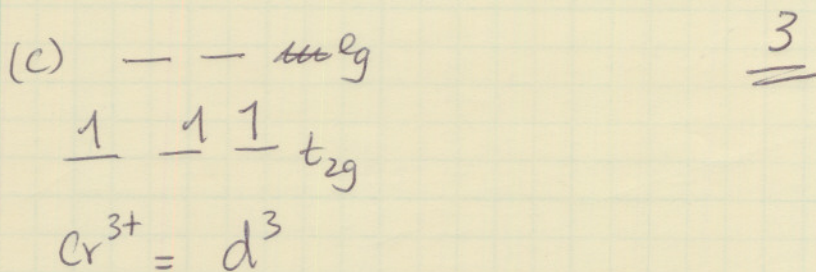
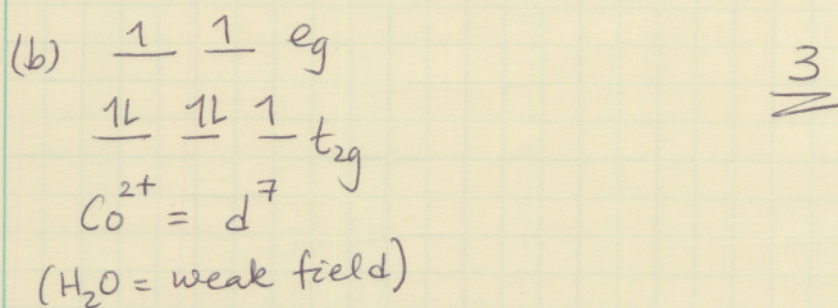
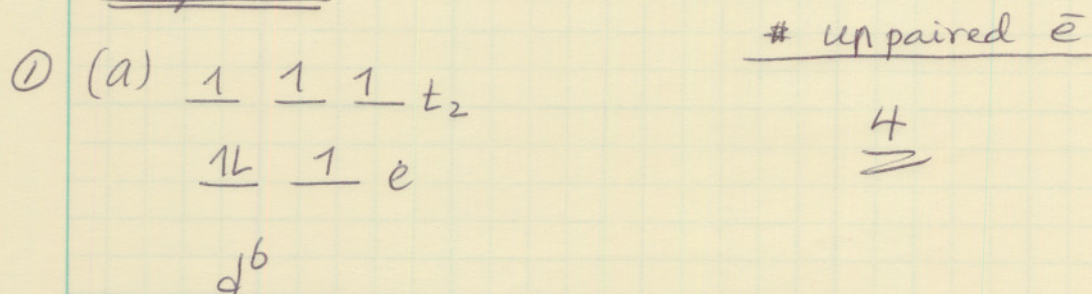


ADVANCED CHEMISTRY

INORGANIC CHEMISTRY - SPRING - WEEK 6

Chapter 10



(d) cannot do this yet

(e) $\mu = 5.1 \text{ BM} = \sqrt{n(n+2)} \text{ BM}$

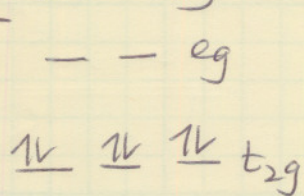
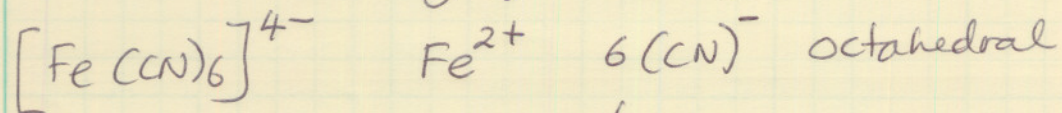
$(5.1)^2 = n(n+2) = 26.01$

