Chemistry 6011
Advanced Inorganic Chemistry I: From Atoms to Coordination Compounds
Exam 3
Name:

Show your work for maximum credit.

1. (10 points) Construct the Latimer diagram for manganese in <u>acidic</u> solution. Fill in the table to help decide what to include in your Latimer diagram. Also note in your diagram which steps are not thermodynamically favorable.

Half-reaction	E^0 (V)	Oxidation State Before	Oxidation State After	Include?
$Mn(OH)_2 + 2e^- \rightarrow Mn + 2OH^-$	-1.565			No
$Mn^{2+} + 2e^- \rightarrow Mn$	-1.182	2+	0	
$Mn_2O_3 + 3H_2O + 2e^- \rightarrow 2Mn(OH)_2 + 2OH^-$	-0.234			No
$MnO_2 + 2H_2O + 2e^- \rightarrow Mn(OH)_2 + 2OH^-$	-0.044			No
$2MnO_2 + H_2O + 2e^- \rightarrow Mn_2O_3 + 2OH^-$	+0.146			No
$MnO_4^{2-} + e^- \rightarrow MnO_4^{3-}$	+0.27	6+	5+	~~Yes~~ No b/c
$MnO_4^- + e^- \rightarrow MnO_4^{2-}$	+0.56	7+	6+	No b/c
$MnO_4^{2-} + 2H_2O + 2e^- \rightarrow MnO_2 + 4OH^-$	+0.60			No
$MnO_4^- + 2H_2O + 3e^- \rightarrow MnO_2 + 4OH^-$	+0.588			No
$MnO_2 + 4H^+ + e^- \rightarrow Mn^{3+}$	+0.90	4+	3+	~~Yes Yes No b/c~~
$MnO_4^- + H^+ + e^- \rightarrow HMnO_4^-$	+0.90	7+	6+	Yes
$MnO_4^{3-} + 2H_2O + e^- \rightarrow MnO_2 + 4OH^-$	+0.93	5+	4+	Yes
$MnO_2 + 4H_3O^+ + 2e^- \rightarrow Mn^{2+} + 2H_2O$	+1.23	4+	2+	Yes
$MnO_4^- + 8H_3O^+ + 5e^- \rightarrow Mn^{2+} + 12H_2O$	+1.507	7+	2+	Yes
$Mn^{3+} + e^- \rightarrow Mn^{2+}$	+1.56	3+	2+	Yes
$MnO_4^- + 4H_3O^+ + 3e^- \rightarrow MnO_2 + 2H_2O$	+1.692	7+	4+	Yes
$HMnO_4^- + 3H^+ + 2e^- \rightarrow MnO_2 + 2H_2O$	+2.09	6+	4+	Yes

$$MnO_4^- \xrightarrow{+0.90} HMnO_4^- \xrightarrow{+2.09} MnO_2 \xrightarrow{+0.90} Mn^{3+} \xrightarrow{+1.56} Mn^{2+} \xrightarrow{-1.182} Mn$$

+1.507 (across MnO₄⁻ to Mn²⁺)

+1.692 (MnO₄⁻ to MnO₂)

+1.23 (MnO₂ to Mn²⁺)

Negative value ∴ Not thermodynamically favorable
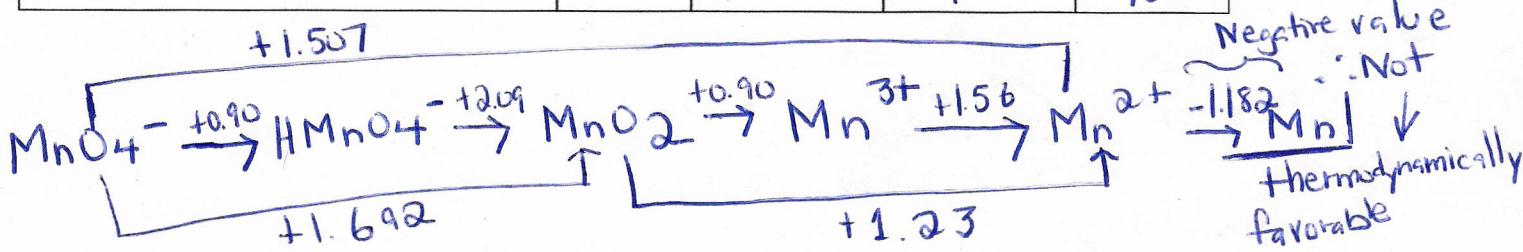
2. (10 points) Explain the following observations. In a series of complexes W(CO)₅L, the stretching frequency of the CO trans- to L varies as follows:

