ATOMS, MOLECULES & RESEARCH

COORDINATION CHEMISTRY – SPRING – WEEK 0

Generate $\Gamma_{t_{2g}^2}$, $\Gamma_{t_{2g}e_g}$ and $\Gamma_{e_g^2}$ and reduce them to irreducible components in the O_h point group.

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

# of times A_{1g} is in $\Gamma_{t_{2g}^2}$ $= \frac{1}{48}[4 + 8 + 12 + 4 + 8 + 12] = 1$

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

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

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

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

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

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

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

# of times A_{1g} is in $\Gamma_{e_g^2}$ $= \frac{1}{48}[4 + 8 + 12 + 4 + 8 + 12] = 1$

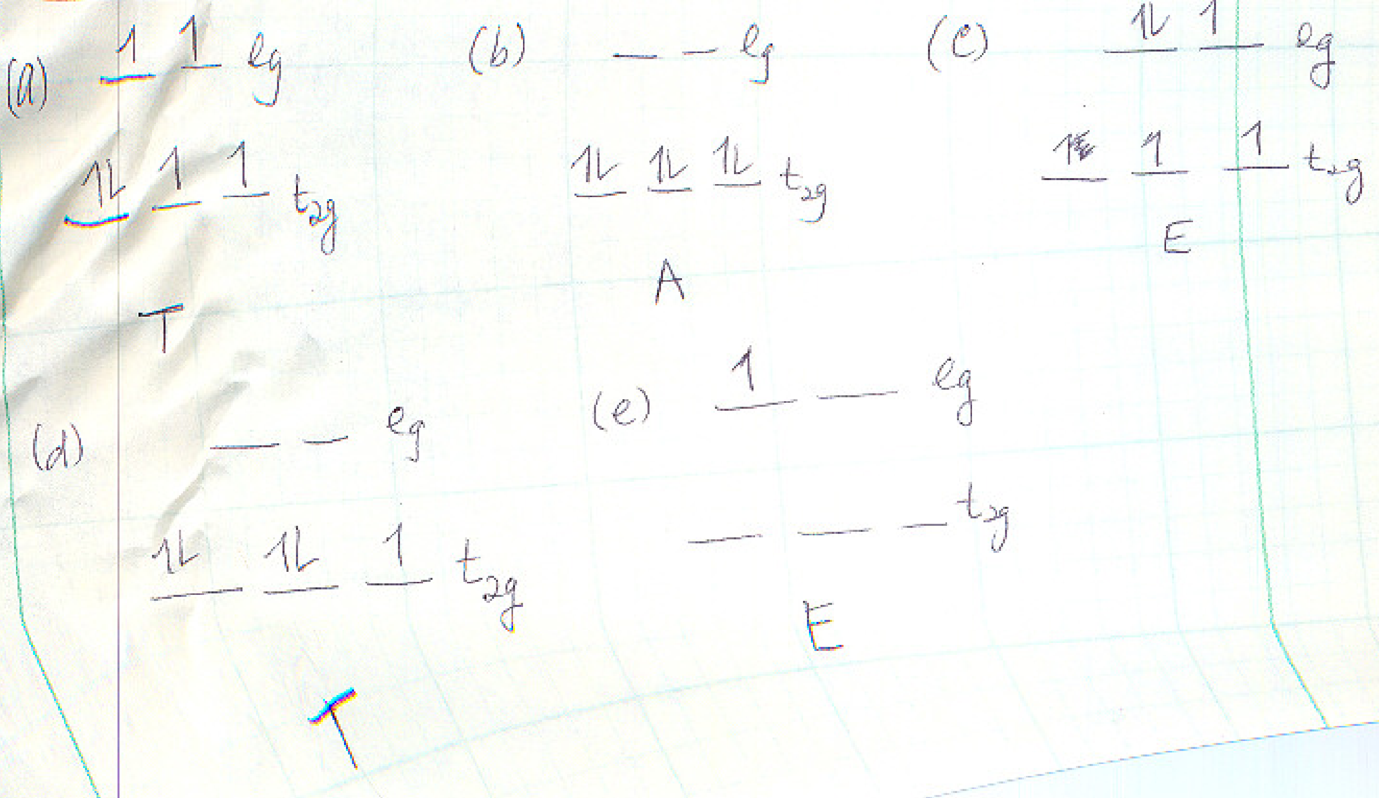
# of times A_{2g} is in $\Gamma_{e_g^2} = \frac{1}{48}[4 + 8 + 12 + 4 + 8 + 12] = 1$

