ADVANCED CHEMISTRY

INORGANIC CHEMISTRY – SPRING – WEEK 7

Chapter 10

(9) $Co(II)$ d^7 configuration

t_2 ↑ ↑ ↑ e_g ↑ ↑   ↑ — e_g

e ↑↓ ↑↓ t_{2g} ↑↓ ↑↓ ↑   ↑↓ ↑↓ ↑↓ t_{2g}

tetrahedral (A)   octahedral high spin (B)   Octahedral low spin (C)

— $d_{x^2-y^2}$

↑ d_{z^2}

↑↓ ↑↓ ↑↓
d_{xz} d_{yz} d_{xy}

Sq-planar (D)

Magnetic moment depends on the number of unpaired electrons.

(A) and (B) have 3 unpaired electrons

$$\mu = \sqrt{n(n+2)}\ BM = \sqrt{3(3+2)}\ BM$$

$$= \underline{\underline{3.9\ B.M}}$$

(D) and (C) have 1 unpaired electron.

$$\mu = \sqrt{1(1+2)} = 1.73\ BM$$

(15)(a) $Co^{2+} = d^7$ $Fe = d^6$

Fe^{2+} (d^6)

$$\begin{array}{ll} e_g & \uparrow \quad \uparrow \\ t_{2g} & \uparrow\downarrow \quad \uparrow \quad \uparrow \end{array} \Big\} \Delta_o$$

d^6 (high spin) (Fe)

$$LFSE = \left[4\left(-\frac{2}{5}\right) + 2\left(\frac{3}{5}\right)\right]\Delta_o$$

$$= -\frac{2}{5}\Delta_o \quad \cancel{-\frac{18}{45}\Delta_o}$$

$$\Delta_t \Big\{ \begin{array}{ll} \uparrow \quad \uparrow \quad \uparrow & e \\ \uparrow\downarrow \quad \uparrow & t_2 \end{array}$$

$$LFSE = \left[3\left(-\frac{3}{5}\right) + 3\left(\frac{2}{5}\right)\right]\Delta_t$$

$$= -\frac{3}{5}\Delta_t \left(\frac{\frac{4}{9}\Delta_o}{\Delta_t}\right)$$

$$= -\frac{12}{45}\Delta_o$$

For Co^{2+} d^7 case

$$\begin{array}{ll} e_g & \uparrow \quad \uparrow \\ t_{2g} & \uparrow\downarrow \quad \uparrow\downarrow \quad \uparrow \end{array} \Big\} \Delta_o$$

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

$$= -\frac{4\Delta_o}{5}$$

$$\Delta_t \Big\{ \begin{array}{ll} \uparrow \quad \uparrow \quad \uparrow & t_2 \\ \uparrow\downarrow \quad \uparrow\downarrow & e \end{array}$$

$$LFSE = 4\left(-\frac{3}{5}\Delta_t\right) + 3\left(\frac{2}{5}\Delta_t\right)$$

$$= -\frac{6\Delta_t}{5} \times \left(\frac{\frac{4}{9}\Delta_o}{\Delta_t}\right)$$

$$= -\frac{24}{45}\Delta_o$$

Ni (d^8 case)

$$\begin{array}{ll} e_g & \uparrow \quad \uparrow \\ t_{2g} & \uparrow\downarrow \quad \uparrow\downarrow \quad \uparrow\downarrow \end{array} \Big\} \Delta_o$$

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

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

$$\begin{array}{ll} t_2 & \uparrow\downarrow \quad \uparrow \quad \uparrow \\ e & \uparrow\downarrow \quad \uparrow\downarrow \end{array} \Big\} \Delta_t$$

$$LFSE = 4\left(-\frac{3}{5}\Delta_t\right) + 4\left(\frac{2}{5}\Delta_t\right)$$

$$= -\frac{4}{5}\Delta_t \times \left(\frac{4/9\,\Delta_o}{\Delta_t}\right) = -\frac{16}{45}\Delta_o$$

The ~~largest~~ LFSE in the decreasing order for tetrahedral geometry is

$$Co^{2+} > Ni^{2+} > Fe^{2+}$$

(The numbers do not explain the given order)

(16) Compare square planar geometry with tetrahedral geometry since they both have 4 ligands.

