Problem Set #4

Chapter 20

1) $[Co(H_2O)_6]^{3+}$

Co^{3+} (d^6)

σ only interactions will be considered.

Each water molecule will donate $2e^-$.

6 H_2O molecules: $12e^-$

— — — — $t_{1u}*$

— $a_{1g}*$

$4p$ — P — t_{1u} — — — e_g*

$4s$ — S a_{1g}

↑↓ ↑↓ ↑↓ ↑↓ ↑↓ ↑↓

σ LGOs

$e_g + a_{1g} + t_{1u}$

$3d$ ↑↓ ↑ ↑ ↑ ↑

d_{z^2} $d_{x^2-y^2}$ d_{xz} d_{yz} d_{xy}

e_g t_{2g}

↑↓ ↑↓ ↑↓ t_{2g}

↑↓ ↑↓ e_g

$Co^{3+}(d^6)$

↑↓ ↑↓ ↑↓ t_{1u}

↑↓ a_{1g}
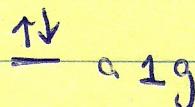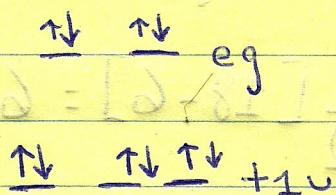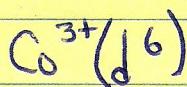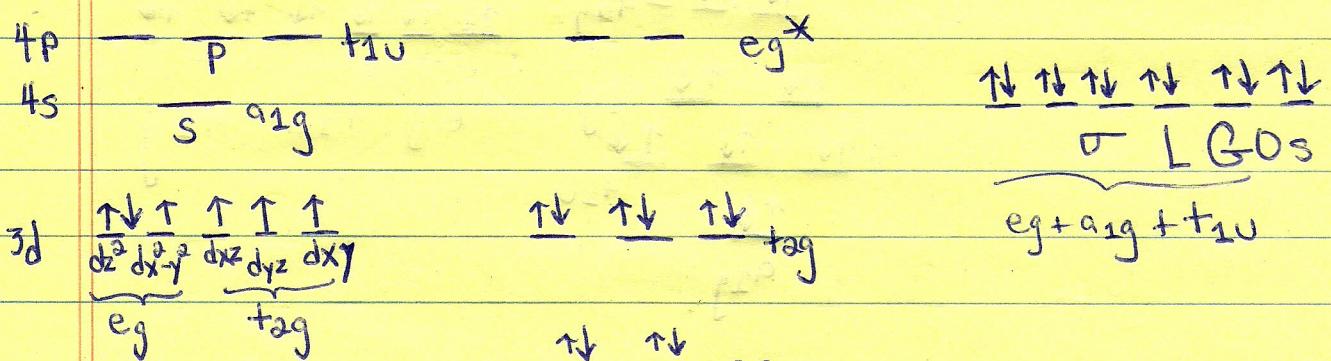
Bond order = $\dfrac{1}{2}$ [bond e^- – antibond e^-] = $\dfrac{1}{2}[12]$

= 6

∴ 6 $Co-OH_2$ bonds

2) $[Co(I)_6]^{3-}$

$Co^{3+}; d^6$

I⁻ is a π donor ligand

— ⤊ — $t_{1u}*$
— $a_{1g}*$

↑ ↑ e_g*

— — — —
t_{1u}

$\overline{a_{1g}}$

⇅ ↑ ↑ $t_{2g}*$

⇅ ↑ ↑ ↑ ↑
$\underbrace{}_{e_g} \underbrace{}_{t_{2g}}$

nonbonding

⇅⇅ ⇅⇅⇅⇅⇅⇅⇅⇅⇅   ⇅ ⇅⇅↓ ⇅⇅↓ ⇅⇅ ⇅⇅⇅⇅
$\underbrace{}_{t_{2g}}$ $\underbrace{}_{t_{1g}+t_{1u}+t_{2u}}$