L	C-O stretch (cm⁻¹)
H₃P	2083
Me₃P	2070
Cl₃P	2095
F₃P	2103

e^- donating ← Me₃P
e^- withdrawing ← Cl₃P, F₃P

The changes in the stretching frequencies are due to the trans influence.
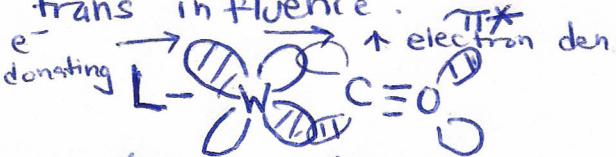
e^- donating $\to$ ↑ electron density in $CO\pi^*$, ↓ bond strength, ↓ νCO

e^- withdrawing $\to$ Decrease e^- density in $CO\pi^*$ orbital, ↑ bond strength, ↑ νCO

3. (10 points) The following pertains to the formation of a metal tri-ligand complex in water.

a. **Write** the series of steps involved in the formation if the ligand is bidentate and its coordination sites are proton affinity sites. Assume that the ligand is fully protonated before it reacts with the metal.

$$H_2L \rightleftharpoons L^{2-} + 2H^+$$

$$3(H_2L \rightleftharpoons HL^- + H^+)$$
$$3(HL^- \rightleftharpoons L^{2-} + H^+)$$

Net $M^{n+} + 3H_2L \rightleftharpoons [ML_3]^{n+-6} + 6H^+$

$3H_2L \xrightarrow{K_{d1}} 3HL^- + 3H^+$

$3HL^- \xrightarrow{K_{d2}} 3L^{2-} + 3H^+$

$M^{n+} + L^{2-} \underset{K_{F1}}{\rightleftharpoons} [ML]^{n+-2}$

$[ML]^{n+-2} + L^{2-} \xrightarrow{K_{F2}} [ML_2]^{n+-4}$

$[ML_2]^{n+-4} + L^{2-} \underset{K_{F3}}{\rightleftharpoons} [ML_3]^{n+-6}$

Net: $M^{n+} + 3H_2L \overset{\beta}{\rightleftharpoons} [ML_3]^{n+-6} + 6H^+$
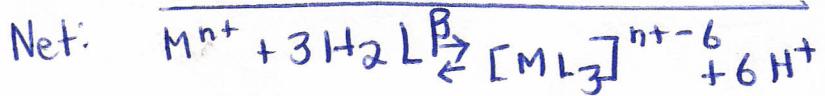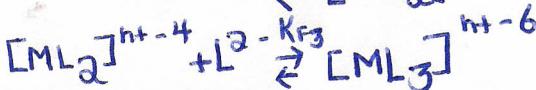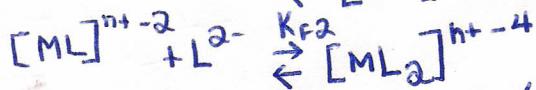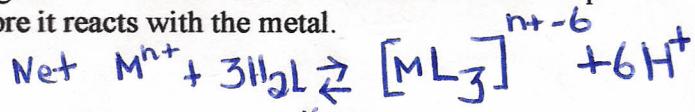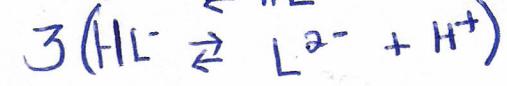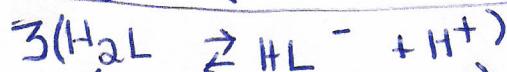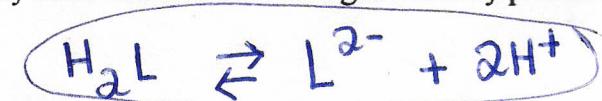
b. Derive the formation constant expression for the metal tri-ligand complex.

$$\beta = K_{d_1}^3 \cdot K_{d_2}^3 \cdot K_{F_1} \cdot K_{F_2} \cdot K_{F_3} = \frac{[ML_3]^{n+-6}[H^+]^6}{[M^{n+}][H_2L]^3}$$

