A complete theory of chemical bonding needs to make no assumptions regarding chemical structure. Unfortunately, except for the simplest compounds such as H₂, HD, etc., a detailed theory is not currently available and is unlikely to be fully developed for many years to come. However, by using empirical and semiempirical structural relationships that have evolved over a number of years, we often can correctly predict molecular structures which usually can be confirmed or rejected by spectroscopic techniques. These predicted or experimentally observed structures can provide a basis for meaningful comments about bonding.

One approach to chemical structure starts with the assumption that similar types of ligands produce similarly structured molecules. If, for example, the anion CoI₄⁻ is tetrahedral, it is reasonable to assume that CoBr₄⁻ also is tetrahedral. This approach has its obvious limitations. However, additional relationships do occur to the extent that a student acquainted with modern concepts of bonding and structure is likely to guess that PtCl₄⁻ is planar and Ni(OH₂)₄²⁺ is octahedral. He might even correctly suggest that the fluoride atoms surrounding manganese in K₂NaMnF₆ are at the corners of a distorted octahedron. Yet in spite of many recent successes in predicting structures, no one supposed
that \( \text{Re}(S_2C_2(C_6H_5)_2)_2 \) would have a structure (Figure 1-1) in which the six sulfur atoms surrounding the rhenium are arranged at the corners of a trigonal prism. Nor did anyone predict that the anionic dimer \( \text{Re}_2\text{Cl}_6^- \) would have the "cubic" structure pictured in Figure 1-2, and contain a quadruple metal–metal bond. A description of the bonding in such systems has had to await structural determinations.
**MOLECULAR SYMMETRY**

The most commonly found structural arrangement for coordination compounds is one in which the groups attached to the central metal atom appear at the corners of an octahedron. Associated with this structure are certain very important symmetry features. There are, for example, three mutually perpendicular axes, $x$, $y$, and $z$, about which a rotation by $n(2\pi/4)$ rad, where $n = 1, 2, 3, \ldots, n$ ($90^\circ$, $180^\circ$, $270^\circ$, etc.), makes the molecule indistinguishable from the original species. If the ligands along the $x$ axis are identical to each other, but different from the four identical ligands along $y$ and $z$, only one such four-fold rotation axis would exist. The octahedral molecule also contains a center of symmetry. This means that each atom has its counterpart at a position with coordinates of identical magnitude and opposite sign (Figure 1-3).

Since symmetry operations such as rotation, inversion, etc., produce no change in the molecule, any model of bonding we choose also must be invariant with respect to these same symmetry operations.

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**Figure 1-3** An octahedral complex.
If, for example, we describe the bond between the metal atom and one of the ligands in an octahedral complex in a particular way, the bonding of the metal to the other five ligands must be described similarly. The bonding model we use must be consistent with the overall structure of the compound. Thus it is apparent that a knowledge of molecular structures can be very important to an understanding of bonding in coordination chemistry—a chemistry noted for its numerous structural types (see Tables 6-3 and 6-4).

Ligand atoms which are appreciably distorted from their free-atom or molecule symmetry by bonding to the metal atom (they are said to be *polarizable*) often produce complexes with nonoctahedral structures. For example, with the polarizable chloride ion, tetrahedral complexes of the type $MCl_4^-$ form for $M = Mn^{II}$, $Fe^{II}$, $Co^{II}$, $Ni^{II}$, $Cu^{II}$, and $Zn^{II}$. A trigonal bipyramidal $CuCl_5^{2-}$ also is known. When the metal is bonded to carbon as in cyanides or carboxyls, or to sulfur, phosphorus, arsenic, and several other easily polarized atoms such as metal atoms themselves, unusual structures appear to be the rule rather than the exception. Chemists are just beginning to find out why."

**COORDINATION NUMBERS**

In a systematic way we will now explore some of the different symmetries that are observed when varying numbers of ligands are attached or coordinated to one metal ion.

