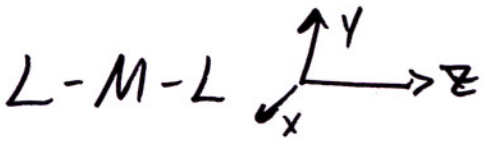
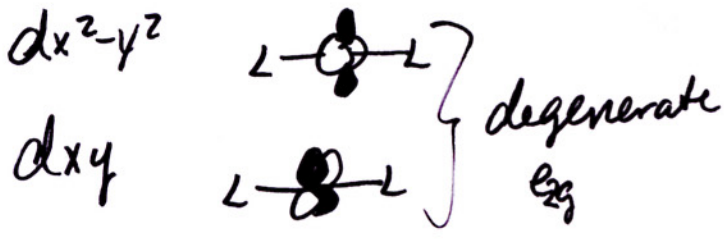
Additional Problems

1.) a) L-M-L Linear



$D_{\infty h}$

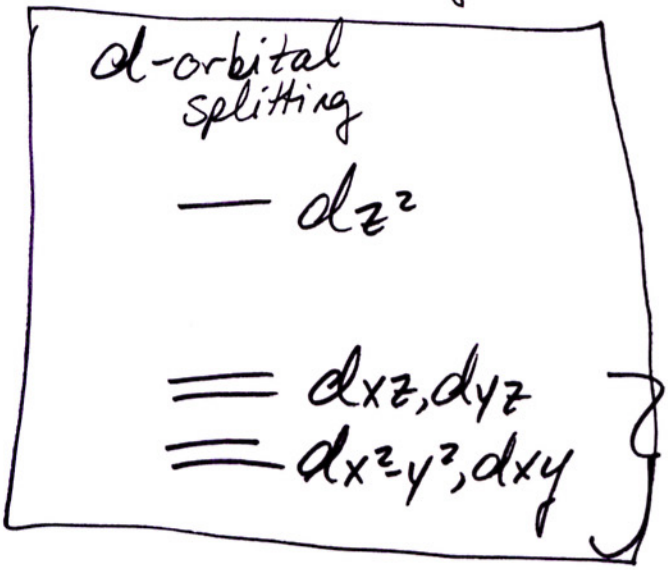
M-orbitals



Least amt of contact w/ Ligand

↓

Most amt. of contact w/ Ligand



Could be at same energy depending on ligand

2. A tetrahedron can be inscribed in a cube so, the d-orbital splitting is the same as a tetrahedral arrangement but only w/ greater Δ_t

d-orbital splitting

$\equiv$ t_2 d_{xz}, d_{yz}, d_{xy}

$=$ e $d_{z^2}, d_{x^2-y^2}$

3.) Both Ni compounds are Ni^{2+} d^8, however, the geometry changes w/ ligand.

Cl^- → weak field ligand → tetrahedral

CN^- → strong field ligand → sq. planar

Square plandr

— $d_{x^2-y^2}$

↿ d_{xy}

↿ d_{z^2}

↿⇂ d_{xz}, d_{yz}

tetrahedral

↿↿↿ d_{xy}, d_{xz}, d_{yz}

↿⇂ $d_{z^2}, d_{x^2-y^2}$

4.) absorption spectra ~ ligand field strength

$[Ti(CN)_6]^{3-}$, $[Ti(H_2O)_6]^{3+}$, $[TiCl_6]^{3-}$

strong field ligand ⟶ weak field ligand

higher energy ⟶ lower energy

5.) a) Mn^{2+} d^5 = 1 e^-

b.) Cr^{4+} d^2 — — — / + + = 2 e^-

c.) Co^{2+} d^7 + + + / # # = 3 e^-

d.) V^{3+} d^2 — — / + + — = 2 e^-

e.) Co^{3+} d^6 — — / # # # = 0 e^-

low spin!

f.) Fe^{2+} d^6 — — / # # # = 0 e^-

octahedral!

g) Mn^{2+} d^5 + + / + + + = 5 e^-

LFSE

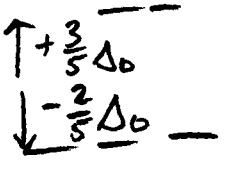
6.) a.) $[Fe(CN)_6]^{3-}$

Fe^{3+} d^5

paramagnetic

$5 \times -\frac{2}{5} = -2$

$LFSE = -2\Delta_o$



b.) $[Ru(NH_3)_6]^{2+}$

Ru^{2+} d^6

diamagnetic

$6 \times -\frac{2}{5} = -\frac{12}{5}$

$LFSE = -\frac{12}{5}\Delta_o$

c.) $[Co(NH_3)_6]^{3+}$

Co^{3+} d^6

diamagnetic

$LFSE = -\frac{12}{5}\Delta_o$

d.) $[CoCl_4]^{2-}$

Co^{2+} d^7

paramagnetic

$-4(\frac{3}{5}) + 3(\frac{2}{5})$

$-\frac{12}{5} + \frac{6}{5} = -\frac{6}{5}$

$LFSE = -\frac{6}{5}\Delta_t$

e.) $[Fe(H_2O)_6]^{2+}$

Fe^{2+} d^6

paramagnetic

$LFSE = -\frac{2}{5}\Delta_o$

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

$4(-\frac{2}{5}) + 2(\frac{3}{5})$

$-\frac{8}{5} + \frac{6}{5} = -\frac{2}{5}$

f.) $[Mn(H_2O)_6]^{2+}$

Mn^{2+} d^5

paramagnetic

$LFSE = 0$

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

$3(-\frac{2}{5}) + 2(\frac{3}{5}) = 0$

g) $[CoF_6]^{3-}$

Co^{3+} d^6

paramagnetic

$LFSE = -\frac{2}{5}\Delta_o$

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

h) $[Cr(H_2O)_6]^{2+}$

Cr^{2+} d^4

paramagnetic

$LFSE = -\frac{3}{5}\Delta_o$

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

$3(-\frac{2}{5}) + \frac{3}{5}$

$-\frac{6}{5} + \frac{3}{5} = -\frac{3}{5}$

i) $[Cr(NH_3)_6]^{3+}$

Cr^{3+} d^3

paramagnetic

$LFSE = -\frac{6}{5}\Delta_o$

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

$3(-\frac{2}{5}) = -\frac{6}{5}$

j) $[PtCl_6]^{2-}$

Pt^{4+} d^6

diamagnetic

$LFSE = \frac{-12}{5}\Delta_o$

$6\left(\frac{-2}{5}\right) = \frac{-12}{5}$

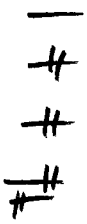
7.)