⇅ ⇅ ⇅ t_{2g}

⇅ ⇅ ⇅ ⇅ ↕ ⇅
$\underbrace{}$

⇅ ↑↓ e_g

⇅ ⇅ ↑↓ e_g e_g t_{1u} a_{1g}

⇅ ⇅ ↑↓
t_{1u}

⇅
a_{1g}
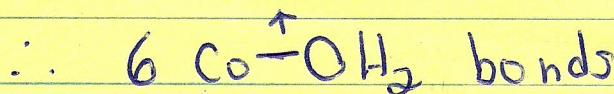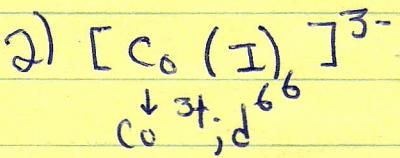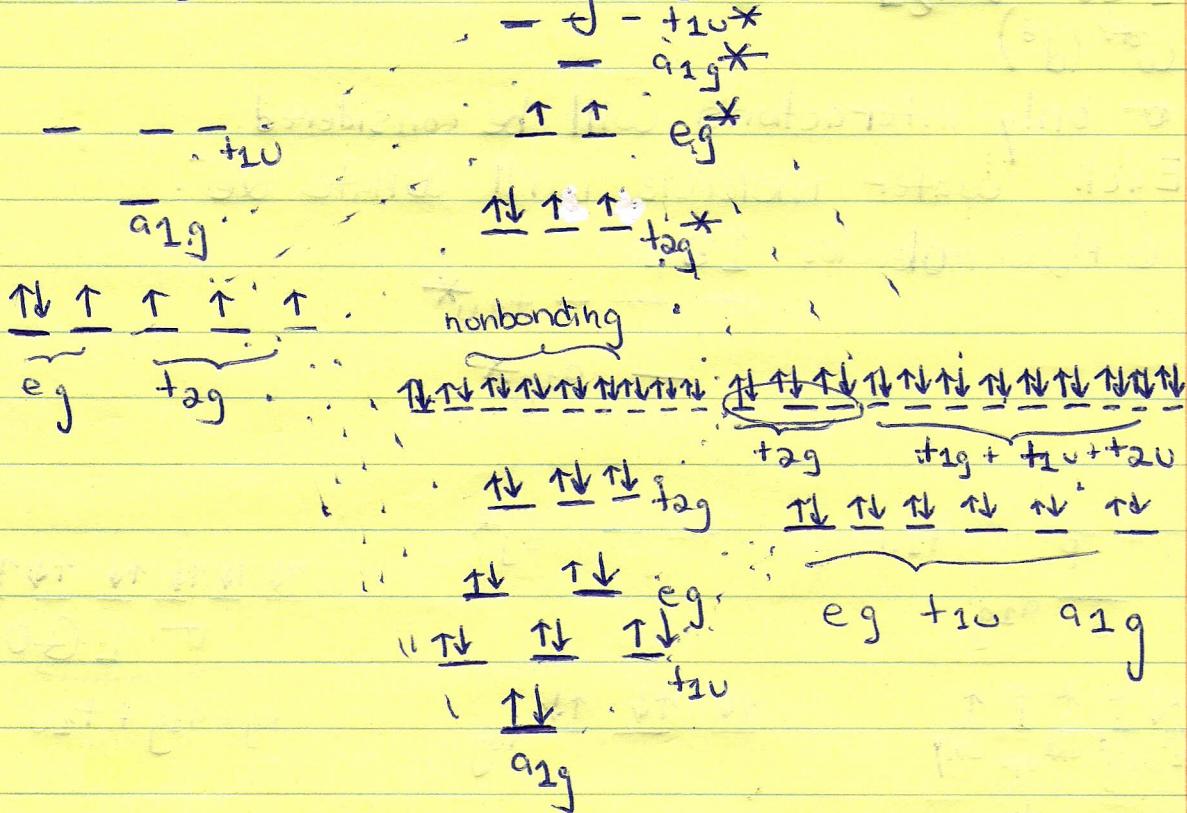
Bond order $= \dfrac{1}{2}[18-6] = 6$

∴ 6 Co–I bonds

3) CFSE

$[Co(I)_6]^{3-}$

d^6 ; weak field

$\uparrow$ $\uparrow$ 0.6

$\uparrow\downarrow$ $\uparrow$ $\uparrow$ 0.4

$\mu_s = \sqrt{4(4+2)} = \sqrt{24} = 4.90$

$$CFSE = \left([4 \times 0.4\, \Delta oct] - [2 \times 0.6 \Delta oct] \right) - 1P$$

$$= 0.4\, \Delta oct - 1P$$

$[Co(CN)_6]^{3-}$

d^6 ; strong field

— —

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

CFSE = $1.6\, \Delta oct - 3P$

$\mu_s = 0$ diamagnetic

4) This question can be answered in several ways. If you use the valence bond theory representation of water, then the lone pairs are in sp^3 orbitals which only engage in sigma interactions.

