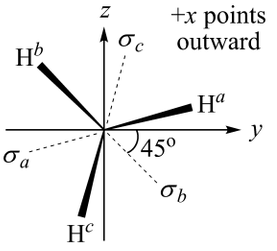
4 Molecular Symmetry

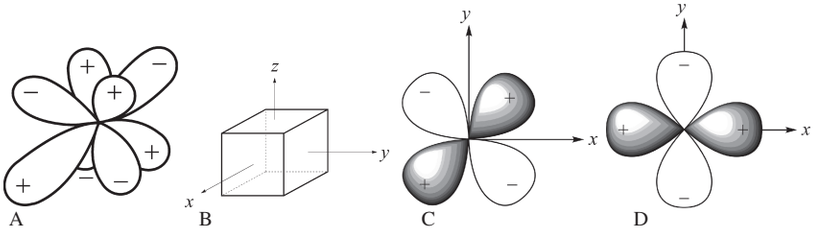
PROBLEMS

4.1 A student sets up the coordinates for NH_3 rather unconventionally, as shown on the right. In this coordinate system, the x-axis is the three-fold axis. One of the σ-planes, σ_b, makes an angle of 45° with the y-axis. By considering the transformation of a general point in space, deduce the six 3×3 matrices which form a set of reducible representations for the C_{3v} point group.

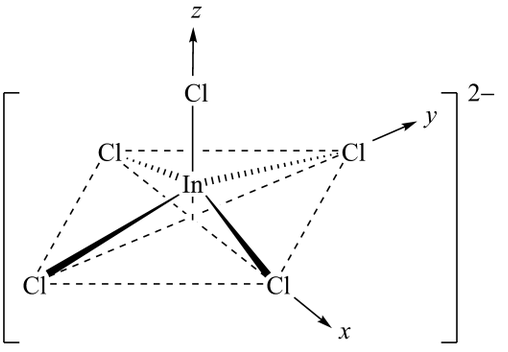


4.2 There are eight equivalent lobes for the f_{xyz} orbital. They point toward the corners of a cube with the origin as its center and have alternating signs, as shown in Fig. A below. The cube is orientated in such a way that x-, y-, and z-axis pass through the centers of the six faces, as shown in Fig. B below. Rotation of f_{xyz} orbital about z-axis by $-45°$ results in $f_{z(x^2-y^2)}$ orbital. The top views of f_{xyz} and $f_{z(x^2-y^2)}$ orbitals are shown below in Figs. C and D, respectively.

Assign these two orbitals to their proper irreducible representation in point groups C_{2v} and D_{4h}.



4.3 The square pyramidal $[InCl_5]^{2-}$ anion has C_{4v} symmetry. Of the four vertical mirror planes, one σ_v is in the xz-plane, the other σ_v in the yz-plane, and the two σ_d's lie in between them.



(i) With reference to the coordinate system based on the orthonormal base vectors $\hat{e}_1$, $\hat{e}_2$, and $\hat{e}_3$ (pointing in the x-, y-, and z-directions, respectively), write down all eight matrices that represent the symmetry operations of the C_{4v} group.

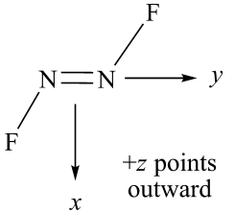
(ii) Deduce the character of Γ_e, the representation based on $\{\hat{e}_1, \hat{e}_2, \hat{e}_3\}$. Reduce Γ_e to the irreducible representations of C_{4v}.

REFERENCE: D. S. Brown, F. W. B. Einstein, and D. G. Tuck, Tetragonal-pyramidal indium(III) species. Crystal structure of tetraethylammonium pentachloroindate(III). *Inorg. Chem.* **8**, 14–8 (1969).

4.4 Point groups S_n, have only two symmetry elements: E and S_n. Explain why n must be an even integer and $n \geq 4$.

4.5 *Trans*-N_2F_2 has C_{2h} symmetry and its coordinates are taken as those shown below. The character table of the C_{2h} point group is shown below.

C_{2h}	$\boldsymbol{E}$	$\boldsymbol{C}_2$	$\boldsymbol{i}$	$\boldsymbol{\sigma}_h$
A_g	1	1	1	1
B_g	1	−1	1	−1
A_u	1	1	−1	−1
B_u	1	−1	−1	1



(i) To which representations do the Cartesian coordinates x, y, and z belong?

(ii) To which representations do the binary products x^2, y^2, z^2, xy, xz, and yz belong?

4.6 In a reference book, the character table of the D_{3d} point group has the following form:

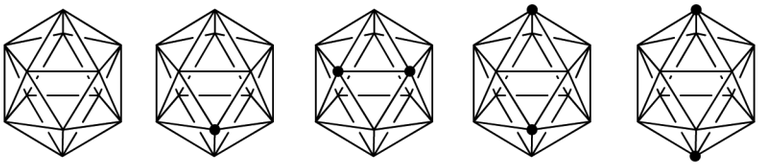
D_{3d}	$\boldsymbol{E}$	$2\boldsymbol{C}_3$	$3\boldsymbol{C}_2$	$\boldsymbol{i}$	$2\boldsymbol{S}_6$	$3\boldsymbol{\sigma}_d$
A_{1g}	1	1	1	1	1	1
A_{2g}	1	1	−1	1	1	−1
E_g	2	−1	0	2	−1	0
A_{1u}	1	1	1	−1	−1	−1
A_{2u}	1	1	−1	−1	−1	1
E_u	2	−1	0	−2	1	0

(i) To which representations do the Cartesian coordinates x, y, and z belong?

(ii) Taking the z-axis as the C_3 axis, to which representations do the binary products x^2, y^2, z^2, xy, xz, and yz belong?