# of times E_g is in $\Gamma_{e_g^2} = \frac{1}{48}[8 - 8 + 24 + 8 - 8 + 24] = 1$

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

Chapter 11

(11)



$[Sc(NH_3)_6]^{3+}$ Sc^{3+} d^0 case, closed shell } No Jahn–Teller distortion

$[Ti(NH_3)_6]^{3+}$ Ti^{3+} d^1 case

— — e_g

1 — — t_{2g}

Gr-state = $^2T_{2g}$

} gr-state is degenerate. ∴ Jahn–Teller distortions possible but weak

$[V(NH_3)_6]^{3+}$ d^2

— — E_g

1 1 — t_{2g} $^3T_{2g}$

Ground state is degenerate. Jahn–Teller distortions are possible, but weak

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

— —

1 1 1 A

Ground state is not degenerate. No Jahn–Teller distortions possible.

$[Mn(NH_3)_6]^{3+}$ d^4 (assume high spin)

1 — e_g

1 1 1 t_{2g} E

ground state is degenerate. strong Jahn–Teller distortions.

$[Fe(NH_3)_6]^{3+}$ d^5

1 1

1 1 1 A

ground state is not degenerate. No Jahn–Teller distortions.

(~~High~~ low spin d^5 will have have Jahn–Teller distortions)

$[Co(NH_3)_6]^{3+}$ d^6

1 1

1↓ 1 1 T

$[Ni(NH_3)_6]^{3+}$ d^7

1 1

1↓ 1↓ 1 T

} ground state is degenerate. Jahn–Teller distortions are possible.

$[Cu(NH_3)_6]^{3+}$ d^8

1 1

1↓ 1↓ 1↓ A — No Jahn–Teller distortions.

$[Zn(NH_3)_6]^{3+}$ d^9 ⥮ ↿ / ⥮ ⥮ ⥮ E Jahn-Teller distortions are possible & strong

[Jahn-Teller distortions are stronger for E terms than for T terms].