If you use molecular orbital theory, the p_x orbital (b_1 symmetry) is available for sigma bonding.

The p_z orbital (a_1) is only partially available for π bonding because it is used in the molecular orbitals formation of the water molecule and would serve as a weak pi donor. The a_1^* orbital does not have the correct symmetry to be a pi acceptor.

$\left. \begin{array}{c} \\ \end{array} \right\} a_1^*$

mismatch $\left\{ \begin{array}{c} \\ \end{array} \right.$

d orbital
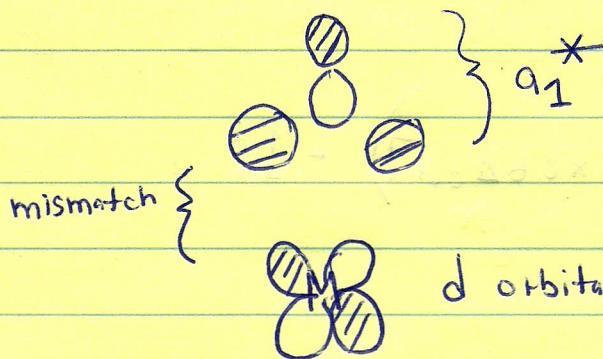
5) Ni^{2+}; d^8

$[Ni(NH_3)_6]^{2+}$: $\dfrac{\nu_2}{\nu_1} = \dfrac{17,500\, cm^{-1}}{10,750\, cm^{-1}} = 1.63$

$\dfrac{\nu_3}{\nu_1} = \dfrac{28,200\, cm^{-1}}{10,750\, cm^{-1}} = 2.62$

@ $\dfrac{\Delta}{B} = 12$ $\dfrac{\nu_2}{\nu_1} = \dfrac{19.5}{12} = 1.63$ $\Big\}$ reasonable

$\dfrac{\nu_3}{\nu_1} = \dfrac{32}{12} = 2.67$

$$^3A_2 \rightarrow {}^3T_2 \qquad \frac{E}{B} = 12 \qquad \frac{10,750 \text{ cm}^{-1}}{B} = 12$$

$$B = 896 \text{ cm}^{-1}$$

$$^3A_2 \rightarrow {}^3T_1 \qquad \frac{E}{B} = 19.5 \qquad \frac{17,500 \text{ cm}^{-1}}{B} = 19.5$$

$$B = 897 \text{ cm}^{-1}$$

$$^3A_2 \rightarrow {}^3T_1 \qquad \frac{E}{B} = 32 \qquad \frac{28,200 \text{ cm}^{-1}}{B} = 32$$

