

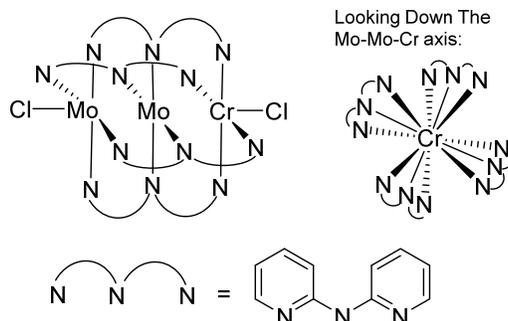
2018 Ch112 – problem set 4

Due: Thursday, Nov. 15 – before class

Problem 1 (2 points)

Consider the MoMoCr heterotrimetallic complex shown below (Berry, et. al. *Inorganica Chimica Acta* **2015**, p. 241). Metal-metal bonds are not drawn. The ligand framework distorts this structure so that it is in the C_4 point group, as seen by looking down the CrMoMo axis. For this problem assume C_{4v} symmetry.

a. Assign an average oxidation state for the metal centers and total number of d-electrons in this molecule:



b. Draw a qualitative MO diagram for the Mo-Mo interaction in the C_{4v} point group, using the ten Mo d-based orbitals as your basis set. Ignore Cr for this part. The z axis is along the M-M vector.

- Assign Mulliken symbols
- Label each orbital with the type of interaction (nb, σ , σ^* , etc)
- Fill in the diagram with electrons assuming the average oxidation state as above. Predict the spin state of this fragment.
- Determine the Mo-Mo bond order

c. Starting from your answer to part b, draw the qualitative MO diagram for the Mo-Mo-Cr interaction. Consider whether atomic orbitals/molecular orbitals will mix significantly based *not only* on their symmetry, but also spatial overlap. Assume that the Mo & Cr based atomic orbitals are approximately equal in energy. Note that the crystallographic Mo-Mo bond distance is 2.098 Å and the Mo-Cr bond distance is 2.689 Å.

- Assign Mulliken symbols
- Label each orbital with the type of interaction (nb, σ , σ^* , etc)
- Fill in the diagram with electrons
- Predict the Mo-Cr and Mo-Mo bond orders.

d. Draw the Mo-Mo-Cr molecular orbitals that correspond to the interactions between the three metals that have σ and π symmetry with respect to the z axis. Comment on their bonding / non-bonding / antibonding character.

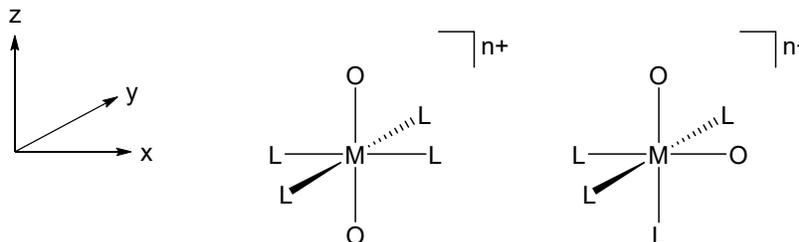
e. Magnetic susceptibility experiments on the Mo-Mo-Cr trimetallic are consistent with a quintet ground state ($S = 2$). Rationalize the experimental result and discuss in the context of potential lower spin electronic configurations.

f. How do you expect the MO diagram to change for an analogous Mo-Mo-Mo complex of D_{4h} symmetry? Predict the bond orders of the two Mo-Mo interactions.

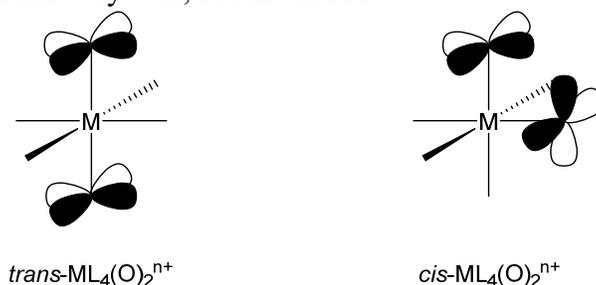
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Problem 2. (3 Points)

For an octahedral metal-dioxo complex ($ML_4(O)_2^{n+}$), there are two possible geometries: one in which the oxo moieties lie *trans* to each other, and one in which they lie *cis*.