**COORDINATION NUMBER TWO**

Compounds of the type $ML_2$ may be linear or bent. In the former case all bonding properties must be the same on rotation by any angle about the molecular axis and on inversion through the center of the molecule (Figure 1-4). With a bent molecule, rotation producing an indistinguishable structure is restricted to $2\pi/2$ rad ($180^\circ$) about an axis through M and bisecting the $L-M-L$ angle. No center of symmetry exists. Moleculeally isolated, condensed-phase (solid or liquid) transition* metal compounds having linear or bent shapes are quite rare. However, some vapor-phase species such as gaseous $ZnI_2$ are known by structural

* Transition elements are defined in Chapter 2.
studies to be linear. Gaseous MCl₂ species with M = Mn^{II}, Fe^{II}, Co^{II}, Ni^{II}, and Cu^{II} are also thought to be linear from spectroscopic studies. Nontransition metal compounds of both structural types are known; H₂S and F₂O are examples of bent compounds, while CO₂ and CS₂ are representative of the linear ML₂ shape.

COORDINATION NUMBER THREE

Either a trigonal planar or a pyramidal shape is expected for ML₃ (Figure 1-5). Both structures have an axis about which a
rotation by either $2\pi/3$ or $4\pi/3$ (120° or 240°) leads to an equivalent structure. The trigonal planar compound also has a symmetry plane which contains all four atoms. Three-coordinate transition metal compounds also are rather uncommon in the condensed phase. Some complexes of CuI, AgI, and HgII are thought to contain essentially a trigonal planar coordination. The species BF₃ and PF₃ are examples of nontransition metal compounds with established planar and pyramidal geometries, respectively.

**COORDINATION NUMBER FOUR**

Two idealized structures are observed for the coordination number four. These are the tetrahedral and square planar arrangements of ligands (Figures 1-6 and 1-7). Since the tetrahedron can be inscribed in a cube, the structure is called “cubic.” This always implies the presence of considerable symmetry. In particular, there are four three-fold rotation axes in every cubic structure (Figure 1-6). These are the principal axes of a tetrahedron. Rotation about these axes by $2\pi/3$ rad or multiples thereof makes the rotated species indistinguishable from the original. There is no center of symmetry in the tetrahedron. Many tetrahedral transition metal compounds are known, especially with anionic halide or

![Figure 1-6](image)

*Figure 1-6* Tetrahedral and octahedral coordination showing the presence of four three-fold axes.
pseudohalide ligands, as indicated earlier. Nickel tetracarbonyl, Ni(CO)$_4$, also is tetrahedral.

A planar ML$_4$ stereochemistry is very commonly observed with bivalent platinum, palladium, copper, and nickel, and nearly always with trivalent gold. Certain chelate* ligands such as

\[
\begin{array}{c}
\text{R} \\
\text{S} \\
\hline
\text{C}
\end{array}
\]

\[
\begin{array}{c}
\text{R} \\
\text{S} \\
\hline
\text{C}
\end{array}
\]


tend to promote the formation of planar compounds with many metal ions.

The square planar† ML$_4$ structure is characterized by a principal four-fold rotation axis (2\pi/4) with four two-fold rotation axes perpendicular to it (Figure 1-7). A center of symmetry also exists. Often planar compounds are found in which three two-fold axes (two in the plane, one from $C_4$), the symmetry plane, and the center are preserved, but the four-fold rotation axis and two two-fold axes of the square are missing. An example is trans-Pt(NH$_3$)$_2$Cl$_2$, neglecting hydrogen atoms.

---

* The word chelate, χελάτo, from the Greek, means claw of a crab.
† While “square” requires “planar,” the use of “square planar” by chemists is so common that no effort will be made to change this practice here.
Exercise 1-1

A square planar structure can be achieved from a tetrahedral one (and vice versa) by a twist or rotation about the two-fold axis of two ligands relative to the other two ligands. A clockwise twist may lead to a different isomer from that produced by a counterclockwise twist. Consider a tetrahedral Mabcd complex with $C_{2a}$ bisecting angle $a$—$M$—$b$, $C_{2b}$ bisecting $c$—$M$—$b$, and $C_{2c}$ bisecting $b$—$M$—$d$. How many different planar isomers are produced from the two (optical) tetrahedral isomers? Draw them.

COORDINATION NUMBER FIVE

A five-fold rotation axis $(2\pi/5)$ has not been found in a compound in which the metal has a coordination number of five. However, the square pyramidal structure (Figure 1-8) is present in some transition metal compounds. While few transition metal compounds with five identical ligand atoms have this shape,* several compounds of the type $\text{MAB}_4$ are known which approximate it. An X-ray structural determination has shown, for example, that $\text{VO} (\text{AcAc})_2$ (Figure 1-9) has nearly a square pyramidal arrangement of the oxygens about the metal. The interaction of planar $\text{Cu}^{II}$ compounds with bases such as pyridine, $\text{C}_5\text{H}_5\text{N}$, may give similarly structured compounds.

