

## Chemical Applications of Topology and Group Theory

### 13. Chirality and Framework Groups [1]

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Pople has recently introduced the concept of a *framework group* to specify the full symmetry properties of a molecular structure. Furthermore, Pople has developed powerful algorithms for the use of framework groups to generate all distinguishable skeletons with a given number of sites. This paper studies the systematics of chirality arising from different framework groups. In this connection framework groups can be classified into four different types: linear, planar, achiral, and chiral. Chiral framework groups lead to chiral systems for any ligand partition including that with all ligands equivalent. Linear framework groups are never chiral even for the ligand partition with all ligands different. Planar framework groups are also never chiral since all sites are in the same plane, which therefore remains a symmetry plane for any ligand partition. However, the mirror symmetry of the molecular plane of a planar framework group can be destroyed by a process called polarization; this process can be viewed as the mathematical analogue of complexing a planar aromatic hydrocarbon to a transition metal. The chirality of four-, five-, and six-site framework groups is discussed in terms of the maximum symmetry ligand partitions resulting in removal of all of the symmetry elements corresponding to improper rotations  $S_n$  (including reflections  $S_1$  and inversions  $S_2$ ) from achiral and polarized planar framework groups. The Ruch-Schönhofer group theoretical algorithms for the calculation of chiral ligand partitions and pseudoscalar polynomials of lowest degree ("chirality functions") are adapted for use with these framework groups. Other properties of framework groups relevant to a study of their chirality are also discussed: these include their transitivity (i.e. whether all sites are equivalent or not), their normality (i.e. whether proper rotations correspond to even permutations and improper rotations correspond to odd permutations), and the number of sites in their symmetry planes.

**Key words:** Framework groups – Chirality functions – Pseudo scalar measurements – Symmetry – Chiral representations.

## 1. Introduction

Many properties of interest to chemists (e.g., optical rotation and circular dichroism) are related to *pseudoscalar measurements*. Such measurements give real numbers which have the following two properties [2]:

- (1) They depend upon the measured object but not its orientation in space.
- (2) They have opposite signs for mirror images such as the two enantiomers of a chiral molecule.

The interest in pseudoscalar measurements makes of chemical significance the geometrical and algebraic study of chirality with the following objectives:

- (1) The systematics of the molecular skeletons and ligand partitions leading to chiral systems, i.e. systems having non-superimposable mirror images and therefore belonging to molecular point groups having no improper rotation symmetry elements [3] including mirror planes ( $S_1 \equiv \sigma$ ) and inversion centers ( $S_2 \equiv i$ ).
- (2) The determination of mathematical functions by which the magnitude and sign of a given pseudoscalar property (the dependent variable) can be calculated for a given skeleton using parameters which depend only upon the ligands located at specific sites on the skeleton (the independent variables). Such mathematical functions are called chirality functions.

The development of the theory of chirality functions was pioneered by Ruch and Schönhofer [4, 5]. A general outline of the algebraic aspects of this theory has been presented by Ruch [2]. A more detailed summary of the mathematics underlying this theory has been presented by Mead [6]. The relative complexity of some of the mathematics has led to considerable confusion over certain specific issues (e.g., qualitative completeness [7–10] and hyperchirality [11–16]) which this paper will try to avoid as much as possible.

The original objective of the work outlined in this paper was the systematic determination of the chiral ligand partitions for skeletons represented by coordination polyhedra, whose topology [17] and symmetry [18] have been previously studied by the author. However, during the course of this work a publication by Pople [19] on framework groups suggested a considerably more elegant approach. His concept of framework groups provides a systematic and powerful method for generating *all* possible skeletons having a given number of sites and distinguishable symmetries. This paper thus presents for the first time detailed information on the chiral ligand partitions for all distinguishable skeletons having four, five, and six sites. In addition, sufficient information is presented on the associated chirality functions of a specific type (pseudoscalar polynomials of lowest degree [2]) so that such functions can be determined with relative ease.

## 2. Symmetry and Framework Groups

Consider a molecule of the type  $ML_n$  in which  $M$  is a metal or other central atom and the  $n$  ligands  $L$  may or may not be equivalent but cannot be chiral

[6]. Removal of the  $n$  ligands  $L$  from  $ML_n$  leads to what may be called the *skeleton* [11]. The symmetry of the skeleton is regarded as that of the framework group [19] based on the locations of the  $n$  ligands  $L$ . Furthermore, the *ligand partition* of a given molecule  $ML_n$  and the *site partition* of the underlying skeleton may be represented by symbols of the type  $(a_1^{b_1} a_2^{b_2} \dots a_k^{b_k})$  where  $a_k$  and  $b_k$  are small positive integers and  $a_m > a_{m+1} (l \leq m \leq k)$ . In this symbol for the ligand partition there are  $b_k$  sets of  $a_k$  identical ligands. Thus a ligand partition  $(n)$  refers to an  $ML_n$  complex in which all  $n$  ligands  $L$  are equivalent. Similarly in this symbol for the site partition there are  $b_k$  different sets of  $a_k$  equivalent sites on the skeleton. Thus a site partition  $(n)$  refers to a skeleton in which all  $n$  sites are equivalent. Such a skeleton with all sites equivalent is called a *transitive* skeleton since its point group operates transitively [20] on the sites. A framework group which is not transitive is called *intransitive*. An intransitive framework group has more than one *orbit*, where an orbit is a set of sites interchanged among each other in some way by symmetry operations in the point group. The number of sites in an orbit is called the *length* of the orbit.

This terminology can be illustrated by the trigonal bipyramidal complex  $MA_2BCD$  in which the ligand partition is  $(21^3)$  and the site partition is  $(32)$ . In the latter symbol the “3” refers to the three equivalent equatorial sites of the trigonal bipyramid and the “2” refers to the two equivalent apical sites of the trigonal bipyramid.