4. (10 points) What is the d orbital splitting for the following ideal coordination geometries:

a. Trigonal bipyramidal

$$— dz^2$$

$$\overline{dxy} \quad \overline{dx^2-y^2}$$

$$\overline{dxz} \quad \overline{dyz}$$
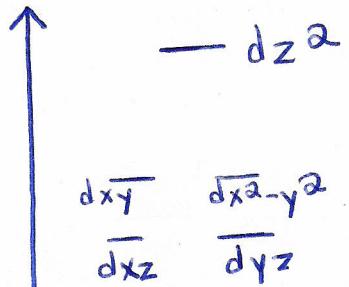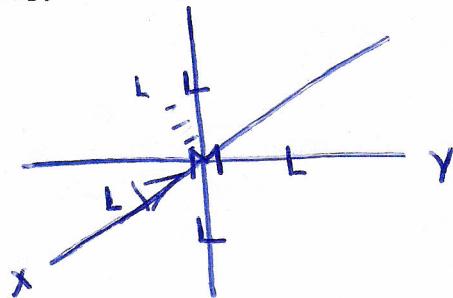
b. Square pyramidal

$$— dx^2-y^2$$

$$— dz^2$$

$$— dxy$$

$$\overline{dxz} \quad \overline{dyz}$$
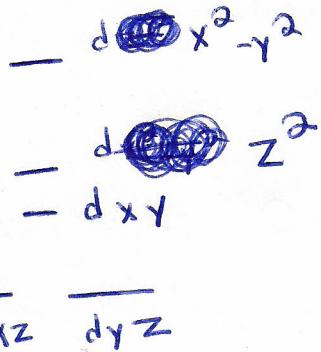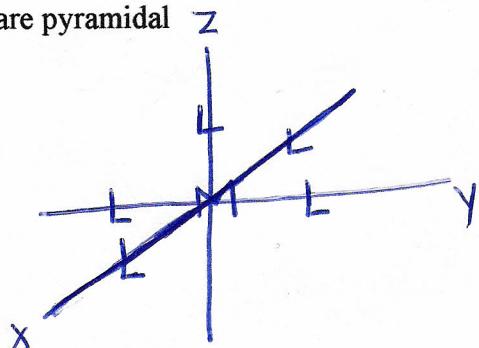
c. Pentagonal bipyramidal

$$\overline{dz^2}$$

$$\overline{dxy} \quad \overline{dx^2-y^2}$$

$$\overline{dxz} \quad \overline{dyz}$$
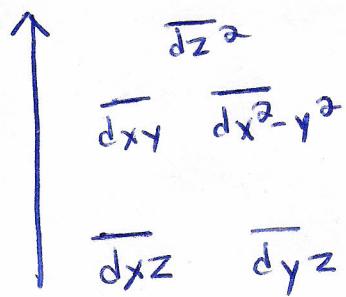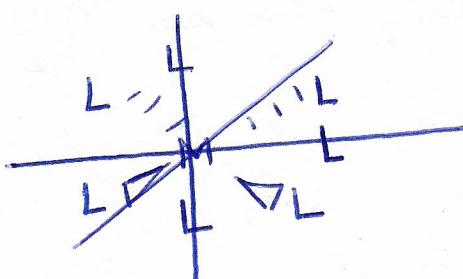
5. (10 points) Give chemical names for the following:

a. [Co(N₃)(NH₃)₅]SO₄   pentaammine azido cobalt (III) sulfate

b. [Ir(CO)Cl(PPh₃)₂]   carbonylchlorobis(triphenyl phosphine) iridium (I)

c. [Fe(NH₃)₆]Cl₃   hexaammine iron (III) chloride

d. [PtCl(NH₂CH₃)(NH₃)₂]Cl   diammine chloromethylamine platinum (II) chloride

e. K₂[PdCl₄]   potassium tetrachloro palladate (II)

6. (10 points) Explain the structure for the $[CuF_6]^{4-}$ complex and predict its UV-Vis spectrum.

Cu^{2+} d^9

$= F^-$
$= Cu^{2+}$

193 pm
227 pm

Elongation along Z-axis.