$n^2 + 2n - 26.01 = 0$

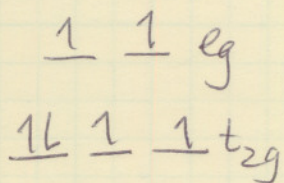
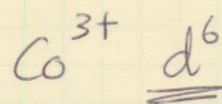
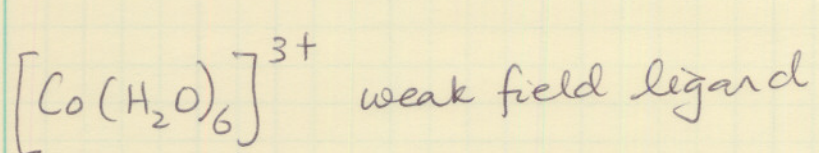
$n = 4.19 \approx 4$

4

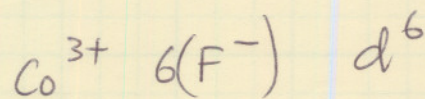
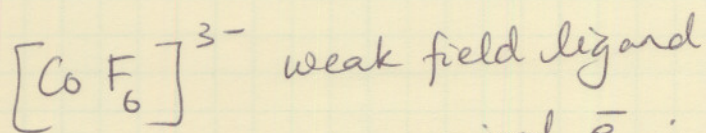
② CN^- is a strong field ligand



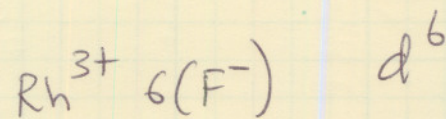
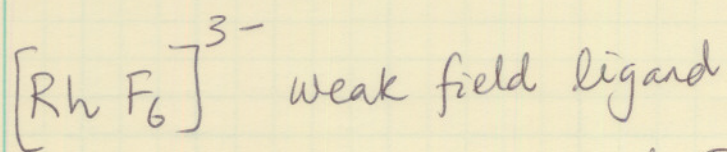
d^6
 no unpaired \bar{e} ; diamagnetic



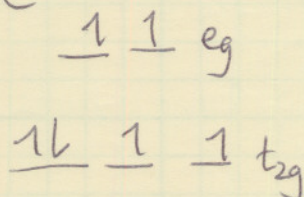
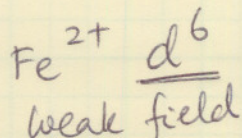
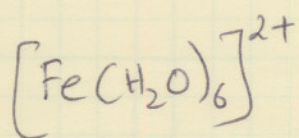
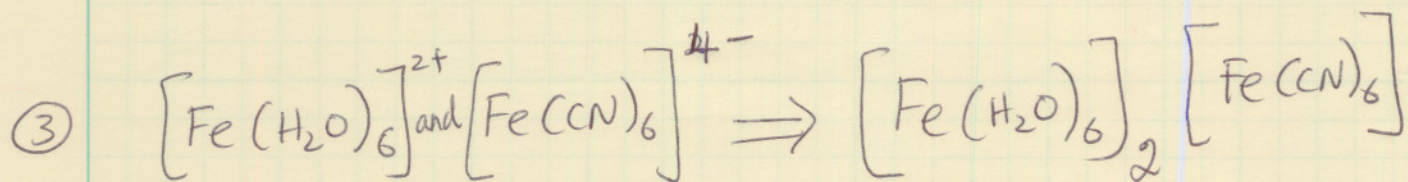
4 unpaired \bar{e} ; paramagnetic



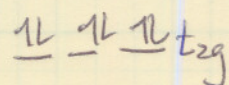
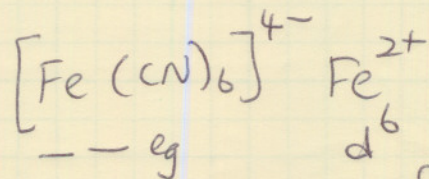
4 unpaired \bar{e} ; paramagnetic



4 unpaired \bar{e} ; paramagnetic



} 4 unpaired \bar{e}



d^6
 strong field

zero unpaired \bar{e}

total # of unpaired \bar{e} ^{one unit of} in the compound = $4 + 4 = 8$

~~$$\mu = \sqrt{n(n+2)} \text{ BM} = \sqrt{8(8+2)} = 4.89 \text{ BM}$$~~

observed data

$2 \frac{2}{3}$ unpaired \bar{e} per iron

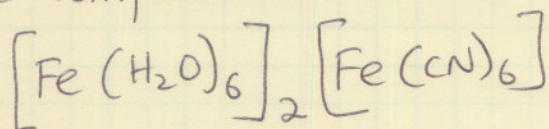
there are 3 irons per unit of compound

total # of unpaired \bar{e} per unit of compound = $3 \left(2 \frac{2}{3} \right) = 3 \left[\frac{8}{3} \right] = 8$