1. Assign the point groups of both *trans*- and *cis*- $[ML_4(O)_2]^{n+}$.
2. Begin with the *trans* isomer only. First, determine the irreducible representations for the ligand-based SALCs in the point group from part 1 and the given coordinate system. Derive the irreducible representations for the four equatorial L ligands ($\Gamma_{4L\sigma}$), the axial oxo σ interaction ($\Gamma_{2O\sigma}$), and the axial oxo π interactions ($\Gamma_{4O\pi}$) in the appropriate symmetry.
3. Provide graphical representations of the SALCs and assign their Mulliken symbols. Represent the σ -symmetry orbitals on L as *s* orbitals. You need not use the projection operator, but rather use the character table and symmetry-associated functions within the table to help construct the SALCs.
4. Construct the σ -only molecular orbital diagram for *trans*- $ML_4(O)_2^{n+}$, using the metal *d*, *s*, and *p* atomic orbitals and the SALCs derived in parts 2 and 3 for the σ symmetry ligand orbitals. You may consider the O and L-based SALCs of σ symmetry to be isoenergetic. Label each molecular orbital with the correct Mulliken symbol and provide the character of the interaction (bonding, non-bonding, anti-bonding). Label the d-based orbitals with their d-orbital parentage.
5. Now construct the full molecular orbital diagram for *trans*- $ML_4(O)_2^{n+}$, including the SALCs derived in parts 2 and 3 for the π symmetry O^{2-} orbitals.
6. Redraw only the d-splitting diagram derived from the MO diagram in part 5 for *trans*- $ML_4(O)_2^{n+}$. Consider now the effect of switching the position of one of the oxo and L ligands to generate *cis*- $ML_4(O)_2^{n+}$. Draw this new d-splitting diagram starting relative to the diagram for *trans*- $ML_4(O)_2^{n+}$. Clearly illustrate which d-orbitals change in energy and which remain the same. Label all orbitals with their d-parentage and bonding/non-bonding/anti-bonding character. Note that both diagrams should be derived under the same coordinate system, as shown above.



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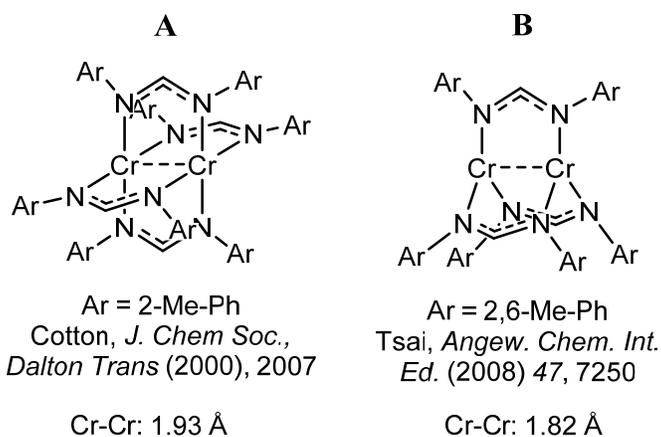
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7. Consider the two hypothetical complexes $\text{Mo}(\text{PR}_3)_4(\text{O})_2$ and $\text{Mo}(\text{PR}_3)_4(\text{O})_2^{2+}$. Assign the oxidation states, d-electron counts, and valence electron counts of both molecules.

8. Which geometry, *trans* or *cis*, would you expect each complex, $\text{Mo}(\text{PR}_3)_4(\text{O})_2$ and $\text{Mo}(\text{PR}_3)_4(\text{O})_2^{2+}$, to prefer? Explain given the molecular orbital and d-splitting diagrams derived above. Indicate the nature of the HOMO in each case and the average M-O bond order. Use only d-orbitals for π bonding.