$\mu_{eff} = 2\sqrt{S(S+1)}\,\mu_B$

a.) $[Ni(CN)_4]^{2-}$

Ni^{2+} d^8

$\mu_{eff} = 0$

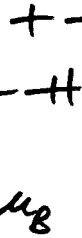


b.) $[Ni(NH_3)_6]^{2+}$

Ni^{2+} d^8

$S = 1$

$\mu_{eff} = 2\sqrt{1(2)} = 2\sqrt{2}\,\mu_B$ $2.83\,\mu_B$



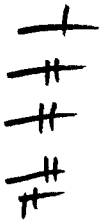
C.) $[Cu(NH_3)_6]^{2+}$

Cu^{2+} d^9

$S = \frac{1}{2}$

Jahn-teller distortion

$\mu_{eff} = 2\sqrt{\frac{1}{2}\left(\frac{3}{2}\right)} = \sqrt{3}\,\mu_B$ $1.73\,\mu_B$



d.) $[Ag(NH_3)_2]^+$

Ag^+ d^{10}

$\mu_{eff} = 0$

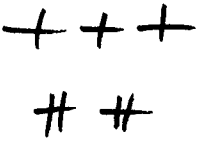
e.) $[Co(NH_3)_6]^{3+}$

Co^{3+} d^6

$\mu_{eff} = 0$

f.) $[CoCl_4]^{2-}$

Co^{2+} d^7



$S = \frac{3}{2}$

$\mu_{eff} = 2\sqrt{\frac{3}{2}\left(\frac{5}{2}\right)} = \sqrt{15}\,\mu_B$ $3.87\,\mu_B$

g) $[Cr(NH_3)]^{3+}$

Cr^{3+} d^3

$S = \frac{3}{2}$

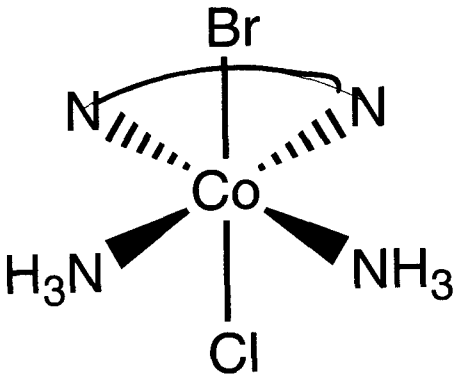
$\mu_{eff} = \sqrt{15}\,\mu_B$ $3.87\,\mu_B$

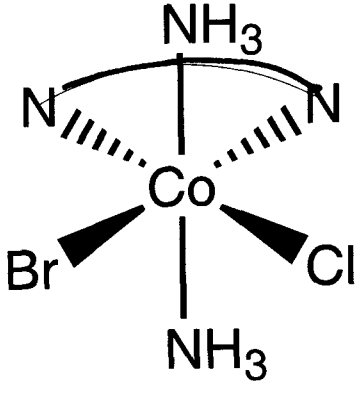
h) $Ni(CO)_4$

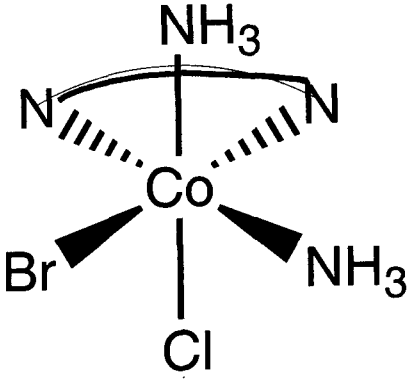
Ni^0 d^{10}

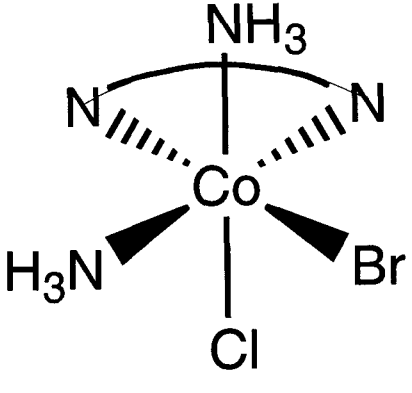
$\mu_{eff} = 0$

8a) full credit if you made a concerted effort!

