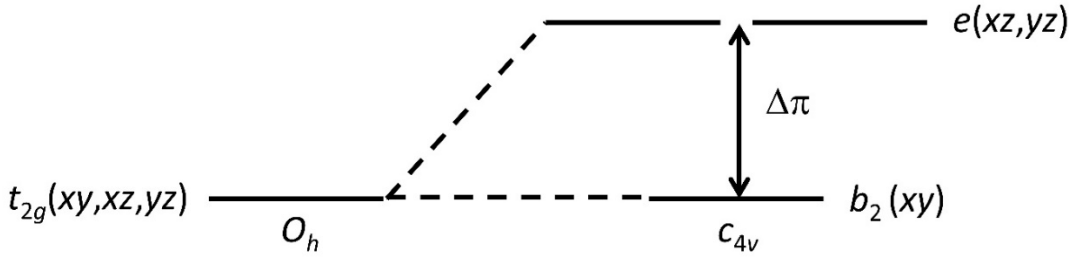
Problem Set 2
Ch153a – Winter 2025
Due: 24 January 2025

1. (10 points) Consider the tetragonal oxo complex, $[L_5MO]^{n+}$ (L is an uncharged ligand, for example, H_2O or NH_3).
   a. Construct an MO diagram for $[L_5MO]^{n+}$ using the following orbitals in the C_{4v} point group: five metal 3d orbitals, one set of five ligand σ 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. (10 points) Electronic Structure and Spectra of Metal Nitrido Complexes



The $d\pi$-orbital splitting for a tetragonal nitrido-metal complex is shown above.

The following states arise from the d^1 and d^2 configurations in this scheme:

d^1:

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

d^2:

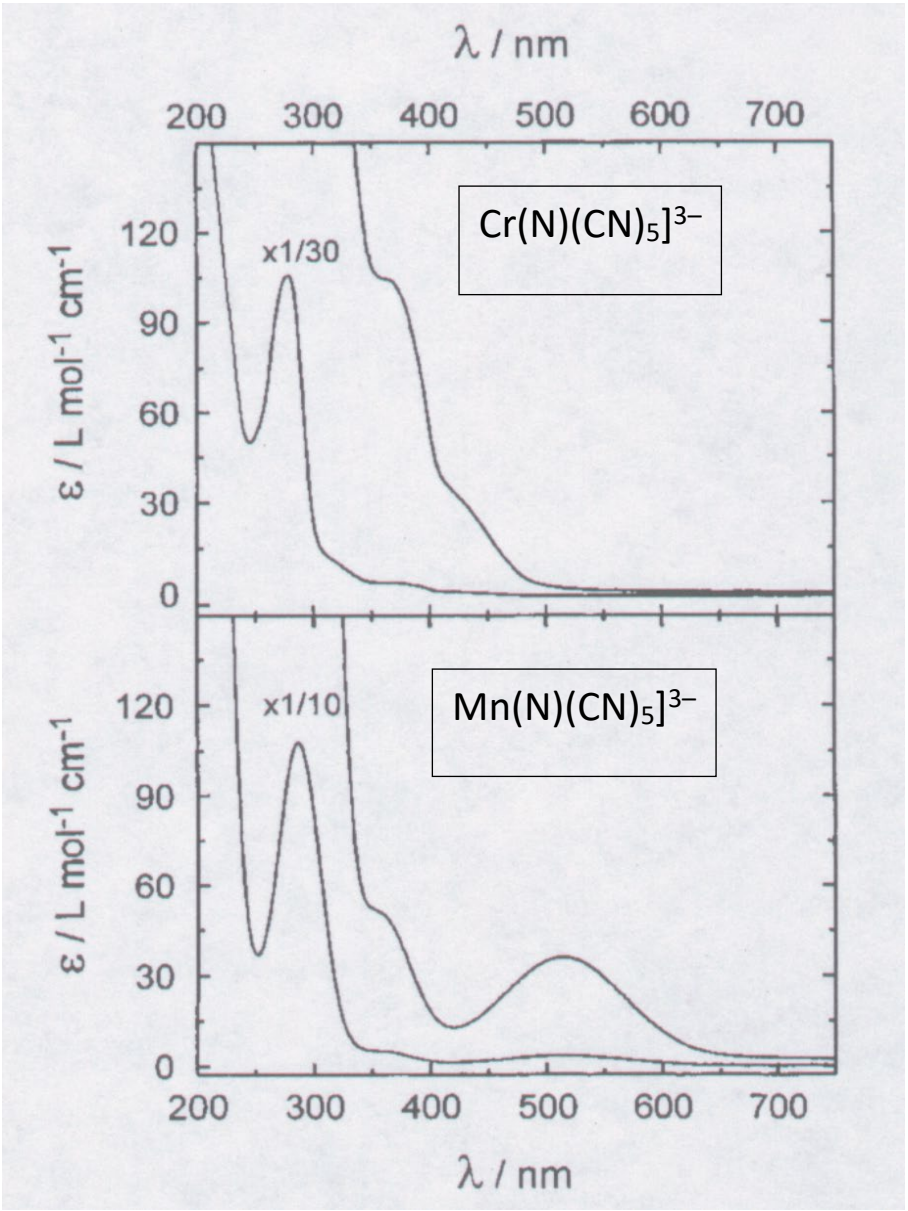
$^3A_2[(xz,yz)^2]$	$E = 2\Delta_\pi + A - 5B$
$^1A_1[(xz,yz)^2]$	$E = 2\Delta_\pi + A + 7B + 4C$
$^1B_1[(xz,yz)^2]$	$E = 2\Delta_\pi + A + B + 2C$
$^1B_2[(xz,yz)^2]$	$E = 2\Delta_\pi + A + B + 2C$
$^1E[(xy)^1(xz,yz)^1]$	$E = \Delta_\pi + A + B + 2C$
$^3E[(xy)^1(xz,yz)^1]$	$E = \Delta_\pi + A - 5B$
$^1A_1[(xy)^2]$	$E = A + 4B + 3C$

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 lowest energy spin-allowed absorption band is at 23,300 cm^{-1}.

In $Mn^{V}(N)(CN)_5^{3-}$, the lowest energy spin-allowed absorption band is at 19,400 cm^{-1}.

a. Provide an assignment for the lowest energy spin-allowed absorption band in each complex.
b. 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.


λ / nm
200
300
400
500
600
700
120
90
60
30
0
ε / L mol-1 cm-1
x1/30
Cr(N)(CN)5]3–
x1/10
Mn(N)(CN)5]3–