ and σ^* orbitals for each. Be sure to demonstrate how the relative energies of the atomic orbitals affect the relative energies of the molecular orbitals generated in each case. *Note: Assume that the sp^3 carbon orbital is lower in energy than both Br and $\text{I } p_z$ orbitals due to the electron withdrawing nature of the fluorines.*

Br

 F_3C-Br $F_3C(sp^3)$ F_3C-I

I

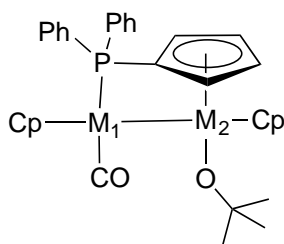


c) Using this molecular orbital picture, explain why CF_3I forms a stronger interaction with dimethyl sulfide than CF_3Br .

Part B

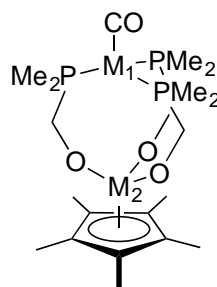
a) Early-late heterobimetallic complexes are of interest due to the unusual cooperative reactivity that can be observed that neither metal individually would be capable of doing. For the following early-late heterobimetallic complexes, assign the metal binding site for the early metal and late metal based on HSAB theory. Provide a short reasoning for your assignment.

Zr^{3+} and Fe^{1+}



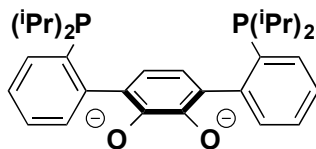
$M_1 =$
 $M_2 =$

Ni^0 and Zr^{4+}

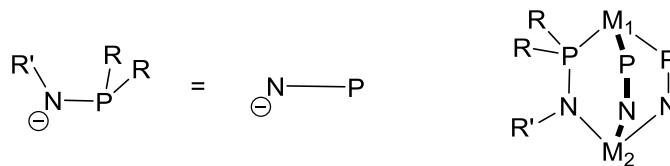


$M_1 =$
 $M_2 =$

b) Consider the ligand below. How do you expect Ni^0 and Ti^{4+} to bind based on HSAB theory?



c) A ligand that has been employed to support early-late heterobimetallic complexes is the phosphine-amide ligand shown below. Three-fold symmetric complexes can be synthesized as shown on the right.

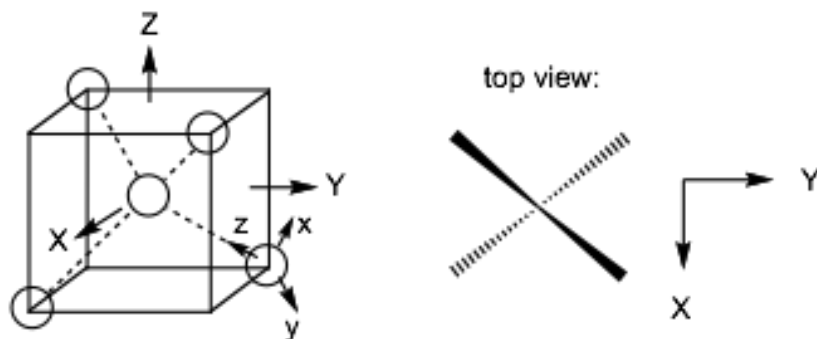


For the following metal combinations, which metal binding site (M₁ or M₂) do you expect each to occupy?

Zr(IV)	Co(II)
Cu(I)	Hf(IV)

Problem 4 (2 points)

Permanganate MnO_4^- is a tetrahedral ion with an intense purple color that is widely used as an oxidizing agent. The figure below shows a convenient coordinate system for a tetrahedral complex that will be useful for generating a molecular orbital diagram for permanganate. You are asked to first examine the structurally similar PO_4^{3-} .



a) Using the coordinate system shown above, generate the reducible and irreducible representations for the ligand σ -bonding interactions (note that there are two orbitals on oxygen that have σ -symmetry with respect to the P-O and Mn-O interaction; for this problem consider only one σ -orbital per oxygen, the second will formally constitute a low energy lone pair on oxygen that should not be included in your analysis).

b) For PO_4^{3-} : Draw an MO diagram incorporating the ligand σ -bonding framework and s and p orbitals on P. For full credit, be sure to do all of the following:

- Label the generated molecular orbitals with the appropriate Mulliken symbols and indicate whether they are σ , σ^* , or nb
- Fill in the correct number of electrons
- Draw the HOMO and LUMO (if degenerate sets, only draw one MO per set)

c) Generate the reducible and irreducible representations for the ligand π -bonding interactions (two π -interactions per ligand)

d) Draw a complete MO diagram incorporating both σ - and π -bonding ligand orbitals and s and p orbitals on P. For full credit, be sure to do all of the following:

- Label the generated molecular orbitals with the appropriate Mulliken symbols and indicate whether they are σ , σ^* , π , π^* , or nb
- Fill in the correct number of electrons
- Draw the HOMO and LUMO (if degenerate sets, only draw one MO per set)

e) For MnO_4^- : Draw an MO diagram incorporating the ligand σ -bonding framework and d, s, and p orbitals on Mn. For full credit, be sure to do all of the following:

- Label metal orbitals with the appropriate Mulliken symbol and designate them as d, s, or p
- Draw the metal and ligand orbitals at the appropriate relative energies (remember that due to oxygen's high electronegativity all of its orbitals will be lower in energy than the manganese orbitals).
- Label the generated molecular orbitals with the appropriate Mulliken symbols and indicate whether they are σ , σ^* , or nb
- Fill in the correct number of electrons
- Draw the HOMO and LUMO (if degenerate sets, only draw one MO per set)

f) Draw a complete MO diagram incorporating both σ - and π -bonding ligand orbitals and d, s, and p orbitals on Mn. For full credit, be sure to do all of the following:

- Label metal orbitals with the appropriate Mulliken symbol and designate them as d, s, or p
- Label ligand orbitals with the appropriate Mulliken symbol and designate them as σ or π
- Draw the metal and ligand orbitals at the appropriate relative energies
- Label the generated molecular orbitals with the appropriate Mulliken symbols and indicate whether they are σ , σ^* , π , π^* , or nb
- Fill in the correct number of electrons
- Draw the HOMO and LUMO (if degenerate sets, only draw one MO per set)

g) Based on the MO diagrams derived at f) and d) what is the correct valence electron count for Mn and P, respectively?

Problem 5 (2 points)

Pick a topic of interest from the recommended reading (descriptive chemistry) in bold at the beginning of this problem set. Prepare two power point slides including relevant *descriptive chemistry* (background on synthesis, applications, reactivity, properties, trend, etc, as applicable), some concepts presented in class (oxidation states, electron count, symmetry, MO theory, vibrational spectroscopy, etc.) and some application of the provided software (since MO theory and vibrational spectroscopy were covered in class, *you are now expected to include some molecular orbital pictures / MO diagram analysis / IR/Raman analysis using the provided software*). Submit the slides in pdf format to the TAs by 12:00 noon (Thursday, May 12, 2015), and turn in a printout of the slides with your problem set.