The framework groups of Pople [19] specify the symmetry of bodies containing a finite number of particles. Framework groups can be described using a general notation [19] specifying the underlying point group in Schoenflies notation [2] followed by an indication of the location of each of the particles in terms of subspaces relating to the symmetry elements of the underlying point group. The subspaces can be classified by their dimensionalities as follows:

*0-dimensional*: a central point (e.g., center of inversion (i) or intersection of a rotation axis with another rotation axis or a perpendicular plane of symmetry) designated as  $O$ .

*1-dimensional*: a rotation axis ( $C_n$ ) designated by  $C_n$  where  $n$  is the order of the rotation.

*2-dimensional*: a reflection plane ( $\sigma$ ) designated by  $\sigma_h, \sigma_v,$  or  $\sigma_d$  depending upon its location in the point group.

*3-dimensional*: the remaining part of full space external to any of the symmetry elements of the point group – designated as  $X$ .

The location of any given particle in the framework group (designated as  $L$  in this paper) is specified in terms of the subspace of the *lowest* possible dimensionality. This leads to the preference order  $O > C_n > \sigma > X$ .

Using this terminology the framework group of the trigonal bipyramid can be expressed as  $D_{3h}[C_3(L_2), 3C_2(L)]$  where the  $C_3(L_2)$  means that the two axial sites are located on the  $C_3$  axis and the  $3C_2(L)$  means that each of the three equatorial sites are located on a different  $C_2$  axis. Pople [19] lists all of the framework groups with up to six sites using this designation.

The symmetry operations in a framework group with  $n$  points can be regarded as permutations of the  $n$  points. There are a total of  $n!$  different possible permutations of the  $n$  points which form a group called the symmetric group generally [21] written as  $S_n$  but written here [18] as  $P_n$  to avoid confusion with the  $S_n$  symbol for improper rotation axes [3]. In the case of the regular tetrahedron, framework group  $T_d[4C_3(L)]$ , the symmetry group is isomorphic to the corresponding symmetric group  $P_4$ . However, all of the other framework groups having  $n$  sites where  $n \geq 4$  do not contain the full  $n!$  symmetries of the corresponding symmetric groups  $P_n$  but contain symmetries corresponding to a subgroup of  $P_n$  (*never a normal* subgroup for  $n \geq 5$  because the alternating groups  $A_n$  ( $n \geq 5$ ) are all simple [21]). Naturally the order (number of elements) in a framework group with  $n$  sites must be a factor of  $n!$  in accord with a fundamental theorem of group theory [21].

Framework groups may also be characterized by their *cycle indices* [22]  $Z(G)$  which are polynomials of the form

$$Z(G) = \sum_{i=1}^{i=c} a_i x_1^{c_i} x_2^{c_i^2} \dots x_n^{c_i^n}. \quad (1)$$

In this equation the terms and indices have the following significance:

$n$  = number of sites in the framework group.

$c$  = number of terms in the cycle index. If the framework group is isomorphic to  $P_n$  then each term corresponds to a conjugacy class.

$a_i$  = number of elements of the framework group with the indicated cycle structure.

$x_k$  = dummy variable referring to cycles of length  $k$ .

$c_{ik}$  = exponent indicating the number of cycles of length  $k$  in term  $i$ .

An individual symmetry element of a framework group may also be represented by its *cycle partition*, which is a symbol of the type  $(k^{c_k}[k-1]^{c_{k-1}}[k-2]^{c_{k-2}} \dots 1^{c_1})$  where  $c_k$  refers to the number of cycles of length  $k$  and all non-existent cycle lengths are omitted from the symbol. In any cycle partition for symmetry operations in a framework group having  $n$  sites, the following equation will hold:

$$\sum_{i=1}^{i=k} ic_i = n. \quad (2)$$

Cycle partitions have a similar general appearance to the ligand partitions and site partitions outlined above. For example, the  $C_3$  rotations in the trigonal bipyramid  $D_{3h}[C_3(L_2), 3C_2(L)]$  have the cycle partition  $(31^2)$ .

The parity of a permutation or symmetry element expressed by a given term of the cycle index or by a cycle partition is odd or even depending upon whether the *total* number of cycles of *even* length is odd or even, respectively. This relates to the parity of the number of two-site transpositions [23] in the permutation

in question. Any permutation group contains either only even permutations or equal numbers of even and odd permutations.

A system which contains no improper rotation axes  $S_n (n \geq 1)$  in its symmetry group is defined as chiral. Systems containing one or more improper rotation axes are thus achiral. In this context the improper rotation axes  $S_1$  and  $S_2$  correspond to a reflection plane  $\sigma$  and an inversion center  $i$ , respectively. Furthermore, a framework group in which a symmetry element is odd if and only if it corresponds to an improper rotation axis  $S_n (n \geq 1)$  may be called *normal*; if this is not the case the framework group may be called *abnormal*.

All achiral framework groups with six or fewer sites other than those having the  $C_i$  point group contain one or more reflection planes  $\sigma$ . These reflection planes can be classified into two types: separating planes and non-separating planes. A *separating plane* in a framework group having  $n$  sites contains exactly  $n - 2$  of these sites. Conversely, a reflection plane containing less than  $n - 2$  sites in a framework group with  $n$  sites is a non-separating plane. Achiral framework groups with at least one reflection plane in which *all* reflection planes are separating planes have been called *shoe-like* framework groups by Ruch [2] since left-handed and right-handed enantiomers can be readily distinguished like left and right shoes. The trigonal bipyramid framework group  $D_{3h}[C_3(L_2), 3C_2(L)]$  is an example of a shoe-like framework group since all four reflection planes ( $\sigma_h + 3\sigma_v$ ) contain exactly 3 ( $= 5 - 2$ ) sites. Framework groups which are not shoe-like have been called *potato-like* by Ruch [2] since although potatoes are chiral, left-handed and right-handed potatoes cannot be distinguished. Shoe-like skeletons are also called "category *a*" and potato-like skeletons are also called "category *b*" by Ruch [2].

