

CHEM 20100 (Inorganic Chemistry I) Problem Sets

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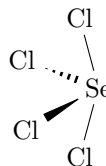
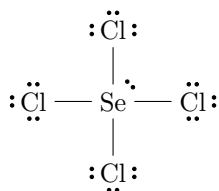
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1 VSEPR and Point Groups

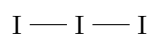
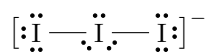
1/21: I) Do the following (VSEPR) problems from your text (Miessler et al. (2014)): Chapter 3: #8, 9f-i, 20, 29.

3.8 Give Lewis dot structures and sketch the shapes of the following:

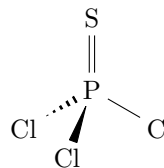
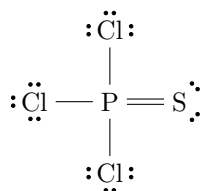
a. SeCl_4



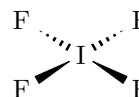
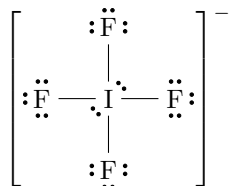
b. I_3^-



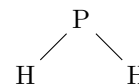
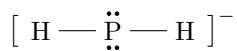
c. PSCl_3



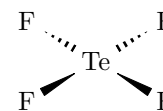
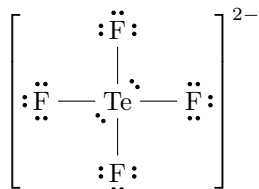
d. IF_4^-



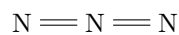
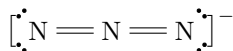
e. PH_2^-



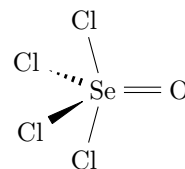
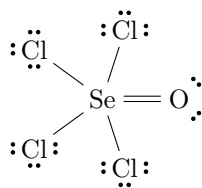
f. TeF_4^{2-}



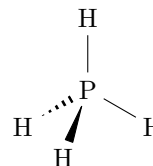
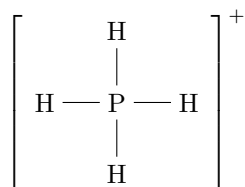
g. N_3^-



h. SeOCl_4

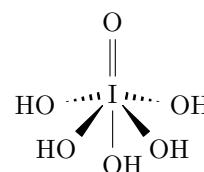
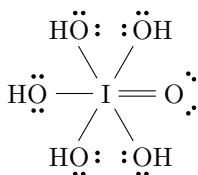


i. PH_4^+

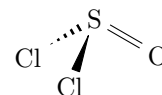
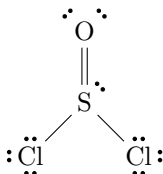


3.9 Give Lewis dot structures and sketch the shapes of the following.

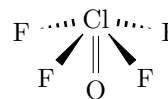
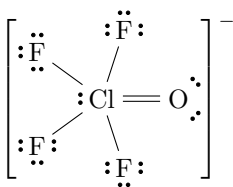
f. $\text{IO}(\text{OH})_5$



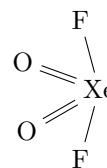
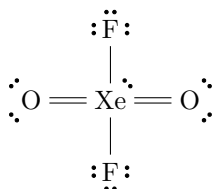
g. SOCl_2



h. $\text{ClOF}_4^{-[1]}$

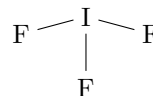
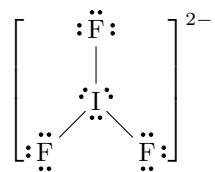


i. XeO_2F_2

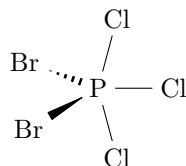


¹Note that it is unclear whether the equatorial fluorines will be bent away from the lone pair and toward the oxygen, or the other way around. Hence, I arbitrarily chose to show them pointed away from the lone pair.

3.20 Predict and sketch the structure of the (as yet) hypothetical ion IF_3^{2-} .



3.29 Sketch the most likely structure of PCl_3Br_2 and explain your reasoning.



Answer. Bromine is more electropositive than chlorine. Thus, by Bent's rule, the bromines will bond to the hybrid orbitals with greater s -character (the equatorial sp^2 ones) first. \square

II) Assign the symmetry point group to the 13 ions and molecules in problems #8, 9f-i in Chapter 3 of your text.

3.8

a. SeCl_4

Answer. Not low or high symmetry. Has a C_2 axis. No perpendicular C_2 axes. No σ_h . Has two perpendicular σ_v planes.

Therefore, SeCl_4 is of the C_{2v} point group. ☐

b. I_3^-

Answer. I_3^- is of the $D_{\infty h}$ point group. ☐

c. PSCl_3

Answer. Not low or high symmetry. Has a C_3 axis. No perpendicular C_2 axes. No σ_h . Has three σ_v planes all offset by 60° .

Therefore, PSCl_3 is of the C_{3v} point group. ☐

d. IF_4^-

Answer. Not low or high symmetry. Has a C_4 axis. Has 4 perpendicular C_2 axes. Has σ_h .

Therefore, IF_4^- is of the D_{4h} point group. ☐

e. PH_2^-

Answer. Not low or high symmetry. Has a C_2 axis. No perpendicular C_2 axes. No σ_h . Has two perpendicular σ_v planes.

Therefore, PH_2^- is of the C_{2v} point group. ☐

f. TeF_4^{2-}

Answer. Not low or high symmetry. Has a C_4 axis. Has 4 perpendicular C_2 axes. Has σ_h .

Therefore, TeF_4^{2-} is of the D_{4h} point group. ☐

g. N_3^-

Answer. N_3^- is of the $D_{\infty h}$ point group. ☐

h. SeOCl_4

Answer. Not low or high symmetry. Has a C_2 axis. No perpendicular C_2 axes. No σ_h . Has two perpendicular σ_v planes.

Therefore, SeOCl_4 is of the C_{2v} point group. ☐

i. PH_4^+

Answer. PH_4^+ is of the T_d point group. ☐

3.9

f. $\text{IO}(\text{OH})_5$

Answer. Not low or high symmetry. Has a C_4 axis. No perpendicular C_2 axes. No σ_h . Has two perpendicular σ_v planes and two perpendicular σ_d planes.

Therefore, $\text{IO}(\text{OH})_5$ is of the C_{4v} point group. ☐

g. SOCl_2

Answer. SOCl_2 is of the C_s point group. ☐

h. ClOF_4^-

Answer. Not low or high symmetry. Has a C_4 axis. No perpendicular C_2 axes. No σ_h . Has two perpendicular σ_v planes and two perpendicular σ_d planes.

Therefore, ClOF_4^- is of the C_{4v} point group. ☐

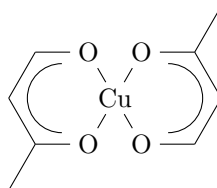
i. XeO_2F_2

Answer. Not low or high symmetry. Has a C_2 axis. No perpendicular C_2 axes. No σ_h . Has two perpendicular σ_v planes.

Therefore, XeO_2F_2 is of the C_{2v} point group. ☐

III) Assign the symmetry point group of the following molecules and objects. Ignore the H atoms in (a), (e), and (g). Note that (e) has pseudooctahedral geometry and (g) is square-planar.

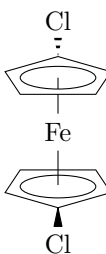
a) The molecule pictured below.



Answer. Not low or high symmetry. Has a C_2 axis. No perpendicular C_2 axes. Has a σ_h .

Therefore, the above molecule is of the C_{2h} point group. □

b) The molecule pictured below.



Answer. Not low or high symmetry. Has a C_2 axis. No perpendicular C_2 axes. Has a σ_h .

Therefore, the above molecule is of the C_{2h} point group. □

c) POCl_3

Answer. Not low or high symmetry. Has a C_3 axis. No perpendicular C_2 axes. No σ_h . Has three σ_v planes all offset by 60° .

Therefore, POCl_3 is of the C_{3v} point group. □

d) Tennis ball (including the seam)

Answer. Not low or high symmetry. Has a C_2 axis. Has 2 perpendicular C_2 axes. No σ_h . Has two perpendicular σ_d planes.

Therefore, a tennis ball is of the D_{2d} point group. □

e) $\text{trans}[\text{CrCl}_2(\text{H}_2\text{O})_4]^+$

Answer. Not low or high symmetry. Has a C_4 axis. Has 4 perpendicular C_2 axes. Has σ_h .

Therefore, $\text{trans}[\text{CrCl}_2(\text{H}_2\text{O})_4]^+$ is of the D_{4h} point group. □

f) 1,3,5-trichlorobenzene.

Answer. Not low or high symmetry. Has a C_3 axis. Has 3 perpendicular C_2 axes. Has σ_h .

Therefore, 1,3,5-trichlorobenzene is of the D_{3h} point group. □

g) $\text{trans-Pt}(\text{NH}_3)_2\text{Cl}_2$

Answer. Not low or high symmetry. Has a C_2 axis. Has 2 perpendicular C_2 axes. Has σ_h .

Therefore, $\text{trans-Pt}(\text{NH}_3)_2\text{Cl}_2$ is of the D_{2h} point group. □

h) SF_5Cl

Answer. Not low or high symmetry. Has a C_4 axis. No perpendicular C_2 axes. No σ_h . Has two perpendicular σ_v planes and two perpendicular σ_d planes.

Therefore, SF_5Cl is of the C_{4v} point group. □

i) BFClBr

Answer. BFClBr is of the C_s point group. □

j) PF_2^+

Answer. Not low or high symmetry. Has a C_2 axis. No perpendicular C_2 axes. No σ_h . Has two perpendicular σ_v planes.

Therefore, PF_2^+ is of the C_{2v} point group. □

- IV) In the octahedral ion FeF_6^{3-} , what symmetry elements are destroyed if two *trans* F ions are moved away from the Fe^{3+} center in an equidistant fashion?

Answer. From the O_h character table, we have that the O_h symmetry *operations* are

$$E \quad 8 C_3 \quad 6 C_2 \quad 6 C_4 \quad 3 C_2(=C_4^2) \quad i \quad 6 S_4 \quad 8 S_6 \quad 3 \sigma_h \quad 6 \sigma_d$$

Most of these operations are in one-to-one correspondence with a symmetry element. For example, each of the six C_2 rotations happens about a different C_2 axis. However, some symmetry elements have multiple symmetry operations happen about them. For example, each of the four C_3 axes has two (conjugate) C_3 symmetry operations (C_3 and C_3^2) occur about it. Thus, accounting for changes like this, we have that the O_h symmetry *elements* are

$$E \quad 4 C_3 \quad 6 C_2 \quad 3 C_4 \quad 3 C_2(=C_4^2) \quad i \quad 3 S_4 \quad 4 S_6 \quad 3 \sigma_h \quad 6 \sigma_d$$

Similarly, we can determine that the D_{4h} symmetry elements are

$$E \quad C_4 \quad C_2(=C_4^2) \quad 2 C_2' \quad 2 C_2'' \quad i \quad S_4 \quad \sigma_h \quad 2 \sigma_v \quad 2 \sigma_d$$

Between the two sets of symmetry elements, some are relabeled and some are lost entirely.

We will first discuss the relabeled ones. In particular...

- The two C_2 axes that lie in the xy plane become $2 C_2''$;
- The two $C_2(=C_4^2)$ axes that do not become the principal axis of the D_{4h} molecule become $2 C_2'^{[2]}$;
- The two σ_h planes that are not perpendicular to the principal axis of the D_{4h} molecule become $2 \sigma_v$.

We now discuss the ones that are lost entirely. These include (of the O_h molecule)...

- All four C_3/S_4 axes;
- The four C_2 axes that do not lie in the xy plane;
- The two C_4/S_4 axes that do not become the principal axis of the D_{4h} molecule;
- The four σ_d planes that do not contain the principal axis of the D_{4h} molecule.

□

²The prime notation is explained in the discussion associated with Figure II.6b of my notes.

2 Representations, Character Tables, and Vibrations

1/28: I) Do the following problem from your text: Chapter 4: #22.

4.22 Using the D_{2d} character table,

a. Determine the order of the group.

Answer. $\boxed{h = 8}$ — count the number of symmetry elements. \square

b. Verify that the E irreducible representation is orthogonal to each of the other irreducible representations.

Answer.

$$\sum_{R_c} g_c \chi_E(R_c) \chi_{A_1}(R_c) = (1)(2)(1) + (2)(0)(1) + (1)(-2)(1) + (2)(0)(1) + (2)(0)(1) = 0$$

$$\sum_{R_c} g_c \chi_E(R_c) \chi_{A_2}(R_c) = (1)(2)(1) + (2)(0)(1) + (1)(-2)(1) + (2)(0)(-1) + (2)(0)(-1) = 0$$

$$\sum_{R_c} g_c \chi_E(R_c) \chi_{B_1}(R_c) = (1)(2)(1) + (2)(0)(-1) + (1)(-2)(1) + (2)(0)(1) + (2)(0)(-1) = 0$$

$$\sum_{R_c} g_c \chi_E(R_c) \chi_{B_2}(R_c) = (1)(2)(1) + (2)(0)(-1) + (1)(-2)(1) + (2)(0)(-1) + (2)(0)(1) = 0$$

\square

c. For each of the irreducible representations, verify that the sum of the squares of the characters equals the order of the group.

Answer.

$$\sum_{R_c} g_c [\chi_{A_1}(R_c)]^2 = 1 \cdot 1^2 + 2 \cdot 1^2 + 1 \cdot 1^2 + 2 \cdot 1^2 + 2 \cdot 1^2 = 8$$

$$\sum_{R_c} g_c [\chi_{A_2}(R_c)]^2 = 1 \cdot 1^2 + 2 \cdot 1^2 + 1 \cdot 1^2 + 2 \cdot (-1)^2 + 2 \cdot (-1)^2 = 8$$

$$\sum_{R_c} g_c [\chi_{B_1}(R_c)]^2 = 1 \cdot 1^2 + 2 \cdot (-1)^2 + 1 \cdot 1^2 + 2 \cdot 1^2 + 2 \cdot (-1)^2 = 8$$

$$\sum_{R_c} g_c [\chi_{B_2}(R_c)]^2 = 1 \cdot 1^2 + 2 \cdot (-1)^2 + 1 \cdot 1^2 + 2 \cdot (-1)^2 + 2 \cdot 1^2 = 8$$

$$\sum_{R_c} g_c [\chi_E(R_c)]^2 = 1 \cdot 2^2 + 2 \cdot 0^2 + 1 \cdot (-2)^2 + 2 \cdot 0^2 + 2 \cdot 0^2 = 8$$

\square

d. Reduce the following representations to their component irreducible representations.

D_{2d}	E	$2S_4$	C_2	$2C'_2$	$2\sigma_d$
Γ_1	6	0	2	2	2
Γ_2	6	4	6	2	0

Answer. For Γ_1 :

$$a_{A_1} = \frac{1}{8} \sum_{R_c} g_c \chi_{\Gamma_1}(R_c) \chi_{A_1}(R_c) = \frac{1}{8} [(1)(6)(1) + (2)(0)(1) + (1)(2)(1) + (2)(2)(1) + (2)(2)(1)] = 2$$

$$a_{A_2} = \frac{1}{8} \sum_{R_c} g_c \chi_{\Gamma_1}(R_c) \chi_{A_2}(R_c) = \frac{1}{8} [(1)(6)(1) + (2)(0)(1) + (1)(2)(1) + (2)(2)(-1) + (2)(2)(-1)] = 0$$

$$a_{B_1} = \frac{1}{8} \sum_{R_c} g_c \chi_{\Gamma_1}(R_c) \chi_{B_1}(R_c) = \frac{1}{8} [(1)(6)(1) + (2)(0)(-1) + (1)(2)(1) + (2)(2)(1) + (2)(2)(-1)] = 1$$

$$a_{B_2} = \frac{1}{8} \sum_{R_c} g_c \chi_{\Gamma_1}(R_c) \chi_{B_2}(R_c) = \frac{1}{8} [(1)(6)(1) + (2)(0)(-1) + (1)(2)(1) + (2)(2)(-1) + (2)(2)(1)] = 1$$

$$a_E = \frac{1}{8} \sum_{R_c} g_c \chi_{\Gamma_1}(R_c) \chi_E(R_c) = \frac{1}{8} [(1)(6)(2) + (2)(0)(0) + (1)(2)(-2) + (2)(2)(0) + (2)(2)(0)] = 1$$

Therefore, we know that

$$\boxed{\Gamma_1 = 2A_1 + B_1 + B_2 + E}$$

For Γ_2 :

$$a_{A_1} = \frac{1}{8} \sum_{R_c} g_c \chi_{\Gamma_2}(R_c) \chi_{A_1}(R_c) = \frac{1}{8} [(1)(6)(1) + (2)(4)(1) + (1)(6)(1) + (2)(2)(1) + (2)(0)(1)] = 3$$

$$a_{A_2} = \frac{1}{8} \sum_{R_c} g_c \chi_{\Gamma_2}(R_c) \chi_{A_2}(R_c) = \frac{1}{8} [(1)(6)(1) + (2)(4)(1) + (1)(6)(1) + (2)(2)(-1) + (2)(0)(-1)] = 2$$

$$a_{B_1} = \frac{1}{8} \sum_{R_c} g_c \chi_{\Gamma_2}(R_c) \chi_{B_1}(R_c) = \frac{1}{8} [(1)(6)(1) + (2)(4)(-1) + (1)(6)(1) + (2)(2)(1) + (2)(0)(-1)] = 1$$

$$a_{B_2} = \frac{1}{8} \sum_{R_c} g_c \chi_{\Gamma_2}(R_c) \chi_{B_2}(R_c) = \frac{1}{8} [(1)(6)(1) + (2)(4)(-1) + (1)(6)(1) + (2)(2)(-1) + (2)(0)(1)] = 0$$

$$a_E = \frac{1}{8} \sum_{R_c} g_c \chi_{\Gamma_2}(R_c) \chi_E(R_c) = \frac{1}{8} [(1)(6)(2) + (2)(4)(0) + (1)(6)(-2) + (2)(2)(0) + (2)(0)(0)] = 0$$

