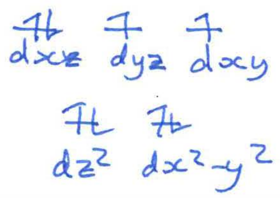
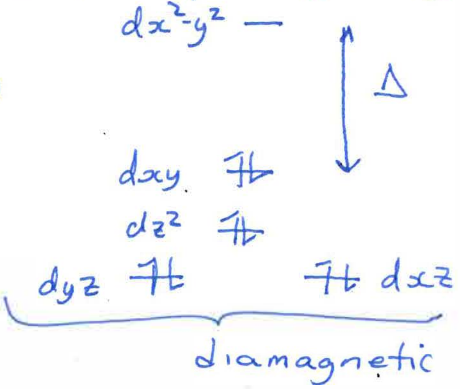
Chemistry 3840
Midterm Examination #2 (March 25, 2026)

1. The nickel complex $[Ni(CN)_4]^{2-}$ is diamagnetic (all electrons are paired), while $[NiBr_4]^{2-}$ is paramagnetic (has unpaired electrons). Fully explain these observations. Include labelled diagrams. (16 points)

$[Ni(CN)_4]^{2-} \rightarrow Ni(II) \rightarrow d^8 \rightarrow CN^-$ is a strong field ligand ∴ expect low spin, square planar geometry

$[NiBr_4]^{2-} \rightarrow Ni(II) \rightarrow d^8 \rightarrow Br^-$ is a weak field ligand ∴ expect ← tetrahedral geometry, which would be paramagnetic.





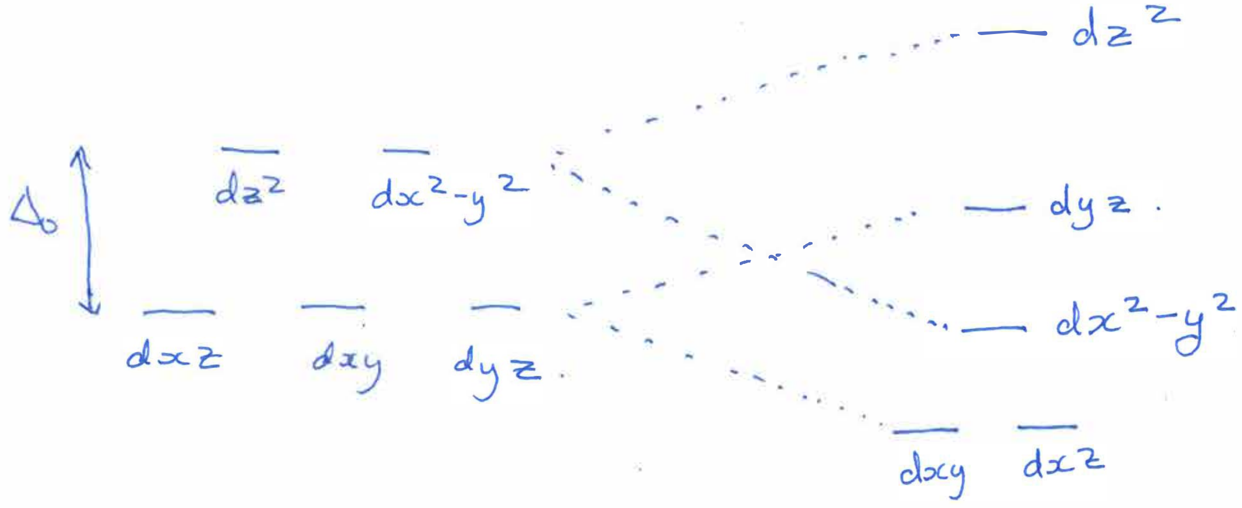
→ Ni(II) complexes can be either square planar or tetrahedral, depending upon the ligands. Since $[NiBr_4]^{2-}$ is paramagnetic, it must have tetrahedral geometry, which makes sense as Br^- is a weak field ligand. Conversely, $[Ni(CN)_4]^{2-}$ is diamagnetic, meaning all e^- are paired. Therefore, it must be square planar which agrees with CN^- being a strong field ligand.

2. Give an example of an ionization isomer of $[CoBr(H_2O)_5]Cl$. No explanation is required. (6 points)

$[CoCl(H_2O)_5]Br$

3. Starting from an octahedral orbital splitting diagram, use the principles of Crystal Field Theory (CFT) to indicate (and discuss) the orbital splitting diagram for a square planar metal complex (complete removal of the two ligands along the x-axis). Be sure to label all orbitals. (12 points)

→ removal of ligands along the x-axis will decrease the energy of orbitals with x-character. Orbitals with y and z character will increase in energy.