In most cases of chemical significance shoe-like framework groups are normal and potato-like framework groups are abnormal. Exceptions to this rule occur only when the number of sites of the framework group becomes large enough so that there are *non-separating* planes with *odd* numbers of *pairs* of sites outside the symmetry plane. The exceptional framework groups of this type with the least number of sites are the six-site  $C_s[X(L_6)]$  in which all three pairs of sites are outside the single symmetry plane and framework groups having  $C_7$  axes (e.g.  $C_{7v}[7\sigma_v(L)]$ ) corresponding to the  $C_7$  ring sites in  $C_7H_7V(CO)_3$  in which there is only one site in each  $\sigma_v$  plane leaving three pairs of sites outside this plane. In general  $C_4$ ,  $C_5$ ,  $C_6$ ,  $S_3$ , and  $S_6$  rotation axes lead to framework groups which are abnormal and potato-like. However, there are also relatively simple abnormal potato-like framework groups lacking these rotation axes (e.g. the rectangular bipyramid  $D_{2h}[C_2(L_2), \sigma(L_4)]$ ).

The general objective of the work outlined in this paper is the determination of how unsymmetrical the ligand partition on a framework group must be before all improper symmetry elements are destroyed to give a chiral system. For the purpose of this study framework groups can be classified into four types as follows:

(1) *Linear*. Framework groups in which all sites are located in a straight line, i.e. in a one-dimensional subspace of three-dimensional space.

(2) *Planar*. Non-linear framework groups in which all sites are located in a flat plane, i.e. in a two-dimensional subspace of three-dimensional space.

(3) *Achiral*. Non-planar framework groups in which the point group contains at least one improper rotation  $S_n$  ( $n \geq 1$ ) (including  $S_1 \equiv \sigma$  and  $S_2 \equiv i$ ).

(4) *Chiral*. Non-planar framework groups in which the point group contains no improper rotations. Chiral framework groups are of no interest in this study since they lead to chiral systems for *any* ligand partition including the ligand partition with all ligands identical. Linear framework groups are also of no interest in this study but for the opposite reason: they can never be chiral even if all ligands are different.

Achiral framework groups are the ones of greatest importance in this study since they can lead to either chiral or achiral systems by varying the ligand partitions. Within this context this paper explores the following questions:

(1) For a given achiral framework group, what ligand partitions lead to chiral systems?

(2) What are the properties of chirality functions for these chiral systems based on achiral framework groups?

In planar framework groups all sites are coplanar; the plane containing these sites can be called the *major plane* of a framework group. Any ligand partition of a planar framework group (even that with all ligands different) retains the major plane as a symmetry plane thereby never leading to a chiral system. Thus before a chiral system can be obtained from a planar framework group, the symmetry of the major plane must be destroyed by a process conveniently called *polarization*.

Consider the major plane in a planar framework group as a bisector of three-dimensional space into two three-dimensional half-spaces. Furthermore, consider one half-space to be positive and the other half-space to be negative (i.e. *polarize* the system). Then the major plane is no longer a plane of symmetry. Furthermore, if the major plane is designated as  $\sigma_h$  (which it generally is in the relevant symmetry point group), then polarization also destroys symmetry elements of the planar framework group of the type  $\sigma_h C_n$  derived by combining reflection through the major plane with *any* proper rotation. This leads to a point group of a polarized planar framework group that is half the size of the point group of the original planar framework group.

The process of polarizing planar framework groups can lead to any of the following three results:

(1) The polarized planar framework group contains no improper rotations and therefore is chiral (for any ligand partition). This case is not interesting in the context of this paper.

(2) The polarized planar framework group is identical to a framework group found by Pople's procedure [19]. For example, polarization of the planar framework group  $D_{3h}[O(L), 3C_2(L)]$  (trigonal planar+center) leads to

$C_{3v}[C_3(L), 3\sigma_v(L)]$  (trigonal pyramid) which is already on Pople's list [19]. This case also is not interesting.

(3) The polarized planar framework group is not on Pople's list [19] because of Pople's "first elimination rule". For example, polarization of the planar framework group  $D_{4h}[2C_2(L_2)]$  (planar square) leads to the polarized planar framework group  $C_{4v}[2\sigma_v(L_2)]$  not found on Pople's list [19]. This is the most important case and appears to occur when the planar framework group is transitive.

The most important application of polarization is the conversion of a planar polygonal framework group  $D_{nh}[nC_2(L)]$  into a framework group of the type  $C_{nv}[\frac{1}{2}n\sigma_v(L_2)]$  for even  $n$  or  $C_{nv}[n\sigma_v(L)]$  for odd  $n$ . This is the mathematical analogue to the chemical process of symmetrically bonding (i.e., by an  $\eta^n$ -hapto bond) a planar aromatic hydrocarbon  $C_nH_n$  ( $3 \leq n \leq 8$ ) to a transition metal. Thus whereas the benzene skeleton can never become chiral because of the molecular plane, complexing a  $Cr(CO)_3$  unit to benzene leads to a non-planar  $C_6H_6Cr(CO)_3$  skeleton which can become chiral with an appropriate ligand partition (i.e., substitution pattern) above a transitive framework group is one in which all sites are equivalent. Thus a transitive framework group with  $n$  sites has a site partition ( $n$ ). In a transitive framework group with  $n$  sites any ligand partition other than the fully symmetrical ligand partition ( $n$ ) (i.e., all ligands identical) will result in a reduction of the point group symmetry. In general, transitive framework groups have fewer chiral ligand partitions than intransitive framework groups with comparable numbers of sites.