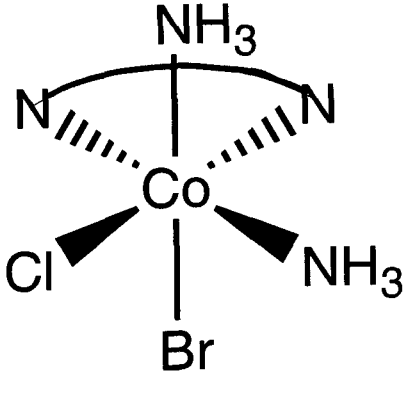


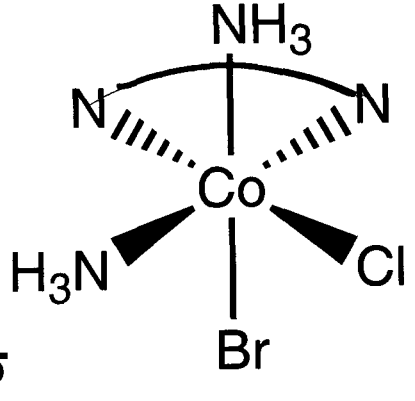






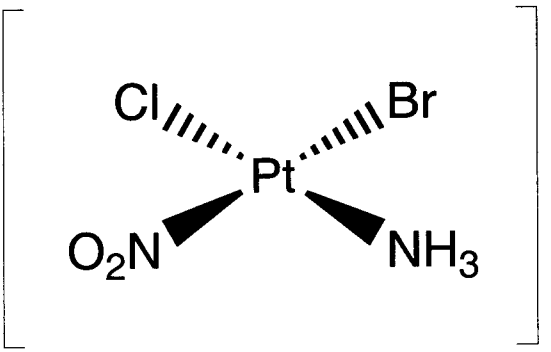
σ

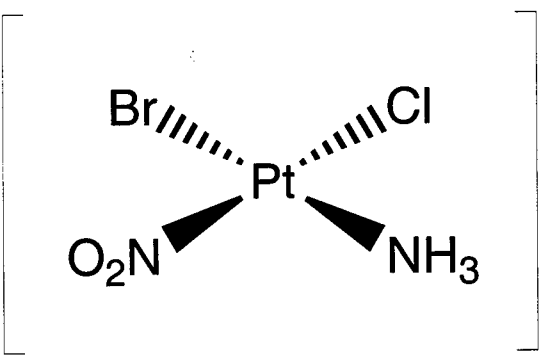


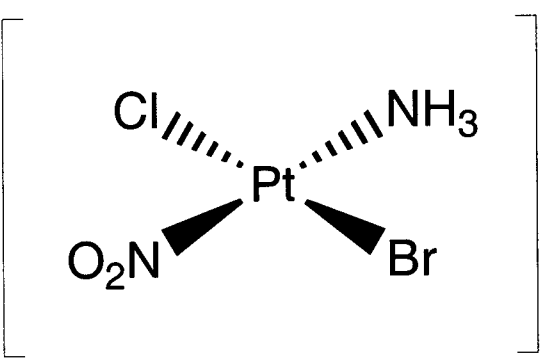


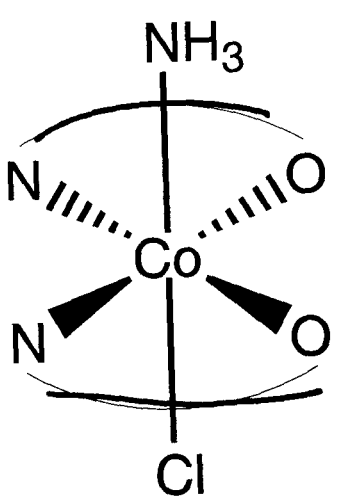
σ

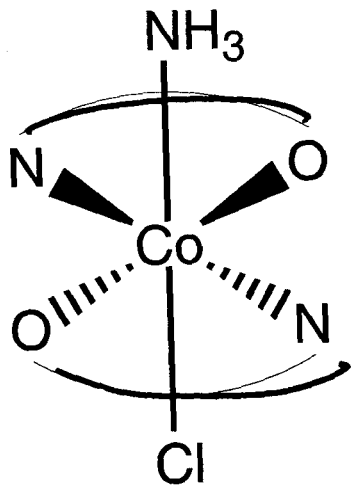
86)








NH3
N
O
Co
N
O
Cl


NH3
N
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Co
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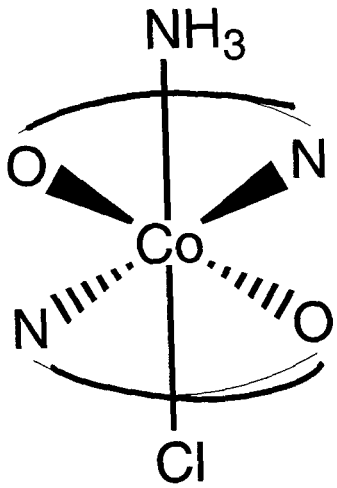
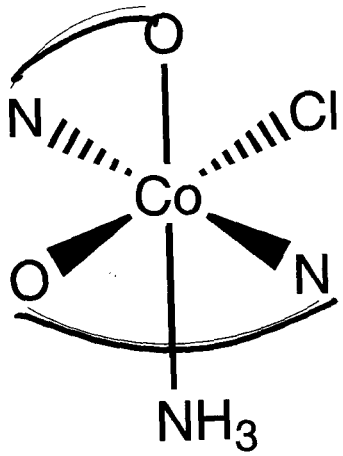
N
Cl


NH3
O
N
Co
N
O
Cl


O
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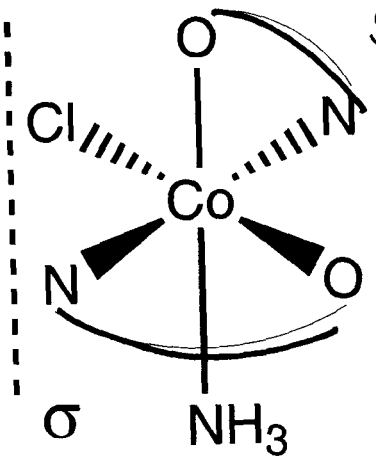
