CHAPTER 3

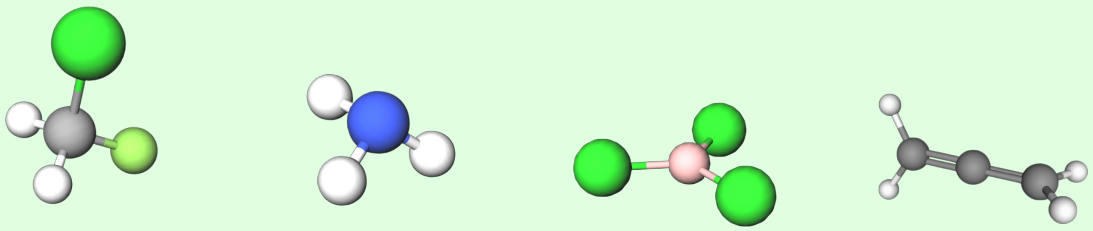
Point Groups

Exercise 3.1

Determine the point groups of the following: (a) CH_2ClF; (b) NH_3; (c) BCl_3; (d) allene; (e) 1,3,5-trichlorobenzene; (f) *trans*-$Pt(NH_3)_2Cl_2$ (considered as square planar); (g) BFClBr.

Solution 3.1

Molecular structures of CH_2ClF, NH_3, BCl_3 and propadiene are illustrated in Fig 3.1. Since 'allene' refers to a general class of compounds rather than a specific molecule, I have used 'propadiene' to ensure chemical specificity.



CH_2ClF NH_3 BCl_3 propadiene

Figure 3.1: Molecular structures of CH_2ClF, NH_3, BCl_3 and propadiene.

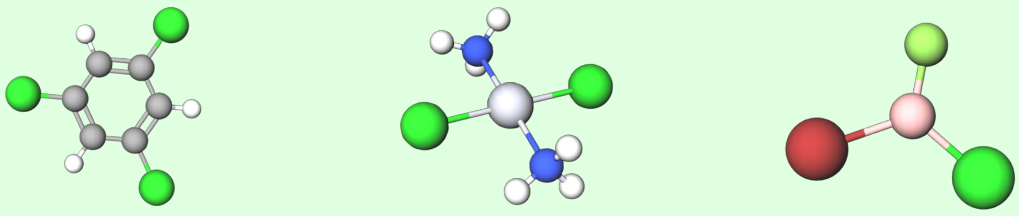
(a) CH_2ClF belongs to the $\mathscr{C}_{\rm s}$ point group. The only symmetry element present is a single mirror plane ($\sigma_{\rm h}$) that bisects the H−C−H angle and contains the Cl−C−F atoms.

(b) NH_3 belongs to the $\mathscr{C}_{3\rm v}$ point group. It has one C_3 axis passing through the N atom and 3 vertical mirror planes ($\sigma_{\rm v}$) each containing one N−H bond.

(c) BCl_3 belongs to the $\mathscr{D}_{3\rm h}$ point group. It has a principal C_3 axis perpendicular to the molecular plane, 3 C_2 axes along the B−Cl bonds, a horizontal mirror plane ($\sigma_{\rm h}$) (the molecular plane), and 3 vertical mirror planes ($3\sigma_v$).

(d) Propadiene belongs to the $\mathscr{D}_{2\rm d}$ point group. It has a principal C_2 axis along the C=C=C chain and two other C_2 axes at 45° to the CH_2 planes. Crucially, it has two dihedral mirror planes ($\sigma_{\rm d}$) but no σ_h or i. It also possesses an S_4 axis (along the C=C=C chain).

Molecular structures of 1,3,5-trichlorobenzene, *trans*-$Pt(NH_3)_2Cl_2$, BFClBr are illustrated in Fig 3.2.



1,3,5-trichlorobenzene *trans*-$Pt(NH_3)_2Cl_2$ BFClBr

Figure 3.2: Molecular structures of 1,3,5-trichlorobenzene, *trans*-$Pt(NH_3)_2Cl_2$ and BFClBr.

(e) 1,3,5-trichlorobenzene belongs to the $\mathscr{D}_{3h}$ point group. It has a principal C_3 axis perpendicular to the ring, 3 C_2 axes passing through the C−H bonds, a horizontal mirror plane (σ_h) (the ring plane), and 3 vertical planes (σ_v).