E

$\uparrow\downarrow$ $\uparrow$
$\overline{d_{z^2}}$ $\overline{d_{x^2-y^2}}$

$\uparrow\downarrow$ $\uparrow\downarrow$ $\uparrow\downarrow$
$\overline{d_{xy}}$ $\overline{d_{xz}}$ $\overline{d_{yz}}$

Z-out

$\uparrow$ $\overline{d_{x^2-y^2}}$ $\uparrow\uparrow$
$\uparrow\downarrow$ $\overline{d_{z^2}}$ ΔE_2 ΔE_1
$\uparrow\downarrow$ $\overline{d_{xy}}$
$\uparrow\downarrow$ $\overline{d_{xz}}$ $\overline{d_{yz}}$

Jahn Teller effect
Two d-d transitions

The structure is distorted by elongating the axial bonds to remove the unequal e^- population of d_{z^2} & $d_{x^2-y^2}$. There will be a contraction of the bonds along equatorial plane. This results in increase in energy of orbitals with x,y components and decrease of those with z component.

Abs

Two not well resolved absorbances.

ΔE_1 ΔE_2

λ

7. (20 points) Explain the following square planar complex $[Pt(NH_3)_4]^{2+}$ in terms of the following bonding theories. Make sure to account for stabilization energy.

a. Valence Bond Theory

$[Pt(NH_3)_4]^{2+}$
d^8

Square planar

$\begin{bmatrix} & NH_3 & \\ & | & \\ H_3N- & Pt & -NH_3 \\ & | & \\ & NH_3 & \end{bmatrix}^{2+}$

:NH_3 Lone pair donor for σ interactions.

The valence bond theory accounts for covalency in metal ligand interactions by invoking metal orbital hybridization. The hybrid orbitals can engage in σ_z interactions. The ligands will interact directly with the metal $d_{x^2-y^2}$, s, and 2 p orbitals.

$p_x + p_y$

$\uparrow\downarrow$ $\uparrow\downarrow$ $\uparrow\downarrow$ $\uparrow\downarrow$ | $\uparrow\downarrow$ $\uparrow\downarrow$ $\uparrow\downarrow$ $\uparrow\downarrow$ —
$\underbrace{\overline{5d}}$ $\underbrace{\overline{6s}\ \overline{6p}}$

The $d^8 e^-$s go here.
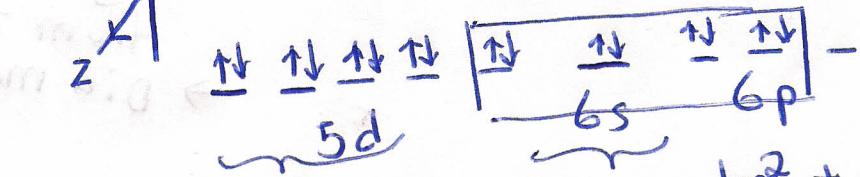
becomes dsp^2 & accepts the $8e^-$ from the ligand

b. Crystal Field Theory

This is an electrostatic model that only considers the impact of ligand interactions on the energy of the metal d orbitals. The ligands are treated as point charges that impose a geometric field on the metal d orbitals, destabilizing the orbitals with direct contact with the point charges (or close to them) & stabilizing those that do not have direct contact.

E

$6p$ ---- ---
$6s$ $\overline{}$
$5d$ $\uparrow\downarrow$ $\uparrow\downarrow$ $\uparrow\downarrow\uparrow$ $\uparrow$

p_z
$\uparrow\downarrow$ $\uparrow\downarrow\uparrow\downarrow\uparrow\downarrow$
dsp^2
$\uparrow\downarrow$ $\uparrow\downarrow\uparrow\downarrow$ $\uparrow\downarrow$

diamagnetic
Inner shell complex.

$\uparrow\downarrow$ $\uparrow\downarrow$ $\uparrow\downarrow$ $\uparrow\downarrow$