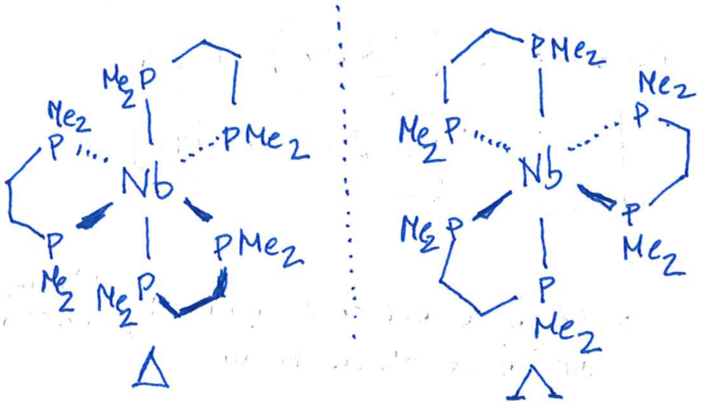


4. **Properly** draw the following complexes using **fully expanded** Lewis structures. Be sure to draw and label all *reasonable* isomers. (dmpe = $Me_2PCH_2CH_2PMe_2$; py = pyridine (C_5H_5N); ^{n}Bu = $CH_2CH_2CH_2CH_3$) (18 points)

a) [Nb(κ^2-dmpe)$_3$]

→ Nb(0), d^5, 17e^-

→ dmpe is a bidentate ligand ∴ Nb is 6 coordinate → octahedral geometry expected

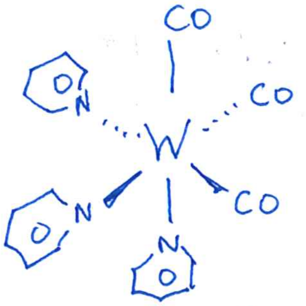


b) [W(CO)$_3$(py)$_3$]

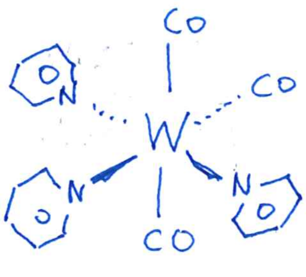
→ W(0), d^6, 18e^-

→ 6 coordinate

↳ expect octahedral geometry.



fac(ial)



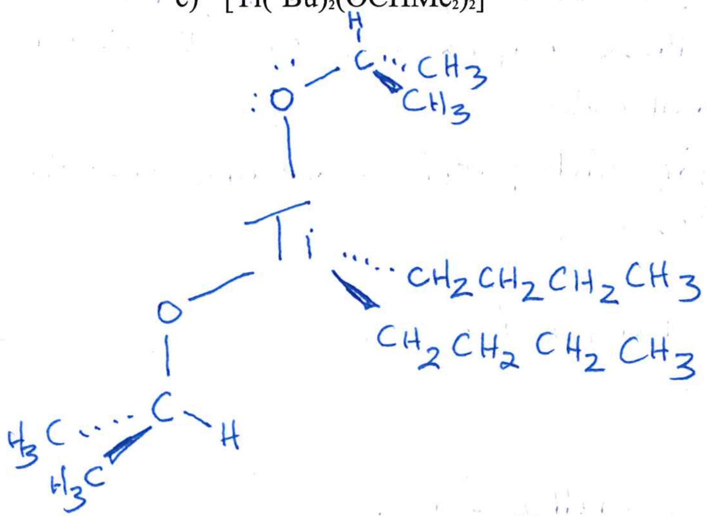
mer(idonal)

c) [Ti(^{n}Bu)$_2$(OCHMe$_2$)$_2$]

→ Ti(IV) d^0, 8e^-

→ 4 coordinate

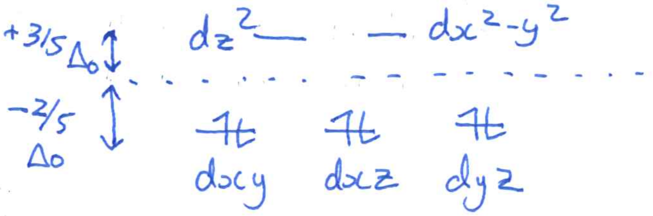
↳ expect tetrahedral geometry.