A well-known example of a trigonal bipyramidal five-coordinate transition metal compound (Figure 1-10) is iron pentacarbonyl, $\text{Fe} (\text{CO})_5$. In this compound, the principal rotation axis is three-fold. In addition to three two-fold axes perpendicular to the three-fold axis, there are four mirror planes, each containing three carbonyls and the iron. The three ligands at the corners of the equilateral triangle perpendicular to the three-fold axis are called equatorial ligands; the other two are called axial.

COORDINATION NUMBER SIX

In addition to the octahedral structure which is very common, the trigonal prismatic structure (Figure 1-1) is also known. The

* One type of $\text{Ni(CN)}_3^{2-}$ ion in $[\text{Cr(NH}_3\text{CH}_2\text{CH}_2\text{NH}_3]_2[\text{Ni(CN)}_3] \cdot 1.5 \text{ H}_2\text{O}$ has a square pyramidal $\text{NiL}_5$ structure, while another is a distorted trigonal bipyramid.
Figure 1-8 Square pyramidal structure.

Figure 1-9 Vanadylacetylacetonate, VO(AcAc)₂.

Figure 1-10 Trigonal bipyramidal structure.
best example of this arrangement is found in crystalline MoS₂. A few sulfur ligand complexes besides Re[SixC₆(C₅H₅)₂]₃ also are thought to have a similar arrangement of atoms around the metal. In this structure, there are three two-fold rotation axes perpendicular to the three-fold axis; four symmetry planes are also present.

COORDINATION NUMBER EIGHT

Three important structural arrangements have been found for compounds in which the coordination number of the metal atom is eight, with identical ligands. These are the square antiprismonic configuration typified by TaF₇⁻⁺, the dodecahedral structure found in Mo(CN)₆⁻⁺ (Figure 1-11) and the cube. A cubic structure has been observed recently for the anions in Na₂MF₈, M = U, Pa, Np. In the dodecahedral structure there exist three two-fold rotation axes and two mirror planes. In the square antiprismonic configuration the principal rotation axis is four-fold. No inversion center is present in either structure.

The symmetry operations of a cube are identical to those of the octahedron. A tetrahedron displays only one-half of these operations.

![Diagram of coordination number eight structures](image)

**Figure 1-11** Square antiprismonic and dodecahedral ML₈ structures.

**Exercise 1-2** By means of a molecular model, prove to yourself that an inversion center combined with all the symmetry
Figure 1-12  The symmetric, face-centered trigonal prism $ML_9$ structure of the ReH$_9^{2-}$ anion in $K_2ReH_6$.

present in a tetrahedron produces the symmetry operations of an octahedron.

Hint Remember that a tetrahedron can be inscribed in a cube.

COORDINATION NUMBERS SEVEN, NINE, AND HIGHER

Since the number of transition metal compounds having these coordination numbers definitely established is limited [some examples are $NbF_7^{2-}$, $TaF_7^{2-}$, and $Nb(H_2O)_{8+}$], the various idealized structures observed will not be described here. However, it is apparent that a trigonal prismatic compound containing atoms in the centers of the rectangular faces represents a reasonably high symmetry (Figure 1-12). The anion $ReH_9^{2-}$ has such a structure.
SYMmetry CLASSIFICATION

As we have observed, the presence of rotation axes, inversion centers, etc. in a molecular structure implies that certain movements of the molecule, symmetry operations, produce structurally identical orientations. These symmetry operations are a direct result of the presence of various symmetry elements, the rotation axes, inversion center, etc. With the square planar PtCl$_4^−$ anion, the presence of the four-fold rotation axis perpendicular to the plane of the molecule (see Figure 1-7) means that the molecule can be rotated around this axis by 90° (2π/4), 180° (2 × 2π/4), 270° (3 × 2π/4), and 360° (4 × 2π/4) to produce an equivalent or, in the latter case, an identical configuration. This axis is labeled C$_4$ or simply 4. In general, a C$_n$ or n operation* implies rotation by 2π/n rad.