Therefore, we know that

$$\boxed{\Gamma_2 = 3A_1 + 2A_2 + B_1}$$

□

II) Decompose the following reducible representations into their irreducible components. Ordering of the classes is the same as in the character tables in Appendix C of your text.

a) D_{3h} : 5, 2, 1, 3, 0, 3

Answer.

$$a_{A'_1} = \frac{1}{12} \sum_{R_c} g_c \chi_{\Gamma}(R_c) \chi_{A'_1}(R_c) = \frac{1}{12} [(1)(5)(1) + (2)(2)(1) + (3)(1)(1) + (1)(3)(1) + (2)(0)(1) + (3)(3)(1)] = 2$$

$$a_{A'_2} = \frac{1}{12} \sum_{R_c} g_c \chi_{\Gamma}(R_c) \chi_{A'_2}(R_c) = \frac{1}{12} [(1)(5)(1) + (2)(2)(1) + (3)(1)(-1) + (1)(3)(1) + (2)(0)(1) + (3)(3)(-1)] = 0$$

$$a_{E'} = \frac{1}{12} \sum_{R_c} g_c \chi_{\Gamma}(R_c) \chi_{E'}(R_c) = \frac{1}{12} [(1)(5)(2) + (2)(2)(-1) + (3)(1)(0) + (1)(3)(2) + (2)(0)(-1) + (3)(3)(0)] = 1$$

$$a_{A''_1} = \frac{1}{12} \sum_{R_c} g_c \chi_{\Gamma}(R_c) \chi_{A''_1}(R_c) = \frac{1}{12} [(1)(5)(1) + (2)(2)(1) + (3)(1)(1) + (1)(3)(-1) + (2)(0)(-1) + (3)(3)(-1)] = 0$$

$$a_{A''_2} = \frac{1}{12} \sum_{R_c} g_c \chi_{\Gamma}(R_c) \chi_{A''_2}(R_c) = \frac{1}{12} [(1)(5)(1) + (2)(2)(1) + (3)(1)(-1) + (1)(3)(-1) + (2)(0)(-1) + (3)(3)(1)] = 1$$

$$a_{E''} = \frac{1}{12} \sum_{R_c} g_c \chi_{\Gamma}(R_c) \chi_{E''}(R_c) = \frac{1}{12} [(1)(5)(2) + (2)(2)(-1) + (3)(1)(0) + (1)(3)(-2) + (2)(0)(1) + (3)(3)(0)] = 0$$

Therefore, we know that

$$\boxed{\Gamma = 2A'_1 + E' + A''_2}$$

□

b) D_{3h} : 3, 0, -1, -3, 0, 1

Answer.

$$a_{A'_1} = \frac{1}{12} \sum_{R_c} g_c \chi_{\Gamma}(R_c) \chi_{A'_1}(R_c) = \frac{1}{12} [(1)(3)(1) + (2)(0)(1) + (3)(-1)(1) + (1)(-3)(1) + (2)(0)(1) + (3)(1)(1)] = 0$$

$$a_{A'_2} = \frac{1}{12} \sum_{R_c} g_c \chi_{\Gamma}(R_c) \chi_{A'_2}(R_c) = \frac{1}{12} [(1)(3)(1) + (2)(0)(1) + (3)(-1)(-1) + (1)(-3)(1) + (2)(0)(1) + (3)(1)(-1)] = 0$$

$$a_{E'} = \frac{1}{12} \sum_{R_c} g_c \chi_{\Gamma}(R_c) \chi_{E'}(R_c) = \frac{1}{12} [(1)(3)(2) + (2)(0)(-1) + (3)(-1)(0) + (1)(-3)(2) + (2)(0)(-1) + (3)(1)(0)] = 0$$

$$a_{A''_1} = \frac{1}{12} \sum_{R_c} g_c \chi_{\Gamma}(R_c) \chi_{A''_1}(R_c) = \frac{1}{12} [(1)(3)(1) + (2)(0)(1) + (3)(-1)(1) + (1)(-3)(-1) + (2)(0)(-1) + (3)(1)(-1)] = 0$$

$$a_{A''_2} = \frac{1}{12} \sum_{R_c} g_c \chi_{\Gamma}(R_c) \chi_{A''_2}(R_c) = \frac{1}{12} [(1)(3)(1) + (2)(0)(1) + (3)(-1)(-1) + (1)(-3)(-1) + (2)(0)(-1) + (3)(1)(1)] = 1$$

$$a_{E''} = \frac{1}{12} \sum_{R_c} g_c \chi_{\Gamma}(R_c) \chi_{E''}(R_c) = \frac{1}{12} [(1)(3)(2) + (2)(0)(-1) + (3)(-1)(0) + (1)(-3)(-2) + (2)(0)(1) + (3)(1)(0)] = 1$$

Therefore, we know that

$$\boxed{\Gamma = A''_2 + E''}$$

□

c) C_{2v} : 4, 0, 0, 0

Answer. We know the following by inspection.

$$\boxed{\Gamma = A_1 + A_2 + B_1 + B_2}$$

□

d) C_{2h} : 5, 1, 1, 1

Answer. We know the following by inspection.

$$\Gamma = 2A_g + B_g + A_u + B_u$$

□

e) T_d : 13, 1, 5, -3, -3

Answer.

$$a_{A_1} = \frac{1}{24} \sum_{R_c} g_c \chi_{\Gamma}(R_c) \chi_{A_1}(R_c) = \frac{1}{24} [(1)(13)(1) + (8)(1)(1) + (3)(5)(1) + (6)(-3)(1) + (6)(-3)(1)] = 0$$

$$a_{A_2} = \frac{1}{24} \sum_{R_c} g_c \chi_{\Gamma}(R_c) \chi_{A_2}(R_c) = \frac{1}{24} [(1)(13)(1) + (8)(1)(1) + (3)(5)(1) + (6)(-3)(-1) + (6)(-3)(-1)] = 3$$

$$a_E = \frac{1}{24} \sum_{R_c} g_c \chi_{\Gamma}(R_c) \chi_E(R_c) = \frac{1}{24} [(1)(13)(2) + (8)(1)(-1) + (3)(5)(2) + (6)(-3)(0) + (6)(-3)(0)] = 2$$

$$a_{T_1} = \frac{1}{24} \sum_{R_c} g_c \chi_{\Gamma}(R_c) \chi_{T_1}(R_c) = \frac{1}{24} [(1)(13)(3) + (8)(1)(0) + (3)(5)(-1) + (6)(-3)(1) + (6)(-3)(-1)] = 1$$

$$a_{T_2} = \frac{1}{24} \sum_{R_c} g_c \chi_{\Gamma}(R_c) \chi_{T_2}(R_c) = \frac{1}{24} [(1)(13)(3) + (8)(1)(0) + (3)(5)(-1) + (6)(-3)(-1) + (6)(-3)(1)] = 1$$

Therefore, we know that

$$\Gamma = 3A_2 + 2E + T_1 + T_2$$

□

f) T_h : 8, -1, -1, 4, 8, -1, -1, 4

Answer. With respect to the two doubly degenerate groups, we must add the two parts together and also double the order that we are dividing out. Note that $\varepsilon = e^{2\pi i/3} = \cos\left(\frac{2\pi}{3}\right) + i \sin\left(\frac{2\pi}{3}\right) = -0.5 + i\frac{\sqrt{3}}{2}$ and, thus, $\varepsilon^* = -0.5 - i\frac{\sqrt{3}}{2}$. It follows that $\varepsilon + \varepsilon^* = -1$.

$$\begin{aligned} a_{A_g} &= \frac{1}{24} \sum_{R_c} g_c \chi_{\Gamma}(R_c) \chi_{A_g}(R_c) \\ &= \frac{1}{24} [(1)(8)(1) + (4)(-1)(1) + (4)(-1)(1) + (3)(4)(1) + (1)(8)(1) + (4)(-1)(1) + (4)(-1)(1) + (3)(4)(1)] \\ &= 1 \end{aligned}$$

$$\begin{aligned} a_{A_u} &= \frac{1}{24} \sum_{R_c} g_c \chi_{\Gamma}(R_c) \chi_{A_u}(R_c) \\ &= \frac{1}{24} [(1)(8)(1) + (4)(-1)(1) + (4)(-1)(1) + (3)(4)(1) + (1)(8)(-1) + (4)(-1)(-1) + (4)(-1)(-1) + (3)(4)(-1)] \\ &= 0 \end{aligned}$$

$$\begin{aligned} 2a_{E_g} &= \frac{1}{24} \sum_{R_c} g_c \chi_{\Gamma}(R_c) \chi_{E_g}(R_c) \\ a_{E_g} &= \frac{1}{48} [(1)(8)(2) + (4)(-1)(-1) + (4)(-1)(-1) + (3)(4)(2) + (1)(8)(2) + (4)(-1)(-1) + (4)(-1)(-1) + (3)(4)(2)] \\ &= 2 \end{aligned}$$

$$2a_{E_u} = \frac{1}{24} \sum_{R_c} g_c \chi_{\Gamma}(R_c) \chi_{E_u}(R_c)$$

$$\begin{aligned} a_{E_u} &= \frac{1}{48} [(1)(8)(2) + (4)(-1)(-1) + (4)(-1)(-1) + (3)(4)(2) + (1)(8)(-2) + (4)(-1)(1) + (4)(-1)(1) + (3)(4)(-2)] \\ &= 0 \end{aligned}$$

$$a_{T_g} = \frac{1}{24} \sum_{R_c} g_c \chi_{\Gamma}(R_c) \chi_{T_g}(R_c)$$

$$\begin{aligned} &= \frac{1}{24} [(1)(8)(3) + (4)(-1)(0) + (4)(-1)(0) + (3)(4)(-1) + (1)(8)(3) + (4)(-1)(0) + (4)(-1)(0) + (3)(4)(-1)] \\ &= 1 \end{aligned}$$

$$a_{T_u} = \frac{1}{24} \sum_{R_c} g_c \chi_{\Gamma}(R_c) \chi_{T_u}(R_c)$$

$$\begin{aligned} &= \frac{1}{24} [(1)(8)(3) + (4)(-1)(0) + (4)(-1)(0) + (3)(4)(-1) + (1)(8)(-3) + (4)(-1)(0) + (4)(-1)(0) + (3)(4)(1)] \\ &= 0 \end{aligned}$$

Therefore, we know that

$$\boxed{\Gamma = A_g + 2E_g + T_g}$$

□

- III) Draw the set of s , p , and d orbitals, indicating the Cartesian axes and the proper phases of the orbitals. By noting how each orbital is affected by the symmetry operations in the C_{2h} point group (E , C_2 , i , σ_h), write an irreducible representation for each orbital. Compare your results with the listing of the orbitals in the character table in Appendix C of the text.

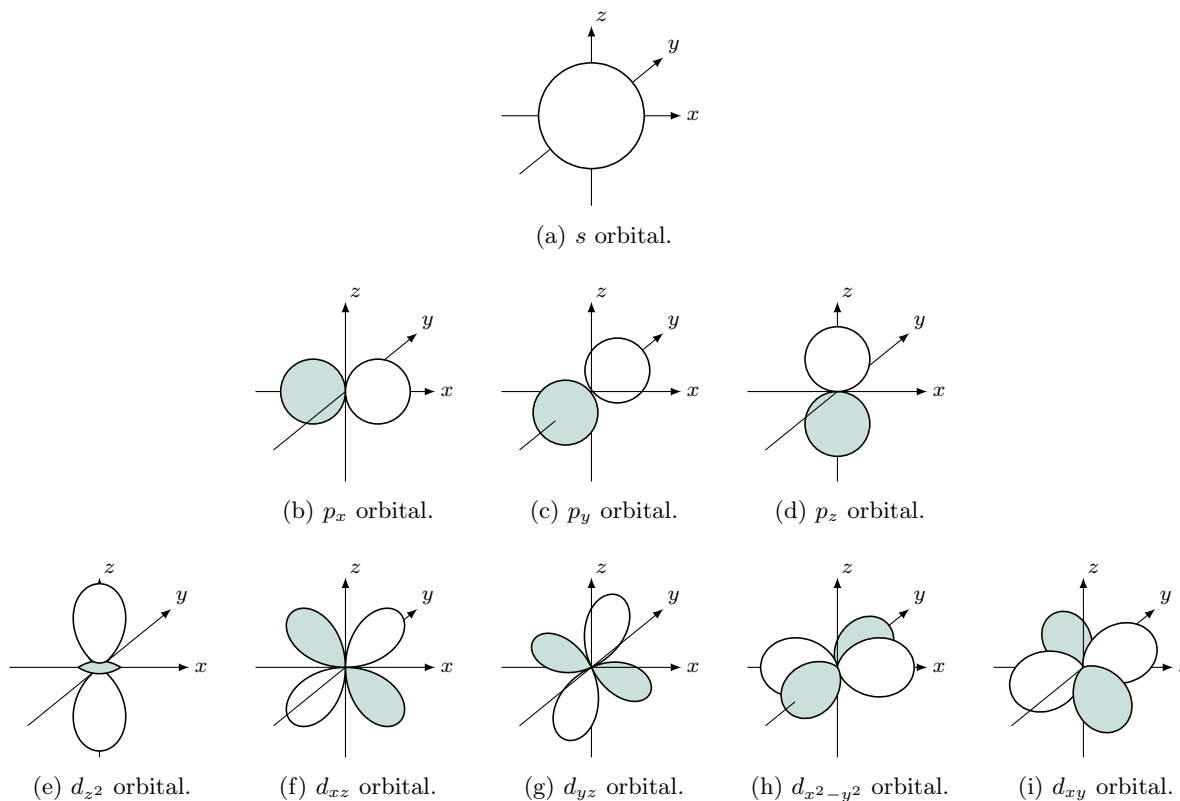


Figure 2.1: s , p , and d orbitals.

Answer. In Figure 2.1, white shading means positive phase and orange means negative phase.

Here are irreducible representations for each orbital:

$$\begin{aligned}\Gamma_s &= (1, 1, 1, 1) = A_g \\ \Gamma_{p_x} &= (1, -1, -1, 1) = B_u \\ \Gamma_{p_y} &= (1, -1, -1, 1) = B_u \\ \Gamma_{p_z} &= (1, 1, -1, -1) = A_u \\ \Gamma_{d_{z^2}} &= (1, 1, 1, 1) = A_g \\ \Gamma_{d_{xz}} &= (1, -1, 1, -1) = B_g \\ \Gamma_{d_{yz}} &= (1, -1, 1, -1) = B_g \\ \Gamma_{d_{x^2-y^2}} &= (1, 1, 1, 1) = A_g \\ \Gamma_{d_{xy}} &= (1, 1, 1, 1) = A_g\end{aligned}$$

□

- IV) The molecule $\text{Co}(\text{CO})_4(\text{SiMe}_3)$ has a structure based on a trigonal bipyramid. The infrared spectrum of $\text{Co}(\text{CO})_4(\text{SiMe}_3)$ exhibits three $\nu(\text{CO})$ stretching vibrations at 2100, 2041, and 2009 cm^{-1} . Draw the two possible structures based on the TBP geometry, assign their proper point groups, and use the infrared data to determine which is the correct structure.

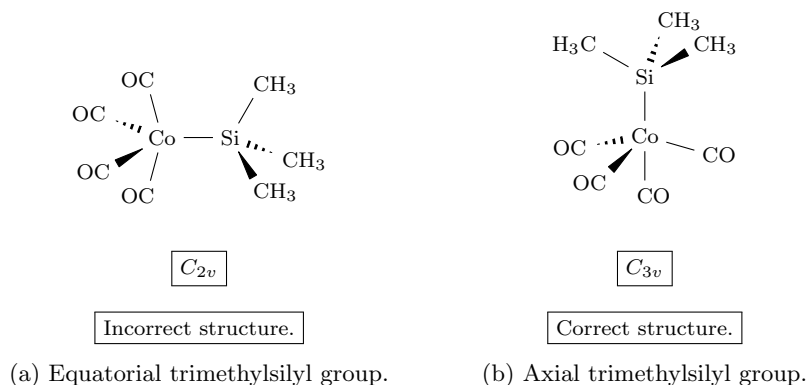


Figure 2.2: Structures of $\text{Co}(\text{CO})_4(\text{SiMe}_3)$.

Explanation. Note that for the sake of point group assignments, the CO ligands will be treated as identical point particles. Additionally, the SiMe_3 ligand will be treated as a point particle distinguishable from the CO point particles.

The structure in Figure 2.2a: Not high or low symmetry. Has a C_2 axis. No perpendicular C_2 axes. No σ_h . Has two perpendicular σ_v planes. Therefore, it is of the C_{2v} point group.

We can determine that $\Gamma_\nu = (4, 0, 2, 2) = 2A_1 + B_1 + B_2$ by counting how many $\overrightarrow{\text{Co}-\text{CO}}$ vectors stay the same under each symmetry operation and decomposing by inspection. With four stretching modes that are all IR active, we can expect there to be four peaks in the infrared spectrum of $\text{Co}(\text{CO})_4(\text{SiMe}_3)$. Therefore, this is not the correct structure.