$$B = 881 \text{ cm}^{-1}$$
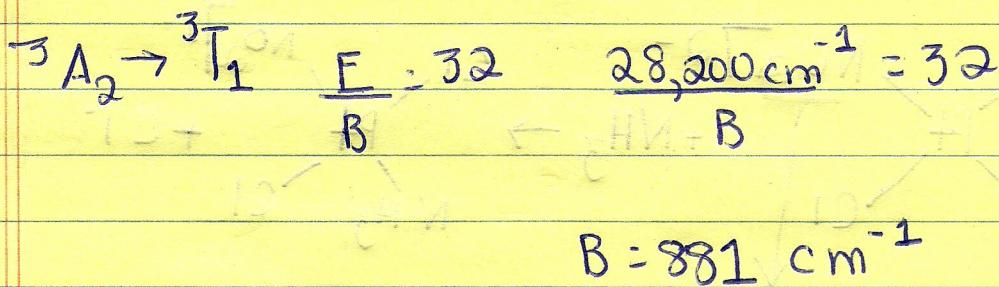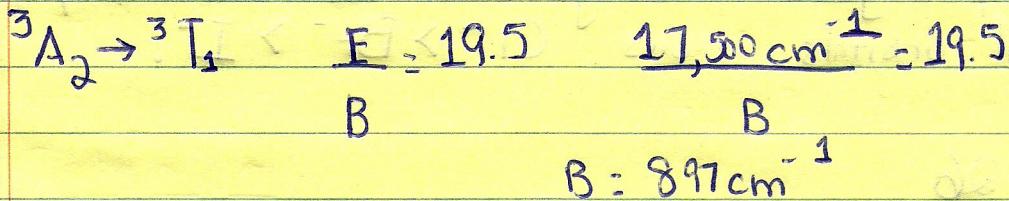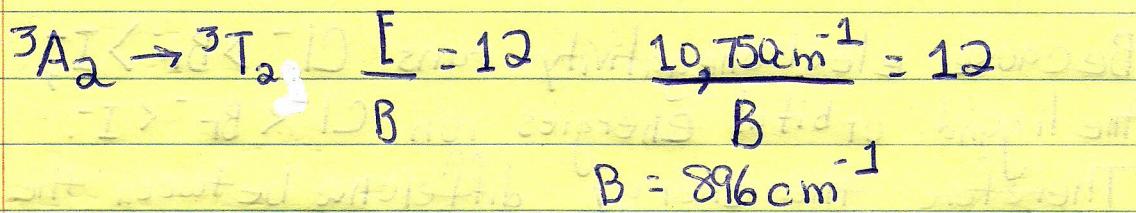
Average $B = 891 \text{ cm}^{-1}$

$$\frac{\Delta}{B} = 12 \qquad \Delta = 10,692 \text{ cm}^{-1}$$

6) Ni^{2+} from T-S diagram, spin-allowed

$$\left.\begin{array}{l} ^3A_2 \rightarrow {}^3T_2 \\ ^3A_2 \rightarrow {}^3T_1 \\ ^3A_2 \rightarrow {}^3T_1 \end{array}\right\} \text{ We saw this already}$$
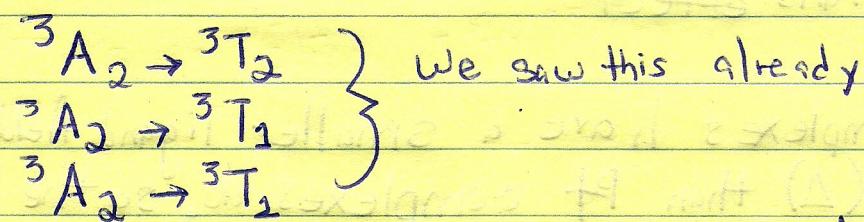
↑ ↑   No Jahn-Teller distortion for the
             ground state because there is only
↑↓ ↑↓ ↑↓   one way to fill the 8 e⁻'s in the
             5 orbitals

7) Because electronegativity runs $Cl^- > Br^- > I^-$, the ligand orbital energies run $Cl^- < Br^- < I^-$. Therefore the energy difference between the mostly ligand bonding MO's and the mostly metal orbitals runs $Cl^- > Br^- > I^-$.

chapter 26

8) a.

greater trans effect

b.