In addition to the symmetry elements we have already considered, there is one additional element called an improper rotation axis. We speak of n-fold improper rotation axes, S$_n$. (The proper rotation axis is C$_n$.) The operation implied by the improper rotation axis is defined as a rotation by 2π/n rad about the axis followed by reflection through a plane perpendicular to this axis. If an equivalent structure results, an S$_n$ axis is present.

If we examine one of the three-fold rotation axes present in an octahedron (Figure 1-6), we see that it is also a six-fold improper rotation axis, S$_6$. Rotation about this axis by 60° (2π/6) followed by reflection in a (hypothetical) plane perpendicular to this axis produces an equivalent structure. Repeating this process six times brings the figure back to its original configuration. This would not be true, however, if n were odd. In such cases, we must repeat the operation 2n times before the structure returns to the original configuration.

Table 1-1 contains a summary of the symmetry elements used to describe molecular structures, together with their required symmetry operations. Two additional symmetry elements are necessary to completely describe three-dimensional crystalline solids, since translational symmetry may be present. To discuss molecular bonding, however, we need consider only those operations which do not change the position of the molecule in space. This means that some point in the molecule, real or imagined, is not moved by any of the symmetry operations associ-

* Spectroscopists use C$_n$, the Schoenflies notation, while crystallographers use the Arabic numeral n, the Hermann–Mauguin notation, to describe an n-fold axis.
Symmetry Point Groups

Table 1-1 Symbols (Hermann–Mauguin and Schoenflies) for symmetry elements and their implied operations

<table>
<thead>
<tr>
<th>Element</th>
<th>Operation</th>
</tr>
</thead>
<tbody>
<tr>
<td>$n, C_n$</td>
<td>Rotation by $2\pi/n$ rad</td>
</tr>
<tr>
<td>$i$</td>
<td>Inversion through a symmetry center</td>
</tr>
<tr>
<td>$S_n$</td>
<td>Rotation by $2\pi/n$ rad followed by reflection through a plane perpendicular to $S_n$ (Schoenflies notation only)</td>
</tr>
<tr>
<td>$n_i$</td>
<td>Rotation by $2\pi/n$ rad followed by inversion (Hermann–Mauguin notation only)</td>
</tr>
<tr>
<td>$m, \sigma$</td>
<td>Reflection through the symmetry plane</td>
</tr>
</tbody>
</table>

ated with the molecule—thus, we speak of a point symmetry. In the case of the planar PtCl$_4^-$, this point and the Pt atom coincide. In fact, with many transition metal compounds, the transition metal itself is at this point. When translations are also considered, we speak of space symmetry.

SYMMETRY POINT GROUPS

A collection of elements related by certain specific rules constitutes an abstract mathematical group. We will state explicitly what these rules are and leave a detailed discussion of their origin to more advanced texts.*

1. “The product of any two elements in the group and the square of each element must be an element in the group.” (CLOSURE)
2. “One element in the group must commute with all the others and leave them unchanged.” (IDENTITY)
3. “The associative law of multiplication must hold.” (ASSOCIATIVE)
4. “Every element must have a reciprocal which is also an element of the group.” (RECPROCAL)

In classifying molecules into point groups it is necessary to realize that an element as referred to in the above rules means

* Since this is a chemistry book, the statements of F. A. Cotton as found in “Chemical Applications of Group Theory,” Wiley (Interscience), New York, 1963, have been used.
a symmetry operation—in other words, action. It should not be confused
with a static element of symmetry discussed previously which indicates
some particular symmetry operation or operations such as a $C_n$ axis. The
elements of rule 1 for a group containing only a $C_n$ axis are the rotations
$C_n$, $C_n^2$, $C_n^3$, $C_n^4$, $C_n^5$, $C_n^6$, $C_n^7$, $C_n^8$, $C_n^9$, $C_n^{10}$.
The mathematical terms such as “product,” “commute,” “associative,” and “reciprocal” will be familiar to most
readers. However, to avoid confusion they will be used only in the following
manner in this book.

The product of the multiplication of elements is the result
obtained by carrying out the implied operations in the order specified. Hence
the product of rotation by $2\pi/4$ with itself is consecutive rotation twice
by $2\pi/4$ or rotation by $\pi$. Thus, $C_4 \times C_4 = C_4^2 = C_2$.