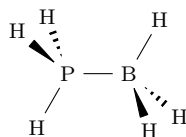
The structure in Figure 2.2b: Not high or low symmetry. Has a C_3 axis. No perpendicular C_2 axes. No σ_h . Has three σ_v planes all offset by 60° . Therefore, it is of the C_{3v} point group.

We can determine that $\Gamma_\nu = (4, 1, 2) = 2A_1 + E$ by counting how many $\overrightarrow{\text{Co}-\text{CO}}$ vectors stay the same under each symmetry operation and decomposing by inspection. With four $\nu(\text{CO})$ stretching modes that are all IR active (but two of the four being degenerate), we can expect there to be three peaks in the infrared spectrum of $\text{Co}(\text{CO})_4(\text{SiMe}_3)$. This confirms that this is the correct structure. \square

V) Determine the number and symmetry types of normal vibrations in the following molecules:

- a) H_3PBH_3 : with a staggered ethane-like geometry.

Answer.



H_3PBH_3 has $3(8) - 6 = 18$ normal vibrations.

Not high or low symmetry. Has a C_3 axis. No perpendicular C_2 axes. No σ_h . Has three σ_v planes all offset by 60° . Therefore, H_3PBH_3 is of the C_{3v} point group.

It follows from the C_{3v} character table that $\Gamma_{x,y,z} = (3, 0, 1)$. We can also figure out that the number of atoms unmoved after applying each symmetry operation is $(8, 2, 4)$. Thus, $\Gamma_{3N} = (24, 0, 4)$. We can reduce this by inspection to $\Gamma_{3N} = 6A_1 + 2A_2 + 8E$.

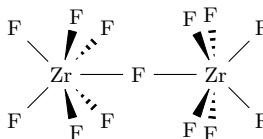
Since $\Gamma_{\text{trans}} = A_1 + E$ and $\Gamma_{\text{rot}} = A_2 + E$ (again from the C_{3v} character table), we have by subtraction that

$$\Gamma_{\text{vibs}} = 5A_1 + A_2 + 6E$$

Thus, of the 18 normal vibrations, 5 have symmetry A_1 , 1 has symmetry A_2 , and 12 have symmetry E (note that these 12 modes pair up into 6 pairs of vibration modes of the same type). \square

- b) $\text{Zr}_2\text{F}_{13}^{5-}$: Each Zr is seven coordinate with monocapped trigonal prismatic geometry. The cap is a bridging F (linear $\text{Zr}-\text{F}-\text{Zr}$ linkage) on the unique square face of the prism. The anionic complex has an eclipsed geometry about the bridging F.

Answer.



$\text{Zr}_2\text{F}_{13}^{5-}$ has $3(15) - 6 = 39$ normal vibrations.

Not high or low symmetry. Has a C_2 axis. Has 2 perpendicular C_2 axes. Has a σ_h plane. Therefore, $\text{Zr}_2\text{F}_{13}^{5-}$ is of the D_{2h} point group.

It follows from the D_{2h} character table that $\Gamma_{x,y,z} = (3, -1, -1, -1, -3, 1, 1, 1)$. We can also figure out that the number of atoms unmoved after applying each symmetry operation is $(15, 3, 1, 1, 1, 1, 7, 3)$.

Thus, $\Gamma_{3N} = (45, -3, -1, -1, -3, 1, 7, 3)$. We can reduce this as follows.

$$\begin{aligned} a_{A_g} &= \frac{1}{8} \sum_{R_c} g_c \chi_{\Gamma_{3N}}(R_c) \chi_{A_g}(R_c) \\ &= \frac{1}{8} [(1)(45)(1) + (1)(-3)(1) + (1)(-1)(1) + (1)(-1)(1) + (1)(-3)(1) + (1)(1)(1) + (1)(7)(1) + (1)(3)(1)] \\ &= 6 \end{aligned}$$

$$\begin{aligned} a_{B_{1g}} &= \frac{1}{8} \sum_{R_c} g_c \chi_{\Gamma_{3N}}(R_c) \chi_{B_{1g}}(R_c) \\ &= \frac{1}{8} [(1)(45)(1) + (1)(-3)(1) + (1)(-1)(-1) + (1)(-1)(-1) + (1)(-3)(1) + (1)(1)(1) + (1)(7)(-1) + (1)(3)(-1)] \\ &= 4 \end{aligned}$$

$$\begin{aligned}
a_{B_{2g}} &= \frac{1}{8} \sum_{R_c} g_c \chi_{\Gamma_{3N}}(R_c) \chi_{B_{2g}}(R_c) \\
&= \frac{1}{8} [(1)(45)(1) + (1)(-3)(-1) + (1)(-1)(1) + (1)(-1)(-1) + (1)(-3)(1) + (1)(1)(-1) + (1)(7)(1) + (1)(3)(-1)] \\
&= 6
\end{aligned}$$

$$\begin{aligned}
a_{B_{3g}} &= \frac{1}{8} \sum_{R_c} g_c \chi_{\Gamma_{3N}}(R_c) \chi_{B_{3g}}(R_c) \\
&= \frac{1}{8} [(1)(45)(1) + (1)(-3)(-1) + (1)(-1)(-1) + (1)(-1)(1) + (1)(-3)(1) + (1)(1)(-1) + (1)(7)(-1) + (1)(3)(1)] \\
&= 5
\end{aligned}$$

$$\begin{aligned}
a_{A_u} &= \frac{1}{8} \sum_{R_c} g_c \chi_{\Gamma_{3N}}(R_c) \chi_{A_u}(R_c) \\
&= \frac{1}{8} [(1)(45)(1) + (1)(-3)(1) + (1)(-1)(1) + (1)(-1)(1) + (1)(-3)(-1) + (1)(1)(-1) + (1)(7)(-1) + (1)(3)(-1)] \\
&= 4
\end{aligned}$$

$$\begin{aligned}
a_{B_{1u}} &= \frac{1}{8} \sum_{R_c} g_c \chi_{\Gamma_{3N}}(R_c) \chi_{B_{1u}}(R_c) \\
&= \frac{1}{8} [(1)(45)(1) + (1)(-3)(1) + (1)(-1)(-1) + (1)(-1)(-1) + (1)(-3)(-1) + (1)(1)(-1) + (1)(7)(1) + (1)(3)(1)] \\
&= 7
\end{aligned}$$

$$\begin{aligned}
a_{B_{2u}} &= \frac{1}{8} \sum_{R_c} g_c \chi_{\Gamma_{3N}}(R_c) \chi_{B_{2u}}(R_c) \\
&= \frac{1}{8} [(1)(45)(1) + (1)(-3)(-1) + (1)(-1)(1) + (1)(-1)(-1) + (1)(-3)(-1) + (1)(1)(1) + (1)(7)(-1) + (1)(3)(1)] \\
&= 6
\end{aligned}$$

$$\begin{aligned}
a_{B_{3u}} &= \frac{1}{8} \sum_{R_c} g_c \chi_{\Gamma_{3N}}(R_c) \chi_{B_{3u}}(R_c) \\
&= \frac{1}{8} [(1)(45)(1) + (1)(-3)(-1) + (1)(-1)(-1) + (1)(-1)(1) + (1)(-3)(-1) + (1)(1)(1) + (1)(7)(1) + (1)(3)(-1)] \\
&= 7
\end{aligned}$$

Therefore, we know that $\Gamma_{3N} = 6A_g + 4B_{1g} + 6B_{2g} + 5B_{3g} + 4A_u + 7B_{1u} + 6B_{2u} + 7B_{3u}$. Since $\Gamma_{\text{trans}} = B_{1u} + B_{2u} + B_{3u}$ and $\Gamma_{\text{rot}} = B_{1g} + B_{2g} + B_{3g}$ (again from the D_{2h} character table), we have by subtraction that

$$\boxed{\Gamma_{\text{vibs}} = 6A_g + 3B_{1g} + 5B_{2g} + 4B_{3g} + 4A_u + 6B_{1u} + 5B_{2u} + 6B_{3u}}$$

Thus, of the 39 normal vibrations, 6 have symmetry A_g , 3 have symmetry B_{1g} , 5 have symmetry B_{2g} , 4 have symmetry B_{3g} , 4 have symmetry A_u , 6 have symmetry B_{1u} , 5 have symmetry B_{2u} , and 6 have symmetry B_{3u} . \square

VI) Benzene (C_6H_6) is a planar molecule.

a) Assign the symmetry group.

Answer. Not high or low symmetry. Has a C_6 axis. Has 6 perpendicular C_2 axes. Has a σ_h plane. Therefore, C_6H_6 is of the D_{6h} point group. \square

b) Determine the number and symmetries of the C–H stretching modes in benzene.

Answer. We can determine that $\Gamma_\nu = (6, 0, 0, 0, 2, 0, 0, 0, 0, 6, 0, 2)$ by counting how many $\overrightarrow{C-H}$ vectors stay the same under each symmetry operation. We can reduce this as follows.

$$\begin{aligned} a_{A_{1g}} &= \frac{1}{24} \sum_{R_c} g_c \chi_{\Gamma_\nu}(R_c) \chi_{A_{1g}}(R_c) \\ &= \frac{1}{24} [(1)(6)(1) + (2)(0)(1) + (2)(0)(1) + (1)(0)(1) + (3)(2)(1) + (3)(0)(1) \\ &\quad + (1)(0)(1) + (2)(0)(1) + (2)(0)(1) + (1)(6)(1) + (3)(0)(1) + (3)(2)(1)] \\ &= 1 \end{aligned}$$

$$\begin{aligned} a_{A_{2g}} &= \frac{1}{24} \sum_{R_c} g_c \chi_{\Gamma_\nu}(R_c) \chi_{A_{2g}}(R_c) \\ &= \frac{1}{24} [(1)(6)(1) + (2)(0)(1) + (2)(0)(1) + (1)(0)(1) + (3)(2)(-1) + (3)(0)(-1) \\ &\quad + (1)(0)(1) + (2)(0)(1) + (2)(0)(1) + (1)(6)(1) + (3)(0)(-1) + (3)(2)(-1)] \\ &= 0 \end{aligned}$$

$$\begin{aligned} a_{B_{1g}} &= \frac{1}{24} \sum_{R_c} g_c \chi_{\Gamma_\nu}(R_c) \chi_{B_{1g}}(R_c) \\ &= \frac{1}{24} [(1)(6)(1) + (2)(0)(-1) + (2)(0)(1) + (1)(0)(-1) + (3)(2)(1) + (3)(0)(-1) \\ &\quad + (1)(0)(1) + (2)(0)(-1) + (2)(0)(1) + (1)(6)(-1) + (3)(0)(1) + (3)(2)(-1)] \\ &= 0 \end{aligned}$$

$$\begin{aligned} a_{B_{2g}} &= \frac{1}{24} \sum_{R_c} g_c \chi_{\Gamma_\nu}(R_c) \chi_{B_{2g}}(R_c) \\ &= \frac{1}{24} [(1)(6)(1) + (2)(0)(-1) + (2)(0)(1) + (1)(0)(-1) + (3)(2)(-1) + (3)(0)(1) \\ &\quad + (1)(0)(1) + (2)(0)(-1) + (2)(0)(1) + (1)(6)(-1) + (3)(0)(-1) + (3)(2)(1)] \\ &= 0 \end{aligned}$$

$$\begin{aligned} a_{E_{1g}} &= \frac{1}{24} \sum_{R_c} g_c \chi_{\Gamma_\nu}(R_c) \chi_{E_{1g}}(R_c) \\ &= \frac{1}{24} [(1)(6)(2) + (2)(0)(1) + (2)(0)(-1) + (1)(0)(-2) + (3)(2)(0) + (3)(0)(0) \\ &\quad + (1)(0)(2) + (2)(0)(1) + (2)(0)(-1) + (1)(6)(-2) + (3)(0)(0) + (3)(2)(0)] \\ &= 0 \end{aligned}$$

$$\begin{aligned}
a_{E_{2g}} &= \frac{1}{24} \sum_{R_c} g_c \chi_{\Gamma_\nu}(R_c) \chi_{E_{2g}}(R_c) \\
&= \frac{1}{24} [(1)(6)(2) + (2)(0)(-1) + (2)(0)(-1) + (1)(0)(2) + (3)(2)(0) + (3)(0)(0) \\
&\quad + (1)(0)(2) + (2)(0)(-1) + (2)(0)(-1) + (1)(6)(2) + (3)(0)(0) + (3)(2)(0)] \\
&= 1
\end{aligned}$$

$$\begin{aligned}
a_{A_{1u}} &= \frac{1}{24} \sum_{R_c} g_c \chi_{\Gamma_\nu}(R_c) \chi_{A_{1u}}(R_c) \\
&= \frac{1}{24} [(1)(6)(1) + (2)(0)(1) + (2)(0)(1) + (1)(0)(1) + (3)(2)(1) + (3)(0)(1) \\
&\quad + (1)(0)(-1) + (2)(0)(-1) + (2)(0)(-1) + (1)(6)(-1) + (3)(0)(-1) + (3)(2)(-1)] \\
&= 0
\end{aligned}$$

$$\begin{aligned}
a_{A_{2u}} &= \frac{1}{24} \sum_{R_c} g_c \chi_{\Gamma_\nu}(R_c) \chi_{A_{2u}}(R_c) \\
&= \frac{1}{24} [(1)(6)(1) + (2)(0)(1) + (2)(0)(1) + (1)(0)(1) + (3)(2)(-1) + (3)(0)(-1) \\
&\quad + (1)(0)(-1) + (2)(0)(-1) + (2)(0)(-1) + (1)(6)(-1) + (3)(0)(1) + (3)(2)(1)] \\
&= 0
\end{aligned}$$

$$\begin{aligned}
a_{B_{1u}} &= \frac{1}{24} \sum_{R_c} g_c \chi_{\Gamma_\nu}(R_c) \chi_{B_{1u}}(R_c) \\
&= \frac{1}{24} [(1)(6)(1) + (2)(0)(-1) + (2)(0)(1) + (1)(0)(-1) + (3)(2)(1) + (3)(0)(-1) \\
&\quad + (1)(0)(-1) + (2)(0)(1) + (2)(0)(-1) + (1)(6)(1) + (3)(0)(-1) + (3)(2)(1)] \\
&= 1
\end{aligned}$$

$$\begin{aligned}
a_{B_{2u}} &= \frac{1}{24} \sum_{R_c} g_c \chi_{\Gamma_\nu}(R_c) \chi_{B_{2u}}(R_c) \\
&= \frac{1}{24} [(1)(6)(1) + (2)(0)(-1) + (2)(0)(1) + (1)(0)(-1) + (3)(2)(-1) + (3)(0)(1) \\
&\quad + (1)(0)(-1) + (2)(0)(1) + (2)(0)(-1) + (1)(6)(1) + (3)(0)(1) + (3)(2)(-1)] \\
&= 0
\end{aligned}$$

$$\begin{aligned}
a_{E_{1u}} &= \frac{1}{24} \sum_{R_c} g_c \chi_{\Gamma_\nu}(R_c) \chi_{E_{1u}}(R_c) \\
&= \frac{1}{24} [(1)(6)(2) + (2)(0)(1) + (2)(0)(-1) + (1)(0)(-2) + (3)(2)(0) + (3)(0)(0) \\
&\quad + (1)(0)(-2) + (2)(0)(-1) + (2)(0)(1) + (1)(6)(2) + (3)(0)(0) + (3)(2)(0)] \\
&= 1
\end{aligned}$$

$$\begin{aligned}
a_{E_{2u}} &= \frac{1}{24} \sum_{R_c} g_c \chi_{\Gamma_\nu}(R_c) \chi_{E_{2u}}(R_c) \\
&= \frac{1}{24} [(1)(6)(2) + (2)(0)(-1) + (2)(0)(-1) + (1)(0)(2) + (3)(2)(0) + (3)(0)(0) \\
&\quad + (1)(0)(-2) + (2)(0)(1) + (2)(0)(1) + (1)(6)(-2) + (3)(0)(0) + (3)(2)(0)] \\
&= 0
\end{aligned}$$

Therefore, we know that

$$\Gamma_{\nu} = A_{1g} + E_{2g} + B_{1u} + E_{1u}$$

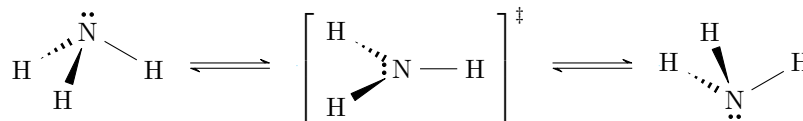
Thus, there are 6 C–H stretching modes in benzene: 1 with symmetry A_{1g} , 2 with symmetry E_{2g} (note that these 2 modes form a pair vibration modes of the same type), 1 with symmetry B_{1u} , and 2 with symmetry E_{1u} (again, these pair up). \square

- c) Determine the Raman and infrared activities for each vibration.

Answer. Since the A_{1g} , E_{1g} , and E_{2g} irreducible representations are Raman active, we know that the A_{1g} and E_{2g} C–H stretching modes are Raman active. The others are Raman silent. Additionally, since the A_{2u} and E_{1u} irreducible representations are IR active and two of the C–H stretching vibration modes are of the E_{1u} type, the E_{1u} vibrations are both IR active. The others are IR silent. \square

3 Constructing Molecular Orbitals

- 2/4: I) Ammonia undergoes a facile inversion (“umbrella flip”) as shown below. The activation barrier for inversion is low ($\Delta G^\ddagger \sim 5$ kcal/mol), and the transition state for this motion is planar NH_3 . Note that the relevant valence shell IP’s are $\text{N}_{2s} = -26.0$ eV, $\text{N}_{2p} = -13.4$ eV, and $\text{H}_{1s} = -13.6$ eV.