~~$$\mu = \sqrt{8(8+2)}$$~~

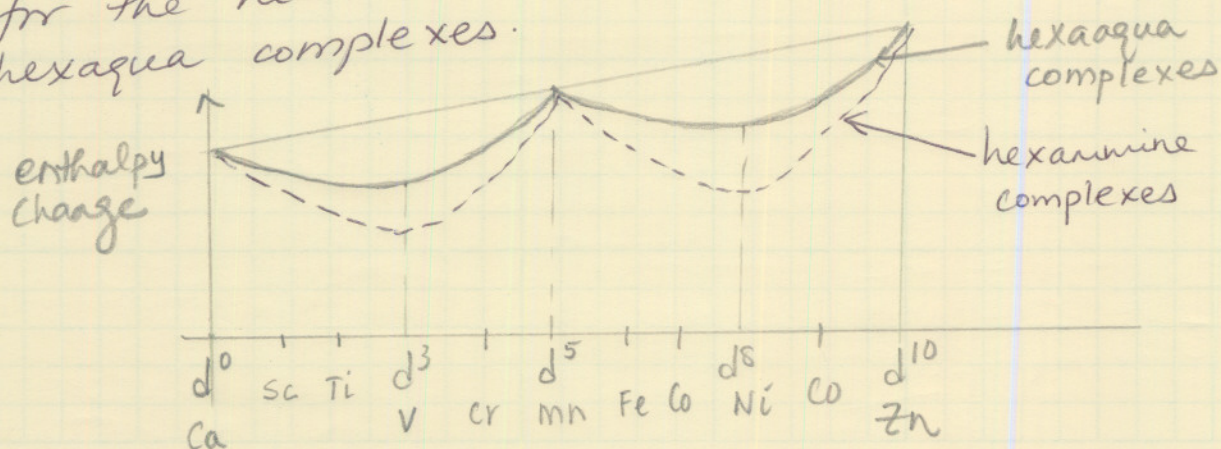
This is consistent with our calculations.

∴ The compound must be

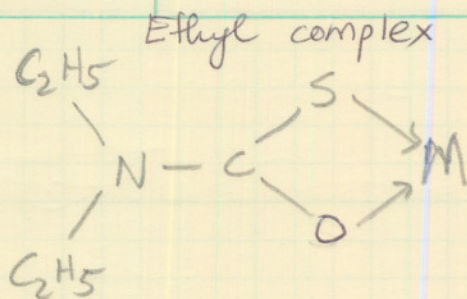
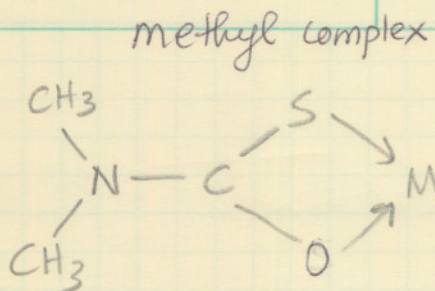


(4)

H_2O is a weaker ligand than NH_3 . Therefore exchanging (NH_3) for (H_2O) should stabilize the metal complex further. This increases the LFSE for the hexamine complexes relative to the hexaqua complexes.