NH3


O
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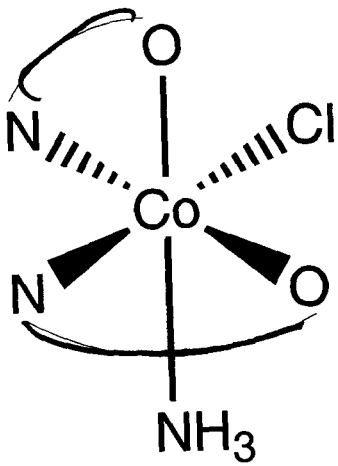
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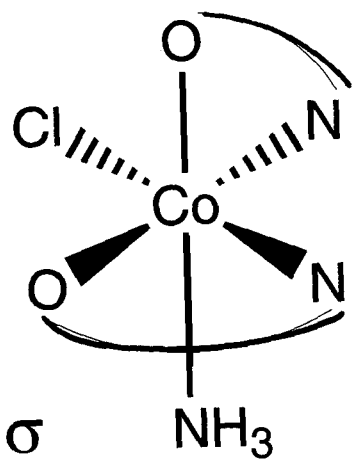
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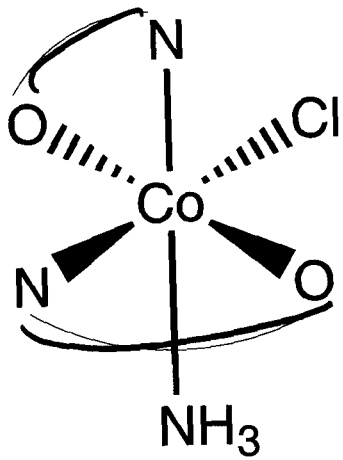
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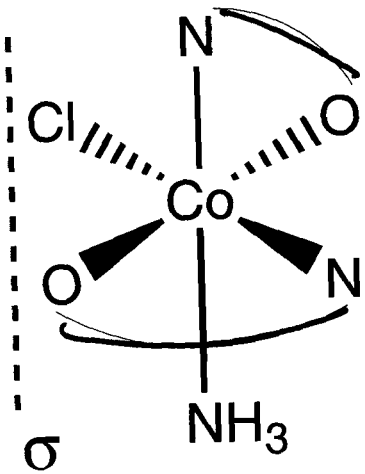
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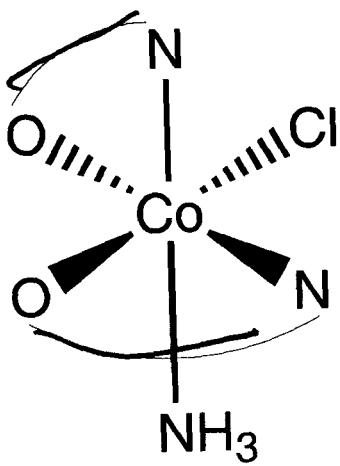
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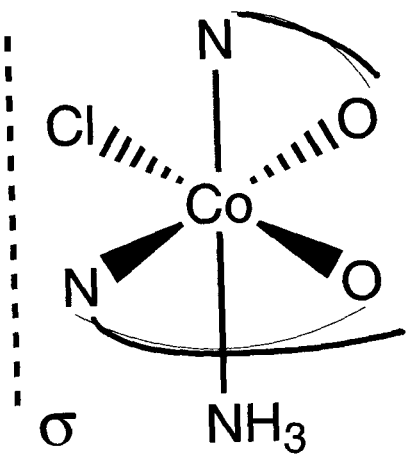
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8e)