(f) *trans*-$Pt(NH_3)_2Cl_2$ belongs to the $\mathscr{C}_{2h}$ point group at most in fact. In a fixed staggered conformation, the 3-fold symmetry of NH_3 breaks the C_2 axes that would otherwise lie along the Pt−N and Pt−Cl bonds. By retaining the center of inversion (i) and the horizontal mirror plane (σ_h), the symmetry is more precisely classified as $\mathscr{C}_{2h}$.

In fact, historically, *trans*-$Pt(NH_3)_2Cl_2$ is often assigned to the $\mathscr{D}_{2h}$ point group by treating the NH_3 ligands as single points or freely rotating groups. It has a principal C_2 axis perpendicular to the plane, two other C_2 axes (one along Cl−Pt−Cl and one along N−Pt−N), a center of inversion (i), a horizontal mirror plane (σ_h), and 2 vertical mirror planes (σ_v).

(g) BFClBr belongs to the $\mathscr{C}_1$ point group. Since all ligands are distinct, there are no rotation axes and no mirror planes. The only symmetry element is the identity (E).

Remark

For *trans*-$Pt(NH_3)_2Cl_2$, while the instantaneous conformation of the ammine ligands typically reduces the molecular symmetry to $\mathscr{C}_1$, the low barrier to N−H bond rotation ensures that the molecule behaves as a $\mathscr{D}_{2h}$ species on a time-averaged scale. This statistical symmetry explains the observed lack of a permanent dipole moment and optical inactivity.

Exercise 3.2

Determine the point groups of the following octahedral compounds: (a) CoN_6; (b) CoN_5A; (c) cis-CoN_4A_2; (d) trans-CoN_4A_2; (e) *cis*-*cis*-CoN_4A_2; (f) *trans*-*cis*-CoN_4A_2.

Solution 3.2

Molecular structures of various cobalt complexes are illustrated in Fig 3.3. In this analysis, the symmetry of these cobalt complexes is evaluated based on the approximation that ligands A and N are either point charges or freely rotating spheres.

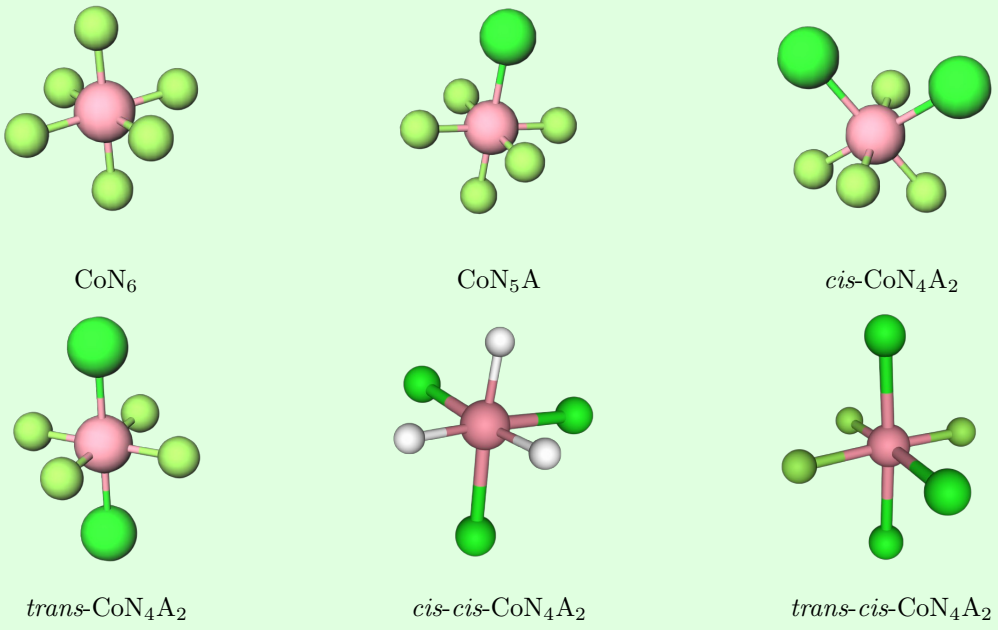


Figure 3.3: Molecular structures of various cobalt complexes.

(a) CoN_6 belongs to the $\mathscr{O}_h$ point group. It possesses 3 C_4 axes, i and no C_5 axes.