4.7 (i) Borane dianions $(BH)_n^{2-}$ adopt structures with high symmetry. For instance, *closo*-dodecaborane(12) dianion, $(BH)_{12}^{2-}$, has the structure of an icosahedron, a polyhedron with 12 vertices and 20 faces. The symmetry point group for this structure is I_h, which has 120 symmetry operations: $\boldsymbol{E}$, $12\boldsymbol{C}_5$, $12\boldsymbol{C}_5^2$, $20\boldsymbol{C}_3$, $12\boldsymbol{C}_2$, $\boldsymbol{i}$, $12\boldsymbol{S}_{10}$, $12\boldsymbol{S}_{10}^3$, $20\boldsymbol{S}_6$, $15\boldsymbol{\sigma}$. The structure of $(BH)_{12}^{2-}$ is shown below (left), where each vertex is occupied by a BH group.

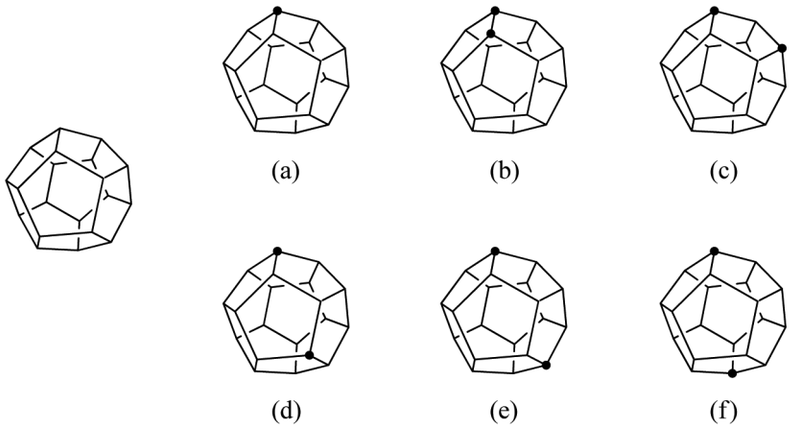
When one or more BH group(s) in $(BH)_{12}^{2-}$ is (are) substituted by C (which is isoelectronic to BH), carborane dianions $C_m(BH)_{12-m}^{2-}$ are obtained. The only possible mono- and di-substituted *closo*-dodecaborane(12) dianions are displayed below [(a) to (d), where C atoms are represented by black dots]. Determine the symmetry point group of each carborane dianion shown.



(ii) Fullerene C_{20} has the structure of a dodecahedron, a polyhedron with 20 vertices and 12 faces. The symmetry point group for this structure is also I_h. The structure of C_{20} is shown below (left), where each vertex is occupied by a C atom.

When one or more C atom(s) of C_{20} is (are) replaced by Si, substituted fullerenes Si_mC_{20-m} are obtained. The only possible mono- and di-substituted C_{20} with the

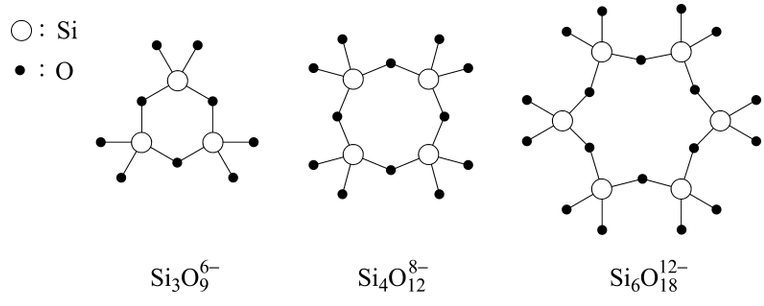
general formula Si_mC_{20-m} (m = 1 or 2) are displayed below [(a) to (f), where Si atoms are represented by black dots]. Determine the symmetry point group of each substituted fullerene shown.



4.8 Determine the point group of each of the following silicate anions:

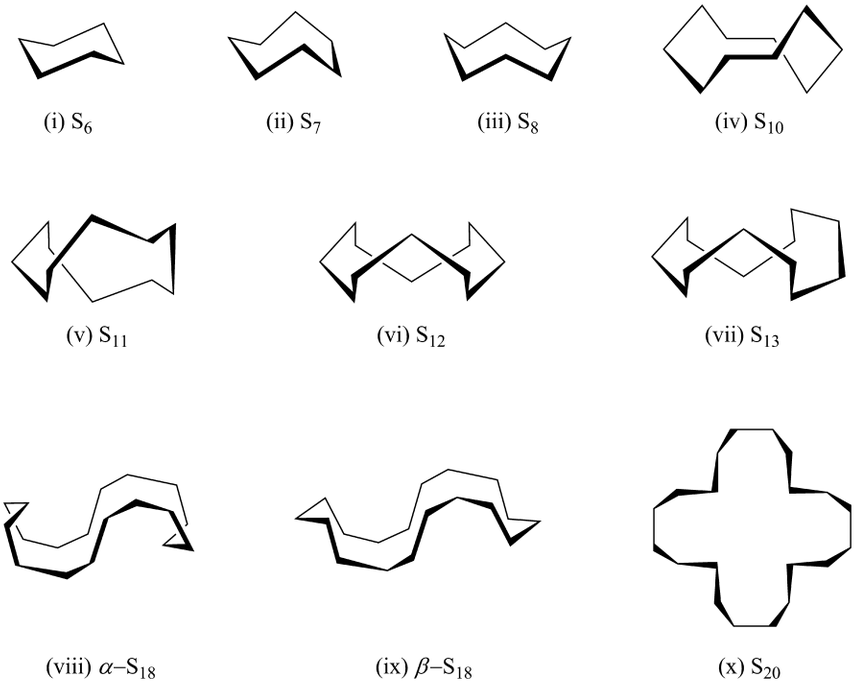
(i) $[SiO_4]^{4-}$
(ii) $[O_3Si{-}O{-}SiO_3]^{6-}$ with linear Si–O–Si linkage. Consider both staggered and eclipsed conformation.
(iii) $[Si_3O_9]^{6-}$
(iv) $[Si_4O_{12}]^{8-}$
(v) $[Si_6O_{18}]^{12-}$

The structures for the last three species are shown below. The $(SiO)_n$ (n = 3, 4, 6) rings are planar.