$4:NH_3$

Crystal Field Theory continuation.
consider the following analysis

E │↑↓ ↑↑↑↓ ↑↑ ─ ─ ─ ─ ─ ─ ─ ─ ─ ─ ─dx²-y²   e⁻ Will have experience
  │   an increase in energy
  │   5d   ↑ ↑   Bary center
  │   d⁸   ─── ───
  │   dz² dx²-y²   ↑↓ dxy
  │   ─── ←   +
  │   ↑↓ dz²
  │   ───
  │   No ligand   ↑↓ ↑↓ ↑↓   e⁻
  │   ─── ─── ───   ↑↓   ↑↓   } will experience
  │   dxy dxz dyz ─── ───   CFSE
  │   dxz dyz
  │   Octahedral   Square planar
  │   field   field
  │   ⎤
  │   overall, there will
  │   be an increase
  │   in the stability of
                                           the d⁸ e⁻ due
         z   z   to CFSE.
         │   │
      ↖ │ ↗   ↖ │ ↗
    L ╲ │ ╱ L   ⌐ ╲ │ ╱
   ─── M ─── Y   L ── M ── L ── Y
      ╱ │ ╲ L   ╱ │ ╲
    L ╱ │   L ╱   │
     X   │ L   X
                  ─ Square planar
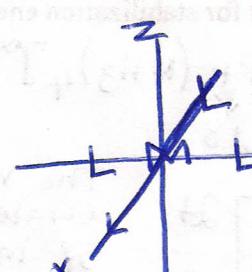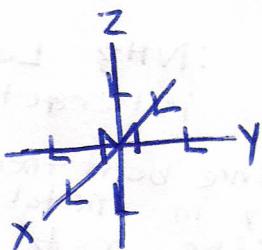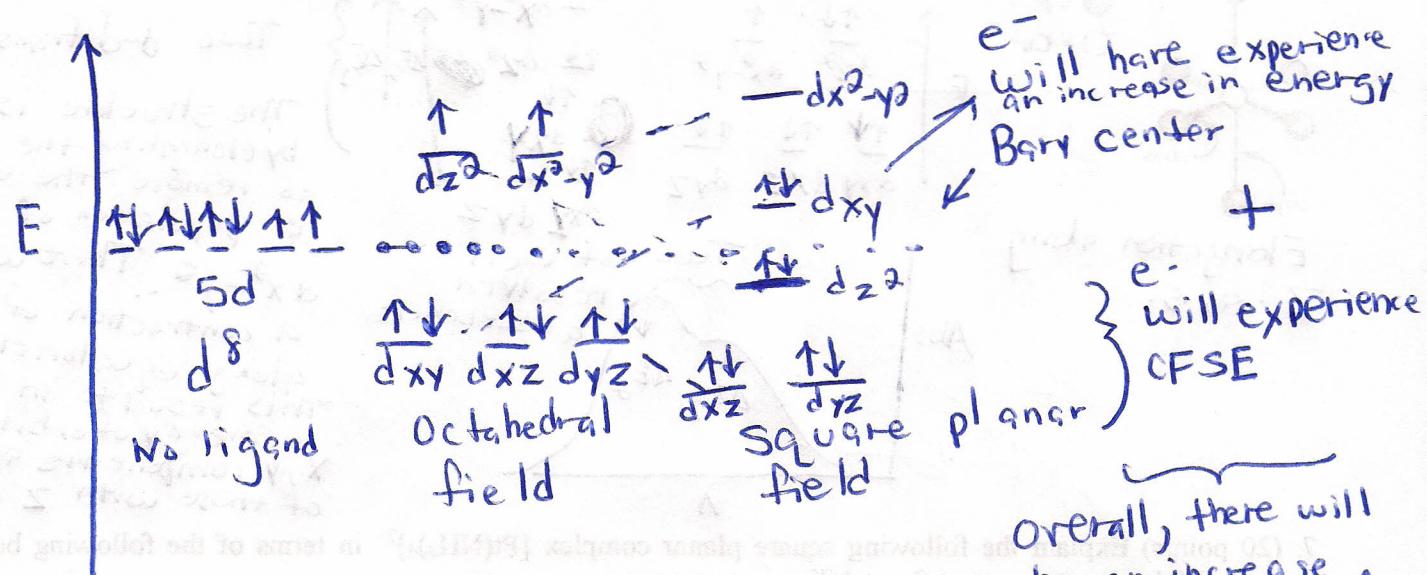
   Coord.# 6   Coord. # 4
                  → Ligands removed
                    from z-axis
                  → Dia magnetic

c. Molecular Orbital Theory (I have started the analysis for you).