N
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N
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N
Cl
Cl

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Cl
N
N

a

Cl
Cl
N
Co
N
N
N

N
N
Cl
Co
N
N
Cl

a

N
Cl
Cl
Co
N
N
N

9.) $Ti^{4+} = [Ar]$

$V^{2+} = [Ar]\,3d^3$

$Cr^{5+} = [Ar]\,3d^1$

$Mn^{6+} = [Ar]\,3d^1$

$Fe^{0} = [Ar]\,3d^6 4s^2$

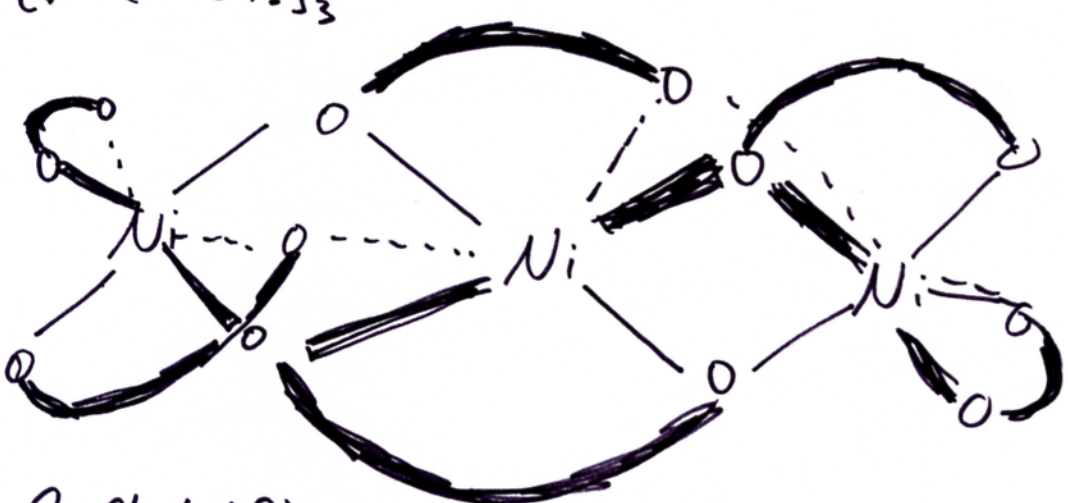
$Co^{+} = [Ar]\,3d^7 4s^1$

$Ni^{2+} = [Ar]\,3d^8$

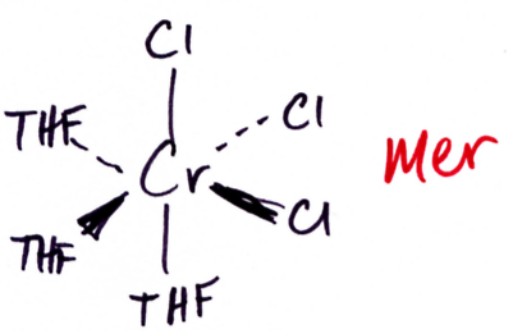
$Cu^{3+} = [Ar]\,3d^8$

$Ti^{3+} = [Ar]\,3d^1$

10.) $[Ni(acac)_2]_3$



$CrCl_3(thf)_3$

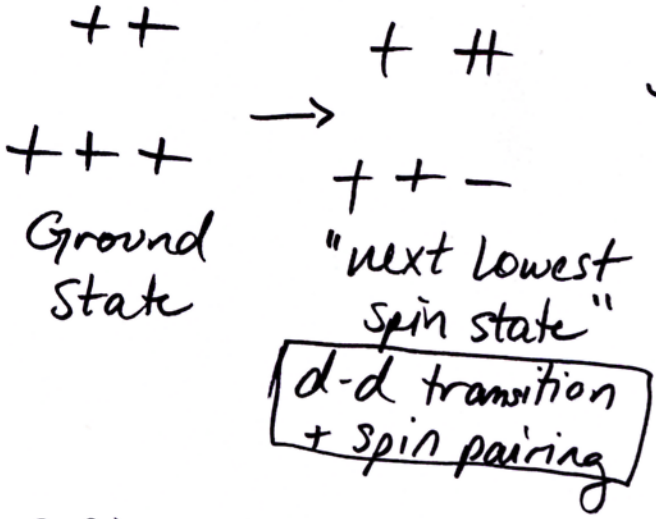


Mer

a.) $Mn^{2+} + OH^- \longrightarrow Mn(OH)_2$ white Mn^{2+} $\xrightarrow{[O]}$ MnO_2 dark Mn^{4+}