(10)



300 K $\mu = 5.7 \mu_B - 5.8 \mu_B$

$\mu = 5.7 - 5.8 \mu_B$

150 K $\mu = 4.7 - 5 \mu_B$

$\mu = 4.7 - 5 \mu_B$

78 K $\mu = 3.6 - 4 \mu_B$

$\mu = 3.6 - 4 \mu_B$

$\mu = 5.7 - 5.9 \approx 5.8$

$\mu = \sqrt{n(n+2)}$

$n(n+2) = \mu^2 = 33.64$

$n = 4.88 \approx 5$ unpaired e^-

∴ at 300k both these compounds have 5 unpaired e^-

Fe(III) has $3d^5 4s^0$ configuration

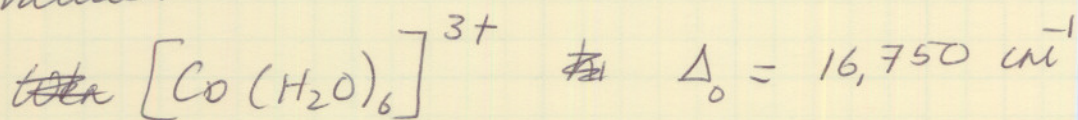
∴ all electrons are unpaired (high spin) for these complexes at 300k.

As temperature is decreased, some electrons begin to pair up, lowering the magnetic moment. from red to orange indicates lowered μ .

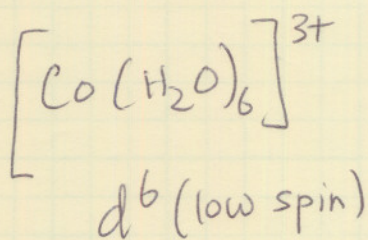
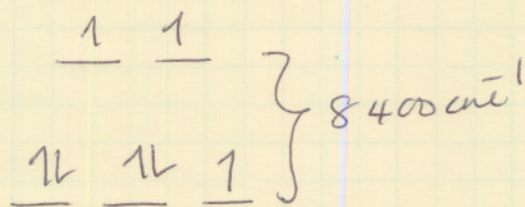
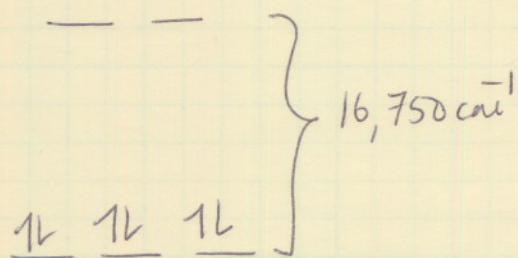
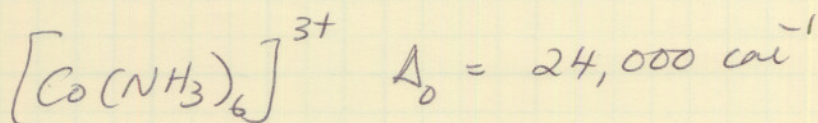
observations.

For the larger R groups the complexes are always high spin, resulting in the larger Δ values.

(ii)



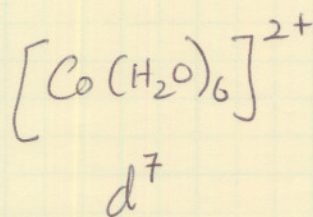
If Co^{3+} is an oxidizing agent, it will be reduced to $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ $\Delta_o = 8,400 \text{ cm}^{-1}$



$$\text{LFSE} = 6(-0.4\Delta_o)$$

$$= -2.4\Delta_o$$

$$= -40,200 \text{ cm}^{-1}$$



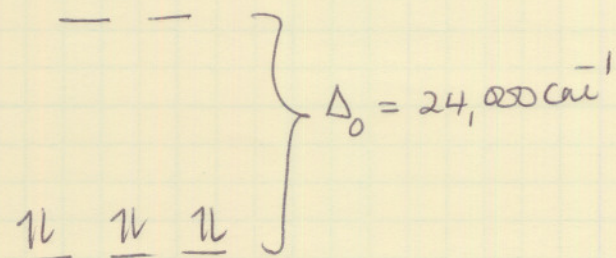
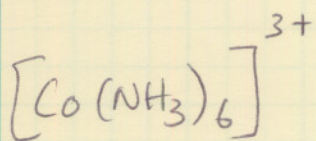
$$\text{LFSE} = 5(-0.4\Delta_o) + 2(0.6\Delta_o)$$