- a) Construct an MO diagram for *planar* NH_3 .

Answer. Point group: D_{3h}

Basis functions: all three H orbitals, N_{2s} , N_{2p_x} , N_{2p_y} , and N_{2p_z} .

Apply operations, generate reducible representations, and reduce to irreducible representations (for orbitals of the center atom, read irreducible representations from the D_{3h} character table):

$$\begin{aligned}\Gamma_{\text{H}} &= (3, 0, 1, 3, 0, 1) = A'_1 + E' \\ \Gamma_{\text{N}_{2s}} &= A'_1 \\ \Gamma_{\text{N}_{2p_x}} &= E' \\ \Gamma_{\text{N}_{2p_y}} &= E' \\ \Gamma_{\text{N}_{2p_z}} &= A''_2\end{aligned}$$

Combine central and peripheral orbitals by their symmetry:

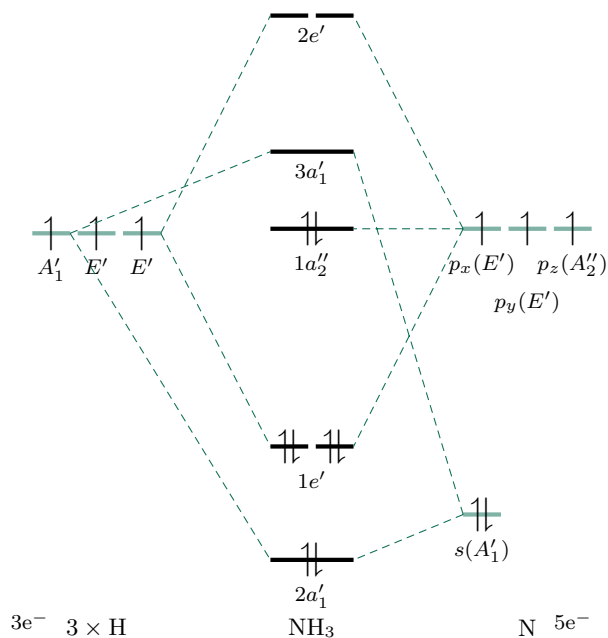


Figure 3.1: Planar NH_3^\ddagger orbital diagram.

□

- b) Label the MOs with the appropriate Mulliken symbols (a_{1g} , e_g , etc.) and add electrons to show the proper orbital occupancies.

Answer. See Figure 3.1.

□

- c) Compare your MO diagram with that for pyramidal NH_3 (Figure 5.30 in your text), and comment qualitatively on why this process is a low-energy one.

Answer. It appears that the only change between the two MO diagrams is that the two $3a_1$ electrons in the pyramidal NH_3 diagram must be excited to the $1a_2''$ orbital in the planar NH_3 diagram. Since $1a_2''$ is higher in energy than $3a_1$, there will be an increase in energy, but since it is only marginally higher, the increase will be very small. \square

- d) What vibrational mode is responsible for the inversion?

Answer.

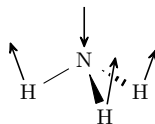


Figure 3.2: The A_1 bending mode.

If any vibrational mode is responsible for the inversion, it certainly won't be a stretching mode since these have no effect on molecular geometry about the central atom. On the other hand, a bending mode could well achieve such a transition. Thus, we will find the bending modes in both pyramidal and planar NH_3 and compare.

For pyramidal NH_3 , the C_{3v} character table tells us that $\Gamma_{x,y,z} = (3, 0, 1)$. We can also figure out that the number of atoms unmoved after applying each symmetry operation is $(4, 1, 2)$. Thus, $\Gamma_{3N} = (12, 0, 2)$. We can decompose this by inspection to $\Gamma_{3N} = 3A_1 + A_2 + 4E$. Since $\Gamma_{\text{trans}} = A_1 + E$ and $\Gamma_{\text{rot}} = A_2 + E$ (again from the C_{3v} character table), we have by subtraction that $\Gamma_{\text{vibs}} = 2A_1 + 2E$.

We can determine that $\Gamma_\nu = (3, 0, 1)$ by counting how many $\overrightarrow{\text{N}-\text{H}}$ vectors stay the same under each symmetry operation. We can decompose this by inspection to $\Gamma_\nu = A_1 + E$. Thus, we have by subtraction that $\Gamma_\delta = A_1 + E$.

For planar NH_3 , the D_{3h} character table tells us that $\Gamma_{x,y,z} = (3, 0, -1, 1, -2, 1)$. We can also figure out that the number of atoms unmoved after applying each symmetry operation is $(4, 1, 2, 4, 1, 2)$. Thus, $\Gamma_{3N} = (12, 0, -2, 4, -2, 2)$. We can decompose this by repeated applications of the reduction formula to $\Gamma_{3N} = A'_1 + A'_2 + 3E' + 2A''_2 + E''$. Since $\Gamma_{\text{trans}} = E' + A''_2$ and $\Gamma_{\text{rot}} = A'_2 + E''$ (again by the D_{3h} character table), we have by subtraction that $\Gamma_{\text{vibs}} = A'_1 + 2E' + A''_2$.

We can determine that $\Gamma_\nu = (3, 0, 1, 3, 0, 1)$ by counting how many $\overrightarrow{\text{N}-\text{H}}$ vectors stay the same under each symmetry operation. We can decompose this by inspection to $\Gamma_\nu = A'_1 + E'$. Thus, we have by subtraction that $\Gamma_\delta = E' + A''_2$.

Since the E pyramidal bending modes transform into the analogous E' planar bending modes, but the A_1 pyramidal bending mode has no planar analogue, it is the A_1 bending mode in pyramidal NH_3 that causes the inversion. This derivation can be rationalized intuitively by noting that the movement that causes the inversion must look like the totally symmetric bending mode in Figure 3.2. \square

II)

- a) Use group theory to construct an MO diagram for octahedral SF_6 . Consider only σ -bonding between S and the F's and use only the sulfur $3s$ and $3p$ valence orbitals (i.e., ignore the $3d$ -orbital involvement). For fluorine, just use a " σ -type" orbital to determine the $6 \times \text{F}$ group orbitals.

Answer. Point group: O_h

Basis functions: all six F orbitals, S_{3s} , S_{3p_x} , S_{3p_y} , and S_{3p_z} .

Apply operations, generate reducible representations, and reduce to irreducible representations (for orbitals of the center atom, read irreducible representations from the O_h character table):

$$\begin{aligned}\Gamma_F &= (6, 0, 0, 2, 2, 0, 0, 0, 4, 2) = A_{1g} + E_g + T_{1u} \\ \Gamma_{S_{3s}} &= A_{1g} \\ \Gamma_{S_{3p_x}} &= T_{1u} \\ \Gamma_{S_{3p_y}} &= T_{1u} \\ \Gamma_{S_{3p_z}} &= T_{1u}\end{aligned}$$

Combine central and peripheral orbitals by their symmetry: □

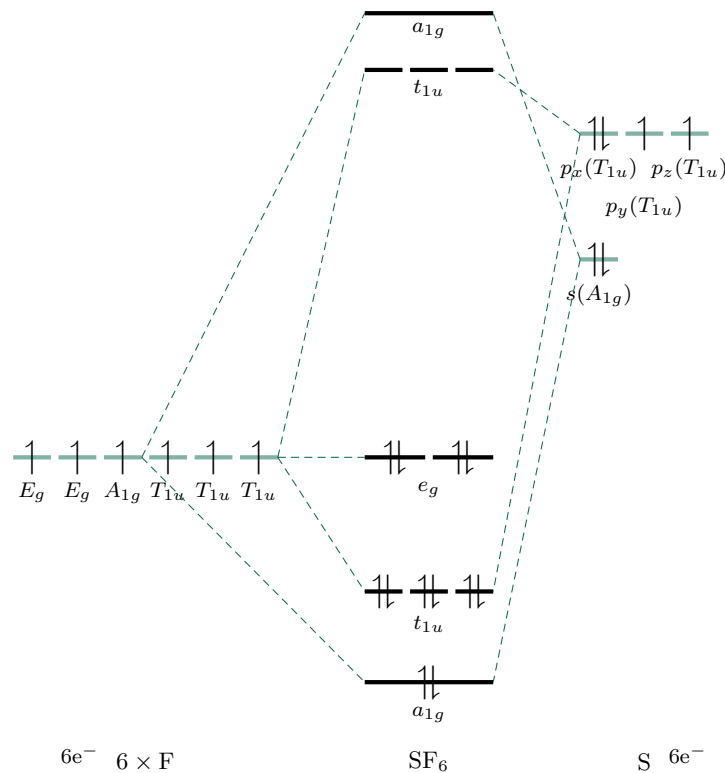


Figure 3.3: SF_6 orbital diagram.

- b) Label the MO's with the appropriate Mulliken symbols and show the orbital occupancies (i.e., fill in the MO levels with the proper number of electrons).

Answer. See Figure 3.3. □

- c) Based on the MO diagram, comment on the number of bonding electrons in SF_6 and the bond-order of each S–F bond.

Answer. There are 8 bonding electrons (the two in the $1a_{1g}$ orbital, and the six in the degenerate $1t_{1u}$ orbitals; the four in the degenerate $1e_g$ orbitals are nonbonding and all anti-bonding orbitals are unfilled). Since the bond order is one half the number of bonding electrons divided by the number of bonds, we have

$$\text{B.O.} = \frac{2}{3}$$

□

4 Band Theory and Acid-Base Interactions

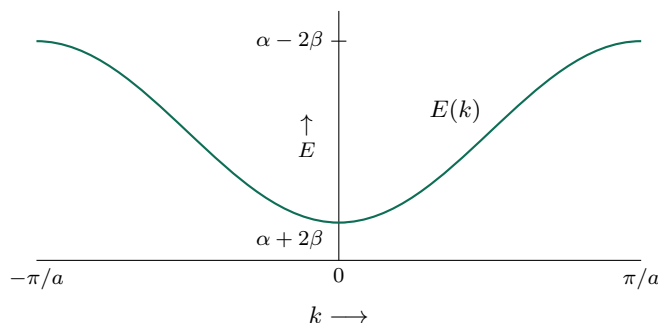
- 2/15: I) In our description for a one-dimensional s -orbital chain with period a , the allowed energy states broaden into a band whose dispersion (dependence of the energy E on the wavevector k) is given by

$$E(k) = \alpha + 2\beta \cos ka$$

where β is the nearest-neighbor interaction energy and is less than zero for neighboring s -type orbitals.

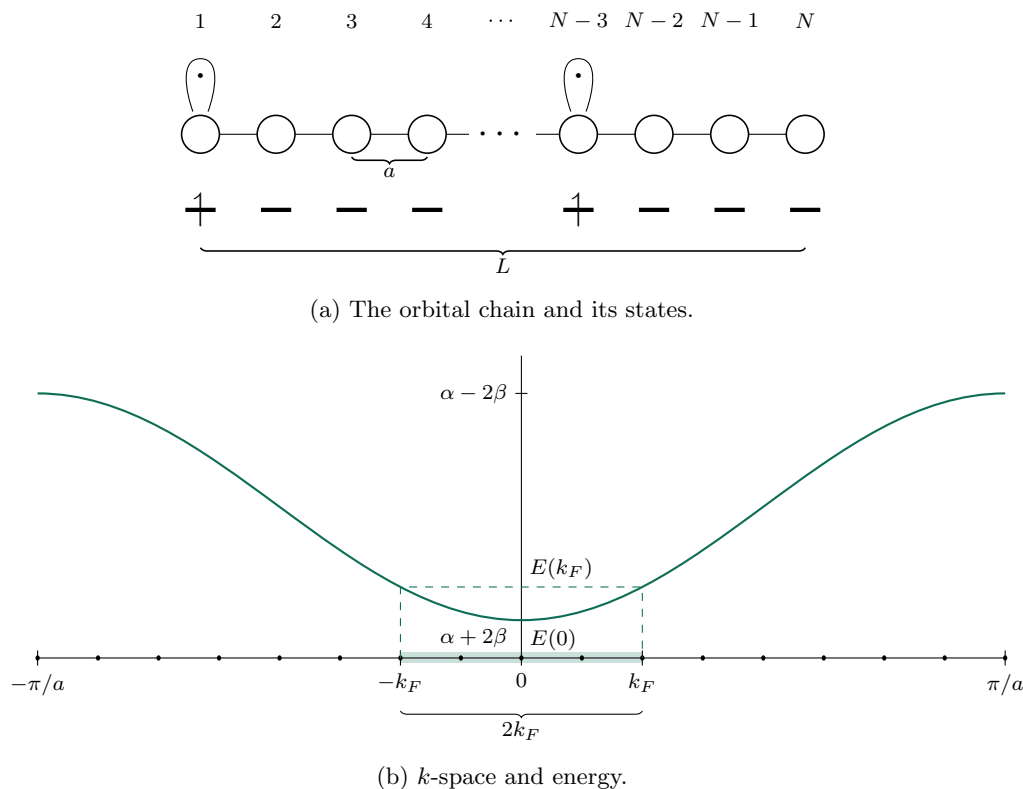
- a. Sketch $E(k)$ over the range $-\frac{\pi}{a} < k < \frac{\pi}{a}$, assuming that $\beta < 0$.

Answer.



□

- b. Suppose there is one electron for every 4 atoms; that is, if there are N atoms in the chain, there are $N/4$ electrons. With $a = 2.00 \times 10^{-10}$ m (i.e., 2.00 Å) and $\beta = -2.00$ eV, calculate the value of k corresponding to the highest occupied electronic state (also known as Fermi wavevector k_F , the wavevector at the Fermi surface) and the height of the Fermi energy E_F above the bottom of the band. Note that a chain of N atoms will have a total length $L = Na$ and that states are uniformly distributed in the k -space.

Figure 4.1: Theory describing a one-dimensional s -orbital chain.

Answer. As in Figure 4.1a, consider a one-dimensional chain of N atoms with one s -orbital each. The orbitals are separated by period a , and the length of the chain is $L = Na$. As in Figure 4.1b, each orbital contributes a state indexed by k . These states are evenly distributed in one-dimensional k -space between $-\frac{\pi}{a}$ and $\frac{\pi}{a}$. Now imagine that the one-dimensional s -orbital chain is devoid of electrons, and we have to fill them in. The first electron will go in the lowest energy state at $k = 0$ (see Figure 4.1b). The second will go into either $k = a$ or $k = -a$, and the third will go into the other one. As we add more and more electrons, the states that they go into will expand outwards evenly from the origin, always filling the lowest energy states available first. Eventually, all electrons will be filled in; however, this does not mean that all states will be filled, as there is one electron for every four atoms and, thus, for every eight states (again, see Figure 4.1a). Indeed, some region evenly surrounding the origin will be completely filled in, and by definition the Fermi surface will be the boundary between occupied and unoccupied states. Since the Fermi wavevector k_F is the radius of the Fermi sphere (i.e., the distance from the origin to the boundary of the Fermi sphere), we can label the boundary points k_F and $-k_F$. Having established the theoretical design, let's start the actual calculations.

Since k -space within the first Brillouin zone runs from $-\frac{\pi}{a}$ to $\frac{\pi}{a}$, the length of the s -orbital chain in k -space is $L = \frac{\pi}{a} - (-\frac{\pi}{a}) = \frac{2\pi}{a}$. It follows that each orbital is separated by $a = \frac{2\pi}{L}$, and that there are $\frac{L}{2\pi}$ orbitals per unit length. Now the length of the occupied region is $k_F - (-k_F) = 2k_F$, so combining this with the previous result gives us that there are $2k_F \times \frac{L}{2\pi} = \frac{k_F L}{\pi}$ occupied orbitals. Since each orbital adds 2 quantum states, we have $\frac{2k_F L}{\pi}$ occupied states. But the number of occupied states is simply equal to the number of electrons $\frac{N}{4}$. Since we also know that $L = Na$,

we have that

$$\begin{aligned}\frac{2k_F Na}{\pi} &= \frac{N}{4} \\ \frac{k_F a}{\pi} &= \frac{1}{8} \\ k_F &= \frac{\pi}{8a}\end{aligned}$$

$$k_F = 1.96 \times 10^9 \text{ m}^{-1}$$

As to the other part of the question, refer to Figure 4.1b once again. It tells us that the height of the Fermi energy above the bottom of the band is given by

$$\begin{aligned}h &= E(k_F) - E(0) \\ &= \alpha + 2\beta \cos\left(\frac{\pi}{8a} \cdot a\right) - (\alpha + 2\beta \cos(0 \cdot a)) \\ &= 2\beta \left(\cos\left(\frac{\pi}{8}\right) - 1\right)\end{aligned}$$

$$h = 0.304 \text{ eV}$$

□

II) Do the following problems from Chapter 6: 13, 25, 30, 37.

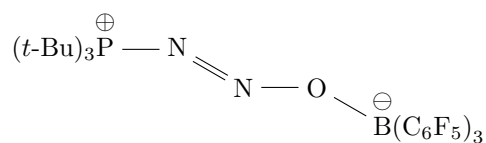
6.13 If an equimolar mixture of $P(t\text{-C}_4\text{H}_9)_3$ and $B(\text{C}_6\text{F}_5)_3$ is mixed with 1 bar of the gas N_2O in bromobenzene solution, a white product is formed in good yield. A variety of NMR evidence has been gathered on the product: there is a single ^{31}P NMR resonance; ^{11}B and ^{19}F NMR are considered consistent with a 4-coordinate boron atom; and ^{15}N NMR indicates two nonequivalent nitrogen atoms. In addition, no gas is released in the reaction.

a. Suggest the role of N_2O in this reaction.