The order in which we carry out the operations may be
important since not all operations will commute. With commutating oper-
ations, $AB$ equals $BA$. However, a reflection followed by rotation will not
always give the same product as a rotation followed by a reflection (unless
the plane of reflection is perpendicular to the rotation axis). Hence these
operations do not always commute, $AB \neq BA$.

An associative law means that we can arrange the elements
together in whatever way we choose providing the order is preserved. Hence
$A \times B \times C \times D$ equals $(A \times B) \times (C \times D)$ or $A \times (B \times C \times D)$, etc.

In algebra the product of a number with its reciprocal
is one. For symmetry groups, an operation ($A$) followed by its reciprocal
($A^{-1}$) leads to a configuration identical to the original. The resultant element
(symmetry operation) is called the identity, $E$. All mathematical groups
must have such an element. This element commutes with all others. For
symmetry groups, $E$ is the element implied in rule 2.

**MULTIPLICATION OF SYMMETRY OPERATIONS**

To see how the rules of group theory can be applied
to molecules and also to introduce some of the symbolism which is associated
with point groups, we consider the symmetry found in the interesting
“sandwich” structure of ferrocene (Figure 1-13). This structure, a twisted
pentagonal prism, contains a five-fold principal rotation axis coincidental
with the axis labeled $z$. The presence of this $C_5$ axis requires that rotation
by $m \times (2\pi/5)$, where $m = 2, 3, 4, and 5$, gives configurations indistin-
guishable from the first one. The last rotation, $C_5^0$, is symbolized by $E$,
the identity operation, since it leaves the molecule unchanged. Along with
the five-fold rotation axis, $z$ contains a ten-fold improper rotation axis. Rotation by $2\pi/10$ ($36^\circ$) followed by reflection in a plane perpendicular to this axis carries the molecule into an equivalent, indistinguishable structure. This ten-fold rotation–reflection axis* is labeled $S_{10}$. As with $C_5$, various products of $S_{10}$ with itself must lead to indistinguishable configurations. However, some of the $(n - 1)$, nine, new operations we might expect to find are not labeled as multiples of $S_{10}$. For example, "$S$ ten taken five times," $S_{10}^5$, gives the same result that would be obtained by inversion, $i$. This operation is labeled $1$, "bar one" in the crystallographic notation. The presence of the symmetry element requires the operation and vice

* Or it is a five-fold rotation–inversion axis, $\bar{5}$ ("bar five").
versa. We will use the rotation–reflection terminology throughout most of this text, but the reader should be able to work with either system.

Parallel to the $C_5$ (or $S_{10}$) axis in ferrocene are five mirror planes. The presence of any one such plane containing a $C_n$ axis requires that $(n - 1)$ additional symmetry planes also contain this axis. These $n$ planes are labeled $\sigma_v$ or $\sigma_d$, depending on whether the planes contain two-fold axes perpendicular to $C_n$ ($\sigma_v$) or bisect the angle between such axes ($\sigma_d$). Rotation of a $\sigma_v$ plane by $C_n$ will produce the other $\sigma_v$ planes. If $\sigma_d$ planes are present, rotation by $C_n$ will generate each of these from an initial one. Only one set of vertical planes is present in ferrocene (Figure 1-13). These are $\sigma_d$ planes, since they bisect the angle between the $C_2$ axes. In planar PtCl$_4^-$ (Figure 1-7) both $\sigma_v$ and $\sigma_d$ planes are present. A plane perpendicular to the principal rotation axis is given the special symbol $\sigma_h$ (horizontal). No such plane is present in ferrocene, but there is one in PtCl$_4^-$.

The presence of one two-fold axis perpendicular to the $C_5$ axis in ferrocene requires that four more $C_2$ axes be present. Rotation by $2\pi/5$ about $z$ carries one such $C_2$ axis into another.

In summary, the following twenty symmetry operations are present in the structure of the molecule ferrocene: $E$, $C_5$, $S_{10}$, $C_2^1$, $C_5^2$, $C_5^3$, $C_5^4$, $S_{10}$, $S_{10}^0$, $i(S_{10}^0)$, $S_{10}^7$, $S_{10}^9$, five $\sigma_d$'s, and five $C_2$'s. Taken together, these constitute the symmetry operations of the point group labeled $D_{4d}$.* By appropriate combination of these operations, it is easy to construct a multiplication table and prove to yourself that the operations listed for $D_{4d}$ constitute a mathematical group. Table 1-2 is the multiplication table for the point group $C_{2v}$. Here each of the four operations leads to $E$ when combined with itself. Thus $E$ appears on the diagonal. In constructing multiplication tables, it is assumed that the product operation appearing at the intersection of any column with any row transforms an

* In point group tables or character tables, the elements are grouped according to the classes to which they belong.