TABLE 10.8 Representations and Orbital Symmetry for Square-Planar Complexes

D_{4h}	E	$2C_4$	C_2	$2C_2'$	$2C_2''$	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$		
A_{1g}	1	1	1	1	1	1	1	1	1	1		x^2+y^2, z^2
A_{2g}	1	1	1	-1	-1	1	1	1	-1	-1	R_z	
B_{1g}	1	-1	1	1	-1	1	-1	1	1	-1		x^2-y^2
B_{2g}	1	-1	1	-1	1	1	-1	1	-1	1		xy
E_g	2	0	-2	0	0	2	0	-2	0	0	(R_x, R_y)	(xz, yz)
A_{1u}	1	1	1	1	1	-1	-1	-1	-1	-1		
A_{2u}	1	1	1	-1	-1	-1	-1	-1	1	1	z	
B_{1u}	1	-1	1	1	-1	-1	1	-1	-1	1		
B_{2u}	1	-1	1	-1	1	-1	1	-1	1	-1		
E_u	2	0	-2	0	0	-2	0	2	0	0	(x, y)	

D_{4h}	E	$2C_4$	C_2	$2C_2'$	$2C_2''$	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$
$\Gamma_\sigma (y)$	4	0	0	2	0	0	0	4	2	0

~~Crystal Field Theory~~ conti

In this theory we consider the covalency of metal ligand interactions. A new set of orbitals are created called molecular orbitals that are formed from the metal atomic orbitals and the ligand group orbitals (LGO). We use group theory to understand which atomic orbitals combine with which LGO based on symmetry. Here we only consider σ interactions.

Four vector: 4 irreducible representations
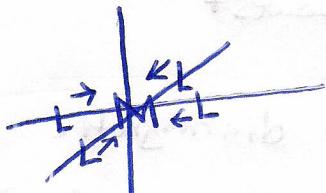
$$\Gamma_\sigma \quad 4 \quad 0 \quad 0 \quad 2 \quad 0 \quad 0 \quad 0 \quad 4 \quad 2 \quad 0$$

$$\Gamma_{red} = A_{1g} + B_{1g} + E_u$$

```
     1  1  1  1  1  1  1  1  1  1
     1 -1  1  1 -1  1 -1  1  1 -1
 +   2  0 -2  0  0 -2  0  2  0  0
 ─────────────────────────────────
     4  0  0  2  0  0  0  4  2  0
```

Atomic orbitals
a_{1g} : s, $\boxed{d_{z^2}}$ → Will not consider because not sufficiently good overlap.
b_{1g} : $d_{x^2-y^2}$
e_u : p_x, p_y

A.O. + LGO matching

a_{1g}

antibonding → 4 nodes

s   bonding → No nodes — Lowest in energy

b_{1g} $d_{x^2-y^2}$ antibonding → 6 nodes

bonding → 2 nodes — Third lowest in energy

e_u

z

p_y → 3 nodes

→ 1 node — Next Lowest

~~B~~ Also same for p_x

- - - $a_{1g}*$
- - - e_u * — diamagnetic

___ ___ ___ Nonbonding — p_z (a_{2u})   Bond order: $\dfrac{8-0}{2} = 4$

$\overline{p_x}\ \overline{p_y}\ \overline{p_z}$
e_u 6p a_{2u}

$\overline{a_{1g}\ 6s}$

— $b_{1g}*$ ∴ 4 Pt–NH₃ bonds

$\underset{d_{z^2}}{\uparrow\downarrow}\ \underset{d_{x^2-y^2}}{\uparrow\downarrow}\ \underset{d_{xy}}{\uparrow\downarrow}\ \underset{d_{xz}}{\uparrow}\ \underset{d_{yz}}{\uparrow}$ · · · $\underset{d_{z^2}}{\uparrow\downarrow}\ \underset{d_{xy}}{\uparrow\downarrow}\ \underset{d_{xz}\ d_{yz}}{\uparrow\downarrow\ \uparrow\downarrow}$ Nonbonding

a_{1g} $\underset{b_{1g}}{\swarrow}$ 5d a_{1g} b_{2g} e_g

Metal Pt²⁺ $\uparrow\downarrow$ b_{1g}
d⁸

$\underset{a_{1g}\ b_{1g}\ e_u}{\uparrow\downarrow\ \uparrow\downarrow\ \uparrow\downarrow\ \uparrow\downarrow}$

LGO
Ordered in terms of
↑ # of nodes

$\uparrow\downarrow\quad \uparrow\downarrow$ e_u

$\uparrow\downarrow$ a_{1g}

8. (20 points) Draw out all the isomers, geometric and optical, of the following: [Co(mer-ONO)Cl₂Br] and [Co(fac-ONO)Cl₂Br].