(27) (a) $[Co(bipy)_3]^{2+}$ bipy is a strong field neutral ligand

$Co^{2+} = d^7$ case

↿ — e_g

3/5 {
2/5 {

⥮ ⥮ ⥮ t_{2g}

Ground state term $= {}^2E_g$

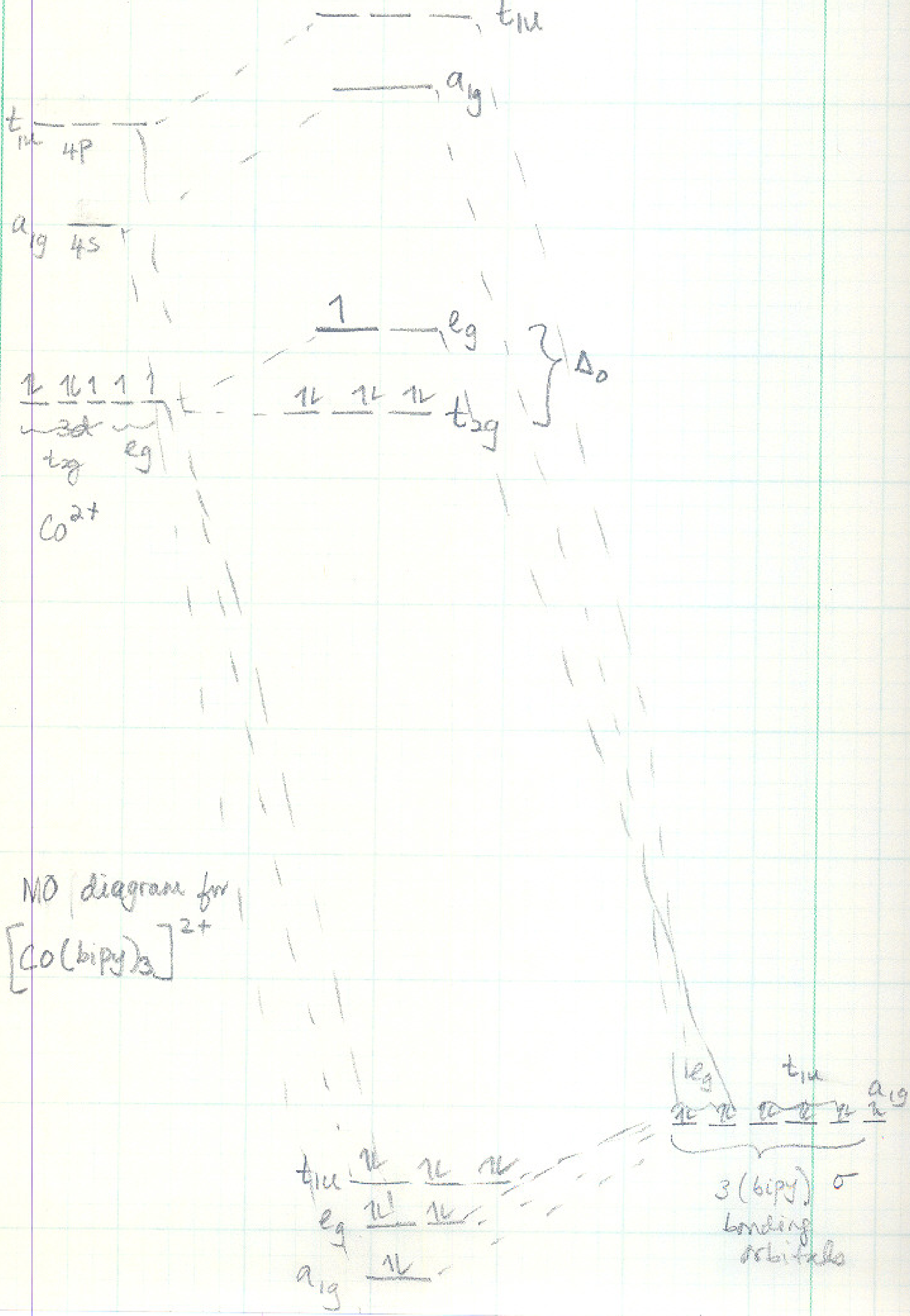
(b) allowed transitions are

$^2E \rightarrow {}^2T_1$ } overlap ∴ broad band spectrum
$^2E \rightarrow {}^2T_2$ } at 11,300 cm^{-1} −12 +3

$^2E \rightarrow {}^2A_1$ — 22,000 cm^{-1}

(c) $LFSE = 6\left[-\frac{2}{5}\Delta_0\right] + 1\left(\frac{3}{5}\Delta_0\right) = -\frac{9}{5}\Delta_0$

(d) broad bands (as in most solids).



MO diagram for $[Co(bipy)_3]^{2+}$

6)

$[Co(NH_3)_6]^{2+}$ NH_3 is a weak field ligand & it is neutral.

$Co^{2+} \equiv d^7$ case

$\underline{1}\ \underline{1}\ e_g$

$\underline{1\downarrow}\ \underline{1\downarrow}\ \underline{1}\ t_{2g}$ $^4T_{1g}$ ground state

3/2

(b) $^4T_{1g} \longrightarrow {}^4T_{2g}$

$^4T_{1g} \longrightarrow {}^4A_{2g}$ } may switch or be very close in energy.

$^4T_{1g} \longrightarrow {}^4T_{1g}$

-10/8

(c) $LFSE = 5\left(-\frac{2}{5}\Delta_0\right) + 2\left(\frac{3}{5}\Delta_0\right) = -\frac{4}{5}\Delta_0$

(d) broad, like most solids.

The MO Diagram is very similar to that of $[Co(bipy)_3]^{2+}$ except Δ_0 will be smaller.