<table>
<thead>
<tr>
<th>Group $C_{2v}$</th>
<th>$E$</th>
<th>$C_2$</th>
<th>$\sigma_v(xz)$</th>
<th>$\sigma_v(yz)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E$</td>
<td>$E$</td>
<td>$C_2$</td>
<td>$\sigma_v$</td>
<td>$\sigma_v'$</td>
</tr>
<tr>
<td>$C_2$</td>
<td>$C_2$</td>
<td>$E$</td>
<td>$\sigma_v'$</td>
<td>$\sigma_v$</td>
</tr>
<tr>
<td>$\sigma_v(xz)$</td>
<td>$\sigma_v$</td>
<td>$\sigma_v'$</td>
<td>$E$</td>
<td>$C_2$</td>
</tr>
<tr>
<td>$\sigma_v'(yz)$</td>
<td>$\sigma_v'$</td>
<td>$\sigma_v$</td>
<td>$C_2$</td>
<td>$E$</td>
</tr>
</tbody>
</table>
Object in exactly the same way that the object would be transformed by sequentially performing the operations given at the top of the column and the left-hand side of the row. In the \( C_{2v} \) point group all operations commute with each other, for example, \( \sigma_v(zz) C_2 = C_2 \sigma_v(zz) \), and such a group is called Abelian. However, most groups of interest to us do not have this property.

**POINT GROUP SYMMETRY**

The point group to which a particular molecular structure belongs now can be determined in a systematic manner. The line chart Figure 1-14 indicates the procedure we will follow. First look for special types of symmetry such as are characterized by linear, cubic, and icosahedral structures. The linear molecule which contains a center of symmetry belongs to the point group \( D_{nh} \); otherwise it is in \( C_{nv} \). The infinity symbol implies that an infinite number of vertical planes may contain the molecule. Since the cubic groups \( T, O, T_d \) (tetrahedral), \( O_h \) (octahedral), and \( T_h \) require the presence of four tetrahedrally oriented three-fold axes, this symmetry is readily recognized, and so is the regular icosahedron, \( I_h \), which has six five-fold axes.

Molecules which do not display any type of rotation axes belong to \( C_{s}, C_{i}, \) or \( C_{1} \). In the latter case there is no symmetry at all; for the others only one element of symmetry is present in addition to the identity element. These point groups are groups of order two; that is, they have only two elements.

If the only symmetry operations present in addition to an \( n \)-fold rotation axis are \( 2n \)-fold improper rotations, the point group is \( S_{2n} \).

The presence of \( n \) two-fold rotation axes perpendicular to the principal axis* places the molecule in a \( D \) point group—either \( D_{nh}, D_{nd}, \) or \( D_{n} \). The subscripts indicate the symmetry planes, if any, that are present. Without the two-fold axes, the molecule belongs to \( C_{nh}, C_{nv}, \) or \( C_{n} \), and again the subscripts indicate the presence or absence of symmetry planes.

The Schoenflies notation for a point group specifies the minimum symmetry required to define a particular point group. This

* Sometimes the principal axis is not unique, as for example in \( D_{2} \) or \( T \). In such cases the choice of axis to be called principal is arbitrary.
Figure 1-14 Line chart identification of point group symmetry.
fact is recognized quickly by the use of a mnemonic called a stereographic projection. (Stereographic projections originally were developed to describe crystal faces, but these details need not concern us here.) We will use stereographic projections simply to represent the symmetry operations present in point groups.

As an example of stereographic projection construction we consider the point group $D_{4h}$ (Figure 1-15). The symmetry present

![Diagram of stereographic projections]

**Figure 1-15** Construction of the stereographic projection for the symmetry operations found in $D_{4h}$. (Reproduced by permission of the International Union of Crystallography.)
will be indicated by symbols on a circle (Figure 1-15a). The z axis projects from the center of the circle. It contains the four-fold rotation axis and is given the symbol of a solid square, the appropriate regular polygon symmetric to rotation by $2\pi/4$ (Figure 1-15b). A two-fold axis is specified by a solid ellipse, a three-fold axis by a solid triangle, etc.