$$= -0.8\Delta_o$$

$$= -6720 \text{ cm}^{-1}$$

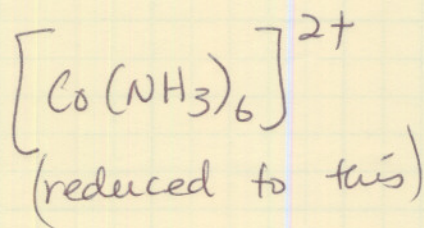
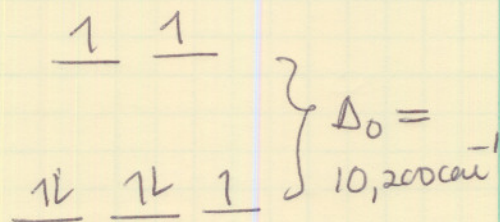
difference
in energy = $33,480 \text{ cm}^{-1}$

In order for $[\text{Co}(\text{H}_2\text{O})_6]^{3+}$ to be oxidized, one must put in $33,480 \text{ cm}^{-1}$ worth of energy.



d^6 (low spin)

$$\begin{aligned} \text{LFSE} &= 6(-0.4\Delta_0) \\ &= -2.4\Delta_0 \\ &= -57,600 \text{ cm}^{-1} \end{aligned}$$

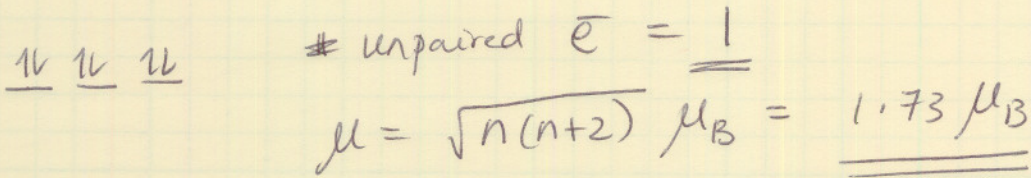
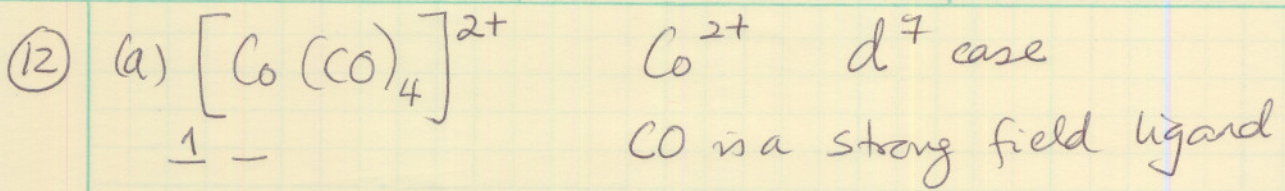


$$\begin{aligned} \text{LFSE} &= 5(-0.4\Delta_0) + 2(0.6\Delta_0) \\ &= -0.8\Delta_0 \\ &= -8160 \text{ cm}^{-1} \end{aligned}$$

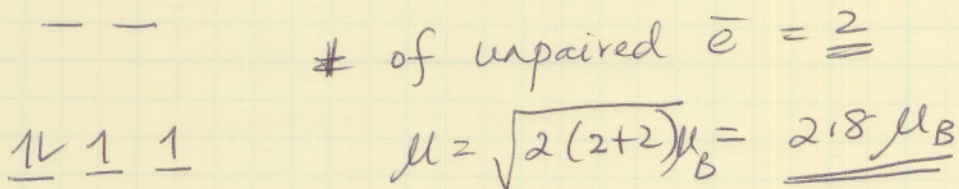
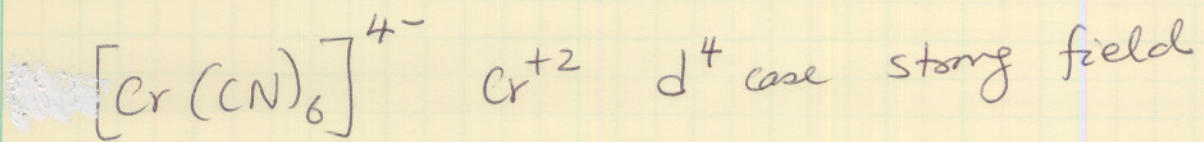
$$\text{difference} = 49,440 \text{ cm}^{-1}$$

For this reduction to occur, we need $49,440 \text{ cm}^{-1}$ of energy.