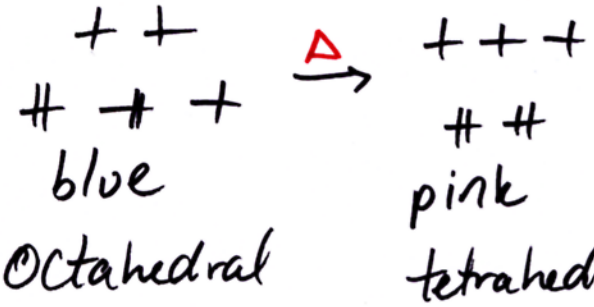
1.) d-d transitions are spin forbidden

2.) a) in Mn^{2+} complex



this is forbidden so it is uncolored

b.) Co^{2+} d^7



C.) Cu^{2+} d^9

$Cu^{2+} + 2OH^- \rightarrow Cu(OH)_2 \xrightarrow{\Delta} CuO + H_2O$

Jahn-Teller distorted Cu^{2+}

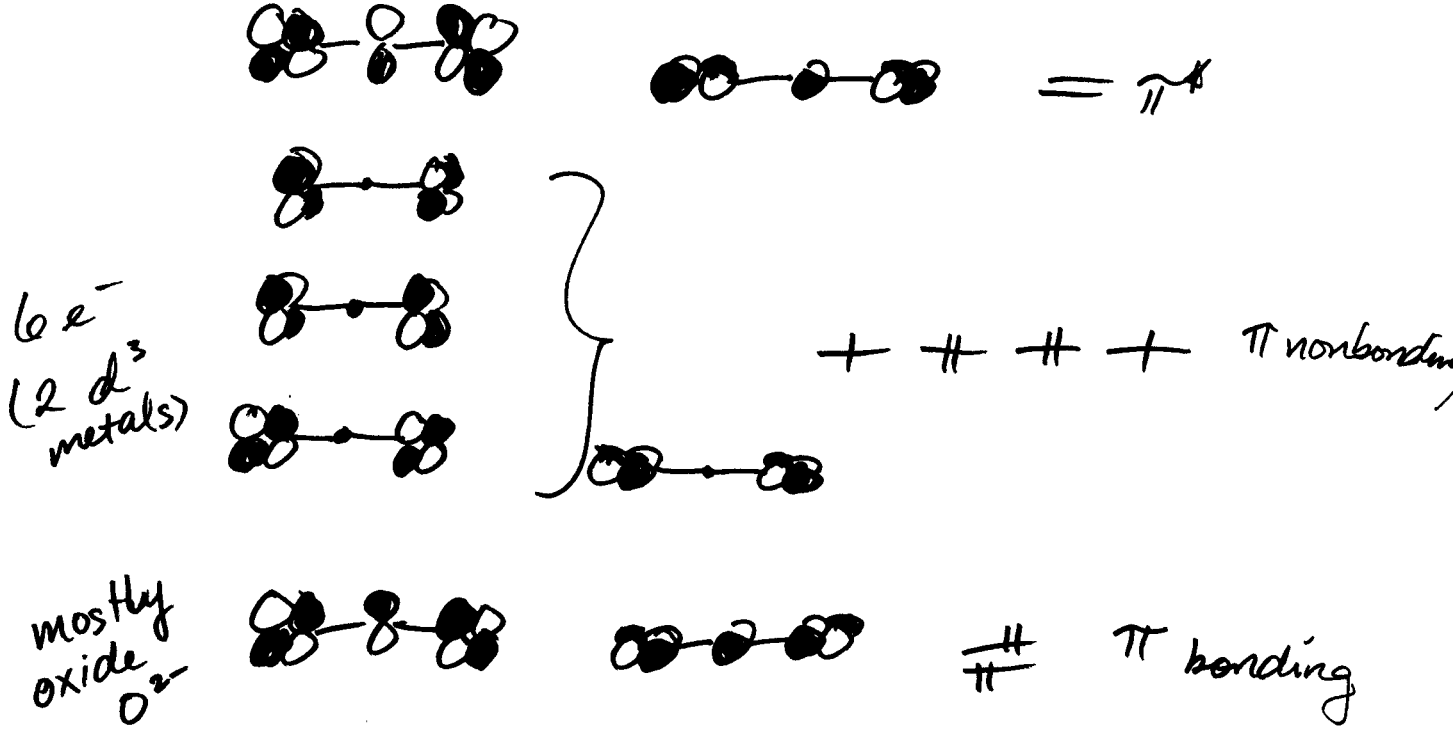
forms a solid state structure

12.) Same as #5.

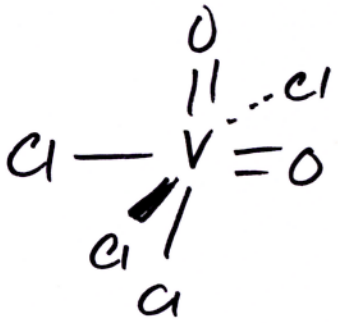
13.) $[(NH_3)_5Cr-O-Cr(NH_3)_5]^{4+}$

Cr^{3+} d^3

There is $Cr=O=Cr$ bonding, i.e. Cr-O $d\pi$-$p\pi$ bonding. This requires sp-hybridization @ the oxygen.

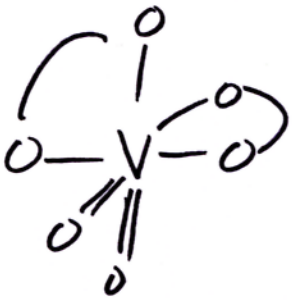


14.)



$[VO_2Cl_4]^{3-}$

V^{5+} d^0



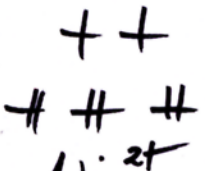
$[VO_2(ox)_2]^{3-}$

V^{5+} d^0

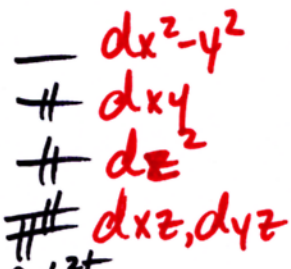
in the cis complex the oxygen atoms can π donate into the t_{2g} set of orbitals without competing w/ each other. in the trans configuration, the e-e repulsion destabilizes the structure.

15.)

a) Ni^{2+} d^8
Pd^{2+} d^8



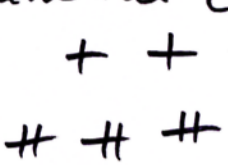
Ni^{2+}



Pd^{2+}

Pd^{2+} forms square planar complexes and Ni^{2+} forms an octahedral complex.

b) NiF_2 and PdF_2 form the rutile structure w/ octahedral coordination

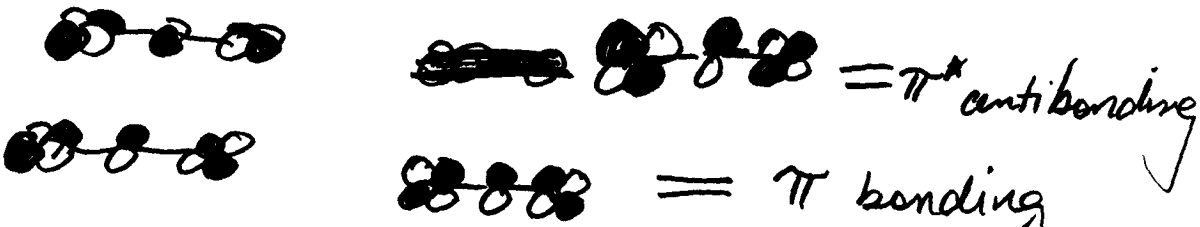


16. $[Ru_2OCl_{10}]^{4-}$

Ru^{4+} d^4

The bonding is very similar to that of the Cr problem (#13)

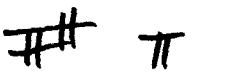
Will form a linear Ru-O-Ru bridge of $d\pi$-$p\pi$ character.