greater trans effect
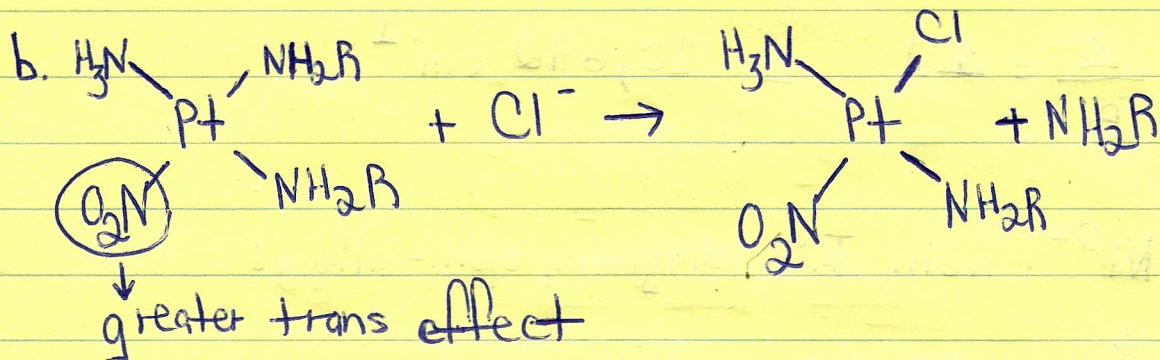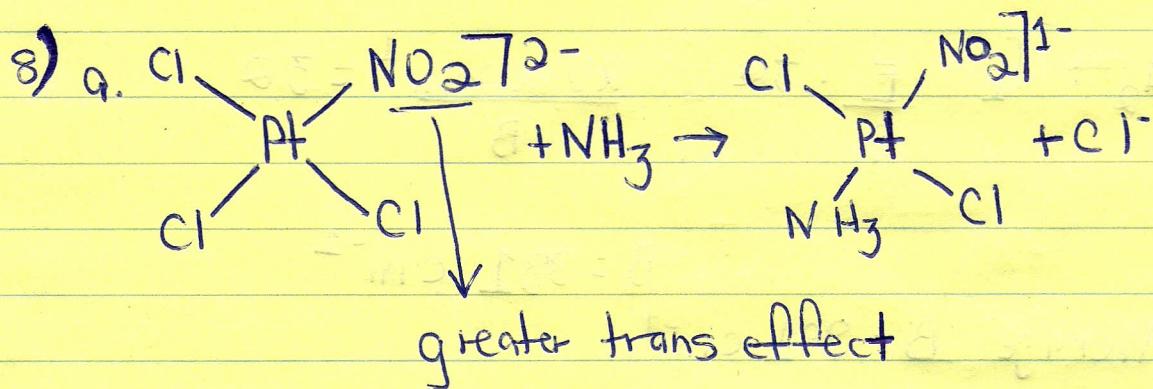
9) Nickel complexes have a smaller ligand field splitting (Δ) than Pt complexes do, so the crystal field stabilization energy is smaller. This means that the activation barrier to substitution is lower for Ni because the complex is starting at a higher energy activation barrier means faster substitution rate.

Ni Pt

E E_a E_a

10. $[Pd(dien)SCN]^+ + py \xrightarrow{k} [Pd(dien)py]^{2+} + SCN^-$
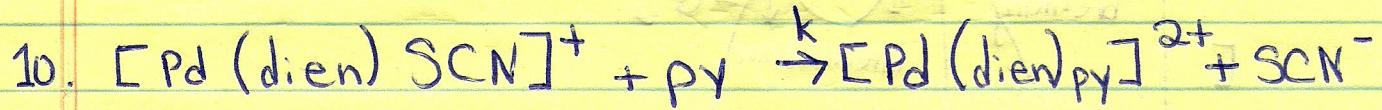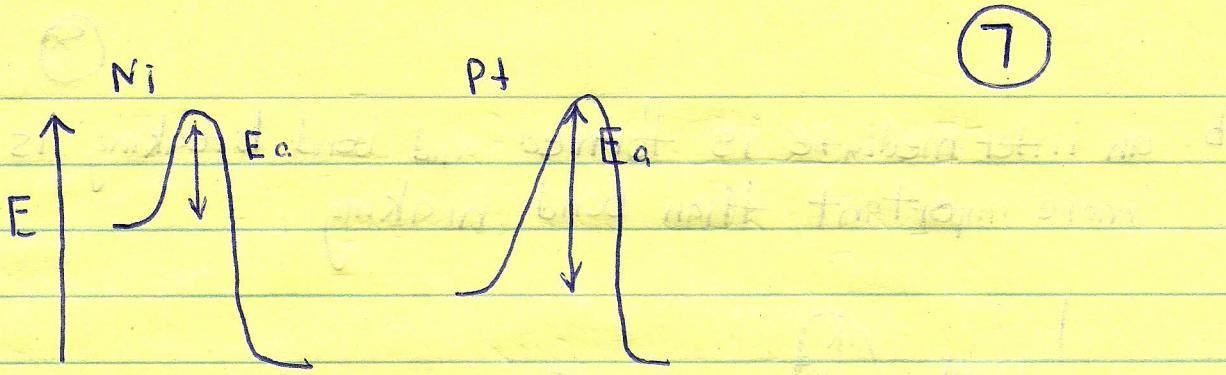
$$\frac{Rate}{\frac{M}{S}} = \underbrace{(k_1 + k_2[py])}_{k_{obs}} [Pd(dien)SCN]^+$$