(b) CoN_5A belongs to the $\mathscr{C}_{4v}$ point group. Firstly, it has a C_4 axis. Secondly, it has no $C_2 \perp$ to C_4. At last, it has no σ_h and possesses 4 σ_v.

(c) *cis*-CoN_4A_2 belongs to the $\mathscr{C}_{2v}$ point group. Firstly, it has a C_2 axis. Secondly, it has no $C_2 \perp$ to C_2. At last, it has no σ_h and possesses 2 σ_v.

(d) *trans*-CoN_4A_2 belongs to the $\mathscr{D}_{4h}$ point group. Firstly, it has a C_4 axis. Secondly, it has 4 $C_2 \perp$ to C_4. At last, it has a σ_h.

(e) *cis-cis*-CoN_4A_2 belongs to the $\mathscr{C}_{3v}$ point group. Firstly, it has a C_3 axis. Secondly, it has no $C_2 \perp$ to C_2. At last, it has no σ_h and possesses 3 σ_v.

(f) *trans-cis*-CoN_4A_2 belongs to the $\mathscr{C}_{2v}$ point group. Firstly, it has a C_2 axis. Secondly, it has no $C_2 \perp$ to C_2. At last, it has no σ_h and possesses 2 σ_v.

Remark

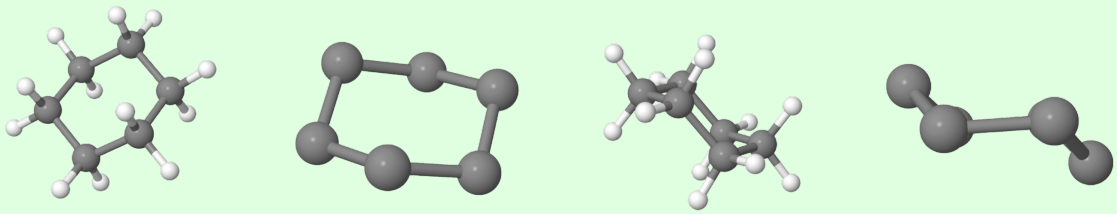
In octahedral nomenclature, '*cis-cis*' typically refers to the *facial* (*fac*) isomer, where three A ligands occupy one face of the octahedron. while '*trans-cis*' typically refers to the *meridional* (*mer*) isomer, where three A ligands are arranged in a 'T-shape' or a meridian.

Exercise 3.3

Determine the point groups of the following: (a) chair form of cyclohexane (ignoring the H's); (b) boat form of cyclohexane (ignoring the H's); (c) staggered C_2H_6; (d) eclipsed C_2H_6; (e) between staggered and eclipsed C_2H_6.

Solution 3.3

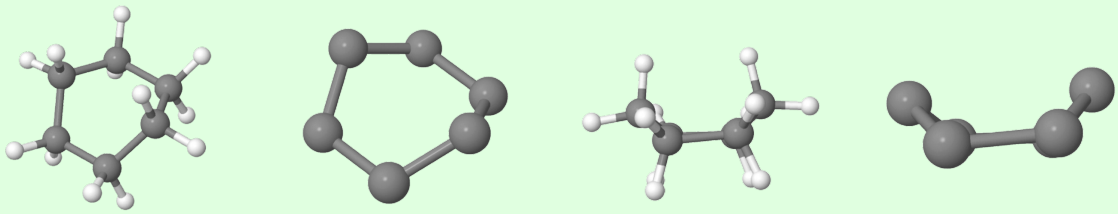
Front and end views of the cyclohexane chair and boat conformation, shown with and without H's are illustrated in Fig 3.4 and Fig 3.5, respectively.



with H's (front view) | without H's (front view) | with H's (end view) | without H's (end view)

Figure 3.4: Front and end views of the cyclohexane chair conformation, shown with and without H's.

(a) Chair form of cyclohexane (ignoring the H's) belongs to the $\mathscr{D}_{3d}$ point group. The carbon ring has a principal C_3 axis perpendicular to the average plane of the ring. It also has 3 C_2 axes passing through the centers of opposite C−C bonds. Moreover, it has no σ_h but 3 σ_v.



with H's (front view) | without H's (front view) | with H's (end view) | without H's (end view)

Figure 3.5: Front and end views of the cyclohexane boat conformation, shown with and without H's.