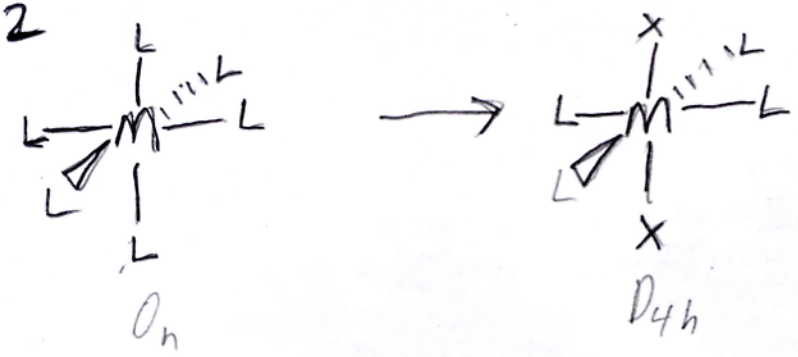
See prob. 13 for rest of orbital configuration

= π^*

nonbonding → 8e⁻ (2 d^4 metals)


π ——→ oxide O^{2-}

7.2



O_h D_{4h}

M orbitals

$O_h \rightarrow D_{4h}$

P

O_h → D_{4h}

t_{1u} $A_{2u} + E_u$

S

O_h → D_{4h}

A_{1g} $A_{2u} + E_u$

d

B_{1g} A_{1g}

O_h → D_{4h}

E_g $A_{1g} + B_{1g}$

B_{2g}

O_h → D_{4h}

t_{2g} $B_{2g} + E_g$

$L_6 \rightarrow L_4X_2$ σ orbitals

O_h D_{4h}

A_{2u}

E_u

$O_h \rightarrow D_{4h}$

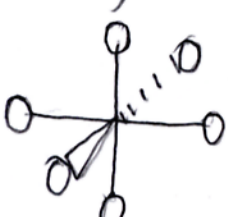
t_{1u} $E_u + A_{2u}$

A_{1g}

B_{1g}

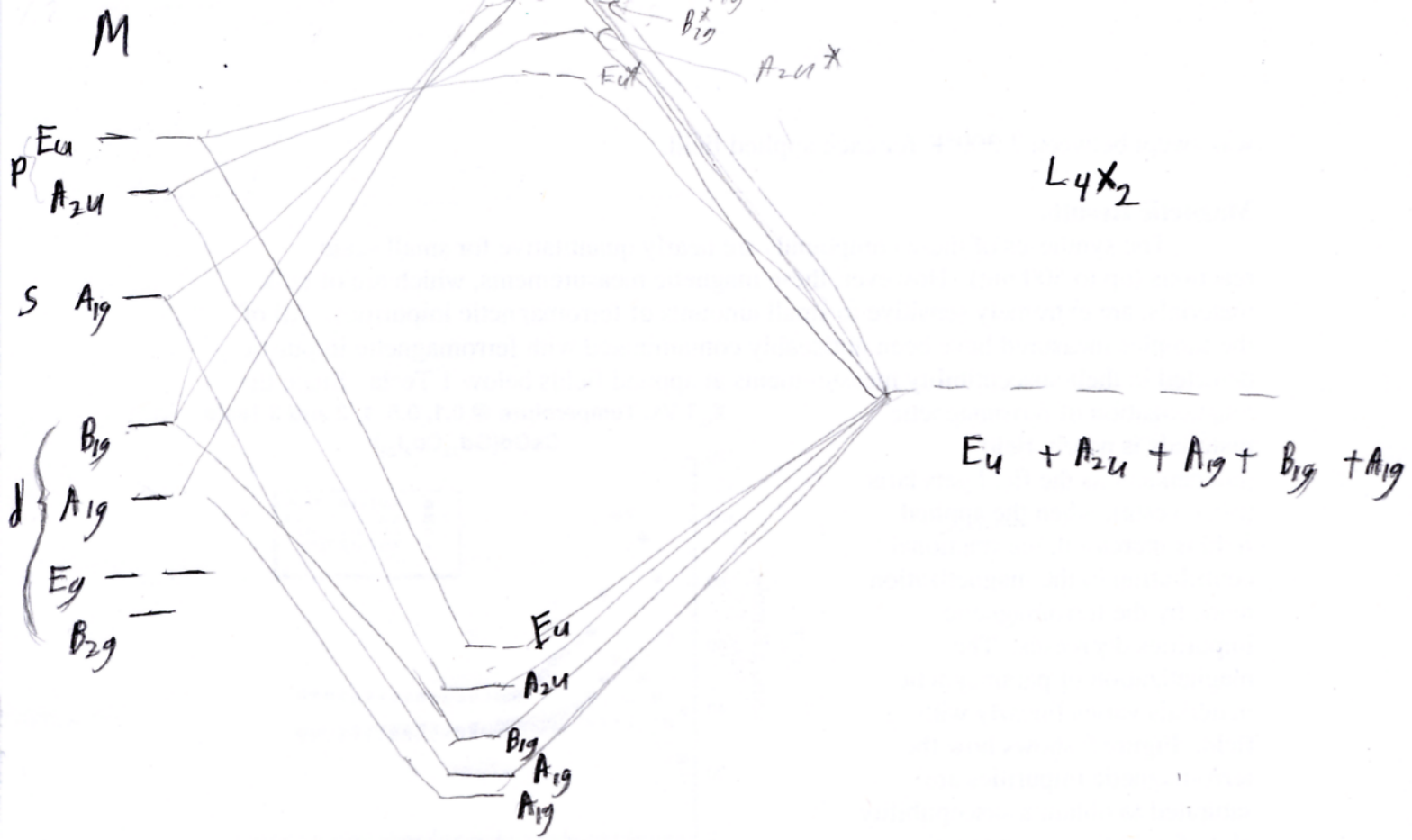
$O_h \rightarrow D_{4h}$

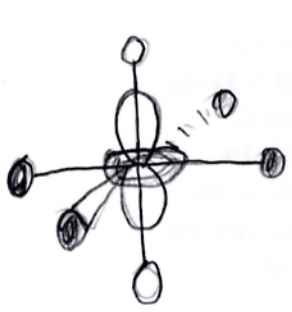
E_g $A_{1g} + B_{1g}$



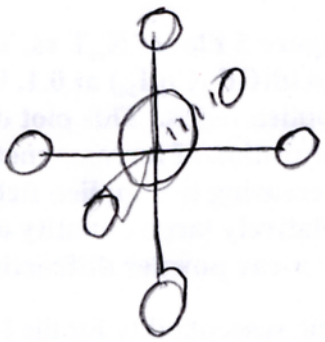
$O_h \rightarrow D_{4h}$

A_{1g} A_{1g}

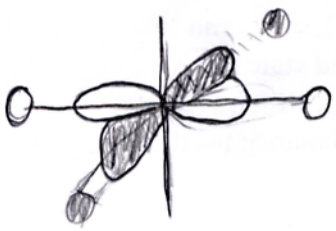

M
E_u
A_{2u}
p
s A_{1g}
B_{1g}
A_{1g}
d
E_g
B_{2g}
B_{1g}^*
E_u^*
A_{2u}^*
L_4X_2
$E_u + A_{2u} + A_{1g} + B_{1g} + A_{1g}$
E_u
A_{2u}
B_{1g}
A_{1g}
A_{1g}



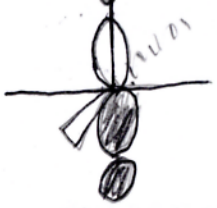
A_{1g}



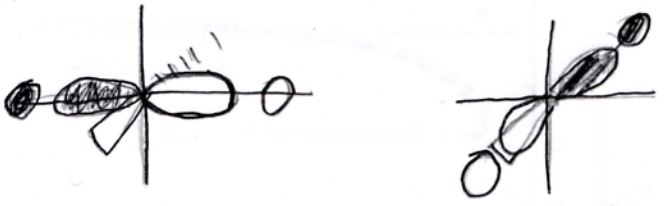
A_{1g}



B_{1g}



A_{2u}



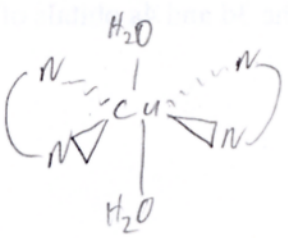
E_u

7.10

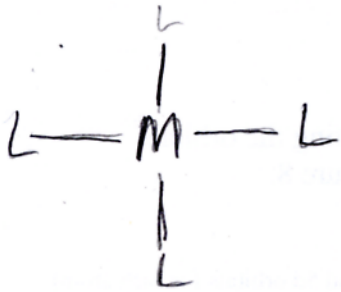
Both trends of successive formation constants and the Irving Williams series are supported by the data.

Cu^{2+}, d^9 is stabilized by a Jahn-Teller distortion of an octahedral complex (as discussed on pg 244 in your book).

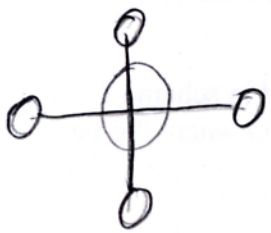
This distortion can occur in a $\left[Cu(en)_2(H_2O)_2\right]^{2+}$ but not in a $\left[Cu(en)_3\right]^{2+}$