Draw mer-ONO:
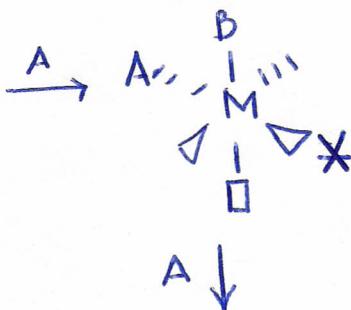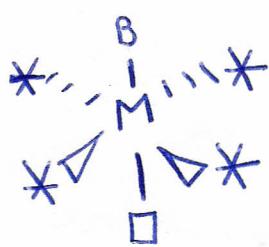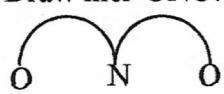
Draw fac-ONO:
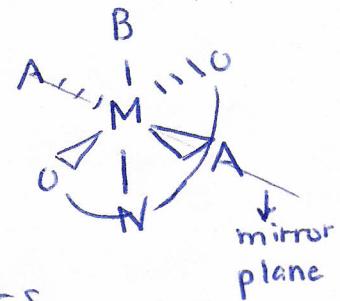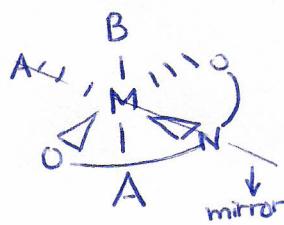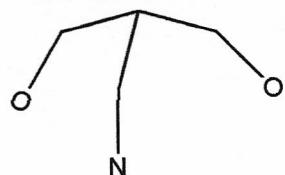
Two geometric isomers
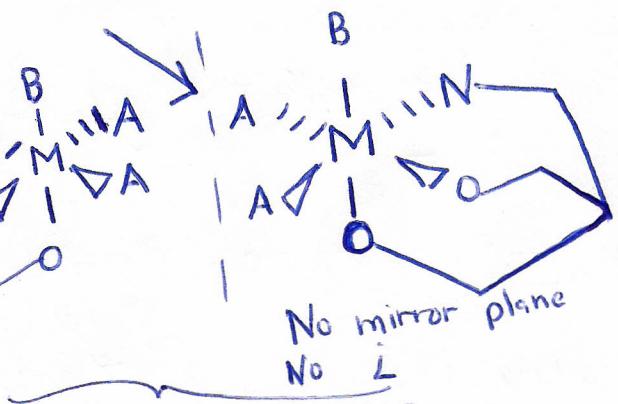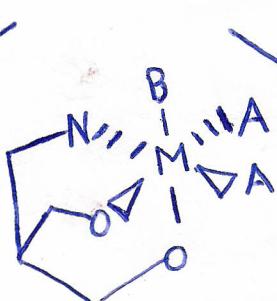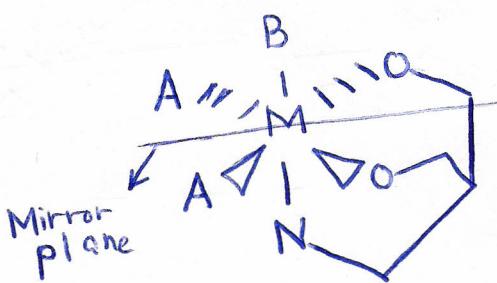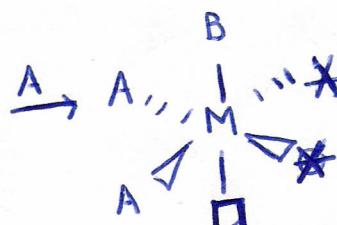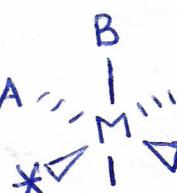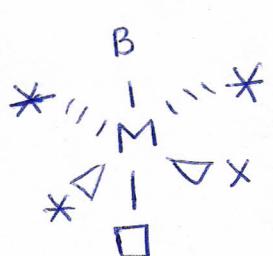
Two geometric isomers, 1 optical isomer

Extra Credit (10 points):

In the graduate seminar on vanadium complexes as antidiabetic agents, the following vanadium complex was discussed. Why does this complex result in the d-orbital splitting below? Also predict its UV-Vis spectrum.