For strong field ligands the tendency is to split the metal d orbitals far apart, which favors square planar geometry since;

$$\Delta_{sp} > \Delta_o > \Delta_t$$

d^7, d^8, d^9 complexes have many d electrons and π acceptor ligands can stabilize the complexes of these metal ions by accepting $\bar{e}$ from the metal.

Also LFSE is higher for ~~Δ_{sp}~~ square planar complexes in d^7, d^8, d^9 configurations.

(17) NH_3 and H_2O ~~can~~ both form σ bonds with the metal by donating the lone pair electrons on N and O atoms respectively. H_2O, because the Oxygen ~~a~~tom has ~~an~~ a second extra pair of electrons can frame a weak π bond (Lewis π base), lowering Δ_o.

Δ_o for H_2 ...

Of the halogen ions

$F^- > Cl^- > Br^- > I^-$

$\longrightarrow$ base strength decreases

F^- is the strongest base, ∴ interacts most readily w/ the metal ion to form a coordinate bond.

∴ Δ_o for $F^- > Cl^- > Br^- > I^-$

(19) Cr(III) d^3 case

e_g — —

t_{2g} 1 1 1

Ground state is not degenerate

Mn(III) d^4 case

1 — e_g

1 1 1 t_{2g}

Ground state is degenerate. ∴ Jahn-Teller distortions will lead to changes in bond lengths.

(20) MnO_4^{2-} Mn is in the +6 oxidation state. There is <u>one</u> d electron in Mn^{+6}

MnO_4^- Mn is in the +7 oxidation state. No d electrons in Mn^{+7}

t_2 __ __ __   __ __ __ t_2

e ↑ __   __ __ e

MnO_4^{2-} MnO_4^{-}

d^1 d^0

This is a degenerate state. Jahn-Teller distortions can elongate bond lengths

non-degenerate No Jahn-Teller distortions.