Straight-line:

$$k_{obs} = \underbrace{k_2}_{slope}\underbrace{[py]}_{x} + \underbrace{k_1}_{y\text{-intercept}}$$

$\underset{y}{}$

$k_1 = 0.0043 \; s^{-1}$

$k_2 = 1.637 \; M^{-1}s^{-1}$

11. a. no intermediate is formed

Reactants

Products
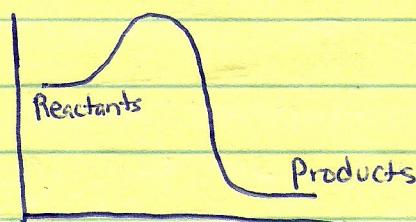
b. an intermediate is formed and bond breaking is more important than bond making
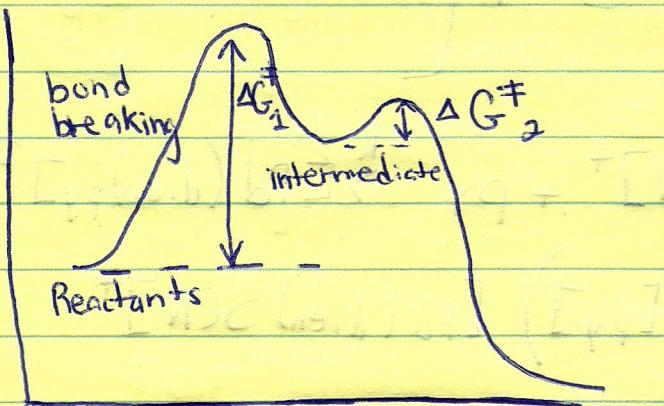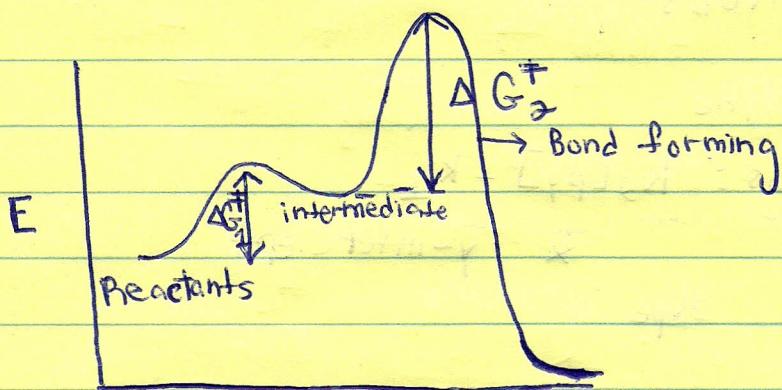
These plots will depend on the mechanism you invoke.

12) From left to right there will be a build-up of electron density on the metal and therefore a higher population of the e_g * molecular orbitals. This would favor a dissociative mechanism.

13)

Inner sphere mechanism
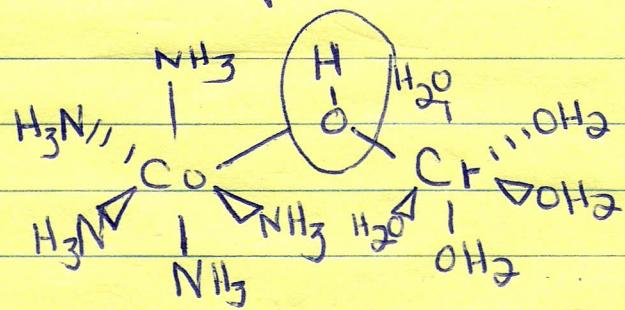
OH^- serves as a bridge

$\ominus : \ddot{O} - H$
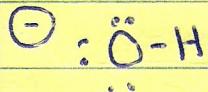
When OH^- is replaced by H_2O, no bridging complex can be formed and so the e^- transfer is forced to occur by an outer sphere mechanism and the rate would be slower. As the H^+ concentration decreases, the water ligand is deprotonated, permitting a bridged structure to form. Thus, the more rapid inner sphere mechanism can occur.