4.9 Assign point group symbols for the following cyclic S_n molecules ($n = 6, 7, 8, 10, 11, 12, 13, 18$ in α and β forms, 20):

(i) S_6; (ii) S_7; (iii) S_8; (iv) S_{10}; (v) S_{11}; (vi) S_{12}; (vii) S_{13}; (viii) α–S_{18}; (ix) β–S_{18}; (x) S_{20}.

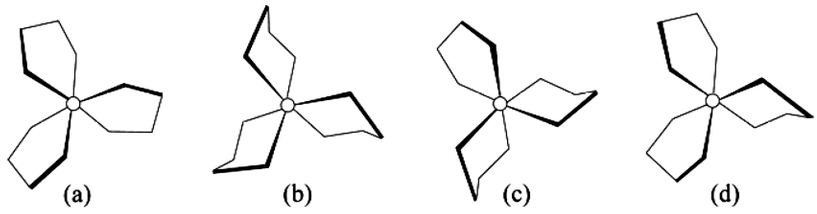


(i) S_6 (ii) S_7 (iii) S_8 (iv) S_{10}

(v) S_{11} (vi) S_{12} (vii) S_{13}

(viii) α–S_{18} (ix) β–S_{18} (x) S_{20}

4.10 (i) Give the point groups and chiral nomenclature for the isomeric forms of tris(ethylenediamine)cobalt(III) illustrated below:

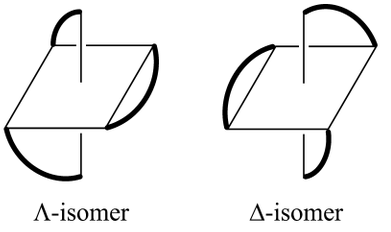


(a) **(b)** **(c)** **(d)**

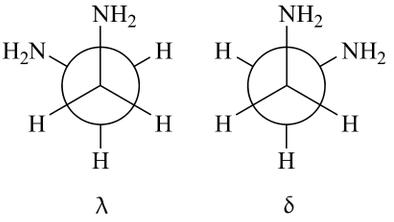
(ii) List the remaining possible configurations of $[Co(en)_3]^{3+}$.

A note on the nomenclature of chiral metal complex:

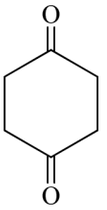
First we view the optically active tris(chelate) complexes down the three-fold rotational axis. If the helix viewed in this way is left-handed, it is called a "Λ-isomer". Its mirror image is the "Δ-isomer". The naming is illustrated in the figure on the right.



Besides the asymmetry due to the tris(chelate) structure of octahedral complexes, asymmetry may also be generated in the ligands such as ethylenediamine. The enantiomeric gauche conformations may be "left-handed" (represented by "λ") or "right-handed" (represented by "δ"), which are shown in the figure on the right. Thus, one of the possible complete notations showing the configuration of tris(ethylenediamine)cobalt(III) is Λ-Mλλλ, where M denotes metal.

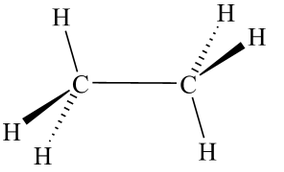


4.11 There are five possible conformations for cyclohexane-1,4-dione: a chair form, two boat forms, a symmetric twist form, and a twist form of lower symmetry generally referred to as the twist-boat form. Sketch all five distinct conformations and identify their point groups.

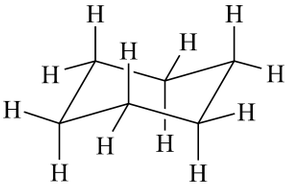


REFERENCE: C.-S. Tse, D. Y. Chang, K.-Y. Law, and T. C. W. Mak, The crystal and molecular structure of *trans*-2,5-di-*p*-bromobenzyl-2,5-diethoxycarbonylcyclohexane 1,4-dione. *Acta Cryst.* **B32**, 1216–9 (1976).

4.12 The structure of ethane, C_2H_6, is shown on the right. Consider the fluoro-substituted ethanes with the general formula $C_2H_{6-n}F_n$, $n = 1, 2, \ldots, 6$. Draw members of this series that have the following symmetries: (i) C_1; (ii) C_2; (iii) C_s; (iv) C_{2h}; (v) C_{3v}; (vi) D_{3d}.



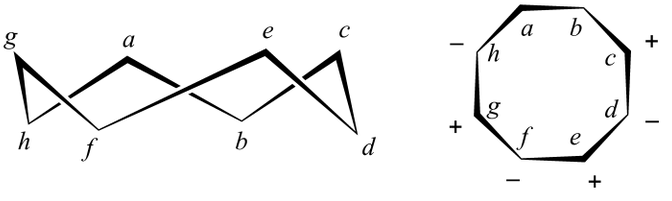
4.13 Cyclohexane molecule (C_6H_{12}, shown on the right) has D_{3d} symmetry. Consider the chloro-substituted cyclohexanes with the general formula $C_6H_mCl_n$, with $n = 1, 2, \ldots$ and $m + n = 12$. Write the structural formulas for members from the $C_6H_mCl_n$ series that have the following symmetries: (i) C_1; (ii) C_2; (iii) C_s; (iv) C_{2h}; (v) C_{3v}.



