**Chemistry 153a**
**Winter 2020**
**Due 7 February, 2020**

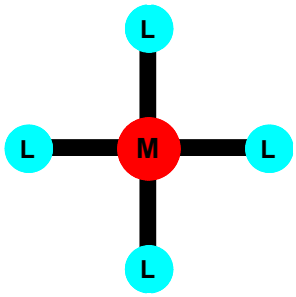
**Problem Set 5**

1. Consider a binuclear metal complex constructed from two square-planar $ML_4$ fragments where the L ligands are σ-donors. There are two limiting conformations in the resulting $M_2L_8$ complex: in one the ligands are eclipsed and in the other they are staggered.

   a) Draw the two conformations of the binuclear metal complex and assign each to a symmetry point group.

   b) Construct an MO diagram for each conformation using the following orbitals: five M *d* orbitals and four L σ orbitals. Assume that M-L σ-bonding is quite strong.

   c) Assume that $ML_4$ has a $d^4$ electron configuration, and that each ligand L contributes two σ electrons.




      i. Predict the preferred ground-state conformation of the corresponding $M_2L_8$ complex, and give the electronic configuration and term symbol for the ground electronic state. Determine the metal-metal bond order.

      ii. Identify the spin-allowed electronic transitions involving the *d*-orbitals, determine the term symbols for the excited states, and predict the relative energy ordering of these states.

      iii. Predict the lowest-energy electric-dipole-allowed transition. Also, predict the polarization of light that will induce the transition.

   d) Assume that $ML_4$ has a $d^6$ electron configuration, and that each ligand L contributes two σ electrons. Predict the preferred ground-state conformation of the corresponding $M_2L_8$ complex, and give the electronic configuration and term symbol for the ground electronic state. Determine the metal-metal bond order.

   e) Assume that $ML_4$ has a $d^7$ electron configuration, and that each ligand L contributes two σ electrons.

      i. Predict the preferred ground-state conformation of the corresponding $M_2L_8$ complex, and give the electronic configuration and term symbol for the ground electronic state. Determine the metal-metal bond order.

      ii. Identify the spin-allowed electronic transitions involving the *d*-orbitals, determine the term symbols for the excited states, and predict the relative energy ordering of these states.

      iii. Predict the lowest-energy electric-dipole-allowed transition that should be M—M axis polarized.

2. The absorption spectrum of $Mn_2(CO)_{10}$ exhibits an intense absorption band at 30,000 $cm^{-1}$, and a lower-energy feature at 27,000 $cm^{-1}$. The 30,000-$cm^{-1}$ absorption band is polarized parallel to the Mn-Mn axis, and the 27,000 $cm^{-1}$ band is polarized perpendicular to this axis. Propose assignments for these bands based on a MO diagram for binuclear $d^7$-$d^7$ complexes.