(b) Boat form of cyclohexane (ignoring the H's) belongs to the $\mathscr{C}_{2v}$ point group. It possesses a single C_2 axis that passes through the center of the quadrilateral formed by the four 'base' carbons (C_2,

C_3, C_5, C_6) and is perpendicular to their plane. Additionally, there is no σ_h but 2 σ_v: one passing through the two 'prow/stern' carbons (C_1 and C_4), and the other bisecting the two parallel C−C bonds on the sides of the 'boat'.

Front and end views of the C_2H_6 staggered, eclipsed, between staggered and eclipsed conformation, shown with and without H's are illustrated in Fig 3.6.

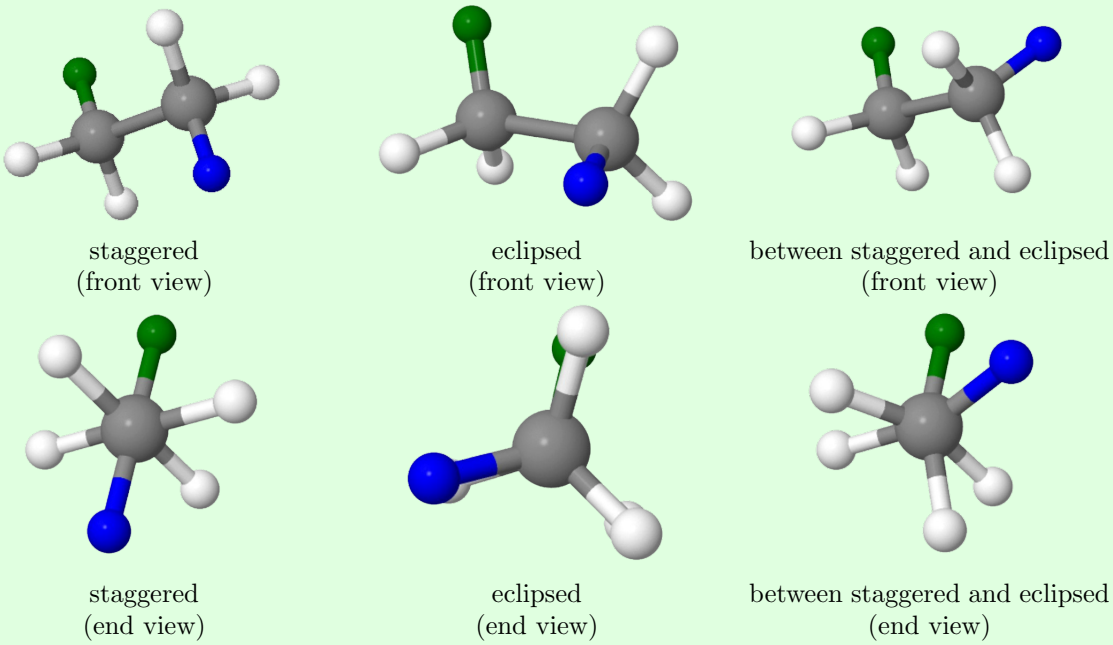


Figure 3.6: Front and end views of the C_2H_6 staggered, eclipsed, between staggered and eclipsed conformations, shown with H's.

(c) Staggered C_2H_6 belongs to the $\mathscr{D}_{3d}$ point group. It has a principal C_3 axis along the C−C bond, perpendicular to this are three C_2 axes. Each C_2 axis passes through the midpoint of the C−C bond and lies exactly halfway between the staggered C−H bonds of the two C atoms. Rotating 180° around any of these axes interchanges the two C atoms and maps each H atom onto an equivalent one on the opposite C atom. At last, it has no σ_h but 3 σ_d.

(d) Eclipsed C_2H_6 belongs to the $\mathscr{D}_{3h}$ point group. It has a principal C_3 axis along the C−C bond, perpendicular to this are three C_2 axes. Each C_2 axis passes through the midpoint of the C−C bond and lies exactly halfway between the eclipsed C−H bonds of the two C atoms. In the end, it has a σ_h.

(e) Between staggered and eclipsed C_2H_6 belongs to the $\mathscr{C}_3$ point group. It has a principal C_3 axis along the C−C bond, perpendicular to this are three C_2 axes. Each C_2 axis passes through the midpoint of the C−C bond and lies exactly halfway between the neither staggered nor eclipsed C−H bonds of the two C atoms. Finally, there is no σ_h and σ_d.