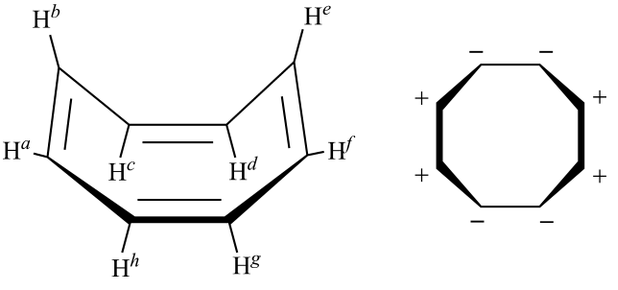
4.14 Elemental sulfur, S_8, has the "crown" structure shown below (left). Viewed from the "top", this structure becomes an octagon. This octagon is also shown below (right), where the "+" sign denotes atoms that are above the paper plane and the "−" sign indicates atoms below. All eight atoms are labeled in the figures.

(i) What is the symmetry point group of S_8? Also, if one of the sulfur atoms in S_8 is replaced by (the isoelectronic) oxygen, the hypothetical compound S_7O is formed. What is the point group of S_7O?

(ii) When four of the sulfur atoms in S_8 are replaced by oxygen atoms, another hypothetical compound, S_4O_4, is formed. Clearly there are several isomers for S_4O_4. Write down which sulfur atoms are to be replaced to obtain the isomers which have the following symmetries: (a) C_1; (b) C_2; (c) C_s; (d) C_{4v}; (e) D_{2d}.



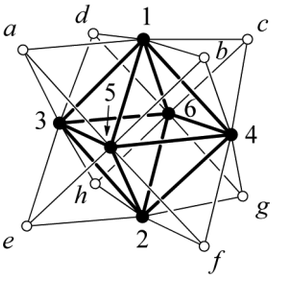
4.15 Cyclooctatetraene, C_8H_8, has the "tub" structure shown below (left). This molecule belongs to the D_{2d} group, whose symmetry operations are easily visualized as in the top view displayed below (right). Here "+" signs indicate atoms that are above the plane of the paper and the "−" signs indicate atoms below.



Consider the halogen-substituted cyclooctatetraenes with general formula $C_8H_{8-n}X_n$, $n = 0, 1, 2, \ldots, 8$. Write down which H atoms are to be replaced to obtain the isomers which have the following symmetries: (i) C_1; (ii) C_s; (iii) C_2; (iv) C_{2v}; (v) S_4; (vi) D_2.

REFERENCE: W.-K. Li, Identification of molecular point groups. *J. Chem. Educ.* **70**, 485–7 (1993).

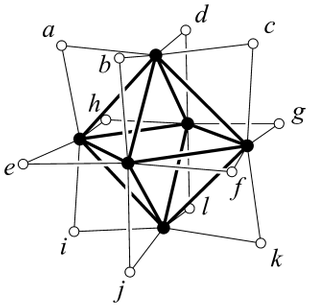
4.16 Shown on the right is the structure of metal cluster $Mo_6Cl_8^{4+}$, with the six Mo atoms forming an octahedron and the eight Cl atoms placed above the eight faces of the octahedron. This cluster has O_h symmetry. Note that Cl atoms *a*, *b*, *c*, *d*, *e*, *f*, *g*, and *h* are above faces 135, 145, 146, 136, 235, 245, 246, and 236, respectively.



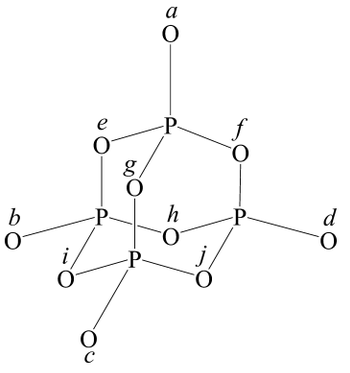
(i) If the following Mo atom(s) is (are) replaced by the isoelectronic W and/or Cr atom(s), determine the symmetry point group of the substituted clusters: (a) 1 = W; (b) 1 = 2 = W; (c) 3 = 5 = W; (d) 1 = 2 = 3 = W; (e) 1 = 3 = 5 = W; (f) 1 = W and 2 = Cr; (g) 3 = W and 5 = Cr; (h) 1 = 5 = W and 2 = 4 = Cr; (i) 1 = 2 = W and 3 = 4 = Cr.

(ii) Replace one or more Cl atoms with F atoms so that the resulting cluster will belong to the following point groups: (a) C_{2v}; (b) C_s; (c) C_{4v}; (d) D_{2h}; (e) C_{3v}; (f) D_{3d}; (g) T_d; (h) C_2. You only need to give the labels of the Cl atoms (*a* to *h*) replaced.

4.17 Shown on the right is the structure of metal cluster $Ta_6Cl_{12}^{2+}$, with the six Ta atoms forming an octahedron and the twelve Cl atoms placed above the twelve edges of the octahedron. This cluster has O_h symmetry. Replace one or more Cl atoms with F atoms so that the resulted cluster will belong to the following point groups: (i) C_{4v}; (ii) D_{4h}; (iii) C_s; (iv) C_1; (v) C_{2v}; (vi) C_2; (vii) C_{2h}; (viii) C_{3v}; (ix) C_3; (x) D_{3d}; (xi) D_3; (xii) D_{2h}; (xiii) D_{2d}; (xiv) D_2. You only need to give the labels of the Cl atoms (*a* to *l*) replaced.