(21) (a) Cr^{+2} d^4 weak field

↑ __

↑ ↑ ↑

4 unpaired $\bar{e}$

$\mu = \sqrt{n(n+2)}$ BM $= \sqrt{4(4+2)}$ BM

$= \underline{\underline{4.9 \text{ BM}}}$

(b) $[Cr(CN)_6]^{4-}$ ~~d~~ Cr^{+2} d^4 strong field

__ __

↑↓ ↑ ↑

$\mu = \sqrt{2(2+2)} = \underline{\underline{2.8 \text{ BM}}}$

(c) $[FeCl_4]^-$ Fe^{3+} d^5 weak field

↑ ↑

↑ ↑ ↑

$\mu = \sqrt{5(5+2)} = \underline{\underline{5.9 \text{ BM}}}$

(d) $[Fe(CN)_6]$ Fe

__ __

↑↓ ↑↓ ↑ $\qquad \mu = \sqrt{1(1+2)} = \underline{\underline{1.73\ BM}}$

(e) $[Ni(H_2O)_6]^{2+}$ $\quad Ni^{2+}$ d^8 weak field

↑ ↑

↑↓ ↑↓ ↑↓ $\qquad \mu = \sqrt{2(2+2)} = \underline{\underline{2.8\ BM}}$

(f) $[Cu(en)_2(H_2O)_2]^{2+}$ $\quad Cu^{2+}$ d^9

↑↓ ↑

↑↓ ↑↓ ↑↓ $\qquad \mu = \sqrt{1(1+2)} = \underline{\underline{1.7\ BM}}$

~~Front the sheet~~

from the worksheet

①

O_h	E	$8C_3$	$6C_2$	$6C_4$	$3C_2$	i	$6S_4$	$8S_6$	$3\sigma_h$	$6\sigma_d$
A_{1g}	1	1	1	1	1	1	1	1	1	1
A_{2g}	1	1	-1	-1	1	1	-1	1	1	-1
E_g	2	-1	0	0	2	2	0	-1	2	0
T_{1g}	3	0	-1	1	-1	3	1	0	-1	-1
T_{2g}	3	0	1	-1	-1	3	-1	0	-1	1
A_{1u}	1	1	1	1	1	-1	-1	-1	-1	-1
A_{2u}	1	1	-1	-1	1	-1	1	-1	-1	1
E_u	2	-1	0	0	2	-2	0	1	-2	0
T_{1u}	3	0	-1	1	-1	-3	-1	0	1	1
T_{2u}	3	0	1	-1	-1	-3	1	0	1	-1
$\Gamma_{t_{2g}^2} = t_{2g} \times t_{2g}$	9	0	1	1	1	9	1	0	1	1
$\Gamma_{t_{2g} \cdot e_g} =$	6	0	0	0	-2	6	0	0	-2	0
$\Gamma_{e_g^2} = e_g \times e_g$	4	1	0	0	4	4	0	1	4	0

in $\Gamma_{t_{2g}^2}$ $\Big\} = \frac{1}{48}\left[9 + 6 + 6 + 3 + 9 + 6 + 3 + 6\right]$

$= 1$

# of time E_g is in $\Gamma_{t_{2g}^2}$ $\Big\} = \frac{1}{48}\left[18 + 6 + 18 + 6\right] = 1$

# of times T_{2g} is in $\Gamma_{t_{2g}^2} = \frac{1}{48}\left[27 + 6 - 6 - 3 + 27 - 6 - 3 + 6\right] = 1$

# of times T_{1g} is in $\Gamma_{t_{2g}^2} = \frac{1}{48}\left[27 - 6 + 6 - 3 + 27 + 6 - 3 - 6\right]$

$= 1$

$$\Gamma_{t_{2g}^2} = A_{1g} + E_g + T_{2g} + T_{1g}$$

# of times T_{1g} is in $\Gamma_{t_{2g}e_g}$ $\Big\} = \frac{1}{48}\left[18 + 6 + 18 + 6\right] = 1$

# of times T_{2g} is in $\Gamma_{t_{2g}e_g}$ $\Big\} = \frac{1}{48}\left[18 + 6 + 18 + 6\right] = 1$

$$\Gamma_{t_{2g}e_g} = T_{1g} + T_{2g}$$

$$\left.\begin{array}{l}\#\text{ of times } \cancel{A_{1g}}\ E_g \text{ is in} \\ \Gamma_{e_g^2}\end{array}\right\} = \frac{1}{48}\left[8 - 8 + 24 + 8 - 8 + 24\right]$$

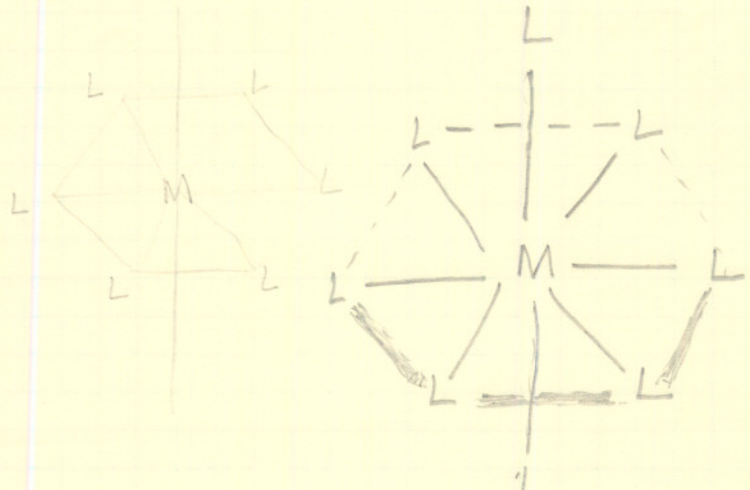
$$= 1$$

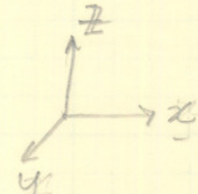
$$\left.\begin{array}{l}\#\text{ of times } \cancel{E_g}\ A_{1g} \text{ is in} \\ \Gamma_{e_g^2}\end{array}\right\} = \frac{1}{48}\left[\cancel{8}\ 4 + 8 + 12 + 4 + 8 + 12\right] = 1$$