Answer. N_2O reorganizes into a bridge linking the phosphorous and boron central atoms of $P(t\text{-C}_4\text{H}_9)_3$ and $B(\text{C}_6\text{F}_5)_3$, respectively. $P(t\text{-C}_4\text{H}_9)_3$ contains a frustrated Lewis pair that could not normally react with the boron in $B(\text{C}_6\text{F}_5)_3$, but by virtue of this bridge, there is enough separation between all of the substituents (i.e., steric hindrance is sufficiently reduced) to permit the formation of a combined product. \square

b. Propose a structure of the product (see Otten et al., 2009).

Answer.



\square

- 6.25** The most common source of mercury is cinnabar (HgS), whereas Zn and Cd in the same group occur as sulfide, carbonate, silicate, and oxide. Why?

Answer. Mercury is soft, so it forms a stable product with the similarly soft sulfide ion. However, zinc and cadmium are intermediate-hard, so they can form stable products with harder anions, such as carbonate, silicate, and oxide. \square

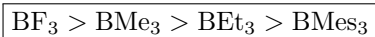
6.30 CsI is much less soluble in water than CsF, and LiF is much less soluble than LiI. Why?

Answer. Cesium iodide is formed from two soft ions, which grants it extra stability in comparison to soft-hard compounds such as cesium fluoride. As such, CsI will dissolve much less in water than CsF since it prefers to be in the molecular state rather than the ionic state.

The same is true for the hard-hard compound lithium fluoride in comparison to the hard-soft compound lithium iodide. \square

- 6.37** List the following acids in order of their acid strength when reacting with NH_3 : BF_3 , $\text{B}(\text{CH}_3)_3$, $\text{B}(\text{C}_2\text{H}_5)_3$, and $\text{B}[\text{C}_6\text{H}_2(\text{CH}_3)_3]_3$, where $\text{C}_6\text{H}_2(\text{CH}_3)_3$ is a mesityl (2,4,6-trimethylphenyl) group.

Answer. We have



BF_3 will be the strongest Lewis acid because it is the only one out of the collection that has electron-withdrawing groups as opposed to electron donating groups. Among the three compounds with electron-donating groups, we rank as stronger acids the ones with smaller alkyl groups, both because smaller groups donate less and steric hindrance is reduced. \square

4.1 Extra Materials

Help with Problem I can be found [here](#).

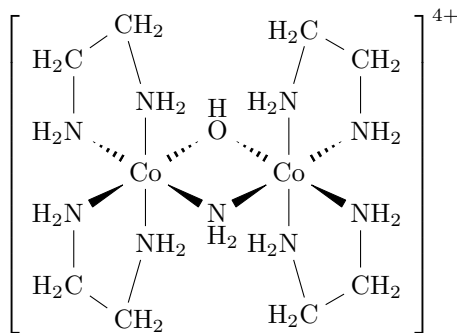
5 Coordination Complexes: Name-Structure Conversions and Isomers

2/19: I) Do the following problems from Chapter 9: 7; 9; 12a,b,e; 20; 23.

9.7 Give structures for the following:

a. Bis(en)Co(III)- μ -amido- μ -hydroxobis(en)Co(III) ion.

Answer.

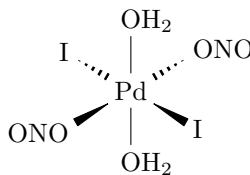


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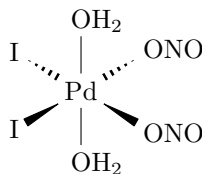
b. DiaquadiiododinitritoPd(IV), all isomers.

Answer. There are six stereoisomers of diaquadiiododinitritoPd(IV). We will classify them into five groups by the relative positions of like ligands as follows. One group will contain two enantiomers.

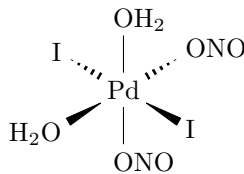
1. All like ligands *trans*.



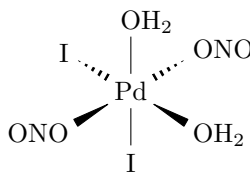
2. *trans*-aqua, *cis*-everything else.



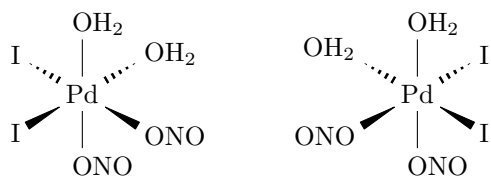
3. *trans*-iodo, *cis*-everything else.



4. *trans*-nitrito, *cis*-everything else.

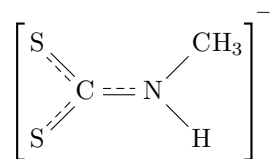


5. All like ligands *cis*.



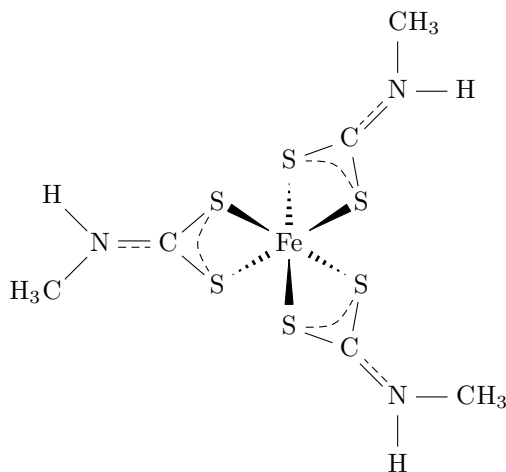
□

c. $\text{Fe}(\text{dtc})_3$, all isomers, where dtc is

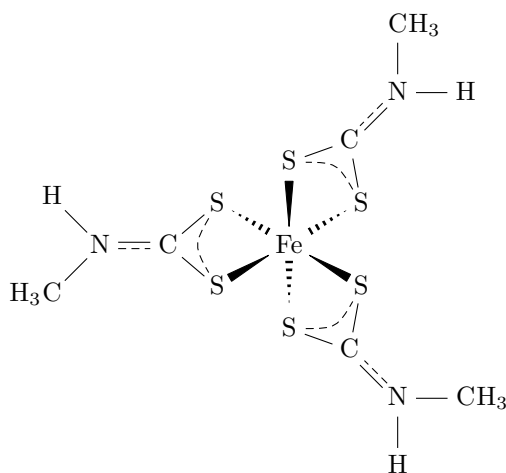


Answer. There are two stereoisomers of $\text{Fe}(\text{dtc})_3$ if we consider the bidentate ligand to be a simple bridge: one Λ form and one Δ form.

1. Λ form.



2. Δ form.

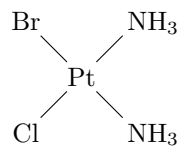


□

9.9 Show structures for the following:

a. *cis*-Diamminebromochloroplatinum(II).

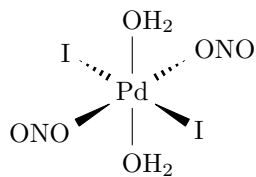
Answer.



□

b. Diaquadiiododinitritopalladium(IV), all ligands *trans*.

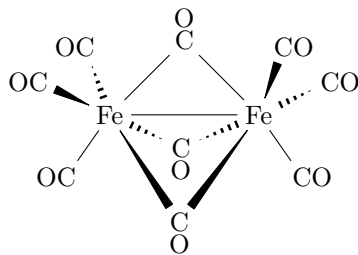
Answer.



□

c. Tri- μ -carbonylbis(tricarbonyliron(0)).

Answer.



□

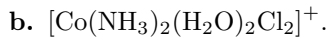
9.12 Sketch all isomers of the following. Indicate clearly each pair of enantiomers.



Answer. There is one facial and one meridional isomer of $[\text{Pt}(\text{NH}_3)_3\text{Cl}_3]^+$. There are no enantiomers.

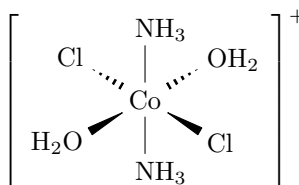


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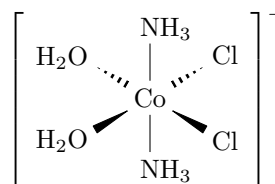


Answer.

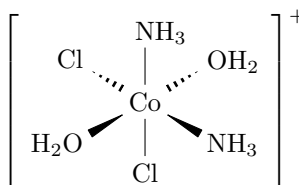
1. All like ligands *trans*.



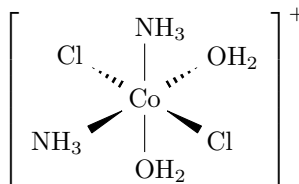
2. *trans*-ammine, *cis*-everything else.



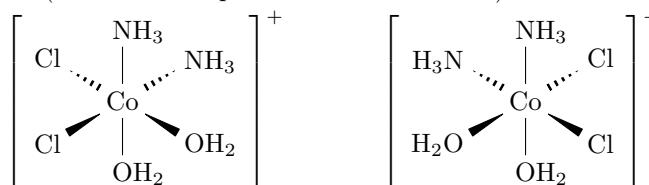
3. *trans*-aqua, *cis*-everything else.



4. *trans*-chloro, *cis*-everything else.



5. All like ligands *cis* (these two compounds are enantiomers).

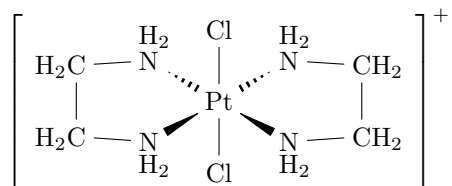


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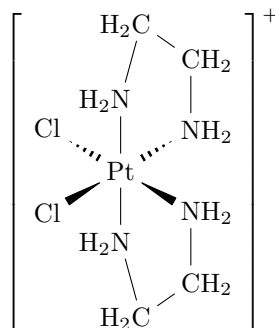
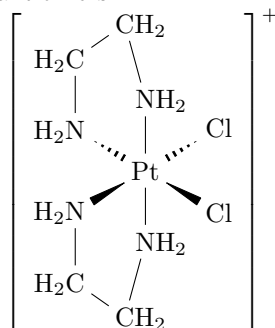
e. $[\text{Pt}(\text{en})_2\text{Cl}_2]^{2+}$.

Answer. There is one achiral isomer and one pair of chiral enantiomers.

1. Achiral isomer.

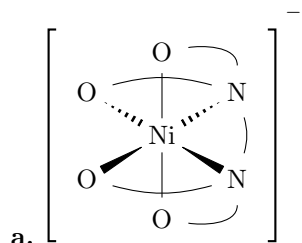


2. Chiral enantiomers.



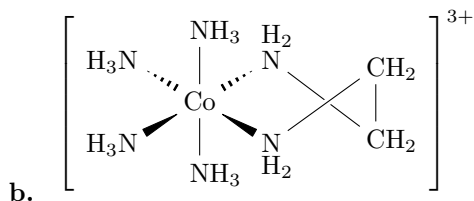
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9.20 Which of the following molecules are chiral?

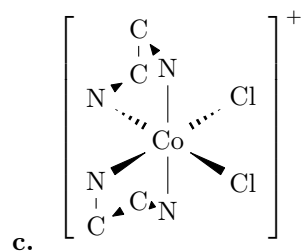


Answer. This molecule is chiral.

□



Answer. This molecule is achiral (if we assume that the ring on the right side largely lies in the plane with quickly reversing buckling or puckering, a reasonable hypothesis given the light N and C atoms). It is chiral if we assume a rigid ring in the pictured conformation. □

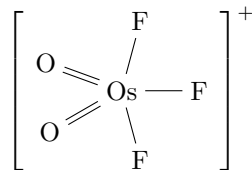


Answer. This molecule is chiral.

□

- 9.23** When *cis*-OsO₂F₄ is dissolved in SbF₅, the cation OsO₂F₃⁺ is formed. The ¹⁹F NMR spectrum of this cation shows two resonances, a doublet and a triplet having relative intensities of 2 : 1. What is the most likely structure of this ion? What is its point group? (See Casteel et al., 1996.)

Answer. From Bent's rule and sterics, we would predict the following structure, which has point group C_{2v} .



Moreover, this structure is supported by the ¹⁹F NMR data, since we have two equivalent (axial) fluorines on the same central atom as one nonequivalent fluorine (causing a doublet by the $n + 1$ rule of relative intensity 2) and, reversing roles, one (equatorial) fluorine on the same central atom as two separate but equivalent fluorines (causing a triplet by the $n + 1$ rule of relative intensity 1). \square

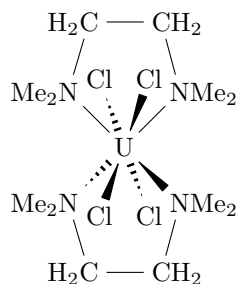
- II) The enthalpies of reaction of trimethylboron with NH_3 , CH_3NH_2 , $(\text{CH}_3)_2\text{NH}$, and $(\text{CH}_3)_3\text{N}$ are -58 , -74 , -81 , and -74 kJ/mol, respectively. Why is trimethylamine out of sequence?

Answer. Trimethylboron is not a very small lewis acid like BH_3 or H^+ . Thus, its own steric bulk clashes with the considerable bulk of $(\text{CH}_3)_3\text{N}$, hindering the reaction in a non-negligible fashion. This hindrance lowers the magnitude of the reaction enthalpy more than the additional electron-donating methyl group can raise it. \square

- III) The complex $\text{UCl}_4(\text{tmeda})_2$ (where tmeda is an abbreviation for $\text{Me}_2\text{N}-\text{CH}_2\text{CH}_2-\text{NMe}_2$, which binds by chelation to metals through both N-atoms) has been shown by X-ray crystallography to have almost perfect D_{2d} symmetry. Carefully draw a stereochemically accurate picture of this 8-coordinate uranium complex based on what you know about geometrical preferences in 8-coordinate complexes.

Answer. The possible molecular geometries for an 8-coordinate species are dodecahedral and square antiprismatic. Assuming all identical, monodentate ligands, the geometries' respective point groups are D_{2d} and D_{4d} . Based on this, dodecahedral might look more appealing, but since we have two bidentate chelating ligands, the D_{4d} square anti-prismatic form provides the wiggle room we need for the "descent in symmetry" these ligands will inevitably cause.

As such, if we take a square antiprismatic geometry and place our bidentate ligands opposite each other, we will have constructed the following D_{2d} molecule.



□

6 Coordination Complexes: Electron Configurations

- 3/1: I) Derive the proper MO diagram for tetrahedral molecules ML_4 using the n d -orbitals, the $(n + l)$ s -orbital, and the $(n + l)$ p -orbitals on the central atom M for

(a) σ -only ligands;

Answer. Point group: T_d .

Basis functions: All four L σ -orbitals, $M(ns)$, $M((n + l)p)$, and $M((n + l)d)$.

Apply operations, generate reducible representations, and reduce to irreducible representations:

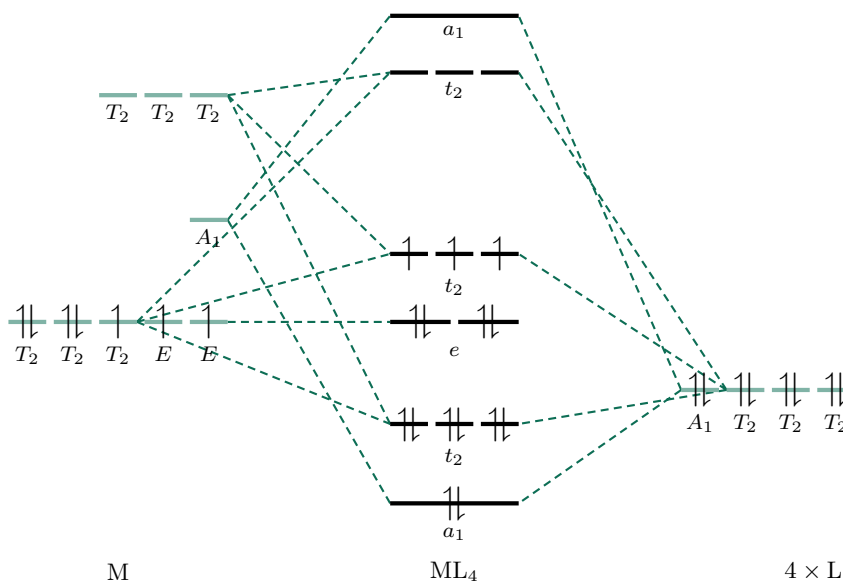
$$\Gamma_{L\sigma} = (4, 1, 0, 0, 2) = A_1 + T_2$$

$$\Gamma_{M_{ns}} = A_1$$

$$\Gamma_{M_{(n+l)p}} = T_2$$

$$\Gamma_{M_{(n+l)d}} = E + T_2$$

Combine orbitals by their symmetry, and fill in electrons for a d^7 metal^[3].



□

³This electron configuration is randomly chosen just to illustrate the point.