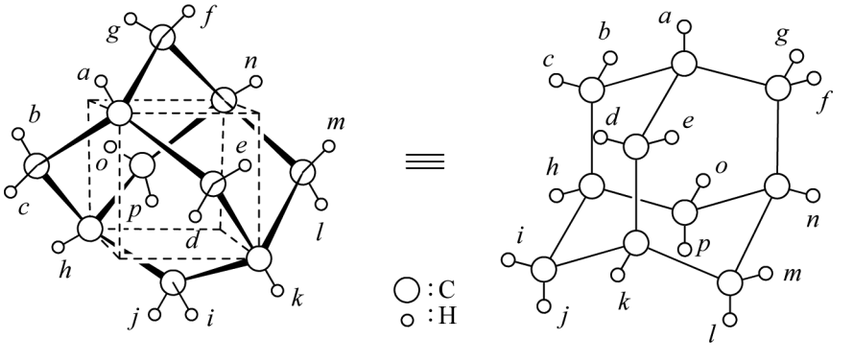
4.18 The structure of P_4O_{10} is shown on the right. In this highly symmetrical and pretty structure, the four P atoms form a perfect tetrahedron. Each P atom is linked to a terminal oxygen (with a double bond); these O atoms are labeled *a* to *d* in the figure. The remaining six oxygens, with labels *e* to *j*, are bridging atoms, located above the edges of the P_4 tetrahedron. So P_4O_{10} has T_d symmetry.



Replace one or more O atoms in P_4O_{10} with S atoms so that the resulting molecules will have the symmetries given below. Also, you need to observe the condition imposed. You only need to give the label(s) of the O atoms replaced. Do not draw the structures of your answers.

(i) D_{2d} [replacing only bridging O atom(s)];
(ii) D_{2d} [replacing both bridging and terminal O atom(s)].
(iii) C_{3v} [replacing only terminal O atom(s)];
(iv) C_{3v} [replacing only bridging O atom(s)];
(v) C_{3v} [replacing both terminal and bridging O atom(s), but each P atom is bonded to only either terminal S atom or bridging S atom(s), and not both];
(vi) C_{2v} [replacing only terminal O atom(s)];
(vii) C_{2v} [replacing only bridging O atom(s)];
(viii) C_{2v} [replacing both terminal and bridging O atom(s), but each P atom is bonded to only either terminal S atom or bridging S atom(s), and not both];
(ix) C_s [replacing only bridging O atom(s)];
(x) C_s [replacing both bridging and terminal O atom(s)];
(xi) C_2 [replacing only bridging O atom(s)];
(xii) C_2 [replacing both bridging and terminal O atom(s)];
(xiii) C_1 [replacing ONE terminal O atom and bridging O atom(s)];
(xiv) C_1 [replacing TWO terminal O atoms and bridging O atom(s)].

4.19 Adamantane, $C_{10}H_{16}$, has the structure shown below. This molecule has T_d symmetry and two types of carbon atoms. There are four methine carbons (each of which is bonded to one hydrogen with label *a*, *h*, *k*, or *n*) which occupy the corners of a tetrahedron. In addition, there are six methylene carbons (each of which is bonded to two hydrogens) which are located above the edges of the aforementioned tetrahedron. All 16 hydrogens are labeled in the figure.



Consider the chloro-substituted adamantanes with the general formula $C_{10}H_{16-n}Cl_n$, $n = 0, 1, 2, \ldots, 16$. Draw members of this series that have the following symmetries: (i) C_1; (ii) C_2; (iii) C_3; (iv) C_s; (v) $C_{2v;}$ (vi) C_{3v}; (vii) D_{2d}. Provide only one answer for each part. In the answers, only list the label(s) of the hydrogen atom(s) to be replaced.

REFERENCE: W.-K. Li, Identification of molecular point groups. *J. Chem. Educ.* **70**, 485–7 (1993).

4.20 In a classic paper on optically active coordination compounds, Mills and Quibell reported the synthesis of a Pt complex containing one molecule of *meso*-stilbenediamine ($H_2N–CHPh–CHPh–NH_2$) and one molecule of isobutylenediamine ($H_2N–CH_2–CMe_2–NH_2$). Also, the complex was successfully resolved into its enantiomers. Determine whether the coordination around the metal ion is tetrahedral or square planar. Also illustrate these modes pictorially.

REFERENCE: W. H. Mills and T. H. H. Quibell, The configuration of the valencies of 4-covalent platinum: the optical resolution of *meso*-stilbenediaminoisobutylenediaminoplatinous salts. *J. Chem. Soc.* 839–46 (1935).

4.21 Consider the series of octahedral complexes with the general formula $[MA_mB_n(XX)_p(XY)_q]$, where $m, n, p, q = 0, 1, 2, \ldots, m + n + 2p + 2q = 6$, A and B are monodentate ligands such as Cl and F, XX is a bidentate ligand with two identical donating groups, and XY is a bidentate ligand with two different donating groups. An example of XX is $H_2NCH_2CH_2NH_2$, and an example of XY is $(CH_3)_2NCH_2CH_2NH_2$. Write the structural formulas for members from this series that have the symmetry requested below and that meet the following requirements. (i) C_1, with at least one monodentate ligand; (ii) C_1, with no monodentate ligand; (iii) C_2, with at least one monodentate ligand; (iv) C_2, with no monodentate ligand; (v) C_3; (vi) C_s; (vii) C_{2v}; (viii) C_{2h}; (ix) D_{2h}; (x) C_{3v}; (xi) D_3; (xii) C_{4v}; (xiii) D_{4h}.

REFERENCE: W.-K. Li, Identification of molecular point groups. *J. Chem. Educ.* **70**, 485–7 (1993).