Pillai, S. I.; Subramanian, S. P.; Kandaswamy, M. A novel insulin mimetic vanadium–flavonol complex: Synthesis, characterization and in vivo evaluation in STZ-induced rats. *Eur. J. Med. Chem.* **2013**, *63*, 109-117.
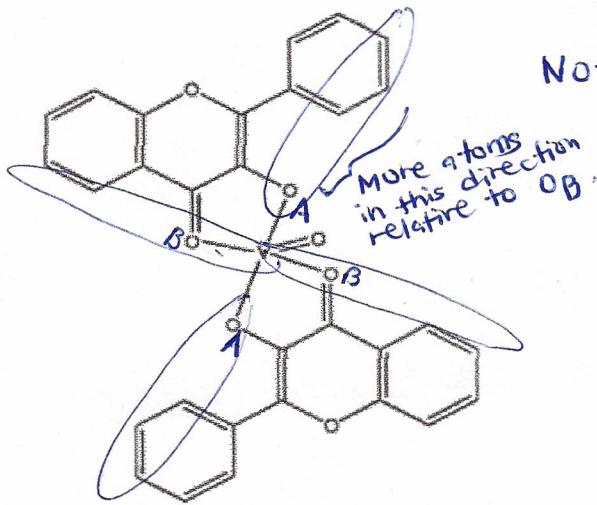
$V(IV)$ d^1

Note: V is above the plane of the four donor oxygen atoms. Therefore the geometry is a distorted square pyramidal.

More atoms in this direction relative to O_B.
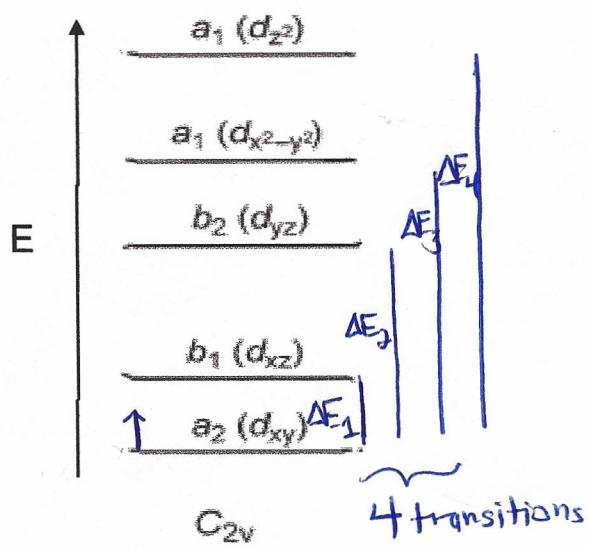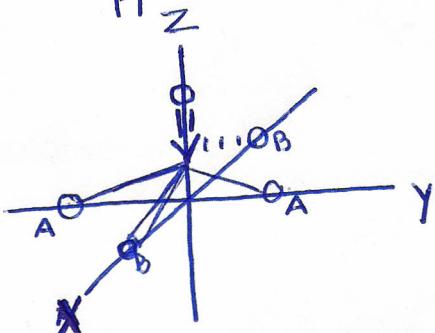
Due to the distortion along the z-axis, the axial oxygen has more V contact with the V d_{z^2} orbital, and the equatorial oxygens have less contact with the V $d_{x^2-y^2}$. This results in an increase of the d_{z^2} orbital energy relative to an octahedral field and even a normal square pyramidal field. All d orbitals with a z component will be higher in energy relative to their x,y component corresponding d orbitals with x,y components. I suspect that d_{yz} is higher in energy than d_{xz} due to the greater # of atoms that would lie on the d_{yz} plane. See my figure above.

$a_1 (d_{z^2})$

$a_1 (d_{x^2-y^2})$

$b_2 (d_{yz})$

ΔE_4

$b_1 (d_{xz})$

ΔE_3

ΔE_2

$a_2 (d_{xy})$ ΔE_1

E

C_{2v}

4 transitions
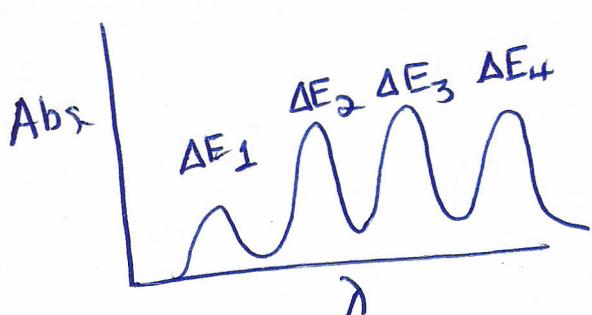
I predict that the UV-Vis spectrum will consist of 4 absorbances.

Abs

ΔE_1 ΔE_2 ΔE_3 ΔE_4

λ