- (b) π -donor ligands (having low-lying, filled π orbitals);

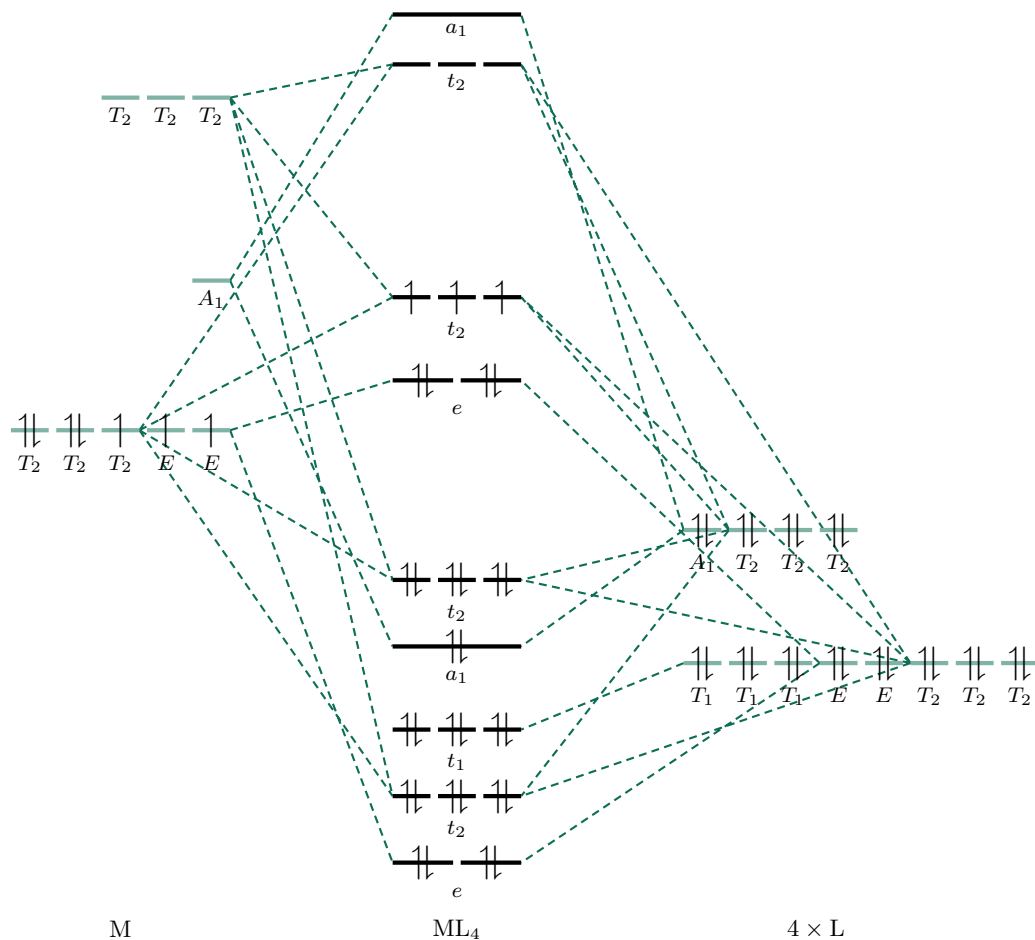
Answer. Point group: T_d .

Basis functions: All four L σ -orbitals, all eight L $\pi_{x,z}$ orbitals, M(ns), M($(n+l)p$), and M($(n+l)d$).

Apply operations, generate reducible representations, and reduce to irreducible representations:

$$\begin{aligned}\Gamma_{L\sigma} &= (4, 1, 0, 0, 2) = A_1 + T_2 \\ \Gamma_{L\pi_{x,z}} &= (8, -1, 0, 0, 0) = E + T_1 + T_2 \\ \Gamma_{M_{ns}} &= A_1 \\ \Gamma_{M_{(n+l)p}} &= T_2 \\ \Gamma_{M_{(n+l)d}} &= E + T_2\end{aligned}$$

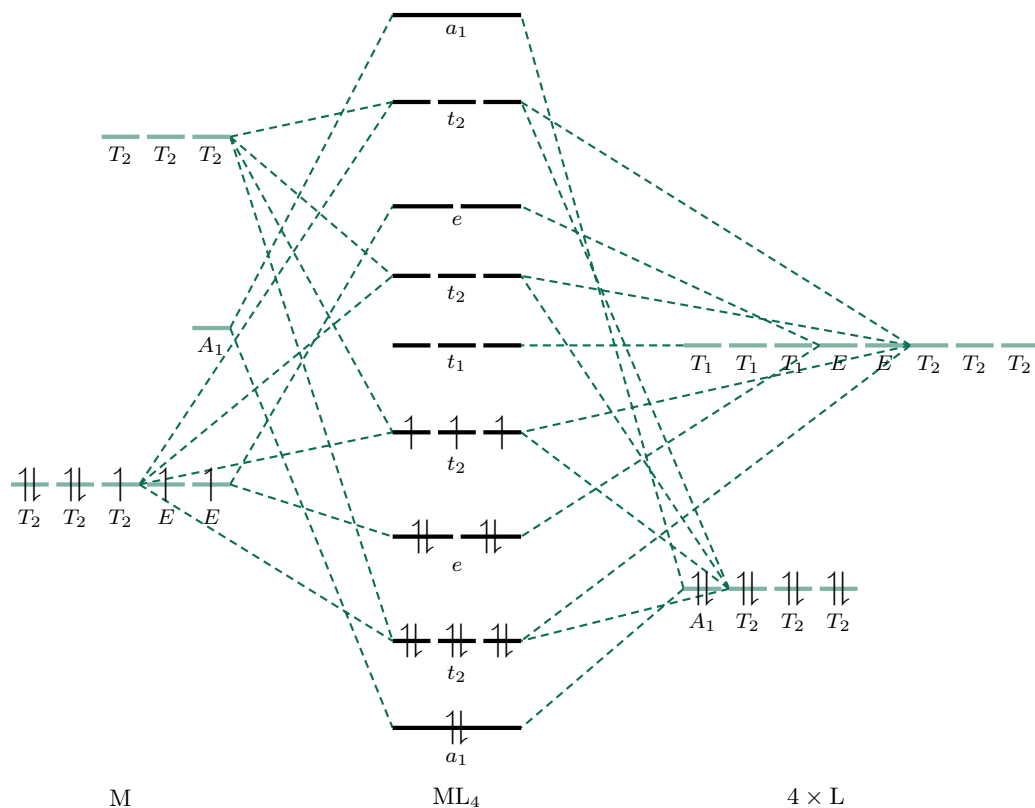
Combine orbitals by their symmetry, and fill in electrons for a d^7 metal.



□

(c) π -acceptor ligands (having high-lying, empty π orbitals).

Answer. Same intro analysis as part (b).



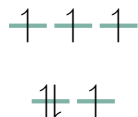
□

II) Do the following problems from Chapter 10: 1, 6, 7, 8, 19, 22.

10.1 Predict the number of unpaired electrons for each of the following:

a. A tetrahedral d^6 ion.

Answer. Tetrahedral means high spin and t_2 orbitals above e . Thus, there will be 4 unpaired electrons.



□

b. $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$.

Answer. Octahedral cobalt with a 2+ oxidation state means high spin. Thus, there will be 3 unpaired electrons.



□

c. $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$.

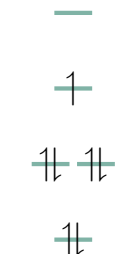
Answer. High spin/low spin doesn't matter here; there will be 3 unpaired electrons, regardless.



□

d. A square-planar d^7 ion.

Answer. Square planar compounds have an orbital arrangement determined by the angular overlap model, and are low spin. Thus, there will be 1 unpaired electron.



□

e. A coordination compound with a magnetic moment of 5.1 Bohr magnetons.

Answer. Using the spin-only magnetic moment formula $\mu_S = \sqrt{n(n+2)}$, we can solve for n with the quadratic formula, take the positive answer, and round.

$$\begin{aligned} 5.1 &= \sqrt{n(n+2)} \\ 0 &= n^2 + 2n - 5.1^2 \\ n &\approx 4 \end{aligned}$$

□

10.6 Predict the magnetic moments (spin-only) of the following species.

a. $[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$.

Answer. We know that $[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$ has four unpaired electrons. Thus,

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

$$\mu \approx 4.90 \text{ B.M.}$$

□

b. $[\text{Cr}(\text{CN})_6]^{4-}$.

Answer. We know that $[\text{Cr}(\text{CN})_6]^{4-}$ has two unpaired electrons. Thus,

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

$$\mu \approx 2.83 \text{ B.M.}$$

□

c. $[\text{FeCl}_4]^-$.

Answer. We know that $[\text{FeCl}_4]^-$ has five unpaired electrons. Thus,

$$\mu = \sqrt{5(5+2)} = \sqrt{35}$$

$$\mu \approx 5.92 \text{ B.M.}$$

□

d. $[\text{Fe}(\text{CN})_6]^{3-}$.

Answer. We know that $[\text{Fe}(\text{CN})_6]^{3-}$ has one unpaired electron. Thus,

$$\mu = \sqrt{1(1+2)} = \sqrt{3}$$

$$\mu \approx 1.73 \text{ B.M.}$$

□

e. $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$.

Answer. We know that $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$ has two unpaired electrons. Thus,.

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

$$\mu \approx 2.83 \text{ B.M.}$$

□

f. $[\text{Cu}(\text{en})_2(\text{H}_2\text{O})_2]^{2+}$.

Answer. We know that $[\text{Cu}(\text{en})_2(\text{H}_2\text{O})_2]^{2+}$ has one unpaired electron. Thus,

$$\mu = \sqrt{1(1+2)} = \sqrt{3}$$

$$\mu \approx 1.73 \text{ B.M.}$$

□

- 10.7** A compound with the empirical formula $\text{Fe}(\text{H}_2\text{O})_4(\text{CN})_2$ has a magnetic moment corresponding to $2\frac{2}{3}$ unpaired electrons per iron. How is this possible? (Hint: Two octahedral Fe(II) species are involved, each containing a single type of ligand.)

Answer. $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$ is a low spin complex with 4 unpaired electrons. $[\text{Fe}(\text{CN})_6]^{4-}$ is a high spin complex with 0 unpaired electrons. The compound $[\text{Fe}(\text{H}_2\text{O})_6]_2[\text{Fe}(\text{CN})_6]$ is the simplest combination of the two with empirical formula equal to $\text{Fe}(\text{H}_2\text{O})_4(\text{CN})_2$. Thus, since this compound has a total of 8 unpaired electrons for 3 Fe atoms, its magnetic moment must correspond to $8/3 = 2\frac{2}{3}$ unpaired electrons. \square

- 10.8** What are the possible magnetic moments of Co(II) in tetrahedral, octahedral, and square-planar complexes?

Answer. For tetrahedral and octahedral complexes, we have $\mu = \sqrt{3(3+2)} = \sqrt{15} \approx 3.87$. For square planar, we have $\mu = \sqrt{1(1+2)} = \sqrt{3} \approx 1.73$. \square

- 10.19** Explain the order of the magnitudes of the following Δ_o values for Cr(III) complexes in terms of the σ and π donor and acceptor properties of the ligands.

Ligand	F^-	Cl^-	H_2O	NH_3	en	CN^-
Δ_o (cm^{-1})	15 200	13 200	17 400	21 600	21 900	33 500

Answer. Cyanide has by far the greatest magnitude Δ_o because it is the only π -accepting ligand. Ethylenediamine and ammonia form the next group down because they are pure π -donating ligands. Lastly, we have water, chloride, and fluoride because they have π -donating character (within this group, chloride has the lowest value because it has fairly good π -donor abilities, fluoride is in the middle because it has lesser π -donor abilities than chloride, and water has the highest value because it only engages in σ bonding). \square

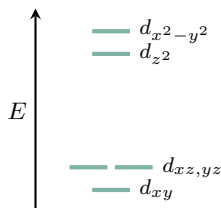
- 10.22** Solid CrF_3 contains a Cr(III) ion surrounded by six F^- ions in an octahedral geometry, all at distances of 190 pm. However, MnF_3 is in a distorted geometry, with $\text{Mn}-\text{F}$ distances of 179, 191, and 209 pm (two of each). Explain.

Answer. The manganese ion has unequally occupied e_g orbitals whereas the chromium one does not, so the former is subject to Jahn-Teller distortion while the latter is not. \square

III) Use the Angular Overlap Model to derive the d -orbital splitting diagrams for $M(\text{CO})_5$ complexes having

(a) Square pyramidal geometry;

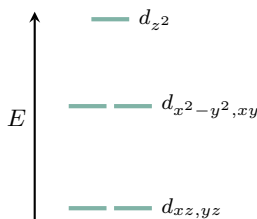
Answer. From the charts in Module 36, we have $e_\sigma = (2, 3, 0, 0, 0)$ and $e_\pi = (0, 0, 4, 3, 3)$. Thus we know that the d -orbital splitting diagram is



□

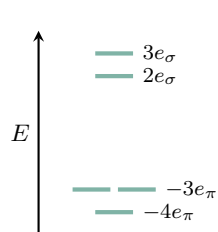
(b) Trigonal bipyramidal geometry.

Answer. From the charts in Module 36, we have $e_\sigma = (\frac{11}{4}, \frac{9}{8}, \frac{9}{8}, 0, 0)$ and $e_\pi = (0, \frac{3}{2}, \frac{3}{2}, \frac{7}{2}, \frac{7}{2})$. Thus we know that the d -orbital splitting diagram is

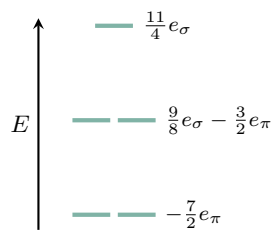


□

(c) Label the orbitals with the appropriate energies in units of e_σ and e_π . Note that degenerate orbitals are those with the same energies — you don't have to use group theory to get this information!



(a) Square pyramidal.



(b) Trigonal bipyramidal.

(d) Determine the relative energies of $\text{Cr}(\text{CO})_5$ (based on orbital population) in these two geometries, and use this to predict the structure of $\text{Cr}(\text{CO})_5$.

Answer. Assuming a low spin configuration since carbonyl ligands are strong field ligands and noting that chromium has a d^6 configuration, we have

$$E_{\text{square pyramidal}} = 2(-4e_\pi) + 4(-3e_\pi) = -20e_\pi$$

$$E_{\text{trigonal bipyramidal}} = 4\left(-\frac{7}{2}e_\pi\right) + 2\left(\frac{9}{8}e_\sigma - \frac{3}{2}e_\pi\right) = \frac{9}{4}e_\sigma - 17e_\pi$$

Since $E_{\text{square pyramidal}} < E_{\text{trigonal bipyramidal}}$, we know that $\text{Cr}(\text{CO})_5$ is square pyramidal.

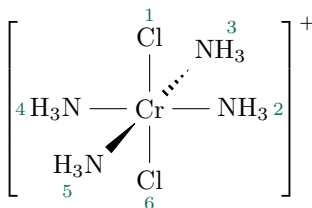
□

7 Coordination Complexes: Bonding Models

3/5: I) Do the following problems from Chapter 10: 13, 14, 27, 30, 33.

10.13 Use the angular overlap method to calculate the energies of both ligand and metal orbitals for $\text{trans}[\text{Cr}(\text{NH}_3)_4\text{Cl}_2]^+$, taking into account that ammonia is a stronger σ -donor ligand than chloride, but chloride is a stronger π donor. Use the 1 and 6 positions for the chloride ions.

Answer.



We have from the question that NH_3 is a pure σ donor whereas Cl^- is a σ and π donor. Thus, we can add up

$\sigma(\text{NH}_3)$	z^2	$x^2 - y^2$	xy	xz	yz
2	$\frac{1}{4}$	$\frac{3}{4}$	0	0	0
3	$\frac{1}{4}$	$\frac{3}{4}$	0	0	0
4	$\frac{1}{4}$	$\frac{3}{4}$	0	0	0
5	$\frac{1}{4}$	$\frac{3}{4}$	0	0	0
Sum:	1	3	0	0	0

$\sigma(\text{Cl})$	z^2	$x^2 - y^2$	xy	xz	yz
1	1	0	0	0	0
6	1	0	0	0	0
Sum:	2	0	0	0	0

$\pi(\text{Cl})$	z^2	$x^2 - y^2$	xy	xz	yz
1	0	0	0	1	1
6	0	0	0	1	1
Sum:	0	0	0	2	2

Adding up the sums for each d orbital reveals that the metal orbitals are destabilized by^[4]:

$$\begin{aligned}
 E(d_{z^2}) &= 1e_{\sigma}(\text{NH}_3) + 2e_{\sigma}(\text{Cl}) \\
 E(d_{x^2-y^2}) &= 3e_{\sigma}(\text{NH}_3) \\
 E(d_{xy}) &= 0 \\
 E(d_{xz}) &= 2e_{\pi}(\text{Cl}) \\
 E(d_{yz}) &= 2e_{\pi}(\text{Cl})
 \end{aligned}$$

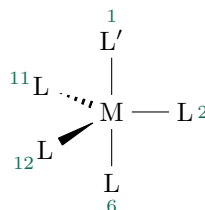
If we now add up the values in the sum rows and divide by the corresponding number of orbitals, we'll get the stabilization energy contribution of each table to its orbitals. For example, the sum in the $\sigma(\text{NH}_3)$ table is 4, and there are 4 $\text{NH}_3(\sigma)$ orbitals; thus, each NH_3 ligand orbital is stabilized, at least in part, by $\frac{4}{4} = 1e_{\sigma}(\text{NH}_3)$. If we continue in this fashion for the other two, we'll eventually end up with four ligand orbitals stabilized by $1e_{\sigma}(\text{NH}_3)$ and two ligand orbitals stabilized by $1e_{\sigma}(\text{Cl}) + 2e_{\pi}(\text{Cl})$. \square

⁴Note that by $e_{\sigma}(\text{NH}_3)$, for example, we mean the angular overlap parameter for a σ bond formed in an MA_2B_4 -type complex containing ammine groups as the B ligands.

10.14 Consider a transition metal complex of formula ML_4L' . Using the angular overlap model and assuming trigonal-bipyramidal geometry, determine the energies of the d orbitals...

a. considering sigma interactions only (assume L and L' are similar in donor ability);

Answer.