Remark

- The content of this exercise is actually explained in detail in many classic organic chemistry textbooks (although it may not necessarily include content on symmetry), and you can refer to their stereochemistry chapters for more information.
- The diagrams in this exercise are generated from https://www.chemtube3d.com.

Exercise 3.4

Determine the point groups of the following: (a) ivy leaf; (b) iris; (c) starflsh; (d) ice crystal; (e) twin-bladed propellor; (f) rectangular bar; (g) hexagonal bathroom tile; (h) swastika; (i) tennis ball (with seam); (j) Chinese abacus (counters all in their lowest positions); (k) ying-yang.

Solution 3.4

The diagrams of various real-world objects and patterns are illustrated in Fig 3.7. Since some of them have variations, such as the many common varieties of ivy, our analysis of the objects or patterns is based on the examples given in these images. The ice crystal serves as a fascinating exception to standard hexagonal symmetry. I have provided diagrams of both its classic hexagonal morphology and its rare pentagonal variant, analyzing each separately.

Figure 3.7: Diagrams of various real-world objects and patterns.

(a) An ivy leaf belongs to the $\mathscr{C}_{\mathrm{s}}$ point group. It has only a σ, not even a C_2 axis or i.

(b) An iris belongs to the $\mathscr{C}_{3\mathrm{v}}$ point group. Firstly, it has a C_3 axis and no C_2 axes. Then, there is no σ_{h} and 3 σ_{v}.

(c) A starfish belongs to the $\mathscr{C}_{5\mathrm{v}}$ point group. It has a C_5 axis and 5 σ_{v}. Since the top (aboral) surface and bottom (oral/tube feet) surface are distinct, it lacks C_2 axes or a σ_h perpendicular to the principal axis.

(d) An ideal hexagonal ice crystal belongs to the $\mathscr{D}_{6\mathrm{h}}$ point group. It possesses a C_6 principal axis, 6 C_2 axes perpendicular to it, and a horizontal mirror plane (σ_{h}).

However, ice crystals have variants. For instance, a pentagonal crystal belongs to the $\mathscr{C}_{5\mathrm{v}}$ point group. While it possesses a C_5 principal axis, it lacks C_2 axes perpendicular to that axis. Furthermore, there is no σ_{h} mirror plane; instead, there are 5 σ_{v} planes. This is because the heterogeneity between the front and back surfaces breaks the σ_{h} mirror plane, which in turn eliminates the C_2 axes.

(e) A twin-bladed propellor belongs to the $\mathscr{C}_2$ point group. Because the blades are slanted, a mirror plane would flip the 'pitch' of the blade, so there are no mirror planes and no i.

(f) A rectangular bar belongs to the $\mathscr{D}_{2\mathrm{h}}$ point group. It has 3 mutually perpendicular C_2 axes and σ_{h}.

(g) A hexagonal bathroom tile belongs to the $\mathscr{C}_{6\mathrm{v}}$ point group. It has a C_6 axis and 6 σ_{v}. Because the top/bottom are different, it lacks the σ_{h} and the 6 C_2 axes, compared to a regular hexagonal prism.

(h) The swastika belongs to the $\mathscr{C}_4$ point group. Because the arms are 'bent' in one direction, it lacks mirror planes (a mirror would reverse the direction of the bends).

(i) A tennis ball (with seam) belongs to the $\mathscr{D}_{2\mathrm{d}}$ point group. Its symmetry is defined not by the sphere itself, but by the undulating, interlocking seam. The seam breaks C_∞ and σ_h due to its 3D 'wave' path. The primary symmetry elements are an S_4 axis and 3 C_2 axes, resulting from the 2 felt pieces being joined at a perpendicular orientation.

(j) A Chinese abacus belongs to the $\mathscr{C}_\mathrm{s}$ point group. It has only one mirror plane bisecting the beads and frame. Due to the presence of a functional front side and a solid backplane, the traditional Chinese abacus lacks a C_2 axis.

(k) The ying-yang symbol belongs to the $\mathscr{C}_1$ point group if color is considered a primary attribute, otherwise, ignoring color variations, it belongs to the $\mathscr{C}_2$ point group.