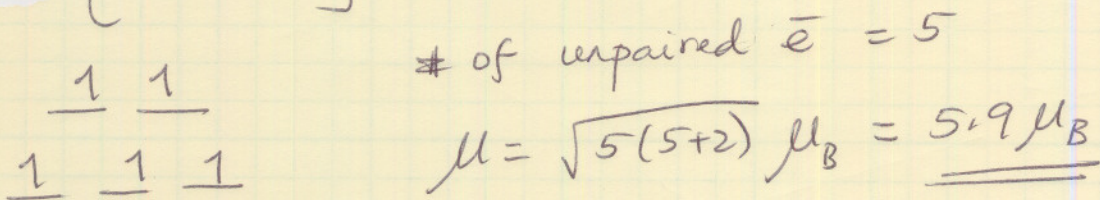
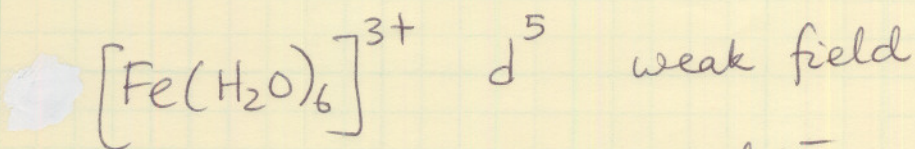
$\therefore [\text{Co}(\text{H}_2\text{O})_6]^{3+}$ is a better oxidizing agent than



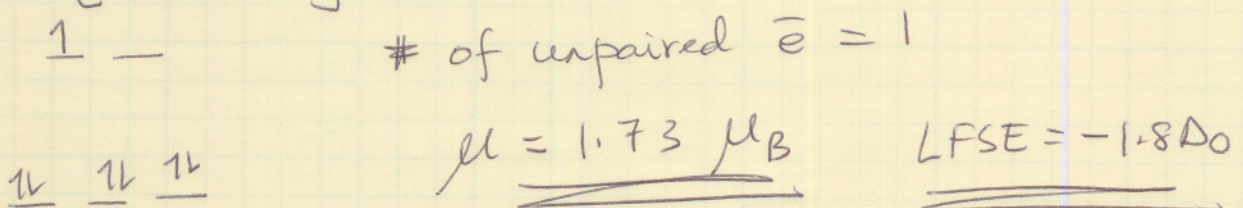
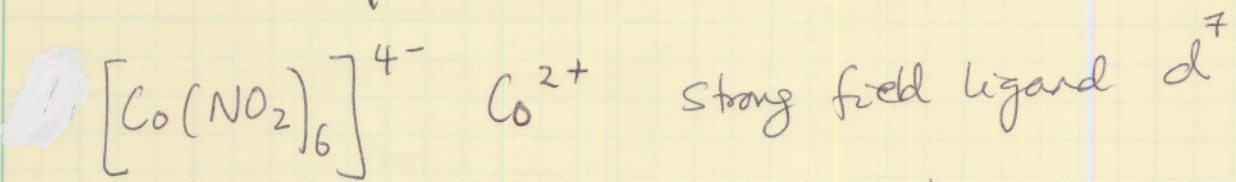
LFSE = $-6(0.4\Delta_0) + 1(0.6\Delta_0) = \underline{\underline{-1.8\Delta_0}}$