Although L' is pictured as axial above, it does not matter where it is because we're considering it to be equivalent to L in σ -donor ability. Having established that, we can add up

σ	z^2	$x^2 - y^2$	xy	xz	yz
1	1	0	0	0	0
2	$\frac{1}{4}$	$\frac{3}{4}$	0	0	0
6	1	0	0	0	0
11	$\frac{1}{4}$	$\frac{3}{16}$	$\frac{9}{16}$	0	0
12	$\frac{1}{4}$	$\frac{3}{16}$	$\frac{9}{16}$	0	0
Sum:	$\frac{11}{4}$	$\frac{9}{8}$	$\frac{9}{8}$	0	0

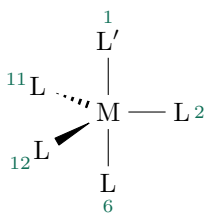
With the sums for each d orbital, we can determine that the metal orbitals are destabilized by^[5]:

$$\begin{aligned}
 E(d_{z^2}) &= \frac{11}{4}e_\sigma \\
 E(d_{x^2-y^2}) &= \frac{9}{8}e_\sigma \\
 E(d_{xy}) &= \frac{9}{8}e_\sigma \\
 E(d_{xz}) &= 0 \\
 E(d_{yz}) &= 0
 \end{aligned}$$

□

b. and considering L' as a π acceptor as well. Consider L' in both (1) an axial position;

Answer.



The σ contributions to the metal orbitals will be identical to part (a). However, we now have to account for the π -acceptor contribution of the axial L' ligand. Since the rows in the table for positions 1 and 6 are equal, arbitrarily consider row 1:

$\pi(L')$	z^2	$x^2 - y^2$	xy	xz	yz
1	0	0	0	1	1
Sum:	0	0	0	1	1

⁵We don't distinguish between $e_\sigma(L)$ and $e_\sigma(L')$ here because we are told that both ligands have comparable σ -donating abilities.

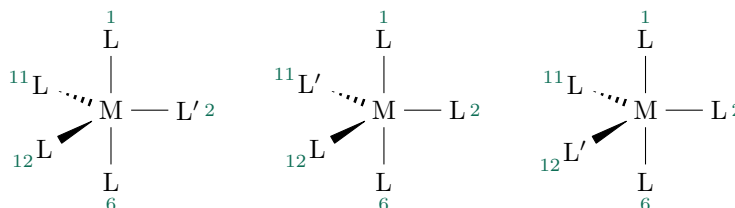
With the sums for each d orbital, we can determine that three of the metal orbitals are destabilized by

$$\begin{aligned} E(d_{z^2}) &= \frac{11}{4}e_{\sigma} \\ E(d_{x^2-y^2}) &= \frac{9}{8}e_{\sigma} \\ E(d_{xy}) &= \frac{9}{8}e_{\sigma} \\ E(d_{xz}) &= -e_{\pi}(L') \\ E(d_{yz}) &= -e_{\pi}(L') \end{aligned}$$

Note that we subtract the $e_{\pi}(L')$ contributions because for π -acceptor ligands, these contributions are stabilizing. Thus, they reduce the destabilization energy (they don't increase it). \square

(2) and an equatorial position.

Answer.



The σ contributions to the metal orbitals will be identical to part (a). However, we now have to account for the π -acceptor contribution of the equatorial L' ligand. Since the rows in the table for positions 2, 11, and 12 vary, we will average the three:

$\pi(L')$	z^2	$x^2 - y^2$	xy	xz	yz
2	0	0	1	1	0
11	0	$\frac{3}{4}$	$\frac{1}{4}$	$\frac{1}{4}$	$\frac{3}{4}$
12	0	$\frac{3}{4}$	$\frac{1}{4}$	$\frac{1}{4}$	$\frac{3}{4}$
Avg:	0	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$

With the average contribution for each d orbital, we can determine that the metal orbitals are destabilized by:

$$\begin{aligned} E(d_{z^2}) &= \frac{11}{4}e_{\sigma} \\ E(d_{x^2-y^2}) &= \frac{9}{8}e_{\sigma} - \frac{1}{2}e_{\pi}(L') \\ E(d_{xy}) &= \frac{9}{8}e_{\sigma} - \frac{1}{2}e_{\pi}(L') \\ E(d_{xz}) &= -\frac{1}{2}e_{\pi}(L') \\ E(d_{yz}) &= -\frac{1}{2}e_{\pi}(L') \end{aligned}$$

As in part (b), we subtract the $e_{\pi}(L')$ contributions because for π -acceptor ligands, these contributions are stabilizing and thus reduce the destabilization energy. \square

- c. Based on the preceding answers, would you expect π -acceptor ligands to preferentially occupy axial or equatorial positions in five-coordinate complexes? What other factors should be considered in addition to angular overlap?

Answer. We can construct orbital diagrams for both the axial L' case and the equatorial L' case.

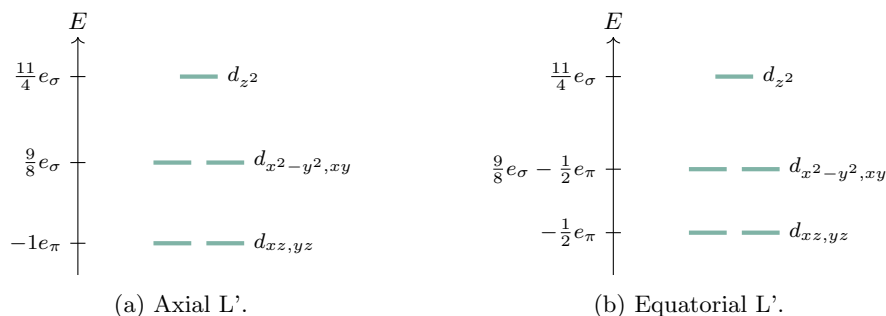


Figure 7.1: Axial and equatorial ML_4L' d -orbital diagrams.

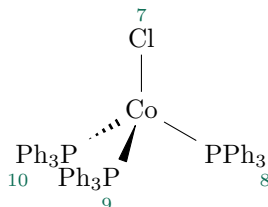
The important factor to be considered in addition to angular overlap is electron configuration — for d^1 to d^7 configurations, the axial complex is preferred; however, for d^8 to d^{10} and d^0 configurations, neither is preferred. We can determine this by calculating the energies of each configuration from Figure 7.1. In the following equations, the axial energy is on the left and the equatorial on the right.

$$\begin{aligned}
 0 &= 0 & (d^0) \\
 -1e_\pi &< -\frac{1}{2}e_\pi & (d^1) \\
 -2e_\pi &< -1e_\pi & (d^2) \\
 -3e_\pi &< -\frac{3}{2}e_\pi & (d^3) \\
 -4e_\pi &< -2e_\pi & (d^4) \\
 \frac{9}{8}e_\sigma - 4e_\pi &< \frac{9}{8}e_\sigma - \frac{5}{2}e_\pi & (d^5) \\
 \frac{9}{4}e_\sigma - 4e_\pi &< \frac{9}{4}e_\sigma - 3e_\pi & (d^6) \\
 \frac{27}{8}e_\sigma - 4e_\pi &< \frac{27}{8}e_\sigma - \frac{7}{2}e_\pi & (d^7) \\
 \frac{9}{2}e_\sigma - 4e_\pi &= \frac{9}{2}e_\sigma - 4e_\pi & (d^8) \\
 \frac{29}{4}e_\sigma - 4e_\pi &= \frac{29}{4}e_\sigma - 4e_\pi & (d^9) \\
 10e_\sigma - 4e_\pi &= 10e_\sigma - 4e_\pi & (d^{10})
 \end{aligned}$$

□

10.27 Cobalt(I) complexes are relatively rare compared to Co(II) and Co(0), but the complexes $\text{CoX}(\text{PPh}_3)_3$ where $\text{X} = \text{Cl}, \text{Br}, \text{I}$ are known with approximate tetrahedral coordination geometry about the high spin d^8 metal center. The angular overlap model was used to analyze the electronic structure of $\text{CoCl}(\text{PPh}_3)_3$, where three independent molecules (with very similar yet statistically different bond lengths and angles) were observed in the unit cell (Krzystek et al., 2012). Using the angular overlap parameters for molecule 1 in Table 3 of this reference, generate an energy-level diagram for $\text{CoCl}(\text{PPh}_3)_3$. Does the electronic structure predicted by this method surprise you? Explain. On the basis of Table 3, the chloride ligands are better π donors, and the triphenylphosphine ligands better σ donors in $\text{NiCl}_2(\text{PPh}_3)_2$ relative to $\text{CoCl}(\text{PPh}_3)_3$. What is probably the most important factor that causes these differences?

Answer.



From Krzystek et al. (2012), we know that

$$\varepsilon_{\sigma}(\text{Cl}) = 5430 \text{ cm}^{-1} \quad \varepsilon_{\pi}(\text{Cl}) = +1380 \text{ cm}^{-1} \quad \varepsilon_{\sigma}(\text{PPh}_3) = 3340 \text{ cm}^{-1} \quad \varepsilon_{\pi}(\text{PPh}_3) = -310 \text{ cm}^{-1}$$

We now add up

$\sigma(\text{Cl})$	z^2	$x^2 - y^2$	xy	xz	yz
7	0	0	$\frac{1}{3}$	$\frac{1}{3}$	$\frac{1}{3}$
Sum:	0	0	$\frac{1}{3}$	$\frac{1}{3}$	$\frac{1}{3}$

$\sigma(\text{PPh}_3)$	z^2	$x^2 - y^2$	xy	xz	yz
8	0	0	$\frac{1}{3}$	$\frac{1}{3}$	$\frac{1}{3}$
9	0	0	$\frac{1}{3}$	$\frac{1}{3}$	$\frac{1}{3}$
10	0	0	$\frac{1}{3}$	$\frac{1}{3}$	$\frac{1}{3}$
Sum:	0	0	1	1	1

$\pi(\text{Cl})$	z^2	$x^2 - y^2$	xy	xz	yz
7	$\frac{2}{3}$	$\frac{2}{3}$	$\frac{2}{9}$	$\frac{2}{9}$	$\frac{2}{9}$
Sum:	$\frac{2}{3}$	$\frac{2}{3}$	$\frac{2}{9}$	$\frac{2}{9}$	$\frac{2}{9}$

$\pi(\text{PPh}_3)$	z^2	$x^2 - y^2$	xy	xz	yz
8	$\frac{2}{3}$	$\frac{2}{3}$	$\frac{2}{9}$	$\frac{2}{9}$	$\frac{2}{9}$
9	$\frac{2}{3}$	$\frac{2}{3}$	$\frac{2}{9}$	$\frac{2}{9}$	$\frac{2}{9}$
10	$\frac{2}{3}$	$\frac{2}{3}$	$\frac{2}{9}$	$\frac{2}{9}$	$\frac{2}{9}$
Sum:	2	2	$\frac{2}{3}$	$\frac{2}{3}$	$\frac{2}{3}$

Adding up the sums for each d orbital (and accounting for the fact that Cl^- is a π donor whereas PPh_3 is a π acceptor) reveals that the metal orbitals are destabilized by

$$E(d_{z^2}) = \frac{2}{3}\varepsilon_{\pi}(\text{Cl}) + 2\varepsilon_{\pi}(\text{PPh}_3) = 300 \text{ cm}^{-1}$$

$$E(d_{x^2-y^2}) = \frac{2}{3}\varepsilon_{\pi}(\text{Cl}) + 2\varepsilon_{\pi}(\text{PPh}_3) = 300 \text{ cm}^{-1}$$

$$E(d_{xy}) = \frac{1}{3}\varepsilon_{\sigma}(\text{Cl}) + 1\varepsilon_{\sigma}(\text{PPh}_3) + \frac{2}{9}\varepsilon_{\pi}(\text{Cl}) + \frac{2}{3}\varepsilon_{\pi}(\text{PPh}_3) = 5250 \text{ cm}^{-1}$$

$$E(d_{xz}) = \frac{1}{3}\varepsilon_{\sigma}(\text{Cl}) + 1\varepsilon_{\sigma}(\text{PPh}_3) + \frac{2}{9}\varepsilon_{\pi}(\text{Cl}) + \frac{2}{3}\varepsilon_{\pi}(\text{PPh}_3) = 5250 \text{ cm}^{-1}$$

$$E(d_{yz}) = \frac{1}{3}\varepsilon_{\sigma}(\text{Cl}) + 1\varepsilon_{\sigma}(\text{PPh}_3) + \frac{2}{9}\varepsilon_{\pi}(\text{Cl}) + \frac{2}{3}\varepsilon_{\pi}(\text{PPh}_3) = 5250 \text{ cm}^{-1}$$

As to the ligand pairs, we must add up the values in the sum rows and divide by the corresponding number of orbitals (note that L_n corresponds to the ligand numbered n), as follows. For the chloride ligand, there is a simple stabilization of the combined σ, π -ligand orbital corresponding to a destabilization of every metal d orbital. For the triphenylphosphine ligands, there is a stabilization of the σ -ligand orbitals corresponding to a destabilization of the metal $d_{xy,xz,yz}$ orbitals, and there is a destabilization of the π -ligand orbitals corresponding to a stabilization of every metal orbital.

$$E(L_7) = -1\varepsilon_{\sigma}(\text{Cl}) - 2\varepsilon_{\pi}(\text{Cl}) = -8190 \text{ cm}^{-1}$$

$$E(L_{8\sigma}) = -1\varepsilon_{\sigma}(\text{PPh}_3) = -3340 \text{ cm}^{-1}$$

$$E(L_{9\sigma}) = -1\varepsilon_{\sigma}(\text{PPh}_3) = -3340 \text{ cm}^{-1}$$

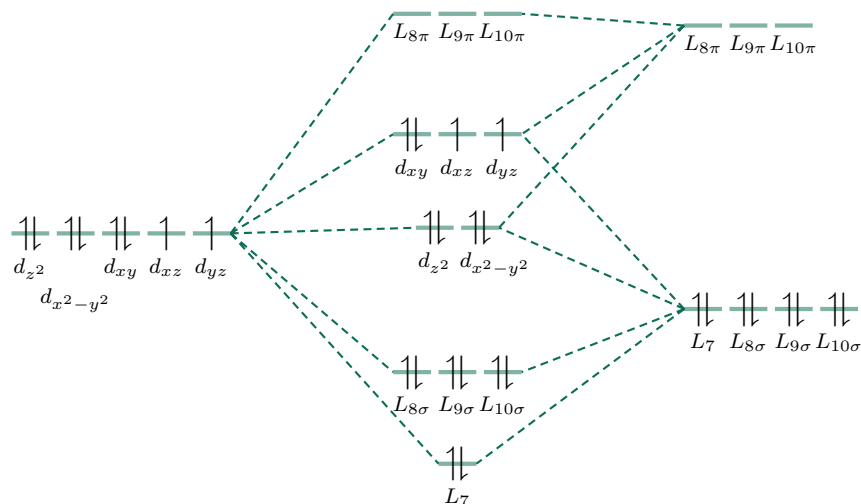
$$E(L_{10\sigma}) = -1\varepsilon_{\sigma}(\text{PPh}_3) = -3340 \text{ cm}^{-1}$$

$$E(L_{8\pi}) = 2\varepsilon_{\pi}(\text{PPh}_3) = 620 \text{ cm}^{-1}$$

$$E(L_{9\pi}) = 2\varepsilon_{\pi}(\text{PPh}_3) = 620 \text{ cm}^{-1}$$

$$E(L_{10\pi}) = 2\varepsilon_{\pi}(\text{PPh}_3) = 620 \text{ cm}^{-1}$$

Putting it all together, we have:

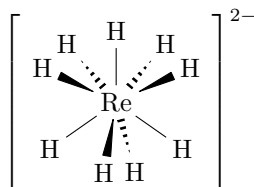


What's surprising: In the angular overlap model, chloride is clearly a stabilizing ligand overall. However, in ligand field theory, π -donor ligands are destabilizing.

Chloride is probably a better π donor in $\text{NiCl}_2(\text{PPh}_3)_2$ than $\text{CoCl}(\text{PPh}_3)_3$ because the increased oxidation state of Ni(II) means it has a greater tendency to attract electrons. On the other hand, triphenylphosphine is likely a better σ donor in $\text{NiCl}_2(\text{PPh}_3)_2$ than $\text{CoCl}(\text{PPh}_3)_3$ because the reduction in steric bulk allows for better head-on overlap with the orbitals of the metal center. \square

- 10.30** One of the more striking hydride complexes is enneahydridorhenate ($[\text{ReH}_9]^{2-}$), which has tricapped trigonal-pyramidal geometry. What is the point group of this ion? Construct a representation using the hydrogen orbitals as a basis. Reduce this to its component irreducible representations, and determine which orbitals of Re are of suitable symmetry to interact with the hydrogen group orbitals.

Answer.



Point group: D_{3h} .

Construct a reducible representation and reduce it to its component irreducible representations:

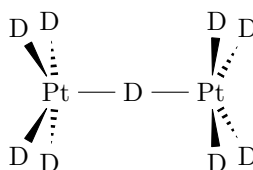
$$\Gamma_{\text{H}} = (9, 0, 1, 3, 0, 3) = 2A'_1 + 2E' + A''_2 + E''$$

Orbital interactions (derived from the D_{3h} character table):

A'_1	s, d_{z^2}
E'	$(p_x, p_y), (d_{x^2-y^2}, d_{xy})$
A''_2	p_z
E''	(d_{xz}, d_{yz})

□

10.33 The ion $[\text{Pt}_2\text{D}_9]^{5-}$, shown below, has eclipsed geometry.



a. What is point group of this ion?