→ No other isomers

5. Calculate the Crystal Field Stabilization Energy (CFSE) **for one of the following two octahedral complexes**. Show your work and explain (in 10 words or less) any assumptions you made. (12 points)

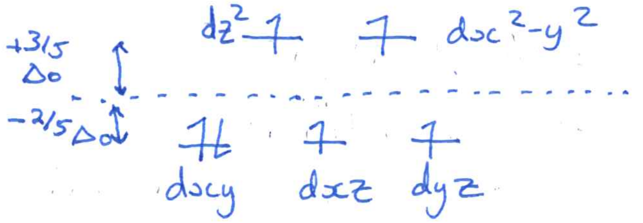
a) $[W(CO)_6]$ → W^0 → d^6 → W is a 3rd row element, CO is a strong field ligand } ∴ strong field environment



$$CFSE = 6\left(-\frac{2}{5}\Delta_o\right) + 3P$$

$$\boxed{= -\frac{12}{5}\Delta_o + 3P}$$

b) $[CoBr_6]^{3-}$ → Co(III) → $d6$ → Co is a 1st row element, Br^- is a weak field } weak field environment



$$CFSE = 4\left(-\frac{2}{5}\Delta_o\right) + 2\left(\frac{3}{5}\Delta_o\right) + P$$

$$= -\frac{8}{5}\Delta_o + \frac{6}{5}\Delta_o + P$$

$$\boxed{= -\frac{2}{5}\Delta_o + P}$$

6. As a recent university graduate with a major in Chemistry, you are very excited about your job interview for a research chemist position at NOVA Chemicals. When you arrive, you are sent into a lab where you find two vials on a bench. One of the vials is filled with a purple powder and the other contains a yellow powder. Nearby you see two labels ($[Co(NH_3)_6]^{3+}$ and $[CoI(NH_3)_5]^{2+}$). If you place the labels on the correct vials you will get the job. Which label do you place on which vial? Why? Explain in four sentences or less. (18 points)

→ Both complexes are Co(III), d^6

→ $I^\ominus$ is a weak field ligand, while NH_3 is a stronger field ligand

↳ since the only difference between these complexes is one I^- vs one NH_3, $[CoI(NH_3)_5]^{2+}$ would have a smaller Δ_o

→ Yellow compounds absorb blue/purple light, while purple compounds absorb green/yellow (lower energy ∴ smaller Δ_o).

∴ $[Co(NH_3)_6]^{3+}$ is yellow (larger Δ_o)

and

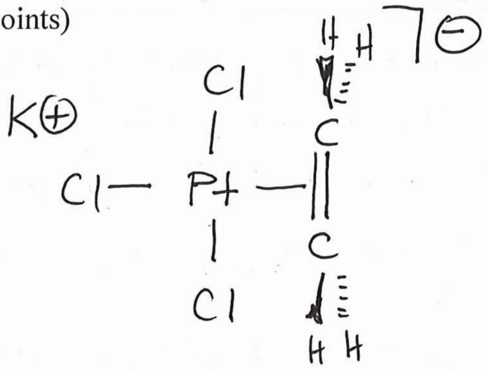
$[CoI(NH_3)_5]^{2+}$ is purple (smaller Δ_o.

7. Match each set of carbonyl stretching frequencies given below with one of the four complexes. No explanation is necessary. (4 points)