$$\left.\begin{array}{l}\#\text{ of times } A_{2g} \text{ is in} \\ \Gamma_{e_g^2}\end{array}\right\} = \frac{1}{48}\left[4 + 8 + 12 + 4 + 8 + 12\right] = 1$$

$$\Gamma_{e_g^2} = A_{1g} + E_g + A_{2g}$$

(2)





symmetry of the metal orbitals

$d_{x^2-y^2}, d_{xy} = E_{2g}$

$d_{zy}, d_{xz} = E_{1g}$

$s, d_{z^2} = A_{1g}$

$p_z = A_{2u}$

$p_x, p_y = E_{1u}$

Geometry = D_{6h}

Generate a Γ to

represent metal–Ligand σ bonds (six of them)

$= \Gamma_{\sigma \text{ bonds}}$

D_{6h}	E	$2C_6$	$2C_3$	C_2	$3C_2'$	$3C_2''$	i	$2S_3$	$2S_6$	σ_h	$3\sigma_d$	$3\sigma_v$
$\Gamma_{\sigma\ \text{bonds}}$	8	2	2	2	2	0	0	0	0	6	2	4

Reduce $\Gamma_{\sigma\ \text{bonds}}$ to its irreducible components.

# of times A_{1g} is in Γ $= \frac{1}{24}\left[8+4+4+2+6+6+6+12\right] = 2$

# of times A_{2g} is in Γ $= \frac{1}{24}\left[8+4+4+2 \overset{-6}{\cancel{+(6)}} +6-6-12\right] = 0$

# of times B_{1g} is in $\Gamma = \frac{1}{24}\left[8-\cancel{4}+\cancel{4}-2+\cancel{6}-\cancel{6}+6-12\right] = 0$

# of times B_{2g} is in $\Gamma = \frac{1}{24}\left[8-\cancel{4}+\cancel{4}-2-6-\cancel{6}-\cancel{6}+\cancel{12}\right] = 0$