Only relatively few framework groups are transitive. Transitive framework groups having 3 to 7 sites are listed below in order of decreasing symmetry for a given number of sites.

#### Three Sites

(1) The planar equilateral triangle  $D_{3h}[3C_2(L)]$  and its polarization  $C_{3v}[3\sigma_v(L)]$ .

#### Four Sites

- (1) The regular tetrahedron  $T_d[4C_3(L)]$ .
- (2) The planar square  $D_{4h}[2C_2(L_2)]$  and its polarization  $C_{4v}[2\sigma_v(L_2)]$ .
- (3) The planar rectangle  $D_{2h}[\sigma(L_4)]$  and its polarization  $C_{2v}[X(L_4)]$ .
- (4) The allene skeleton  $D_{2d}[2\sigma_d(L_2)]$ .

#### Five Sites

(1) The planar pentagon  $D_{5h}[5C_2(L)]$  and its polarization  $C_{5v}[5\sigma_v(L)]$ .

#### Six Sites

- (1) The regular octahedron  $O_h[3C_4(L_2)]$ .
- (2) The planar hexagon  $D_{6h}[3C_2(L_2)]$  and its polarization  $C_{6v}[3\sigma_v(L_2)]$ .
- (3) The trigonal prism  $D_{3h}[3C_2(L_2)]$  and permutationally equivalent trigonal antiprism  $D_{3d}[3\sigma_d(L_2)]$ .

### Seven Sites

(1) The regular heptagon  $D_{7h}[7C_2(L)]$  and its polarization  $C_{7v}[7\sigma_v(L)]$ .

The following observations can be made concerning this list of transitive framework groups:






(1) The order  $n$  of each  $C_n$  rotation axis ( $n > 2$ ) must be a factor of the number of sites. Therefore, transitive framework groups with a prime number  $p$  of sites require a point group having a  $C_p$  rotation axis. This means that the only transitive framework groups with a prime number of sites are the planar  $p$ -gons  $D_{ph}[pC_2(L)]$  and their polarizations  $C_{pv}[p\sigma_v(L)]$ . This is illustrated above by the transitive framework groups having 3, 5, and 7 sites.

(2) The square, rectangle, their polarizations, and all transitive framework groups having 5, 6, and 7 sites are all potato-like. All of these potato-like transitive framework groups except for the regular heptagon and its polarization are abnormal.

### 3. Ligand Partitions and Group Representation Theory

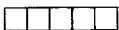






Consider a fully symmetric group  $P_n$  containing  $n!$  elements. This group contains exactly one conjugacy class [23] for each possible set of positive integers  $m_1, m_2, \dots, m_k$  whose sum  $\sum_{i=1}^k m_i = n$  (Ref. [3]). Such a set of positive integers is called a *partition of  $n$* . A given partition of  $n$  can be depicted by  $n$  boxes as indicated in Tables 1, 2, and 3 for all possible partitions of 4, 5, and 6, respectively. Such a collection of boxes is called a Young diagram. [23].

**Table 1.** Young diagrams and ligand partitions for four ligand sites

Ligand partition	Young diagram	Complex type	Chirality order (o)	Chirality index (u)	Chirality polynomial degree (g)
(4)		MA <sub>4</sub>	4	1	0
(31)		MA <sub>3</sub> B	3	2	1
(2 <sup>2</sup> )		MA <sub>2</sub> B <sub>2</sub>	2	2	2
(21 <sup>2</sup> )		MA <sub>2</sub> BC	2	3	3
(1 <sup>4</sup> )		MABCD	1	4	6



**Table 2.** Young diagrams and ligand partitions for five ligand sites

Ligand partition	Young diagram	Complex type	Chirality order (o)	Chirality index (u)	Chirality polynomial degree (g)
(5)		MA <sub>5</sub>	5	1	0
(41)		MA <sub>4</sub> B	4	2	1
(32)		MA <sub>3</sub> B <sub>2</sub>	3	2	2
(31 <sup>2</sup> )		MA <sub>3</sub> BC	3	3	3
(2 <sup>2</sup> 1)		MA <sub>2</sub> B <sub>2</sub> C	2	3	4
(21 <sup>3</sup> )		MA <sub>2</sub> BCD	2	4	6
(1 <sup>5</sup> )		MABCDE	1	5	10

In any group there is a one-to-one correspondence between conjugacy classes and irreducible representations [3], as is readily apparent from inspection of character tables. Therefore, the Young diagrams containing  $n$  boxes correspond not only to conjugacy classes of the symmetric group  $P_n$  but also to the irreducible representations of  $P_n$ .

Young diagrams can also be used to depict ligand partitions, site partitions, and cycle partitions. Of these uses of Young diagrams, their use to depict ligand partitions is important in the study of chirality. In using Young diagrams to represent ligand partitions the rows represent identical ligands. The top row is always the longest row and the left column is always the longest column.

