

Problem Set 5

Ch153a – Winter 2023

Due: 3 February 2023

1. The d^6 hexacyanometallates of Fe, Os, Ru, and Co exhibit the following intense absorption bands:

	$\tilde{\nu}_1, \text{cm}^{-1} (\epsilon, \text{M}^{-1}\text{cm}^{-1})$	$\tilde{\nu}_2, \text{cm}^{-1}$
$\text{Fe}(\text{CN})_6^{4-}$	45,900 (24,200)	50,000
$\text{Ru}(\text{CN})_6^{4-}$	48,800 (37,000)	52,000
$\text{Os}(\text{CN})_6^{4-}$	47,000 (47,400)	51,000
$\text{Co}(\text{CN})_6^{3-}$	50,600 (35,400)	

Propose assignments for the strong d^6 hexacyanometallate absorption features. Explain your reasoning.

2. Consider the C_{4v} complex $\text{W}(\text{CO})_5\text{L}$, where L is an uncharged ligand.
- Draw the molecular structure of the complex with L aligned along the Cartesian z axis.
 - Construct an MO diagram for $\text{W}(\text{CO})_5\text{L}$ using the following orbitals: 5 W 5d, one W 6s, three W 6p, five CO σ , ten CO π^* , and one L σ . Give the electronic configuration and term symbol for the ground electronic state.
 - Identify the spin-allowed ligand-field electronic transitions; determine term symbols for the excited states; and predict the relative energy ordering for these states.
 - The UV-visible absorption spectrum of $\text{W}(\text{CO})_5(\text{pyridine})$ features bands with peaks at 440 ($\epsilon = 627 \text{ M}^{-1}\text{cm}^{-1}$) and 380 nm ($\epsilon = 6904 \text{ M}^{-1}\text{cm}^{-1}$). Propose electronic transition assignments for these bands.
 - UV-visible irradiation of $\text{W}(\text{CO})_5(\text{pyridine})$ results either in loss of CO (reaction 1) or loss of L (reaction 2). The quantum yields for these two processes have been found to be wavelength dependent, as shown in the table on the following page. Using the MO diagram derived above, suggest an interpretation for the observed photochemistry.
 - The product of reaction 1 reacts with excess L to form $\text{M}(\text{CO})_4(\text{L})_2$. Based on the interpretation you gave in part (e), do you expect the *cis* or *trans* isomer to form preferentially? Explain.



Table: Wavelength Dependence for Processes 1 and 2 for W(CO)₅(pyridine)

Irradiation, λ /nm	$\Phi_{\text{eq } 1}$	$\Phi_{\text{eq } 2}$
436	0.00	0.63
366	0.01	0.50
313	0.03	0.38
254	~0.04	0.34

3. A persistent question in complexes of metals coordinated to Lewis-acidic ligands is the relative π -accepting strength of CO and PF₃ ligands. Explore the literature to find a series of complexes and associated *experimental* data that provide insight(s) into this question (computational studies, as always, will not suffice). On the basis of this literature, explain why you believe CO or PF₃ is the better π -acceptor.