4.22 Draw all geometrical isomers of $[Co(trien)Cl_2]^+$, where "trien" is the tetradentate ligand triethylenetetramine which may be conveniently represented by "N–N–N–N" in your drawings. Also, ignoring the conformation of chelate rings, identify the symmetry point group of each isomer and predict whether it is optically active or not.

SOLUTIONS

A4.1

$$\boldsymbol{E} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}, \quad \boldsymbol{C}_3 = \begin{bmatrix} 1 & 0 & 0 \\ 0 & -\frac{1}{2} & -\frac{\sqrt{3}}{2} \\ 0 & \frac{\sqrt{3}}{2} & -\frac{1}{2} \end{bmatrix},$$

$$\boldsymbol{C}_3^{-1} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & -\frac{1}{2} & \frac{\sqrt{3}}{2} \\ 0 & -\frac{\sqrt{3}}{2} & -\frac{1}{2} \end{bmatrix}, \quad \boldsymbol{\sigma}_b = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 0 & -1 \\ 0 & -1 & 0 \end{bmatrix},$$

$$\boldsymbol{\sigma}_a = \boldsymbol{C}_3 \times \boldsymbol{\sigma}_b = \begin{bmatrix} 1 & 0 & 0 \\ 0 & \frac{\sqrt{3}}{2} & \frac{1}{2} \\ 0 & \frac{1}{2} & -\frac{\sqrt{3}}{2} \end{bmatrix}, \quad \boldsymbol{\sigma}_c = \boldsymbol{\sigma}_b \times \boldsymbol{C}_3 = \begin{bmatrix} 1 & 0 & 0 \\ 0 & -\frac{\sqrt{3}}{2} & \frac{1}{2} \\ 0 & \frac{1}{2} & \frac{\sqrt{3}}{2} \end{bmatrix}.$$

A4.2

C_{2v}	$\boldsymbol{E}$	$\boldsymbol{C}_2(z)$	$\boldsymbol{\sigma}_v(xz)$	$\boldsymbol{\sigma}'_v(yz)$	
$\Gamma(f_{xyz})$	1	1	−1	−1	$= A_2$
$\Gamma(f_{z(x^2-y^2)})$	1	1	1	1	$= A_1$

D_{4h}	$\boldsymbol{E}$	$2\boldsymbol{C}_4(z)$	$\boldsymbol{C}_2$	$2\boldsymbol{C}'_2$	$2\boldsymbol{C}''_2$	$\boldsymbol{i}$	$2\boldsymbol{S}_4$	$\boldsymbol{\sigma}_h$	$2\boldsymbol{\sigma}_v$	$2\boldsymbol{\sigma}_d$
$\Gamma(f_{xyz})$	1	−1	1	1	−1	−1	1	−1	−1	1
$\Gamma(f_{z(x^2-y^2)})$	1	−1	1	−1	1	−1	1	−1	1	−1

Thus, $\Gamma(f_{xyz})$ transforms as B_{1u}; $\Gamma(f_{z(x^2-y^2)})$ transforms as B_{2u}.

A4.3 (i) For the symmetry operations $\boldsymbol{\sigma}_{va}$, $\boldsymbol{\sigma}_{vb}$, $\boldsymbol{\sigma}_{da}$ and $\boldsymbol{\sigma}_{db}$, $\boldsymbol{\beta} = 0, 90, 45$, and $-45°$, respectively.

$$\boldsymbol{E}: \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \qquad \boldsymbol{C}_4: \begin{bmatrix} 0 & -1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

$$\boldsymbol{C}_4^3: \begin{bmatrix} 0 & 1 & 0 \\ -1 & 0 & 0 \\ 0 & 0 & 1 \end{bmatrix} \qquad \boldsymbol{C}_2: \begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

$$\boldsymbol{\sigma}_{va}: \begin{bmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \qquad \boldsymbol{\sigma}_{vb}: \begin{bmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

$$\boldsymbol{\sigma}_{\mathrm{d}a}: \begin{bmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{bmatrix} \qquad \boldsymbol{\sigma}_{\mathrm{d}b}: \begin{bmatrix} 0 & -1 & 0 \\ -1 & 0 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

(ii)

C_{4v}	$\boldsymbol{E}$	$2\boldsymbol{C}_4$	$\boldsymbol{C}_4^2$	$2\boldsymbol{\sigma}_v$	$2\boldsymbol{\sigma}_d$	
Γ_e	3	1	−1	1	1	$= A_1 + E.$

A4.4 If n is an odd number, $\boldsymbol{S}_n^n$ generates an additional operation $\boldsymbol{\sigma}$ perpendicular to the S_n axis and hence group S_n becomes $C_{n\mathrm{h}}$. So n cannot be odd. In addition, $\boldsymbol{S}_2 = \boldsymbol{i}$ and hence the point groups S_2 and C_i are equivalent. To sum up: $S_1 = C_s$, $S_2 = C_i$, and $S_3 = C_{3h}$. Hence n must be equal to or larger than 4.

A4.5

C_{2h}	$\boldsymbol{E}$	$\boldsymbol{C}_2$	$\boldsymbol{i}$	$\boldsymbol{\sigma}_h$		
A_g	1	1	1	1		x^2, y^2, z^2, xy
B_g	1	−1	1	−1		xz, yz
A_u	1	1	−1	−1	z	
B_u	1	−1	−1	1	x, y	

Reasoning:

(i) Functions x, y, z must have u symmetry. It is easily seen that z is symmetric with respect to $\boldsymbol{C}_2$, while both x and y are antisymmetric with respect to $\boldsymbol{C}_2$.