Tables 1, 2, and 3 show the use of Young diagrams to depict all possible ligand partitions for skeletons with 4, 5, and 6 ligand sites, respectively. All Young

**Table 3.** Young diagrams and ligand partitions for six ligand sites

Ligand partition	Young diagram	Complex type	Chirality order (o)	Chirality index (u)	Chirality polynomial degree (g)
(6)		MA <sub>6</sub>	6	1	0
(51)		MA <sub>5</sub> B	5	2	1
(42)		MA <sub>4</sub> B <sub>2</sub>	4	2	2
(3 <sup>2</sup> )		MA <sub>3</sub> B <sub>3</sub>	3	2	3
(41 <sup>2</sup> )		MA <sub>4</sub> BC	4	3	3
(321)		MA <sub>3</sub> B <sub>2</sub> C	3	3	4
(2 <sup>3</sup> )		MA <sub>2</sub> B <sub>2</sub> C <sub>2</sub>	2	3	6
(31 <sup>3</sup> )		MA <sub>3</sub> BCD	3	4	6
(2 <sup>2</sup> 1 <sup>2</sup> )		MA <sub>2</sub> B <sub>2</sub> CD	2	4	7
(21 <sup>4</sup> )		MA <sub>2</sub> BCDE	2	5	10
(1 <sup>6</sup> )		MABCDEF	1	6	15

diagrams representing ligand partitions including those depicted in Tables 1, 2, and 3 can be classified by the following three parameters:

- (1) *Order* ( $o$ ): This represents the maximum number of identical ligands in the ligand partition and is simply the length of the top row.
- (2) *Index* ( $i$ ): This represents the number of different ligands in the ligand partitions and is simply the length of the left column.
- (3) *Degree* ( $g$ ): This provides a basis for ordering Young diagrams and represents the minimum degree of the corresponding ligand-specific chirality polynomial. The degree of a Young diagram can be calculated by the following equation:

$$g = \frac{1}{2} \sum_{k=1}^{k=\text{order}} c_k(c_k - 1). \quad (3)$$

In Eq. (3)  $c_k$  represents the length of column  $k$ .

Tables 1, 2, and 3 list the relevant Young diagrams in order of increasing degree. For Young diagrams with 6 or more boxes, there are cases where more than one Young diagram has the same degree. Thus both the  $(41^2)$  and  $(3^2)$  Young diagrams each of degree 3 may be regarded as the next lower Young diagram from the  $(321)$  Young diagram of degree 4 (see Table 3). In general Young diagrams with high degrees depict unsymmetrical ligand partitions of  $ML_n$  (i.e. many of the  $n$  ligands  $L$  are different from each other) and Young diagrams with low degrees depict relatively symmetrical ligand partitions (i.e. all or most of the ligands  $L$  are identical). Thus the degree of a Young diagram may be viewed as a measure of the “asymmetry” of the corresponding ligand partition.

In the study of chirality, minimum asymmetry ligand partitions leading to chiral systems based on an achiral framework group are especially significant. Such *chiral ligand partitions* represent the minimum asymmetry ligand partition (i.e. that of *lowest* degree,  $g$ ) necessary to destroy all  $S_n$  ( $n \geq 1$ ) symmetry elements (reflection planes, inversion centers, and improper rotation axes) in an achiral framework group to give a chiral system: such achiral framework groups may have more than one chiral ligand partition. This is particularly true of intransitive framework groups in which the presence of non-equivalent sites creates several distinguishable routes for the destruction of all  $S_n$  symmetry elements. These ideas will be clarified by specific examples later in this paper.

The following group theoretical algorithm has been demonstrated [4–6] to select among the irreducible representations of the symmetrical group  $P_n$ , those which have Young diagrams corresponding to *chiral* ligand partitions for a skeleton having point group  $G$ :

- (1) Initially the characters for the skeletal point group  $G$  subduced [4–6] by each irreducible representation  $\Gamma_r$  of  $P_n$  must be determined. These can be obtained from character tables of  $P_n$  by copying down the characters of each irreducible representation  $\Gamma_r$  for the operations of  $P_n$  which are also in  $G$ . In order to recognize which operation of  $P_n$  corresponds to a given operation of  $G$ , the cycle partition of the operation in  $G$  is determined and the characters of the unique operation in  $P_n$  with that cycle partition are used.

(2) The characters of the chiral representation  $\Gamma_*$  of  $G$  are determined simply by using +1 for the proper rotations ( $E, C_{n_3}$ ) and -1 for the improper rotations ( $\sigma, i, S_n$ ).

(3) Standard group theoretical methods are used to determine which representations  $\Gamma_r$  of  $P_n$  when restricted only to operations in  $G$  contain the chiral representation  $\Gamma_*$  of  $G$ . Note that representations which are irreducible in systems with full  $P_n$  symmetry are no longer necessarily irreducible when the symmetry is reduced to  $G$ .

(4) The Young diagrams corresponding to these irreducible representations of  $P_n$  correspond to chiral ligand partitions for a skeleton with point  $G$ . This skeleton may be represented by one of the framework groups [19].

The following features of the above algorithm are of interest:

(1) The chiral representation  $\Gamma_*$  of  $G$  has characters of -1 for the improper rotations  $S_n$  (including  $S_1 \equiv \sigma$  and  $S_2 \equiv i$ ) and +1 for the proper rotations  $C_n$  (including  $C_1 \equiv E$ ). In a normal framework group the chiral representation has characters of +1 for the even site permutations and -1 for the odd site permutations but such is no longer true for abnormal framework groups. Also in any symmetric group  $P_n$  the irreducible representation ( $1^n$ ) corresponding to all ligands different has characters of +1 for the even permutations and -1 for the odd permutations. As a consequence of this a framework group with  $n$  sites will have ( $1^n$ ) as a chiral ligand partition if and only if it is normal.

(2) Character tables for  $P_n$  ( $n \geq 5$ ) required for this procedure are not found in the usual places [3] since they do not correspond to three-dimensional point groups. However, character tables of  $P_n$  up to  $n = 10$  have been published [24, 25]. Mathematical methods are available [24] for determining the characters of any irreducible representations of any  $P_n$  but these get rather messy rather quickly as  $n$  exceeds 8.