Exercise 3.5

Determine the point groups of the following: (a) a square-based pyramid; (b) a right circular cone; (c) a square lamina; (d) a square lamina with the top and bottom sides painted differently; (e) a right circular cylinder; (f) a right circular cylinder with the two ends painted differently; (g) a right circular cylinder with a stripe painted parallel to the axis.

Solution 3.5

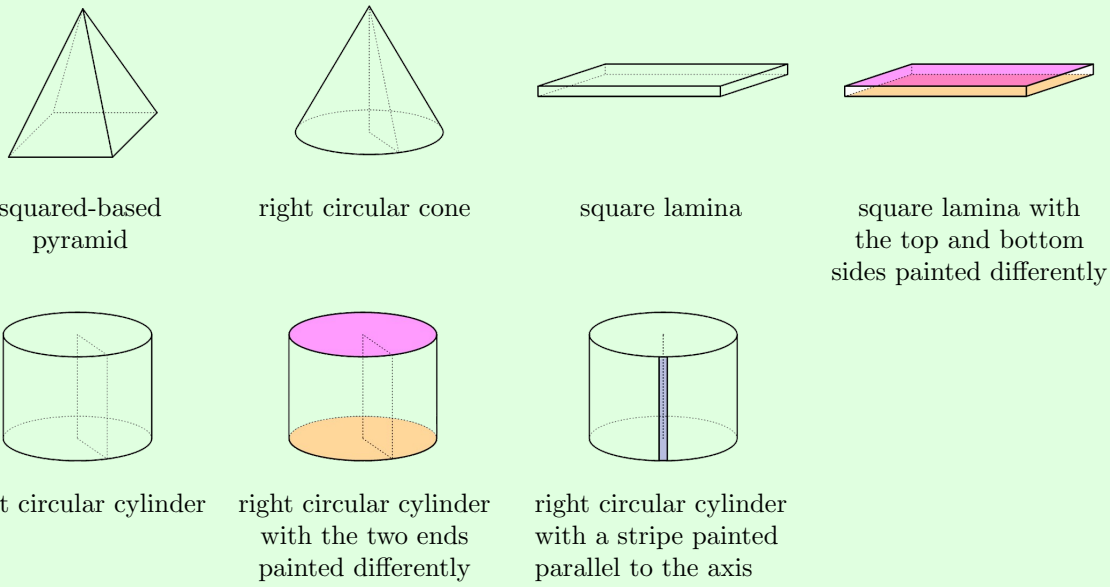


Figure 3.8: Diagrams of various geometric shapes.

(a) The square-based pyramid belongs to the $\mathscr{C}_{4\mathrm{v}}$ point group. It has a C_4 axis passing through the apex and the center of the base. There is no σ_h. It also has 4 σ_v: two passing through opposite corners and two bisecting the sides.

(b) The right circular cone belongs to the $\mathscr{C}_{\infty\mathrm{v}}$ point group. It has a C_∞ axis passing through the apex and the center of the base. There is no σ_h but infinite σ_v.

(c) The square lamina belongs to the $\mathscr{D}_{4\mathrm{h}}$ point group. It has a C_4 axis perpendicular to the face, 4 C_2 axes in the plane of the square, and a σ_h.

(d) The square lamina with the top and bottom sides painted differently belongs to the $\mathscr{C}_{4\mathrm{v}}$ point group. It has a C_4 axis perpendicular to the face but no C_2 axes in the plane of the square and no σ_h. There are 4 σ_v: two passing through opposite corners and two bisecting the sides.

(e) The right circular cylinder belongs to the $\mathscr{D}_{\infty\mathrm{h}}$ point group. It has a C_∞ axis, infinite C_2 axes perpendicular to the principal axis and a σ_h,

(f) The right circular cylinder with the two ends painted differently belongs to the $\mathscr{C}_{\infty\mathrm{v}}$ point group. It has a C_∞ axis but no C_2 axes perpendicular to the principal axis. There is no σ_h but infinite σ_v.