# of times E_{1g} is in $\Gamma = \frac{1}{24}\left[16+\cancel{4}-\cancel{4}-4-12\right] = 0$

# of times E_{2g} is in $\Gamma = \frac{1}{24}\left[16-4-\cancel{4}+\cancel{4}+12\right] = 1$

# of times A_{1u} is in $\Gamma = \frac{1}{24}\left[8+\cancel{4}+4+2+2-6-6-\cancel{12}\right] = 0$

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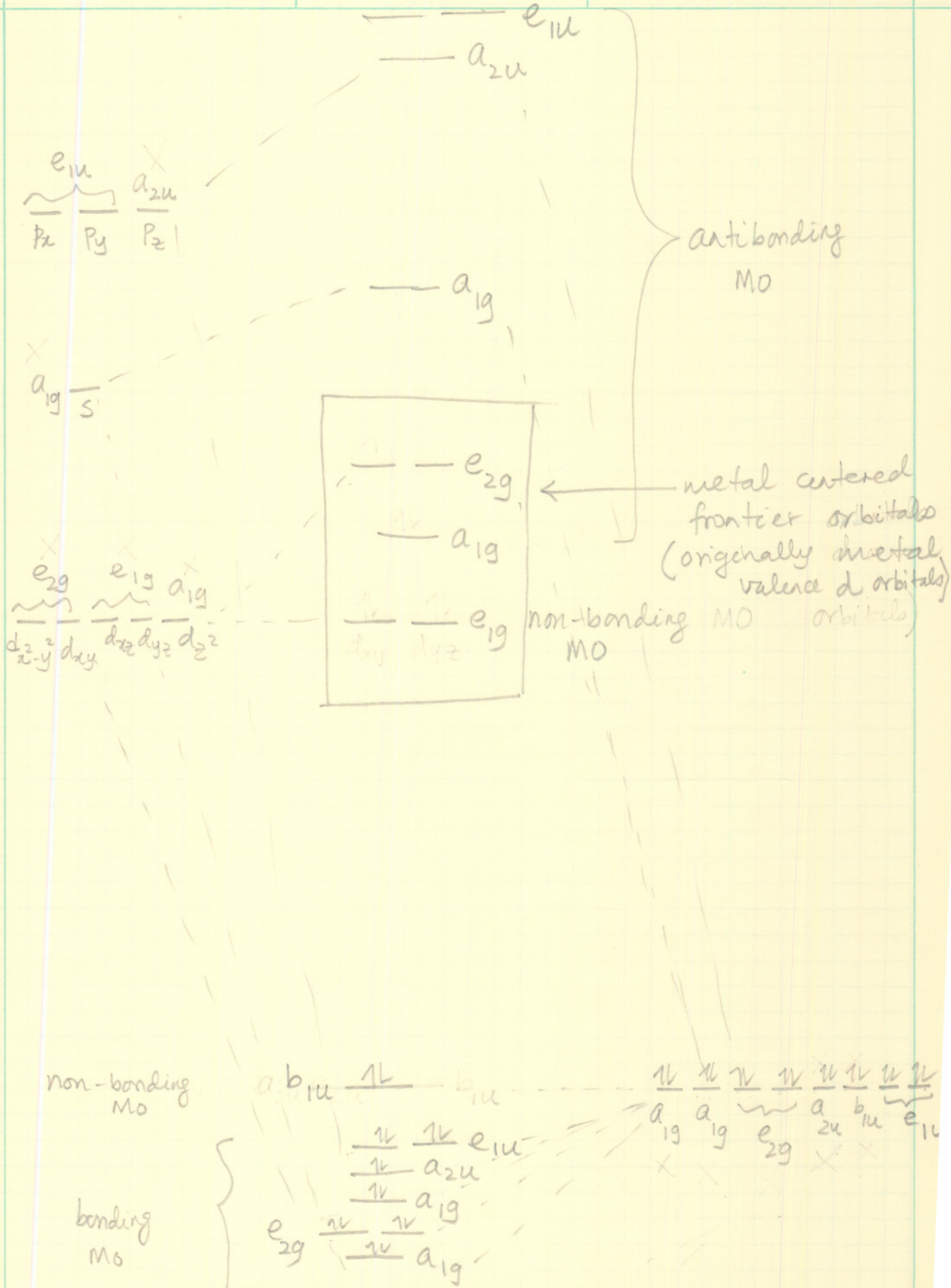
# of times A_{2u} is in $\Gamma = \frac{1}{24}\left[8+4+4+2-\cancel{6}-\cancel{6}+6+\cancel{12}\right] = 1$

# of times B_{1u} is in $\Gamma = \frac{1}{24}\left[8-\cancel{4}+\cancel{4}-2+6+\cancel{6}-\cancel{6}+12\right] = 1$

# of times E_{1u} is in $\Gamma = \frac{1}{24}\left[16+\cancel{4}-\cancel{4}-4+12\right] = 1$

$$\Gamma_{\sigma\ \text{bonds}} = 2A_{1g} + E_{2g} + A_{2u} + B_{1u} + E_{1u}$$



e_{1u}
a_{2u}
e_{1u} a_{2u}
p_x p_y p_z
antibonding MO
a_{1g}
a_{1g} s
e_{2g}
metal centered frontier orbitals (originally metal valence d orbitals)
a_{1g}
e_{2g} e_{1g} a_{1g}
$d_{x^2-y^2}$ d_{xy} d_{xz} d_{yz} d_{z^2}
e_{1g}
non-bonding MO
d_{xy} d_{yz}
non-bonding MO
b_{1u}
b_{1u}
a_{1g} a_{1g} e_{2g} a_{2u} b_{1u} e_{1u}
e_{1u}
a_{2u}
a_{1g}
bonding MO
e_{2g}
a_{1g}

The following d electron configurations
can show Jahn-Teller distortions.

d^1, d^3, d^7, d^9 (~~because~~ all of these have
degenerate states).