(3) Reducing the symmetry of a framework group with  $n$  sites from  $G$  to a smaller (less symmetrical) point group  $H$  will have the following two general effects:

(a) The number of irreducible representations  $\Gamma_r$  of  $P_n$  containing the chiral representation  $\Gamma_*$  will be larger when restricted to  $H$  than when restricted to  $G$ . If  $H$  is a normal [21] subgroup of  $G$ , every irreducible representation  $\Gamma_r$  of  $P_n$  which contains the chiral representation  $\Gamma_*$  when restricted to  $G$  will also contain  $\Gamma_*$  when restricted to  $H$ .

(b) The degree of the lowest chiral ligand partition will be lower for  $H$  than for  $G$ . These effects relate to the obvious fact that a less symmetrical framework group requires fewer different ligands to become chiral. Thus the symmetry of the skeleton is inversely related to the chirality order  $o$  and directly related to the chirality index  $u$ .

#### 4. The Algebraic Form of Chirality Functions

In this paper we will consider chirality functions of the type  $X(s_1, s_2, \dots, s_n)$  which are polynomials of the lowest degree in ligand-specific parameters  $s$  where

$s_k$  refers to the value of the parameter for the ligand located at site  $k$  in the framework group. For such functions to be useful the value of  $s$  must depend only upon the ligand, the framework group, and the pseudoscalar property but *not* on the site where the ligand is located.

Also, of course, a valid chirality function must have equal magnitudes but opposite signs for the two members of an enantiomeric pair (i.e., mirror images).

The algebraic form of these chirality polynomials depends only upon the framework group and the ligand partition. The degree of the polynomial is the same as the degree of the corresponding ligand partition. Normally the chirality polynomials are expressed as a product and/or sum of *differences* between pairs of ligand parameters  $s_k^a - s_i^a$  ( $a$  = small integer) since this depicts most clearly the effects of ligand non-equivalences on pseudoscalar properties.

Before discussing the general group theoretical algorithm for deriving the lowest degree chirality polynomials for a given framework group and ligand partition, there are two special cases where the form of the chirality polynomial is very readily derived without using the full group theoretical algorithm. These correspond to the shoe-like framework groups and the intransitive framework groups. Use of these special rules when possible to determine chirality functions for shoe-like framework groups and intransitive framework groups reduces drastically the complexity of the algebra and the frequency of cases where the considerably more complicated full theoretical algorithm must be used.

(A) *Shoe-like Framework Groups*. Consider a shoe-like framework group with  $n$  sites and  $p$  planes of symmetry. Any given plane of symmetry of a shoe-like group is a separating plane and contains exactly  $n-2$  sites. Consider one of these planes  $P_k$  and label the two sites outside this plane  $a_k$  and  $b_k$ . The symmetry operation represented by the separating plane  $P_k$  interchanges sites  $a_k$  and  $b_k$  but leaves all of the other sites unchanged. The chirality polynomial  $X(s_1, s_2, \dots, s_n)$  is the product of the differences [2]

$$X(s_1, s_2, \dots, s_n) = \prod_{k=1}^{k=p} (s_{a_k} - s_{b_k}). \quad (4)$$

The following points are of interest concerning Eq. (4):

- (1) Sometimes for two different symmetry planes  $P_k$  and  $P_i$ ,  $b_k$  or  $b_i$  may be the same site as  $a_i$ .
- (2) From Eq. (4) it is readily apparent that for a shoe-like framework group the degree of the lowest degree chirality polynomial is equal to the number of symmetry planes.
- (3) For the regular tetrahedron  $T_d[4C_3(L)]$ , which is a shoe-like framework group with 6 separating planes ( $6\sigma_d$ ) Eq. (4) gives the familiar chirality polynomial

$$X\{T_d[4C_3(L)]\} = (s_4 - s_3)(s_4 - s_2)(s_4 - s_1)(s_3 - s_2)(s_3 - s_1)(s_2 - s_1). \quad (5)$$

(B) *Intransitive Framework Groups*: Consider an intransitive framework group with  $n$  sites and  $q$  orbits. The chirality polynomial for each orbit can be determined separately using the procedure above if it is shoe-like or the general algorithm below if it is potato-like. Let  $X_k$  be the chirality polynomial for orbit  $k$ . Then the chirality polynomial for the intransitive framework group may be obtained from the following relationship:

$$X(s_1, s_2, \dots, s_n) = \prod_{k=0}^{k=q} X_k. \quad (6)$$

The chirality polynomial for an intransitive framework group is thus the product of the chirality polynomials of the individual orbits, where each orbit is considered as a smaller framework group. Frequently, the smaller framework groups of the individual orbits are shoe-like and therefore have chirality polynomials that can be readily determined from their separating planes by Eq. (4) without using the full group theoretical algorithm. Also orbits of length 1 (i.e. isolated points invariant under *all* symmetry operations such as central points) can be completely ignored in the calculation of chirality polynomials of intransitive framework groups.

The rules for intransitive framework groups and many of these other concepts can be illustrated by the determination of the lowest degree chirality polynomial for the trigonal bipyramid  $D_{3h}[C_3(L_2), 3C_2(L)]$  which has site partition (32) corresponding to two orbits, one of length 3 (the equatorial sites, labelled 1, 2, and 3) and the other of length 2 (the axial sites, labelled 4 and 5). The framework group of the equatorial sites is  $D_{3h}[3C_2(L)]$  which can be polarized to  $C_{3v}[3\sigma_v(L)]$ , a shoe-like framework group whose chirality polynomial is

$$X_e = X\{C_{3v}[3\sigma_v(L)]\} = (s_3 - s_2)(s_3 - s_1)(s_2 - s_1). \quad (7)$$

Similarly, the orbit corresponding to the 2 axial sites 4 and 5 has a single separating plane leading to the chirality polynomial

$$X_a = (s_5 - s_4). \quad (8)$$

The chirality polynomial of the trigonal bipyramid is the product of  $X_e$  and  $X_a$ , i.e.,

$$X\{D_{3h}[C_3(L_2), 3C_2(L)]\} = (X_e)(X_a) = (s_3 - s_2)(s_3 - s_1)(s_2 - s_1)(s_5 - s_4). \quad (9)$$

In this specific case, the chirality polynomial (Eq. (9)) can also be obtained by treating the whole trigonal bipyramid as a shoe-like framework group with 4 separating planes ( $\sigma_h + 3\sigma_v$ ) and then using Eq. (4).