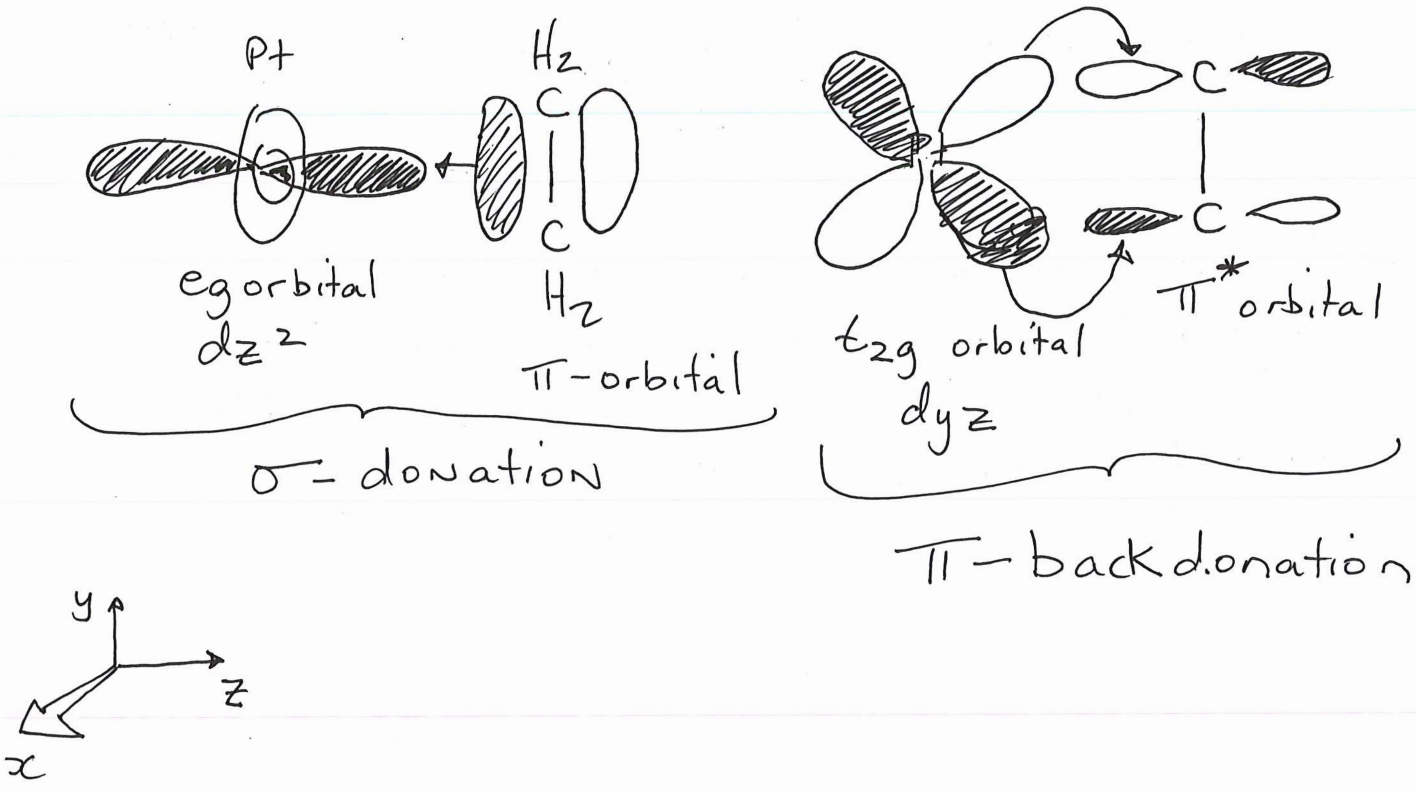
ν(CO) in cm^{-1}	COMPLEXES
1957, 1933	$[Cu(CO)_4]^+$
1944, 1902	*fac*-$[Cr(CO)_3(CNC_6H_4Cl\text{-}p)_3]$
1989, 1841	$[Cp_2Rh_2(CO)_2(\mu\text{-}CO)_2]$
2184	*fac*-$[Cr(CO)_3(CN^tBu)_3]$

8. a) Draw a fully expanded (show every bond and lone pair) Lewis structure for $K^+[Cl_3Pt(H_2C{=}CH_2)]^-$ (2 points)

- Pt(II), d8
4 coordinate
∴ square planar



b) Draw all of the bonding interactions between the Pt and $H_2C{=}CH_2$ in question 8a. For each one, label the type of interaction (*e.g.* σ-donation, π-donation, *etc.*), the constituent d-orbital and the type of alkene orbital (*e.g.* σ, σ^*, π, π^*, *etc.*) involved. (8 points)



9. Which complex in the following pair of molecules would you expect to be more stable? Explain in 10 words or less. (4 points)

Pt(0), d^{10}, 16e^- ← $\boxed{Pt(H_2C{=}CH_2)_3]}$ vs. $[TiCl_4(H_2C{=}CH_2)_2]$ → Ti (iv), d^0, 12e^-

↳ excellent backbonding

↓

no capacity for backbonding to // ligands.

Bonus

Alfred Werner is often considered the "Father of Modern Coordination Chemistry" and was awarded the Nobel Prize in Chemistry in 1913 for his work that established the prevalence of octahedral geometry for late transition metal complexes. Briefly explain how conductivity experiments were essential for providing support for the structures he proposed for various cobalt complexes. Use examples. (4 points)

→ Werner proposed octahedral geometry for a series of Co complexes and by precipitating AgCl and performing conductivity measurements he was able to distinguish between inner and outer sphere ligands.

$CoCl_3(NH_3)_6 \rightarrow 3\,AgCl$, 4 ions ∴ $[Co(NH_3)_6]Cl_3$

$CoCl_3(NH_3)_5 \rightarrow 2\,AgCl$, 3 ions ∴ $[CoCl(NH_3)_5]Cl_2$

2 isomers { $CoCl_3(NH_3)_4 \rightarrow 1\,AgCl$, 2 ions ∴ $\underbrace{[CoCl_2(NH_3)_4]Cl}_{\text{cis \& trans isomers.}}$

$CoCl_3(NH_3)_3 \rightarrow 0\,AgCl$, 0 ions

∴ $[CoCl_3(NH_3)_3]$

→ Werner also made chiral molecules using en, separated them, and also created the first chiral complexes (and separated them) that did not contain any carbon atoms.