(ii) All the binary products must have g symmetry. Also: $\Gamma(z^2) = \Gamma(z) \times \Gamma(z) = A_u \times A_u = A_g$; $\Gamma(x^2) = \Gamma(y^2) = \Gamma(xy) = B_u \times B_u = A_g$; $\Gamma(xz) = \Gamma(yz) = A_u \times B_u = B_g$.

A4.6

D_{3d}	$\boldsymbol{E}$	$2\boldsymbol{C}_3$	$3\boldsymbol{C}_2$	$\boldsymbol{i}$	$2\boldsymbol{S}_6$	$3\boldsymbol{\sigma}_d$		
A_{1g}	1	1	1	1	1	1		$x^2 + y^2, z^2$
A_{2g}	1	1	−1	1	1	−1		
E_g	2	−1	0	2	−1	0		$(x^2 - y^2, xy); (xz, yz)$
A_{1u}	1	1	1	−1	−1	−1		
A_{2u}	1	1	−1	−1	−1	1	z	
E_u	2	−1	0	−2	1	0	(x, y)	

Reasoning:

(i) It is straightforward to obtain $\Gamma(z)$ by applying all the operations on z. On the other hand, each of x and y is neither symmetric nor antisymmetric with respect to $\mathbf{C}_3$, so they must form a degenerate set. Since they have u symmetry, they form an E_u set.

(ii) $\Gamma(z^2) = \Gamma(z) \times \Gamma(z) = A_{2u} \times A_{2u} = A_{1g}$.
Since $x^2 + y^2 = r^2 - z^2$ and $\Gamma(r^2) = \Gamma(z^2) = A_{1g}$, $\Gamma(x^2 + y^2)$ is also A_{1g}.
$\Gamma(xz, yz) = \Gamma(x, y) \times \Gamma(z) = E_u \times A_{2u} = E_g$.

None of the remaining $x^2 - y^2$ and xy is symmetric or antisymmetric with respect to $\mathbf{C}_3$, so they also form a degenerate set. Since they have g symmetry, they form another E_g set.

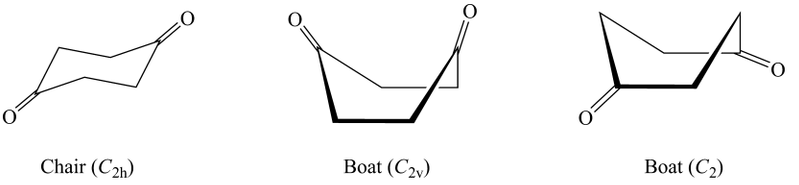
A4.7 (i) (a) C_{5v}; (b) C_{2v}; (c) C_{2v}; (d) D_{5d}.
(ii) (a) C_{3v}; (b) C_{2v}; (c) C_s; (d) C_2; (e) C_{2v}; (f) D_{3d}.

A4.8 (i) T_d. (ii) D_{3d} for staggered conformation and D_{3h} for eclipsed. (iii) D_{3h}. (iv) D_{4h}. (v) D_{6h}.

A4.9 (i) D_{3d}; (ii) C_s; (iii) D_{4d}; (iv) D_2; (v) C_2; (vi) D_{3d}; (vii) C_2; (viii) C_{2h}; (ix) C_{2h}; (x) D_4.

A4.10 (i) (a) Δ-M$\delta\delta\delta$, D_3;
(b) Δ-M$\lambda\lambda\lambda$ (more stable than Δ-M$\delta\delta\delta$ form by about 7.5 kJ mol^{-1}), D_3;
(c) Λ-M$\delta\delta\lambda$, C_2;
(d) Δ-M$\lambda\delta\delta$, C_2.
(ii) Λ-M$\lambda\lambda\lambda$, Λ-M$\delta\delta\delta$, Δ-M$\lambda\lambda\delta$, and Λ-M$\delta\lambda\lambda$, which are enantiomers of (a), (b), (c), and (d), respectively.