Problem 3 (2 points)

Many bimolecular amidinate complexes of chromium have been synthesized; various coordination numbers have been achieved based on different steric profiles of the amidinate ligands, or the synthetic route to arrive at the binuclear complexes. Two examples of reported $[(\text{RNCHNR})_n\text{Cr}_2]$ species are listed below, with their respective Cr-Cr distances.

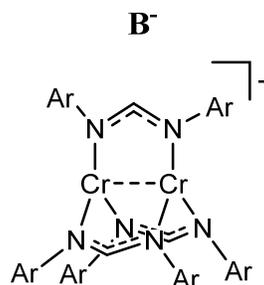


1. Assign oxidation state and d-count for the Cr centers in complexes **A** and **B**.
2. Interact the two $[\text{CrL}_4]$ fragments to arrive at an MO diagram depicting the M-M interactions, similar to $[\text{ReCl}_4]^-$ from lecture to construct $[\text{Re}_2\text{Cl}_4]^{2-}$. We will assume an eclipsed geometry (D_{4h}) even though these structures display some distortions. Label each orbital with its Mulliken symbol, and label the type of interaction (σ , σ^* , π , etc) with respect to both M-M and M-ligand interactions. For simplicity assume that the ligands only act as σ donors.
3. Fill in the d-splitting diagram from question 3 with the appropriate number of electrons. What is the Cr-Cr bond order?
4. Starting from the MO diagram of $[\text{CrL}_4]$, derive a d-splitting diagram for one of the $[\text{CrL}_3]$ fragments in **B** clearly showing how you expect the orbital energies to change. Label each orbital with its d-parentage, Mulliken symbol, and type of interaction with L (σ , σ^* , or nonbonding).
5. Interact two $[\text{CrL}_3]$ fragments from question 4 to arrive at a qualitative MO diagram of complex **B**. Make sure your diagram reflects the change in Cr-Cr bond length (shortening is indicative of an increase in Cr-Cr bond order). What is the Cr-Cr bond order? Label each orbital with its d-parentage, type of M-M and M-ligand interaction, and Mulliken symbol.

Complex **B** can be reduced with 1 equivalent of KC_8 to form the anionic species **B**⁻.

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6. What is the oxidation state, d-electron count of each Cr center in **B⁻**?

7. Do you expect the Cr–Cr distance to lengthen or shorten when reducing **B** to **B⁻**? What is the Cr–Cr bond order of **B⁻**? What is the Cr–Cr bond order for the hypothetical molecule **A⁻**?

Problem 4 (3 points)

Part A

In class, we considered the carbon atom, with the $1s^2 2s^2 2p^2$ electronic configuration. Consider now the case on nitrogen, with the configuration $1s^2 2s^2 2p^3$.

1. Determine the total number of possible microstates for the $1s^2 2s^2 2p^3$ configuration. Determine the ground state term using the shortcut presented in class.
2. Prepare a microstate table and populate with all possible microstates.
3. Using the microstate table for the $1s^2 2s^2 2p^3$ configuration, derive the state symbols. Include the terms resulting from spin-orbit coupling. Order all terms based on energy strictly following Hund's rules (ignoring J).

Part B

Consider now the electron configuration $1s^2 2s^2 2p^2 3s^1$.

1. Determine the total number of possible microstates for the $2p^2 3s^1$ configuration. Determine the ground state term using the shortcut presented in class.
2. Prepare a microstate table and populate with all possible microstates. Remember that all microstates will maintain a $1s^2 2s^2 2p^2 3s^1$ configuration. Example notation: $(1p^+, 0p^-, 0s^+)$
3. Using the microstate table for the $1s^2 2s^2 2p^2 3s^1$ configuration, derive the state symbols. Include the terms resulting from spin-orbit coupling. Order all terms based on energy strictly following Hund's rules (ignoring J).