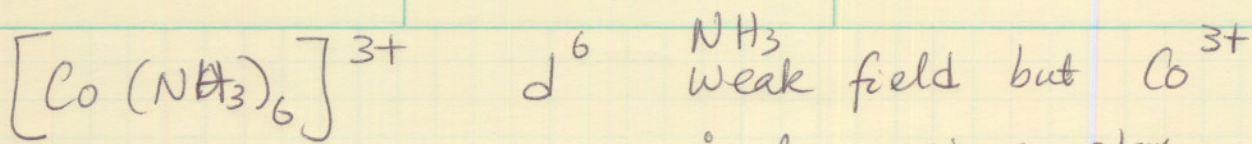


LFSE = $4(-0.4\Delta_0) = \underline{\underline{-1.6\Delta_0}}$

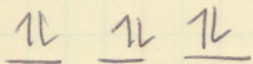


LFSE = $3(-0.4\Delta_0) + 2(0.6\Delta_0) = \underline{\underline{0}}$





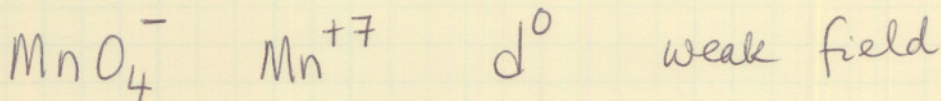
∴ low spin complex
(see problem 10.11)



of unpaired $\bar{e} = \underline{\underline{0}}$

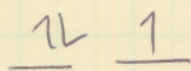
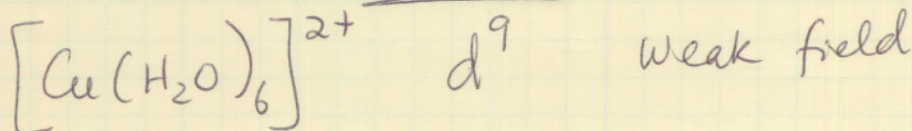
$\underline{\underline{\mu = 0}}$

LFSE = $6(-0.4\Delta_0) = \underline{\underline{-2.4\Delta_0}}$



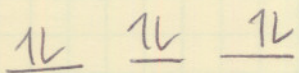
of unpaired $\bar{e} = \underline{\underline{0}}$ $\underline{\underline{\mu = 0}}$

$\underline{\underline{LFSE = 0}}$



of unpaired $\bar{e} = \underline{\underline{1}}$

$\underline{\underline{\mu = 1.73 \mu_B}}$



LFSE = $6(-0.4\Delta_0) + 3(0.6\Delta_0) = \underline{\underline{-0.6\Delta_0}}$

Leave out parts (b) and (c).

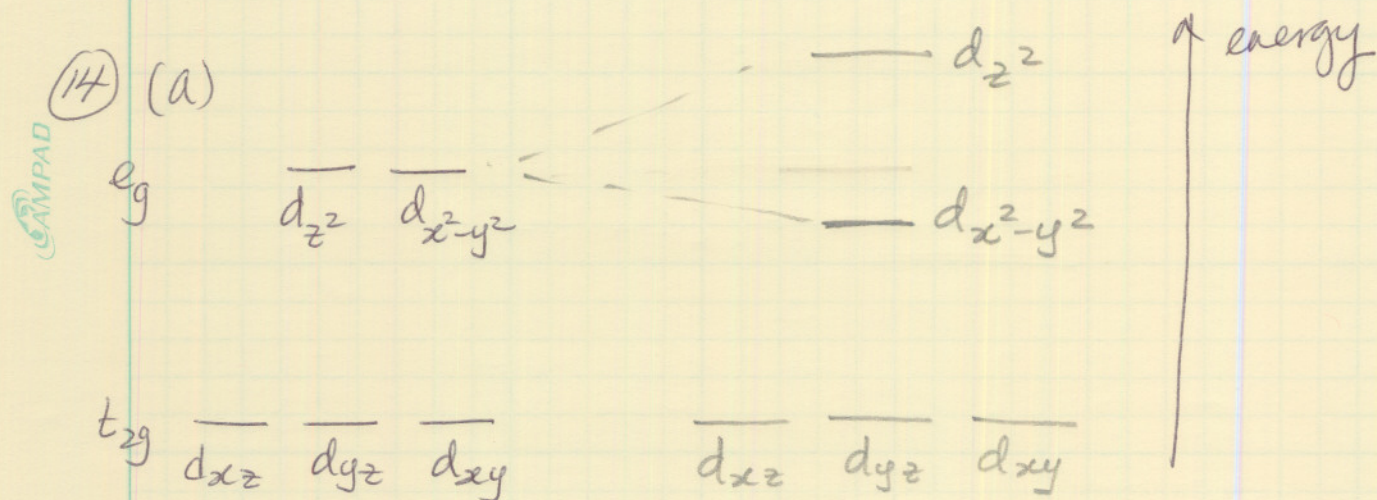
- (13) Since Δ_0 is lowest for Cl^- its π donor ability (π Lewis base) is stronger than that of F^- (next higher Δ_0)