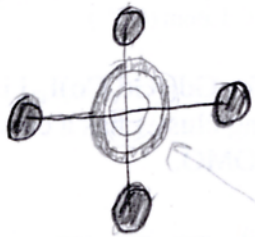
7.3



D_{4h}

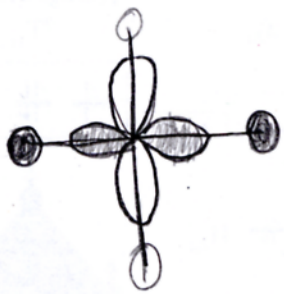


A_{1g}

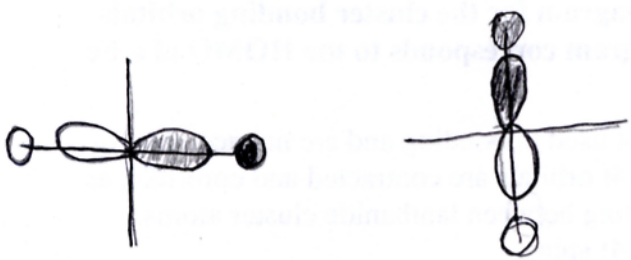


looking down on d_{z^2}

A_{1g}

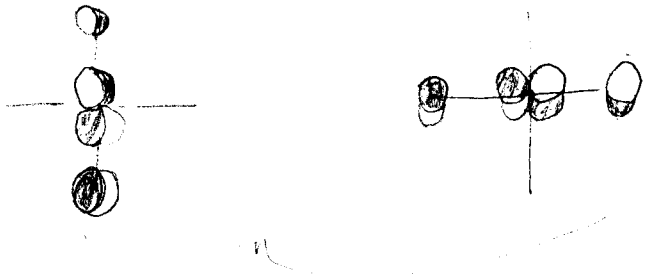


B_{1g}

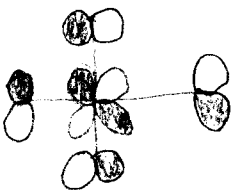


E_u

π - orbitals

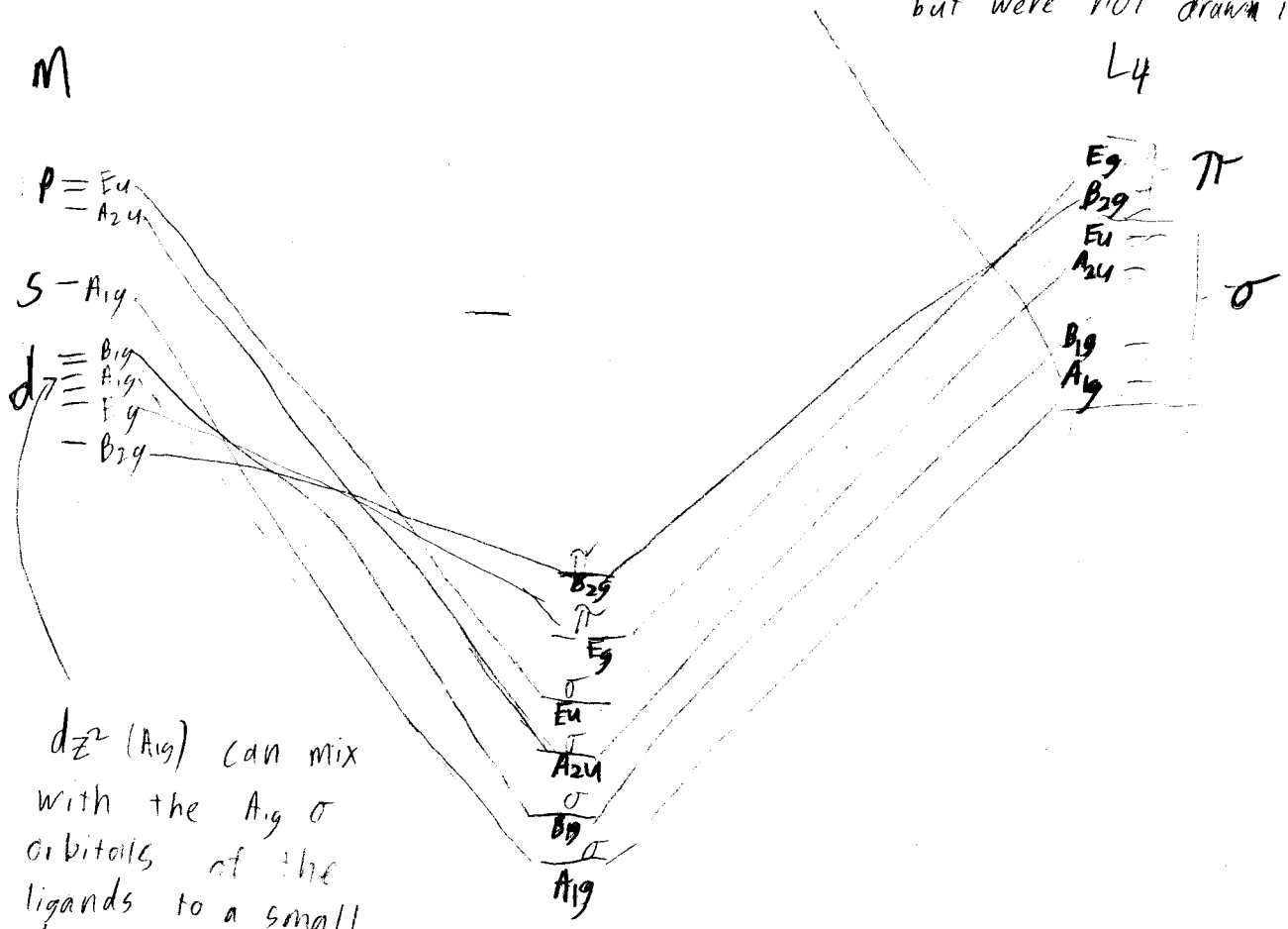


E_g



B_{2g}

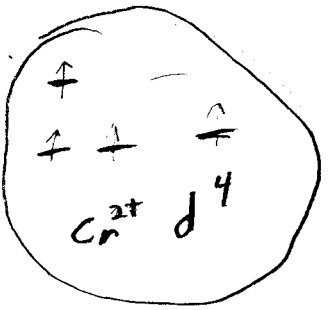
anti-bonding combinations but were not drawn in.

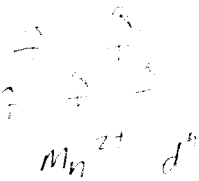


d_{z^2} (A_{1g}) can mix with the A_{1g} σ orbitals of the ligands to a small degree.

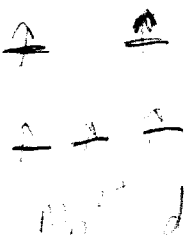
7.12

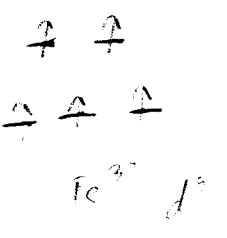
a)





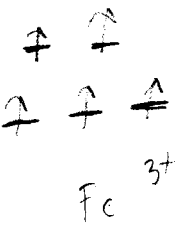
b)



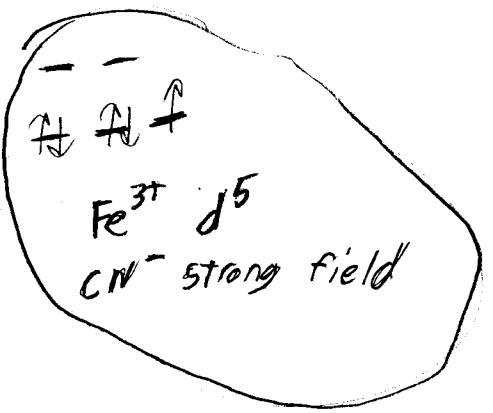


same

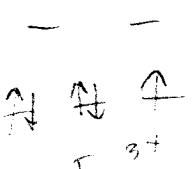
c)

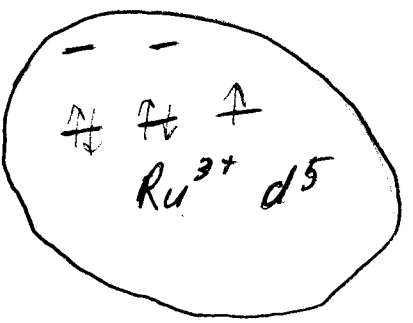
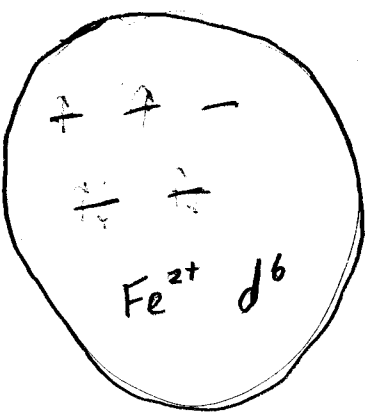
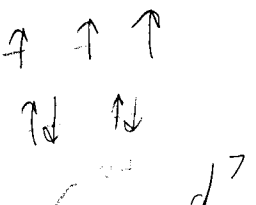


H_2O weak feild



d)





e)