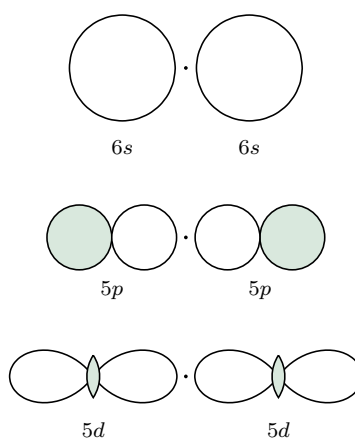
Answer. D_{4h} .

□

b. Assume that the platinum atoms can potentially use s , p , and d orbitals to interact with the central deuterium. If the z -axis is chosen to be collinear with the principal axis of rotation:

1. Sketch the group orbitals of the platinum atoms that potentially could interact with the central D. Be sure to label all orbitals.

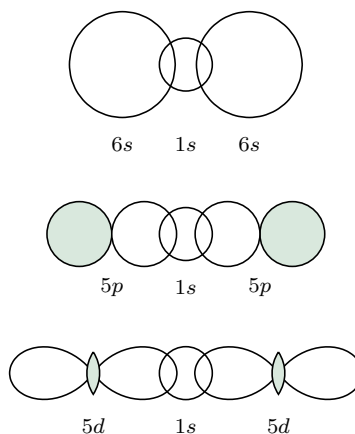
Answer.



□

2. Show how the group orbitals and the central atom would interact.

Answer.



□

3. Which interaction would you expect to be the strongest, and why?

Answer. The d_{z^2} interaction should be the strongest. In the MO energy diagram for MH_6 bonding, the hydrogen orbitals are closest in energy to the metal d orbitals. It stands to reason that it would be similar for square pyramidal bonding and deuterium.

□

- II) We derived in class the MO diagram for $\text{Re}_2\text{Cl}_8^{2-}$, a complex with a Re–Re quadruple bond. Two chloride ligands on each Re can be replaced with two (neutral) PMe_2Ph ligands to give the cationic complex $\text{Re}_2(\text{PMe}_2\text{Ph})_4\text{Cl}_4^{2+}$, which has a similar $\sigma^2\pi^4\delta^2$ electronic configuration and a Re–Re quadruple bond of 2.215 Å in length. The 1-electron and 2-electron reduced species $\text{Re}_2(\text{PMe}_2\text{Ph})_4\text{Cl}_4^+$ and $\text{Re}_2(\text{PMe}_2\text{Ph})_4\text{Cl}_4$ can be prepared, and their structures show Re–Re bond lengths of 2.218 Å and 2.241 Å, respectively. Give the electronic configurations for the 1- and 2-electron reduced species (as given above for the unreduced species), and suggest how this could account for the different Re–Re bond lengths in the three compounds.

Answer. From the MO diagram discussed in lecture, we know that adding more electrons to a complex isoelectronic to $\text{Re}_2\text{Cl}_8^{2-}$ will begin to occupy the δ^* molecular orbitals. Thus, the electronic configuration of $\text{Re}_2(\text{PMe}_2\text{Ph})_4\text{Cl}_4^+$ is $\sigma^2\pi^4\delta^2\delta^{*1}$, and the electronic configuration of $\text{Re}_2(\text{PMe}_2\text{Ph})_4\text{Cl}_4$ is $\sigma^2\pi^4\delta^2\delta^{*2}$.

Because the increasingly reduced species have increasing antibonding character, it stands to reason that the bond will weaken and lengthen. \square

8 Coordination Complexes: Spectra and Reactions

I) Do problem 16 from Chapter 11 of your text.

11.16 Classify the following configurations as A , E , or T in complexes having O_h symmetry. Some of these configurations represent excited states.

a. $t_{2g}^4 e_g^2$

Answer. T: Because the triply degenerate state is asymmetrically occupied and the doubly degenerate state is symmetrically occupied. ☐

b. t_{2g}^6

Answer. A: Because both states are nondegenerate and symmetrically occupied. ☐

c. $t_{2g}^3 e_g^3$

Answer. E: Because the triply degenerate state is symmetrically occupied and the doubly degenerate state is asymmetrically occupied. ☐

d. t_{2g}^5

Answer. T: Because the triply degenerate state is asymmetrically occupied and the doubly degenerate state is symmetrically occupied. ☐

e. e_g

Answer. E: Because the triply degenerate state is symmetrically occupied and the doubly degenerate state is asymmetrically occupied. ☐

- II) For $\text{Co}(\text{NH}_3)_6^{3+}$ (O_h symmetry), the spin-allowed transitions $^1A_{1g} \rightarrow ^1T_{1g}$ and $^1A_{1g} \rightarrow ^1T_{2g}$ are orbitally forbidden. Use symmetry arguments to determine which (if any) are vibronically allowed.

Answer. We will first consider the $^1A_{1g} \rightarrow ^1T_{1g}$ transition. Since $\int \Gamma_2 \Gamma_\mu \Gamma_1 d\tau = \int 0 d\tau = 0$ for the $^1A_{1g} \rightarrow ^1T_{1g}$ transition (as can readily be confirmed), the transition is orbitally forbidden. Thus, we must determine if it can be vibronically allowed.

From its definition, we can determine Γ_1 and Γ_2 , the irreducible representations of the ground state and excited state, respectively. From the O_h character table, we can determine $\Gamma_{\mu_{x,y,z}}$. And from the lecture slides, we can determine Γ_{gv} and Γ_{ev} , the irreducible representations of the ground state and excited state vibrations, respectively. All values are listed below.

$$\begin{aligned}\Gamma_{\text{ev}} &= A_{1g} + E_g + 2T_{1u} + T_{2g} + T_{2u} \\ \Gamma_2 &= T_{1g} \\ \Gamma_\mu &= T_{1u} \\ \Gamma_1 &= A_{1g} \\ \Gamma_{\text{gv}} &= A_{1g}\end{aligned}$$

We want to determine if the direct product $\Gamma_{\text{ev}} \otimes \Gamma_2 \otimes \Gamma_\mu \otimes \Gamma_1 \otimes \Gamma_{\text{gv}}$ contains the totally symmetric irreducible representation. To do so, we will first take the direct product of the right four terms and then distribute it to each of the five terms in Γ_{ev} and see which distributed products contain the totally symmetric representation. Let's begin.

The product of the right four terms is

$$\begin{aligned}\Gamma_2 \otimes \Gamma_\mu \otimes \Gamma_1 \otimes \Gamma_{\text{gv}} &= T_{1g} \otimes T_{1u} \otimes A_{1g} \otimes A_{1g} \\ &= T_{1g} \otimes T_{1u} \\ &= A_{1u} + E_u + T_{1u} + T_{2u}\end{aligned}$$

By Theorem 2, the direct product of the above and any of A_{1g} , E_g , and T_{2g} does not contain the totally symmetric representation, but the direct product of the above and any of T_{1u} and T_{2u} does. Therefore, the $^1A_{1g} \rightarrow ^1T_{1g}$ transition is vibronically allowed. This means that $\text{Co}(\text{NH}_3)_6^{3+}$ can vibrate along either the T_{1u} or T_{2u} mode to break octahedral symmetry temporarily, removing the inversion center. This relaxes Laporte's rule, thus allowing the transition.

We will now consider the $^1A_{1g} \rightarrow ^1T_{2g}$ transition. Using the same method as before, we can determine that

$$\begin{aligned}\Gamma_{\text{ev}} &= A_{1g} + E_g + 2T_{1u} + T_{2g} + T_{2u} \\ \Gamma_2 &= T_{2g} \\ \Gamma_\mu &= T_{1u} \\ \Gamma_1 &= A_{1g} \\ \Gamma_{\text{gv}} &= A_{1g}\end{aligned}$$

As before, the product of the right four terms is

$$\begin{aligned}\Gamma_2 \otimes \Gamma_\mu \otimes \Gamma_1 \otimes \Gamma_{\text{gv}} &= T_{2g} \otimes T_{1u} \otimes A_{1g} \otimes A_{1g} \\ &= T_{2g} \otimes T_{1u} \\ &= A_{2u} + E_u + T_{1u} + T_{2u}\end{aligned}$$

By Theorem 2, the direct product of the above and any of A_{1g} , E_g , and T_{2g} does not contain the totally symmetric representation, but the direct product of the above and any of T_{1u} and T_{2u} does. Therefore, the $^1A_{1g} \rightarrow ^1T_{2g}$ transition is vibronically allowed. \square

- III) “Optical pumping” consists of irradiating a molecule with near monochromatic high intensity light. A short-lived molecule in an electronically excited state is therefore produced. Optically pumping $[\text{Cr}(\text{NCS})_6]^{3-}$ at $13\,000\text{ cm}^{-1}$ yields an electronically excited state whose absorption spectrum is shown in the figure below. This spectrum showed no detectable bands between 9000 and $16\,000\text{ cm}^{-1}$; experimental difficulties prohibited looking below 9000 cm^{-1} . The table gives the normal electronic absorption spectrum (i.e., from the ${}^4A_{2g}$ level).

Energy (cm^{-1})	Assignment	ϵ
13 000	${}^4A_{2g} \rightarrow {}^2E_g$	10
18 870	${}^4A_{2g} \rightarrow {}^4T_{2g}$	159
21 000	${}^4A_{2g} \rightarrow {}^2T_{2g}$	8
25 000	${}^4A_{2g} \rightarrow {}^4T_{1g}$	129
31 600	${}^4A_{2g} \rightarrow {}^2A_{1g}$	12
38 200	${}^4A_{2g} \rightarrow {}^2T_{1g}, {}^2T_{2g}$	~ 10
40 300	${}^4A_{2g} \rightarrow {}^2E_g$	~ 10

Table 8.1: Absorption spectrum of ${}^4A_{2g} \text{Cr}(\text{NCS})_6^{3-}$.

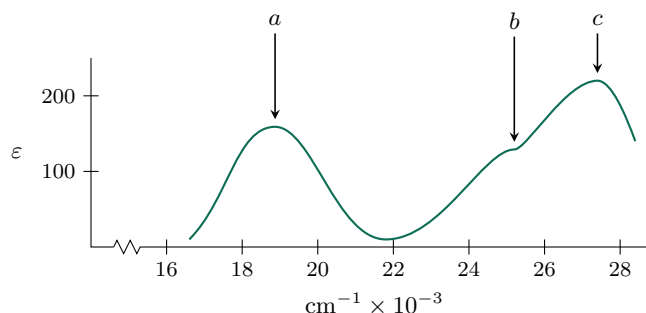


Figure 8.1: Excited state absorption spectrum of $\text{K}_3\text{Cr}(\text{NCS})_6$.

- (a) What excited state is produced by $13\,000\text{ cm}^{-1}$ light (give the molecular term symbol)?

Answer. From Table 8.1, we can read that $13\,000\text{ cm}^{-1}$ light excites a ground state electron to the 2E_g excited state. \square

- (b) Assign the three transitions in the absorption spectrum of the optically pumped ion (and show your reasoning).

Answer. We have that

$$\begin{aligned} a &= {}^2E_g \rightarrow {}^2A_{1g} \\ b &= {}^2E_g \rightarrow {}^2T_{1g}, {}^2T_{2g} \\ c &= {}^2E_g \rightarrow {}^2E_g \end{aligned}$$

Consider a (gaseous) sample of $\text{K}_3\text{Cr}(\text{NCS})_6$. Before it is optically pumped, the electrons of the vast majority of the molecules in the sample lie in the ${}^4A_{2g}$ ground state. While the sample is being irradiated, the electrons' energy is raised (by $13\,000\text{ cm}^{-1}$) to the 2E_g excited state in the vast majority of molecules, essentially making 2E_g a new “ground state.” After the light is shut off, the molecules in the sample retain their excited state for a very short but measurable amount of time. In this window, we can irradiate the sample with different wavenumbers of light

to explore the electronic transitions accessible to the complex if 2E_g were its ground state, with electrons being excited from 2E_g and falling back down to it.

What we see in Figure 8.1 is the absorption spectrum of this optically pumped compound. It tells us things like, “if we have a sample of $\text{K}_3\text{Cr}(\text{NCS})_6$ and raise its electrons’ energy by $13\,000\text{ cm}^{-1}$ to an excited state, this excited state will absorb significant quantities of photons with energy approximately equal to $18\,600\text{ cm}^{-1}$, i.e., there is an energy level $18\,600\text{ cm}^{-1}$ above the $13\,000\text{ cm}^{-1}$ -excited state to which electrons are excited and from which they fall back down to the $13\,000\text{ cm}^{-1}$ -excited state.”

With this understanding, we are now ready to interpret Figure 8.1. Peak *a* corresponds to an energy level approximately $18\,600\text{ cm}^{-1}$ above the 2E_g excited state. From the original reference frame, this means that peak *a* corresponds to an energy level approximately $18\,600\text{ cm}^{-1} + 13\,000\text{ cm}^{-1} = 31\,600\text{ cm}^{-1}$ above the ${}^4A_{2g}$ ground state. It follows from Table 8.1 that the energy level being accessed by this transition is ${}^2A_{1g}$. Therefore, the assignment of this transition is ${}^2E_g \rightarrow {}^2A_{1g}$. The argument is symmetric for the other two peaks, so we know that peak *b*’s assigned transitions are ${}^2E_g \rightarrow {}^2T_{1g}$ and ${}^2E_g \rightarrow {}^2T_{2g}$, and peak *c*’s assigned transition is ${}^2E_g \rightarrow {}^2E_g$. \square

- (c) Explain qualitatively the observed intensities in the spectrum shown.

Answer. Table 8.1 shows the three transitions of interest all having very small ϵ from the ground state, but Figure 8.1 shows that they are considerably (approximately an order of magnitude) larger from the excited state. The reason for this discrepancy is that the transitions from the ground state are Laporte (all $g \rightarrow g$) and spin (all $4 \rightarrow 2$) forbidden, while the transitions from the excited state are still Laporte forbidden (all $g \rightarrow g$) but now spin allowed (all $2 \rightarrow 2$). Moreover, since chromium is a relatively light transition metal, the Laporte selection rule is of negligible importance, so the change in the spin selection rule is what truly accounts for the difference in intensity.

Also note that peak *b* is not just slightly smaller than peak *a*, but represents a much lesser absorption than peak *a*. We know this because it is close enough to peak *c* that much of its absorption intensity is borrowed from its neighbor. \square

- (d) How might this technique be useful in assigning electronic spectra?

Answer. Some transitions (such as the three in Figure 8.1) are heavily forbidden from the ground state (as we can see from the corresponding molar absorptivities in Table 8.1) and thus hard to spot in the ground state absorption spectrum. Consequently, if we want to be able to identify *all* of the energy levels in a compound, we will need to reconcile the absorption spectra of a number of optically pumped spectra with the original ground state spectrum. \square

IV) Do the following problems from Chapter 12: 4, 15, 20.

- 12.4** The yellow “prussiate of soda” $\text{Na}_4[\text{Fe}(\text{CN})_6]$ has been added to table salt as an anticaking agent. Why have there been no apparent toxic effects, even though this compound contains cyano ligands?

Answer. $[\text{Fe}(\text{CN})_6]^{4-}$ is a low-spin d^6 compound, meaning that it has a high CFSE, meaning that it is highly chemically inert. Thus, the cyano ligands do not significantly separate from it. \square

- 12.15** When the two isomers of $\text{Pt}(\text{NH}_3)_2\text{Cl}_2$ react with thiourea [$\text{tu} = \text{S}=\text{C}(\text{NH}_2)_2$], one product is $[\text{Pt}(\text{tu})_4]^{2+}$ and the other is $[\text{Pt}(\text{NH}_3)_2(\text{tu})_2]^{2+}$. Identify the initial isomers and explain the results.

Answer. $\boxed{\text{cis-Pt}(\text{NH}_3)_2\text{Cl}_2 \text{ reacts with thiourea to form } [\text{Pt}(\text{tu})_4]^{2+}}$. Chloride has a strong trans-effect; thus, the amine groups are replaced first by thiourea groups. Since the thiourea groups, in turn, have a stronger trans-effect than chloride ($\text{SR}_2 > \text{Cl}^-$ from Miessler et al., 2014, p. 460)^[6], both chlorides are then replaced by thiourea groups. Alternatively, it is possible that one amine group is replaced, then the tu group (being very strong) replaces the chloride opposite it, and then the process repeats for the other chloride/amine pair.

$\boxed{\text{trans-Pt}(\text{NH}_3)_2\text{Cl}_2 \text{ reacts with thiourea to form } \text{trans-}[\text{Pt}(\text{NH}_3)_2(\text{tu})_2]^{2+}}$. The strong trans-effect of the chlorides causes one to boot the other off. The stronger thiourea then boots off the other chloride, but nothing is able to kick out the amine groups. \square

⁶Miessler et al. (2014) only places SH_2 into the trans-effect list, but so we have to assume that SR_2 occupies an equivalent place.

- 12.20** Is the reaction $[\text{Co}(\text{NH}_3)_6]^{3+} + [\text{Cr}(\text{H}_2\text{O})_6]^{2+}$ likely to proceed by an inner-sphere or outer-sphere mechanism? Explain your answer.

Answer. The chromium complex is d^4 high spin, and would pursue an inner-sphere mechanism. However, the ammine ligands of the cobalt complex have no occupied nonbonding or antibonding orbitals, making it a poor ligand for quantum tunneling, and necessitating an outer-sphere mechanism. Additionally, the cobalt complex is d^6 low spin, hence inert, meaning that it cannot transfer ligands; this further promotes the use of an outer-sphere mechanism. \square

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Note that the (mostly correct) solutions to all book problems can be found [here](#).