H_2O, NH_3, en } σ bonding only.

∴ better overlap of

CN^- σ bonding + π acceptor (deuss π acid) ^{strong} ability

$\therefore \Delta_0$ is highest for CN^-



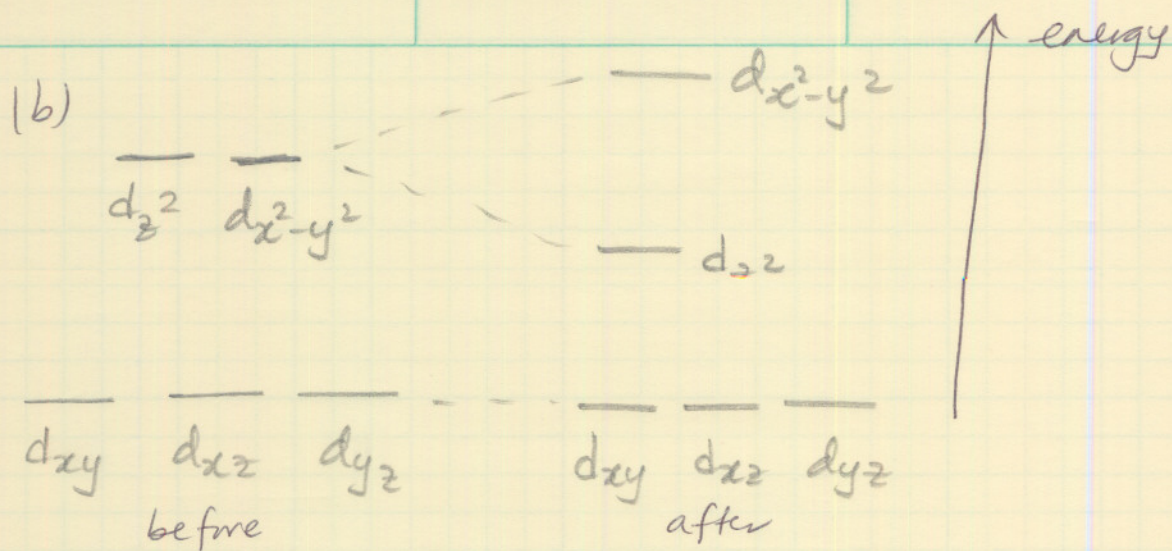
Octahedral
Complex
frontier orbitals

When d orbitals
are compressed along the
z axis

The metal-ligand bonds along the z axis shortened.
 \therefore electron-electron repulsion increases along the
orbitals along the z axis (d_{z^2} orbital).
This raises the energy of the d_{z^2} orbital.

To maintain center of mass, ~~orbitals~~ metal-ligand
bonds along x and y axes ($d_{x^2-y^2}$) are
elongated. This reduces e^-e^- repulsion along
x and y axes
 \therefore Energy of $d_{x^2-y^2}$ orbital is slightly decreased.

No effect on d_{xy} , d_{xz} , d_{yz} because they are in
between the axes.



The metal-ligand bond along the z axis is lengthened. This stabilizes the d_{z^2} orbital. Since the metal-ligand bonds along the x & y axes are compressed to maintain center of mass, the $d_{x^2-y^2}$ orbital is destabilized. d_{xy} , d_{yz} , d_{xz} orbitals remain unchanged since they lie between the axes.