(C) *The Full Group Theoretical Algorithm*. The special procedures outlined above for shoe-like framework groups and intransitive framework groups can be shown to be valid by the use of the full group theoretical algorithm outlined below. The full group theoretical algorithm is also necessary to determine the chirality polynomials for the following framework groups:

- (a) Transitive potato-like framework groups.
- (b) Intransitive framework groups having one or more potato-like orbits.

In addition the full group theoretical algorithm may be necessary for the determination of the chirality polynomial for a framework group with a chiral ligand partition having a degree higher than that of the minimum degree chirality polynomial. Mechanical application of the full group theoretical algorithm for the attempted determination of a chirality polynomial for a framework group using a ligand partition which is not chiral will instead lead identically to zero. Thus the group theoretical method outlined in the previous section for the determination of the chiral ligand partitions for a given framework group is a useful prerequisite to the determination of the algebraic form of chirality polynomials.

The full group theoretical algorithm for the determination of the lowest degree chirality polynomials in ligand-specific parameters  $s_k$  corresponding to a given framework group and ligand partition is based on a procedure first developed by Ruch and Schönhofer [4, 5] and also discussed by Mead [6]. This algorithm can be outlined as follows (keeping non-essential mathematical details to a minimum):

- (1) Label the boxes in the Young diagram for the ligand partition of interest with the indices of the sites corresponding to the particular chiral species of interest with that ligand partition. These labels correspond to the indices  $k$  of the parameters  $s_k$ .
- (2) Determine from the columns of the labelled Young diagram the monomial arising from the following double product:

$$\prod_{e=1}^{e=\text{order}} \prod_{f=0}^{f=i-1} s_{k_{ef}}^f = M(s_1, s_2, \dots, s_n). \quad (10)$$

In Eq. (10) the following should be noted:

- (a) The product over  $e$  contains one factor for each column of the Young diagram. The variable  $e$  corresponds to the position of the column relative to the left column ( $e = 1$ ).
  - (b) The product over  $f$  contains one factor for each box in the Young diagram in column  $e$  except for the bottom box where  $f = 0$  and hence  $s_{k_{ef}}^f = 1$  regardless of the value of  $k_{ef}$ . If column  $e$  has only one box in it then this product is unity for that column and therefore does not contribute to the monomial in Eq. (10). The variable  $f$  corresponds to the position of the box relative to the *bottom* box of the column  $e$ . In the bottom box  $f = 0$ .
  - (c) The variable  $k_{ef}$  refers to the index entered in the Young diagram box corresponding to column  $e$  and row  $f$ .
- (3) Apply each of the symmetry operations of the point group to the monomial  $M(s_1, s_2, \dots, s_n)$  obtained from Eq. (10). This process can be represented schematically by

$$g * M(s_1, s_2, \dots, s_n) \quad (11)$$

where  $g$  refers to a symmetry operation in the point group  $G$  and the star “\*” means that the indices  $1, 2, \dots, n$  are permuted by the symmetry operation  $g$ .

A similar notation to that in Eq. (11) has been used by Dugundji, Marquarding, and Ugi [11].

(4) The chirality polynomial can be expressed by the following equation:

$$X(s_1, s_2, \dots, s_n) = \sum_{g \in G} (-1)^t [g * M(s_1, s_2, \dots, s_n)]. \quad (12)$$

In Eq. (12),  $t$  is 2 for proper rotations  $C_m$  (including  $C_1 \equiv E$ ) and 1 for improper rotations  $S_m$  (including  $S_1 \equiv \sigma$  and  $S_2 \equiv i$ ). This leads to a plus sign in front of the terms corresponding to proper rotations and a minus sign in front of the terms corresponding to improper rotations. The summation is taken over all of the operations  $g$  in the point group  $G$ .

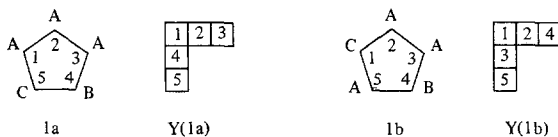
(5) After obtaining the chirality polynomial  $X(s_1, s_2, \dots, s_n)$  from Eq. (12), further somewhat creative algebra may be needed to obtain the chirality function as a product and/or sum of differences between pairs of ligand parameters  $s_k^a - s_i^a$ . Sometimes it is useful to add zero to the result of Eq. (12) in the form of vanishing sums of the following type where  $K$  is a constant and  $a$  is a small integer exponent:

$$K \sum_{k=1}^{k=n} s_k^a - s_k^a. \quad (13)$$

Such addition of zero may be followed by factoring into powers of the type  $(s_k^a - s_m^a)^b$  where  $b$  is a small integer.

The full group theoretical algorithm may be illustrated by the determination of the chirality function of the lowest degree chiral ligand partition  $(31^2)$  for the five-site framework group  $C_{5v}[5\sigma_v(L)]$  arising from polarization of the framework group  $D_{5h}[5C_2(L)]$ . The framework group  $C_{5v}[5\sigma_v(L)]$  can correspond to ring substitution sites in  $C_5H_5Mn(CO)_3$  derivatives. This case is also instructive since it provides the first example of *metacyclic groups* [26] arising in a system of chemical significance.

