**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 σ orbitals, and the oxo σ + 2pπ 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
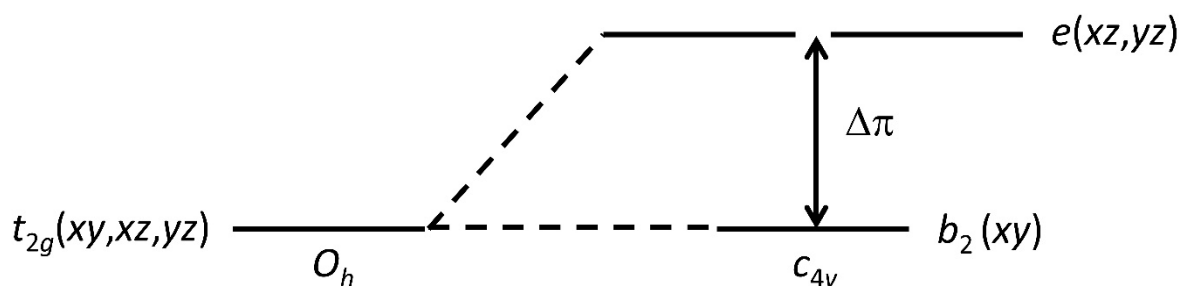
The $d\pi$-orbital splitting for a tetragonal oxo- or nitrido-metal complex is shown above.

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:

$^2E[(xz,yz)^3]$	$E = 3\Delta_\pi + 3A - 3B + 4C$
$^4B_1[(xy)^1(xz,yz)^2]$	$E = 2\Delta_\pi + 3A - 15B$
$^2B_1[(xy)^1(xz,yz)^2]$	$E = 2\Delta_\pi + 3A - 6B + 3C$
$^2A_1[(xy)^1(xz,yz)^2]$	$E = 2\Delta_\pi + 3A - 6B + 3C$
$^2B_2[(xy)^1(xz,yz)^2]$	$E = 2\Delta_\pi + 3A + 5C$
$^2A_2[(xy)^1(xz,yz)^2]$	$E = 2\Delta_\pi + 3A - 6B + 3C$
$^2E[(xy)^2(xz,yz)^1]$	$E = \Delta_\pi + 3A - 3B + 4C$

