Problem Set 2
Ch153a – Winter 2023
Due: 13 January 2023

1a. Construct an MO diagram for $C_4v [L_5MO]^{n+}$ (L is an uncharged ligand, for example, $H_2O$ or $NH_3$) using the following orbitals: five metal 3d orbitals, one set of five ligand $\sigma$ orbitals, and the oxo $\sigma^+ 2p_\pi$ orbitals.

b. Predict the ground state electronic configuration and the metal-oxo bond order for each of the following:

- $[L_5VO]^{2+}$  $V^{IV}$  $d^1$
- $[L_5CrO]^3+$  $Cr^{V}$  $d^1$
- $[L_5CrO]^{2+}$  $Cr^{IV}$  $d^2$
- $[L_5MnO]^3+$  $Mn^{V}$  $d^2$
- $[L_5MnO]^{2+}$  $Mn^{IV}$  $d^3$
- $[L_5FeO]^{2+}$  $Fe^{IV}$  $d^4$

c. Do you think that $[L_5CoO]^2+$ is a stable complex? Why or why not?

2. Electronic Structure and Spectra of Metal Oxo and Nitrido Complexes

The $d\pi$-orbital splitting for a tetragonal oxo- or nitrido-metal complex is shown above. The following states arise from the $d^1$, $d^2$, and $d^3$ configurations in this scheme:

$d^1$:

- $^2E[(xz, yz)1]$  $E = \Delta\pi$
- $^2B_2[(xy)1]$  $E = 0$

$d^2$:

- $^3A_2[(xz, yz)2]$  $E = 2\Delta\pi + A - 5B$
- $^1A_1[(xz, yz)2]$  $E = 2\Delta\pi + A + 7B + 4C$
- $^1B_1[(xz, yz)2]$  $E = 2\Delta\pi + A + B + 2C$
- $^1B_2[(xz, yz)2]$  $E = 2\Delta\pi + A + B + 2C$
- $^1E[(xy)^1(xz, yz)^1]$  $E = \Delta\pi + A + B + 2C$
- $^3E[(xy)^1(xz, yz)^1]$  $E = \Delta\pi + A - 5B$
- $^1A_1[(xy)^2]$  $E = A + 4B + 3C$
\( d^3: \)
\[
\begin{align*}
^2E[(xz,yz)^3] & \quad E = 3\Delta_\pi + 3A - 3B + 4C \\
^4B_1[(xy)^1(xz,yz)^2] & \quad E = 2\Delta_\pi + 3A - 15B \\
^2B_1[(xy)^1(xz,yz)^2] & \quad E = 2\Delta_\pi + 3A - 6B + 3C \\
^2A_1[(xy)^1(xz,yz)^2] & \quad E = 2\Delta_\pi + 3A - 6B + 3C \\
^2B_2[(xy)^1(xz,yz)^2] & \quad E = 2\Delta_\pi + 3A + 5C \\
^2A_2[(xy)^1(xz,yz)^2] & \quad E = 2\Delta_\pi + 3A - 6B + 3C \\
^2E[(xy)^2(xz,yz)^1] & \quad E = \Delta_\pi + 3A - 3B + 4C \\
\end{align*}
\]

The absorption spectra of \( \text{Cr}^\text{IV}(\text{N})(\text{CN})_5^{3-} \) and \( \text{Mn}^\text{IV}(\text{N})(\text{CN})_5^{3-} \) are shown below.

In \( \text{Cr}^\text{IV}(\text{N})(\text{CN})_5^{3-} \), the \( ^2B_2[(xy)]\rightarrow ^2E[(xz,yz)] \) absorption band is at 23,300 cm\(^{-1}\).

In \( \text{Mn}^\text{IV}(\text{N})(\text{CN})_5^{3-} \), the \( ^1A_1[(xy)^2]\rightarrow ^1E[(xy)(xz,yz)] \) absorption band is at 19,400 cm\(^{-1}\).

Use the foregoing orbital splitting diagram and the state energies to determine the values of \( \Delta_\pi \) in the Cr and Mn complexes. Assume that \( B = 500 \text{ cm}^{-1} \) and \( C/B = 4 \).
3. Spin Crossover in $d^2$ and $d^3$ Oxo- and Nitrido Complexes

The value of $\Delta_\pi$ is not the same in all of the states of a $d^2$ or $d^3$ nitrido or oxo complex. The $M\equiv N$ (or $M\equiv O$) bond should be longer in a $(xy)^1(xz, yz)^1$ excited state than in the $(xy)^2$ ground state. Consequently, in the relaxed $(xy)^1(xz, yz)^1$ excited state, $\Delta_\pi$ will be smaller than it was in the ground state.

You can estimate the change in $\Delta_\pi$ from the shape of the absorption band. In $\text{Mn}^{IV}(\text{N})(\text{CN})_5^{3-}$, the parameter $\lambda$ is about $3,400 \text{ cm}^{-1}$. So if $E_{\text{abs}} = 19,400 \text{ cm}^{-1}$, then $E_{\text{em}} = 12,600 \text{ cm}^{-1}$. The energy gap between $^3E$ and $^1A_1$ is $\Delta_\pi - 9B - 3C \approx \Delta_\pi - 21B$.

For thermal population of a high-spin state, the relevant energy is $E_{\text{TH}}$ (or $E_{00}$), which is less than the vertical energy difference: $E_{\text{TH}} = E_{\text{abs}} - \lambda$. 
a. Find the $\Delta_\pi$ values at the high-spin/low-spin crossover points for $d^2$ and $d^3$ tetragonal oxo- and nitrido-metal complexes. Assume that $B = 500 \text{ cm}^{-1}$ and $C/B = 4$.

b. Assume that you have a high-spin/low-spin equilibrium in a $d^2$ tetragonal oxo- or nitrido-metal complex in which $E_{TH} = 0$. What are the $\Delta_\pi$ values for high- and low-spin forms?

c. Assume that you have a high-spin/low-spin equilibrium in a $d^3$ tetragonal oxo- and nitrido-metal complex in which $E_{TH} = 0$. What are the $\Delta_\pi$ values for high- and low-spin forms?

d. What are the relative populations of the high- and low-spin states in problems (b) and (c)?

e. Karl Wieghardt reported (Angew. Chem. Int. Ed. 2005, 44, 2908-2912) that, unexpectedly, the ground-state total spin of the [(cyclam-acetato)FeV(N)]$^+$ core is $S=1/2$ and not $S=3/2$. Discuss whether you think that this result is “unexpected”.