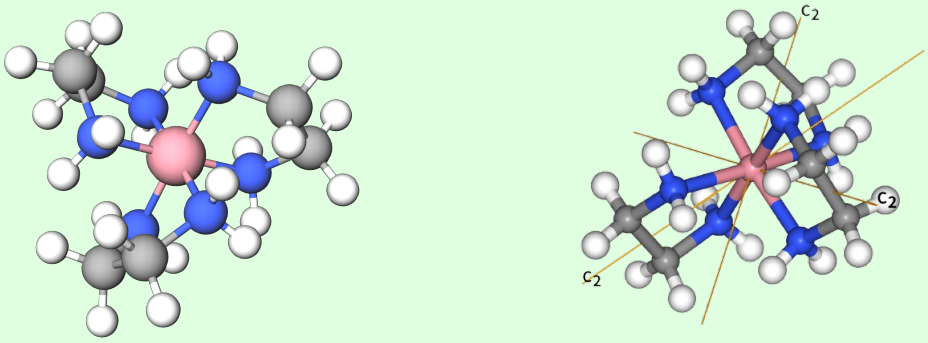
(g) The right circular cylinder with a stripe painted parallel to the axis belongs to the $\mathscr{C}_{2v}$ point group. There is a C_2 axis where the planes intersect and two σ_v.

Exercise 3.6

What is the point group for the tris(ethylenediamine)cobalt(III) ion?

Solution 3.6

The Molecular structure of tris(ethylenediamine)cobalt(III) ion is illustrated in Fig 3.9. It belongs to the $\mathscr{D}_3$ point group. It has a C_3 axis with 3 C_2 axes perpendicular to the principal axis, but it has neither σ_h nor σ_d.



the obvious C_3 axis 3 C_2 axes

Figure 3.9: Molecular structure of $[Co(en)_3]^{3+}$.

Exercise 3.7

For which point groups can a molecule (a) have a dipole moment, (b) be optically active?

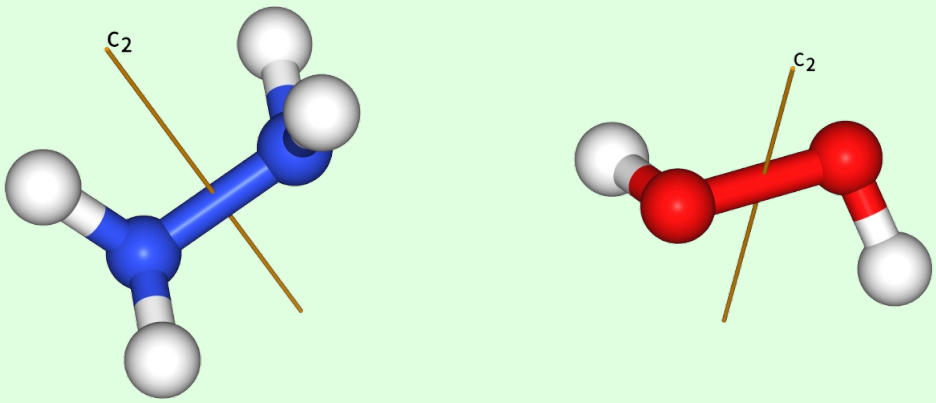
Solution 3.7

Firstly, we analyse the necessary and sufficient condition for a molecule to have a dipole moment and exhibit optical activity.

- A molecule has a permanent dipole moment if and only if its centers of positive and negative charges do not coincide. Note that point groups with multiple non-parallel axes of rotation (e.g., the $\mathscr{D}$ group, the octahedral group $\mathscr{O}_h$, etc.) must have zero dipole moments. In point group symmetries, only molecules belonging to the following 4 point groups have dipole moments:
  - $\mathscr{C}_1$,
  - $\mathscr{C}_s$,
  - $\mathscr{C}_n$,
  - $\mathscr{C}_{nv}$.
- A molecule is optically active if and only if it does not coincide with its mirror image. From the perspective of symmetry elements, a molecule cannot contain any inappropriate rotation axis (S_n). This includes:
  - symmetry plane (σ): which is equivalent to S_1.
  - inversion center (i): which is equivalent to S_2.

  Point groups that are chiral (and thus allow for optical activity) include: $\mathscr{C}_n$, $\mathscr{D}_n$, $\mathscr{T}$, $\mathscr{O}$, and $\mathscr{I}$.

Finally, we take the intersection of these two sets. Thus, the only solution is the $\mathscr{C}_n$ (including $\mathscr{C}_1$).
By the way, except the 1,1-dichloroethene in the FIG.3-6-4 in the text book, we list some molecules of $\mathscr{C}_2$, as illustrated in Fig 3.10.



N_2H_4 H_2O_2

Figure 3.10: Molecular structure of N_2H_4 and H_2O_2.