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

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

In $Mn^V(N)(CN)_5^{3-}$, 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 Δ_π in the Cr and Mn complexes. Assume that $B = 500$ cm^{-1} and $C/B = 4$.
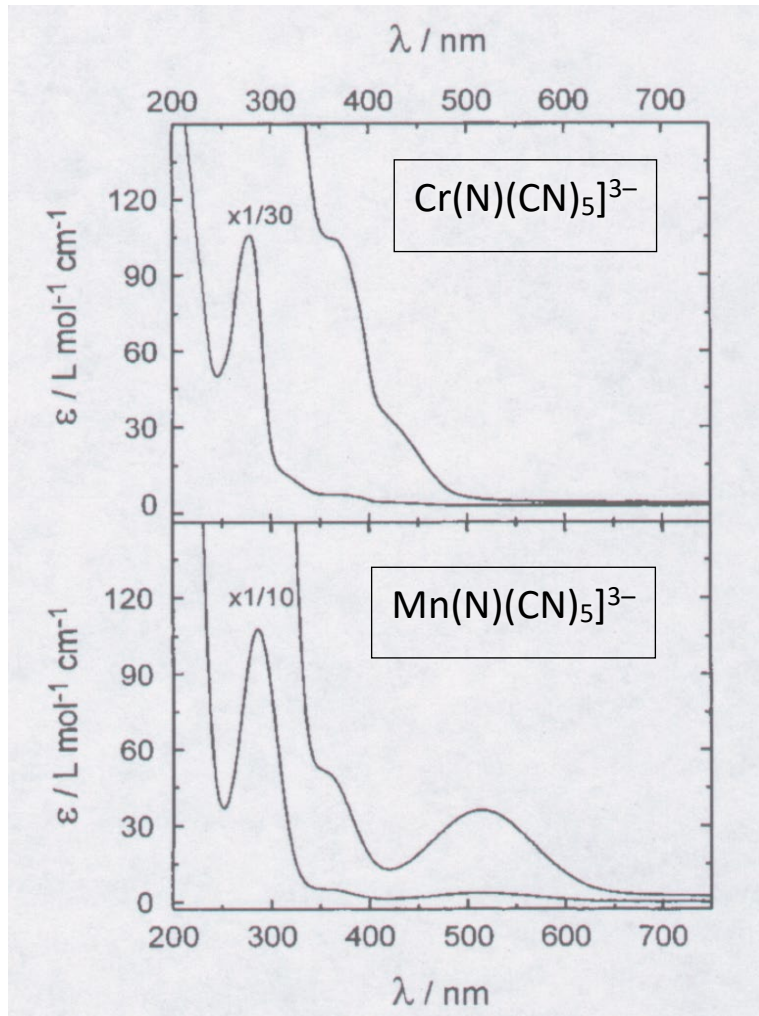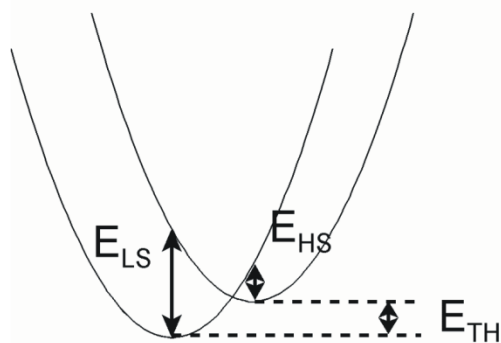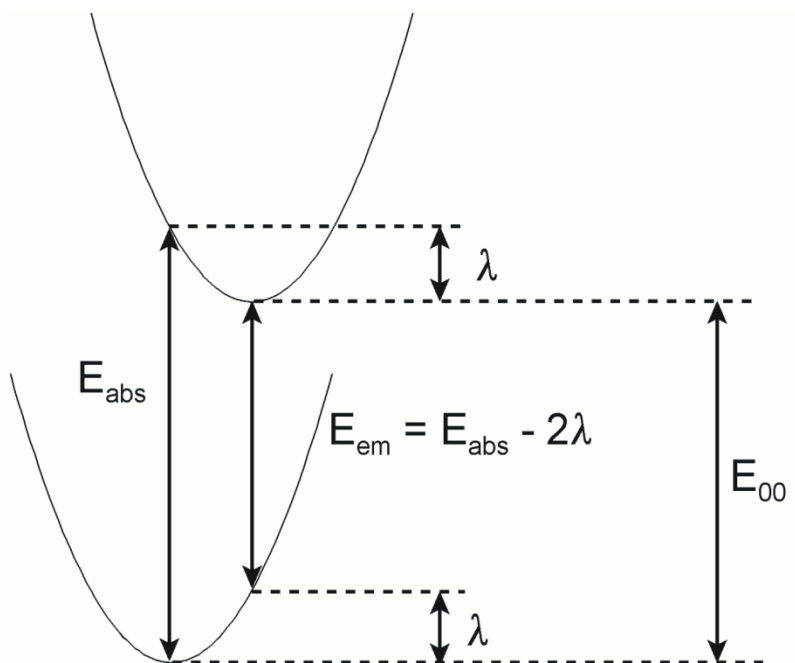
3. Spin Crossover in d² and d³ Oxo- and Nitrido Complexes

The value of Δ_π is not the same in all of the states of a d^2 or d^3 nitrido or oxo complex. The M≡N (or M≡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, Δ_π will be smaller than it was in the ground state.

You can estimate the change in Δ_π from the shape of the absorption band. In $Mn^V(N)(CN)_5^{3-}$, the parameter λ is about 3,400 cm^{-1}. So if E_{abs} = 19,400 cm^{-1}, then E_{em} = 12,600 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_{TH} (or E_{00}), which is less than the vertical energy difference: $E_{TH} = E_{abs} - \lambda$.

a. Find the Δ_π 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 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 Δ_π 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 Δ_π 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)Fe^V(N)]$^+$ core is S=1/2 and not S=3/2. Discuss whether you think that this result is "unexpected".