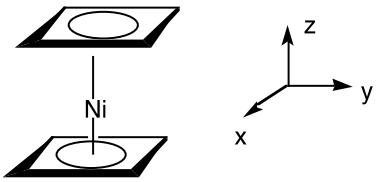
Chemistry 6330 ***Problem Set 5***

(1) Bis(cyclobutadiene)nickel consists of a Ni atom sandwiched between two planar cyclobutadiene ligands. In this complex (shown below), the metal orbitals overlap with the pπ molecular orbitals of cyclobutadiene (the Huckel pπ MO's of cyclobutadiene are shown in Chapter 7 and you should have worked them out in Problem Set 5). Assume that the complex is reduced by two electrons to yield the 2- ion.



(a) Derive the symmetries of the orbitals resulting from the eight linear combinations of the cyclobutadiene pπ Huckel orbitals. Label each orbital according to the irreducible representation for which it forms a basis.

(b) Indicate which Nickel orbitals are of the correct symmetry to overlap with the ligand orbitals

(c) Decide which interactions are likely moderate, strong, or weak and construct the MO diagram for the nickel complex.

(d) Derive the symmetries of the ground state, dipole moment operator, and the two lowest-lying excited states. Assign the allowed and forbidden electronic transitions.

(e) What type of transitions are these? What intensities (ε) would you expect?

(2) The square planar geometry is ubiquitous for transition metals with d^8 electronic configuration. By following the procedure outlined in lecture, derive the following MO diagrams for square planar ML_4 complexes.

(a) σ-donor ligands

(b) π-acceptor ligands

(c) π-donor ligands

(d) Assign the low-lying allowed transitions you would expect for the complexes in (a) - (c)

(3) Consider the fictitious dinuclear hydride complex $Mn_2H_8^{2-}$, which we will assume consists of two face-to-face square planar MnH_4^- fragments.

(a) Using the Mn 3d, 4s, and 4p AO's and the SALCs of four H 1s orbitals, construct a qualitative MO diagram for square planar (D_{4h}) MnH_4^-.

(b) One of the H SALCs can interact with two different Mn AOs. Which interaction should be stronger? Why?

(c) In order to describe the Mn-Mn bonding, we will "throw out" those Mn AOs that are strongly destabilized by interaction with the H atoms. Which orbitals do you think should be discarded?

(d) Assume that the $Mn_2H_8^{2-}$ ion is eclipsed (D_{4h}) and has very short Mn-Mn distance. By taking the sums and differences of the orbitals that are left on the Mn atoms, determine which irreducible reps are spanned by the Mn-Mn bonding and antibonding orbitals. Construct a qualitative MO diagram for the Mn-Mn bonding. What is the Mn-Mn bond order?

(e) Repeat part (d) under staggered (D_{4d}) geometry. Does the Mn-Mn bond order change? Would you expect staggered $Mn_2H_8^{2-}$ to be diamagnetic or paramagnetic?