The point group $D_{4h}$ requires the presence of a two-fold axis (Figure 1-15c) and a mirror plane perpendicular to the four-fold axis. The mirror plane is indicated (Figure 1-15d) by the heavy circle. Now, by placement of a general point $O\ (x, y, z)$ as in Figure 1-15d, the three symmetry elements already listed cause the generation of fifteen other points (Figure 1-15e). Eight of the sixteen points lie above the plane of the paper and are labeled $O$, while those below are given the symbol $X$. It is now easy to add the other symmetry operations suggested by the arrangement of $O$'s and $X$'s. Heavy lines represent planes, and the hole in the polygon indicates a center of symmetry. The number of points in the projection is equal to the number of symmetry operations present in the point group—its order.

An additional symbol is used when a rotation–reflection axis and a rotation axis are collinear but of different order. The rotation–reflection axis is labeled with an “empty” polygon, while the rotation axis is represented by the solid figure. Thus

indicates collinear $S_6$ and $C_3$ axes. Cubic groups require the introduction of additional curved lines that intersect at positions representing the corners of a cube inscribed within a sphere. The symbol for the point group T is presented in Figure 1-16.

![Figure 1-16](image)
Exercise 1-3  By means of a stereographic projection, develop the multiplication table for the point group C\textsubscript{3v}.

Example  For C\textsubscript{3v}, the stereographic projection is

![Stereographic projection diagram]

From this figure it is apparent that C\textsubscript{3} (\sigma'\textsubscript{v}) [point a] is \sigma'\textsubscript{v} [point a] = point b, followed by C\textsubscript{3} [point b] = point d. The same result is obtained by (\sigma\textsubscript{v}) [point a] = point d. Thus, C\textsubscript{3} (\sigma'\textsubscript{v}) = \sigma\textsubscript{v}, etc.

Exercise 1-4  Deduce the point group for the molecular structures pictured in Figures 1-1, 1-2, 1-8, 1-9, and 1-12.

Exercise 1-5  The anion NiBr\textsubscript{4}\textsuperscript{2-} belongs to the point group T\textsubscript{d} as a regular tetrahedron. Distortion of the anion by stretching one Ni—Br bond without bending the bonds and while leaving the other three bonds alone reduces the symmetry. Stretching two bonds simultaneously reduces the symmetry further. Considering all possible Ni—Br extensions, what point groups describe the structures? What point groups describe the structures of species in which Ni—Br bonds are allowed to be compressed relative to the equilibrium bond length?

Exercise 1-6  Carbon monoxide is linear, as is CO\textsubscript{2}. What symmetry feature distinguishes these two molecules? Would this be true if CO\textsubscript{2} were C—O—O?

Exercise 1-7  A bunch of marbles on a tray can be made to pack together with all marbles in maximum contact. Maximum
density is achieved with a very symmetric structure. What is the highest-order rotational axis found perpendicular to the tray? What others are present? Can a five-fold axis appear in any packing arrangement which has a well-defined number of marbles in a group which repeats as a unit on the whole tray?

Exercise 1-8

By means of models, deduce the symmetry operations present and the point group for the following molecular species:

(a) Tetrahedral NiBrCl$_3^-$
(b) Octahedral $cis$-CoCl$_4$F$_2^-$
(c) Octahedral $trans$-CoCl$_4$F$_2^-$
(d) Linear HgCl$_2$
(e) Bent H$_2$S
(f) Tetrahedral CoCl$_4^{2-}$
(g) Planar $cis$-PtCl$_2$Br$_2^{2-}$
(h) Planar $trans$-PtCl$_2$Br$_2^{2-}$
(i) Trigonal bipyramidal PF$_3$
(j) Trigonal bipyramidal $cis$-PF$_3$Cl$_2$
(k) Trigonal bipyramidal $trans$-PF$_3$Cl$_2$
(l) Square pyramidal CuCl$_5^{2-}$

Exercise 1-9

Sketch a stereographic projection for the point group $D_3$. Add a center of symmetry to the figure. What new points are developed? To what point group does the new figure belong?

SUPPLEMENTARY READING