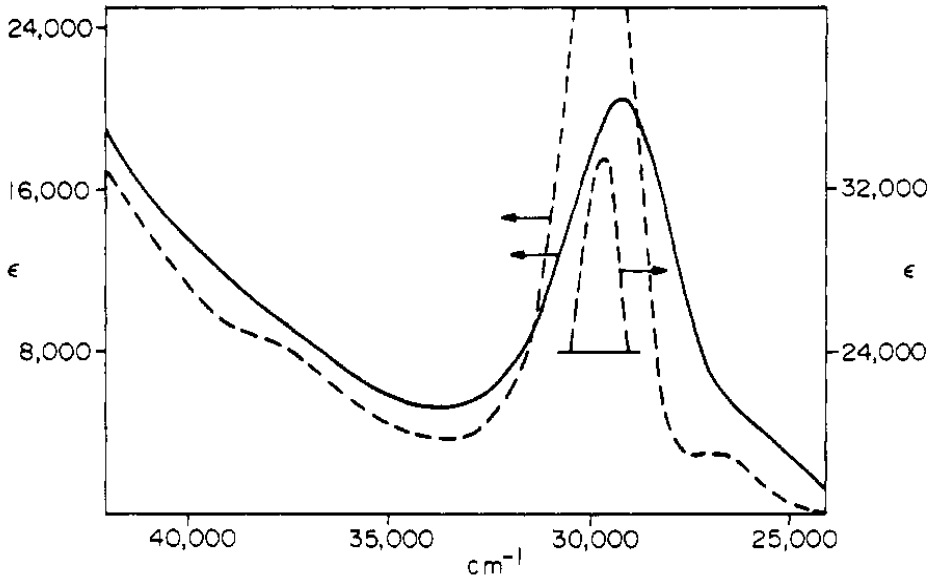
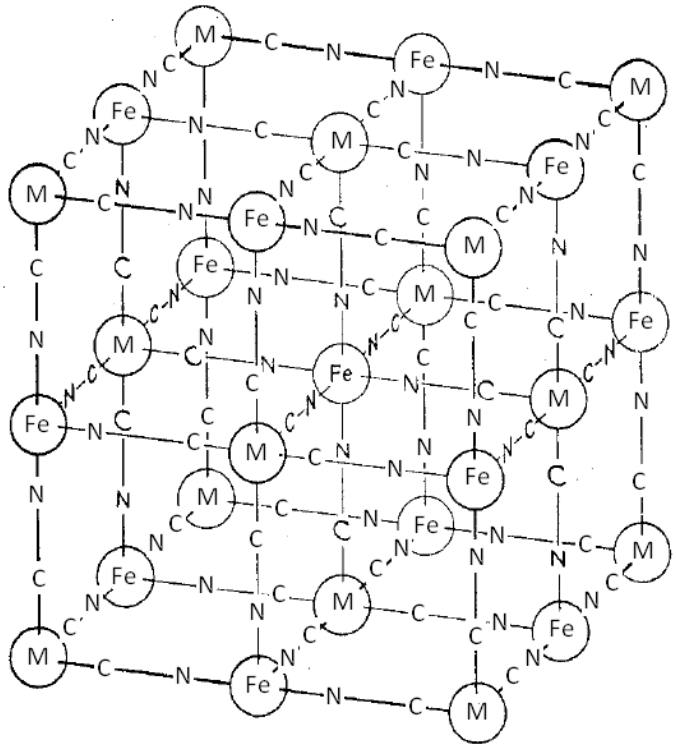
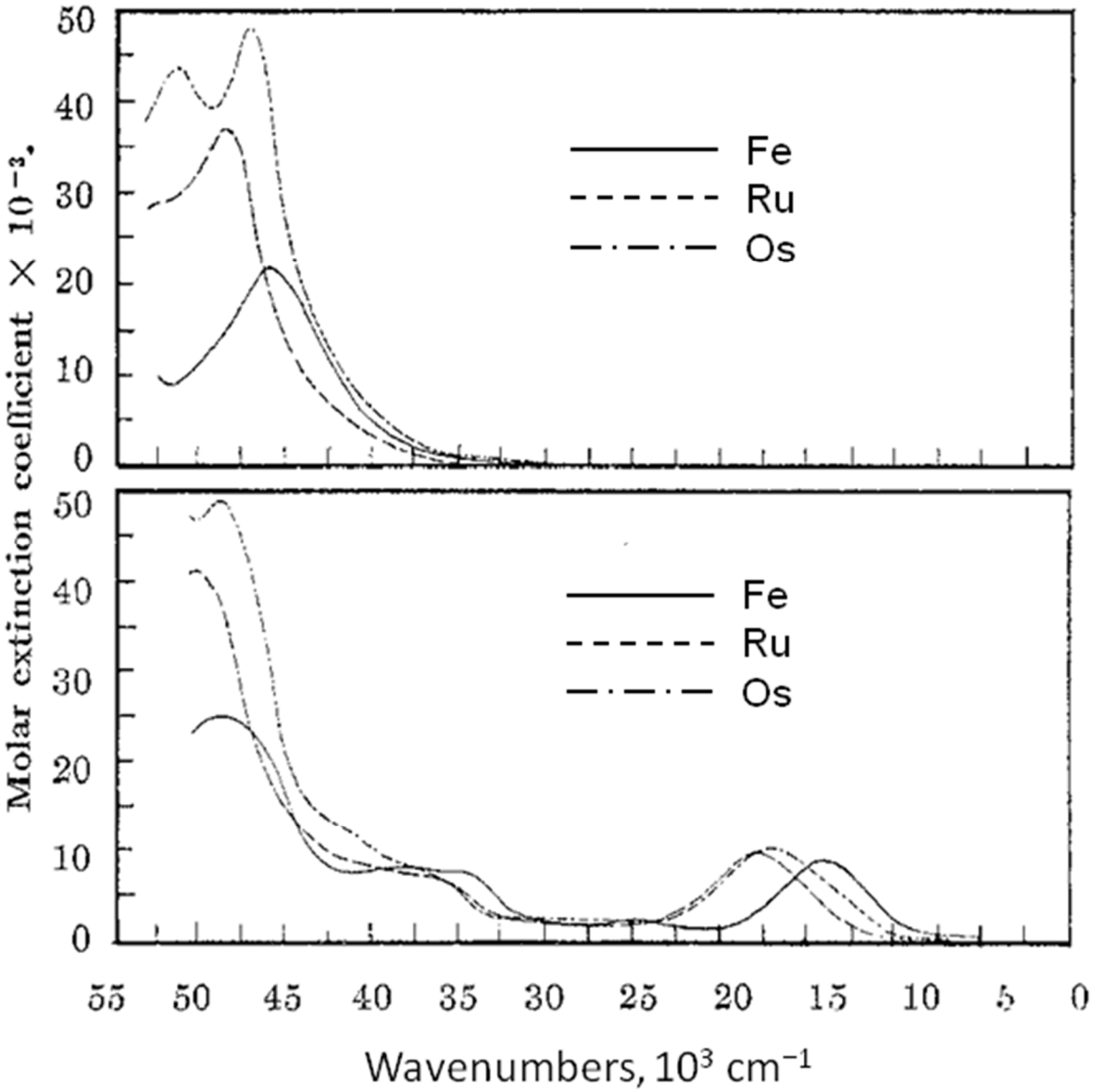



**Figure 2.** Electronic spectra of $Mn_2(CO)_{10}$ in 3-PIP: —, 300 K; - - -, 77 K.

3. The three ferric hexacyanometallates, Prussian blue, ruthenium purple, and osmium purple ($Fe_4[M(CN)_6]_3 \bullet xH_2O$, M = Fe, Ru, Os) are prepared by mixing solutions of the corresponding hexacyanometallates with a ferric perchlorate solution. The general structure of the three compounds is shown below.



The absorption spectra (below) of the hexacyano-metallates are shown in the upper panel, and the spectra of the ferric hexa-cyanometallates appear in the lower panel.




Propose assignments for the absorption bands in the ferric hexacyanometallates spectra. Explain your reasoning.