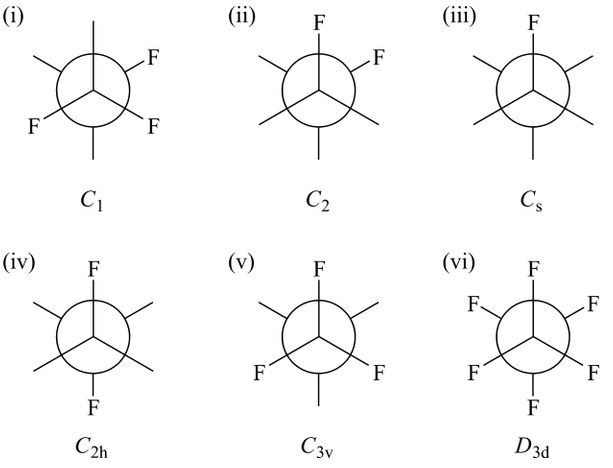
A4.11



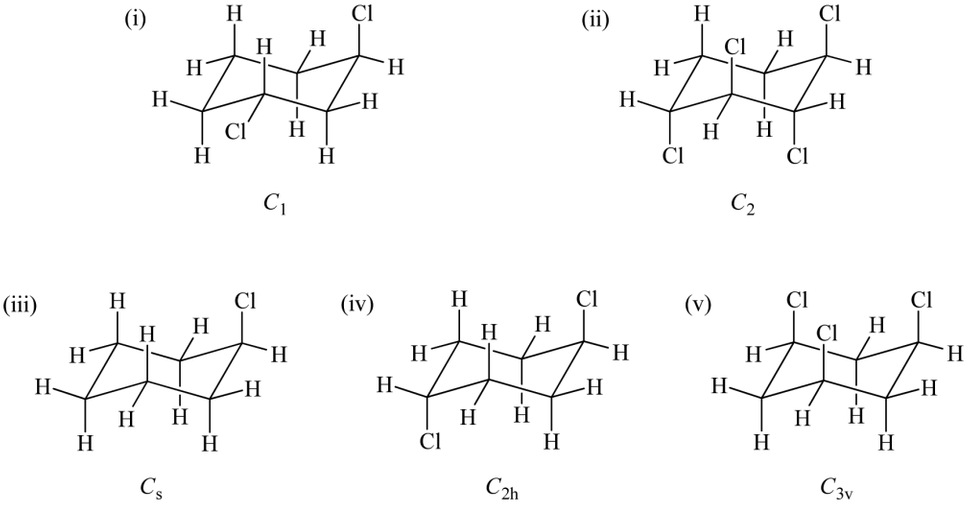
Chair (C_{2h}) Boat (C_{2v}) Boat (C_2)

Symmetric twist (D_2) Twist-boat (C_2)

A4.12



A4.13



A4.14 (i) S_8: D_{4d}; S_7O: C_s.
(ii) (a) *abdf* or *abce*; (b) *abcd* or *abdg*; (c) *abde* or *abcf*; (d) *aceg*; (e) *abef*.

A4.15 (i) *a*; (ii) *ab*; (iii) *ah*; (iv) *abef*; (v) *aceg*; (vi) *adeh*.

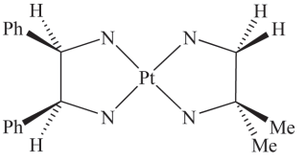
A4.16 (i) (a) C_{4v}; (b) D_{4h}; (c) C_{2v}; (d) C_{2v}; (e) C_{3v}; (f) C_{4v}; (g) C_s; (h) C_1; (i) D_{2h}.
(ii) (a) *ab, ac*; (b) *abc, abg*; (c) *abcd*; (d) *abgh*; (e) *a*; (f) *ag*; (g) *acfh*; (h) *abdf*.

A4.17 (i) *abcd*; (ii) *efgh*; (iii) *ab*; (iv) *ace*; (v) *e*; (vi) *aj*; (vii) *abkl*; (viii) *abe*; (ix) *abcehj*; (x) *abegkl*; (xi) *chj*; (xii) *ak*; (xiii) *acjl*; (xiv) *acegjl*.

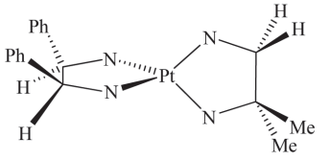
A4.18 (i) *ej*; (ii) *abcdej*; (iii) *a*; (iv) *efg*; (v) *ahij*; (vi) *ab*; (vii) *e*; (viii) *abj*; (ix) *ef*; (x) *aef*; (xi) *efi*; (xii) *abfi*; (xiii) *aeh*; (xiv) *abfj*.

A4.19 (i) *af*; (ii) *bm*; (iii) *bdf*; (iv) *b*; (v) *de*; (vi) *a*; (vii) *gfij*.

A4.20

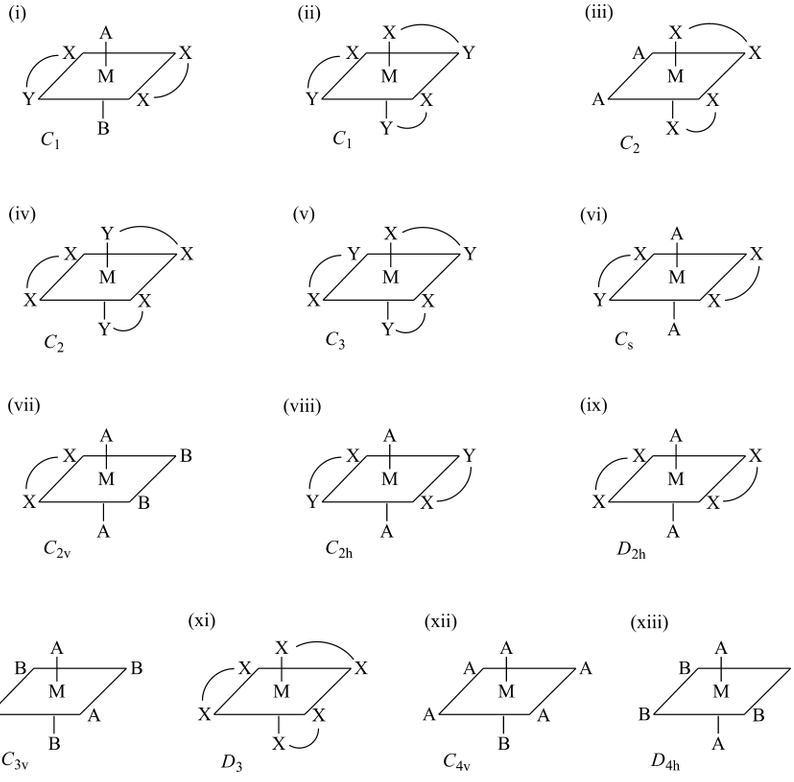


Square planar (optically active, as found by Mills and Quibell)

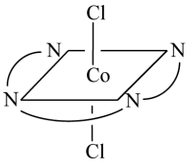


Tetrahedral (may show slight optical activity since the chelate rings are non-planar)

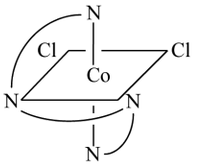
A4.21 There are other possible answers, in addition to the ones given below.



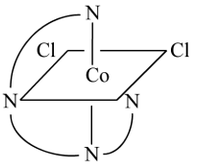
A4.22



C_{2v}



C_2 (optically active)



C_1 (optically active)