The only ligand partitions which are chiral in  $C_{5v}[5\sigma_v(L)]$  are  $2(31^2)$  in which the coefficient 2 arises from the different chiral species 1a and 1b with the corresponding labelled Young diagrams Y(1a) and Y(1b). The detailed calculations of the chirality polynomial will be illustrated for the chirality polynomial



corresponding to 1a, namely  $X_{1a}(s_1, s_2, \dots, s_5)$ . Thus application of Eq. (10) to Y(1a) gives the monomial

$$M_{1a}(s_1, s_2, \dots, s_5) = s_4 s_1^2. \quad (14)$$

Application of Eq. (12) to the monomial in Eq. (14) using the 10 symmetry operations of  $C_{5v}$  (i.e.  $E + 2C_5 + 2C_5^2 + 5\sigma_v$ ) and putting minus signs (i.e.  $(-1)^1 =$



–1) before the terms corresponding to the  $5\sigma_v$  gives

$$\begin{aligned} X_{1a}(s_1, s_2, \dots, s_5) &= s_4(s_1^2 - s_2^2) + s_5(s_2^2 - s_3^2) \\ &\quad + s_1(s_3^2 - s_4^2) + s_2(s_4^2 - s_5^2) + s_3(s_5^2 - s_1^2). \end{aligned} \quad (15)$$

Now add zero in the form of Eq. (13) where  $K = \frac{1}{3}$ ,  $n = 5$ , and  $a = 3$ . Rearranging the terms then gives

$$3X_{1a}(s_1, s_2, \dots, s_5) = (s_4 - s_1)^3 + (s_5 - s_2)^3 + (s_1 - s_3)^3 + (s_2 - s_4)^3 + (s_3 - s_5)^3. \quad (16)$$

These results and an analogous result for  $X_{1b}(s'_1, s'_2, \dots, s'_5)$  were already obtained by Ruch and Schönhofer [5]. A qualitatively complete [5, 6] chirality function  $X_{QC}$  for the framework group  $C_{5v}[5\sigma_v(L)]$  is the sum

$$X_{QC} = X_{1a}(s_1, s_2, \dots, s_5) + X_{1b}(s'_1, s'_2, \dots, s'_5) \quad (17)$$

in which the ligand parameters  $s_1, s_2, \dots, s_5$  for  $X_{1a}$  and  $s'_1, s'_2, \dots, s'_5$  for  $X_{1b}$  are not necessarily the same. The concept of qualitative completeness will not be discussed further in this paper since it is already treated extensively in earlier papers [2, 5].

The  $C_{5v}$  symmetry group of the  $C_{5v}[5\sigma_v(L)]$  framework group has 10 symmetry operations as noted above. There is also a larger permutation group with 20 operations which consists of those operations which convert configuration 1a into either an equivalent configuration (a symmetry operation) or a configuration equivalent to configuration 1b. Groups of this type are metacyclic groups [26] and may be designated as  $M_p$  where  $p \geq 5$  is a prime. The metacyclic groups are significant in group theory [26] since they are the largest *soluble* groups permuting  $p$  objects ( $p$  is a prime). The cycle index (Eq. (1)) of  $M_5$  has the following form:

$$Z(M_5) = x_1^5 + 4x_5 + 5x_1x_2^2 + 10x_1x_4. \quad (18)$$

Note that  $M_5$  is *not* isomorphic to the point group  $D_{5h}$  even though both groups have 20 elements. Metacyclic groups  $M_p$  with  $[p(p-1)]/2$  elements arise naturally in the study of chirality in  $C_{pv}[p\sigma_v(L)]$  framework groups ( $p = \text{prime}$ ) obtained by polarization of the planar framework groups  $D_{ph}[pC_2(L)]$ . The metacyclic groups of potential chemical significance are  $M_5$  (e.g. the  $C_5H_5Mn(CO)_3$  skeleton) with 20 elements and  $M_7$  (e.g. the  $C_7H_7V(CO)_3$  skeleton) with 42 elements.

The following are the lowest degree chirality polynomials for some other potato-like transitive framework groups which are particularly significant in exemplifying the minimum number of sites necessary to define the indicated symmetry element:

(1)  $C_4$  axis: The chirality polynomial for the  $(21^2)$  ligand partition ( $g = 3$ ) of the framework group  $C_{4v}[2\sigma_v(L_2)]$  (polarized planar square) is

$$X(s_1, s_2, s_3, s_4) = (s_2 - s_1)(s_4 - s_3)[(s_1 - s_3) + (s_2 - s_4)]. \quad (19)$$

The chirality polynomial for the lowest degree chiral representation (31) with  $g = 1$  of the polarized planar rectangle (i.e., the framework group  $C_{2v}[X(L_4)]$ ) consists of the final factor of Eq. (19) taken alone, i.e.

$$X(s_1, s_2, s_3, s_4) = (s_1 - s_3) + (s_2 - s_4) . \quad (20)$$

This corresponds to the "quadrant rule" used to estimate the optical activity of complex organic molecules with this particular symmetry [2, 27, 28].

(2)  $C_5$  axis. See Eq. (16).

(3)  $S_3$  or  $S_6$  axis. The chirality polynomial for the (42) ligand partition ( $g = 2$ ) of the framework group  $D_{3h}[3C_2(L_2)]$  for  $S_3$  (trigonal prism) or the permutationally equivalent  $D_{3d}[3\sigma_d(L_2)]$  for  $S_6$  (trigonal antiprism) is

$$X(s_1, s_2, \dots, s_6) = (s_6 - s_5)(s_3 - s_1) - (s_6 - s_4)(s_3 - s_2) . \quad (21)$$

(4)  $C_7$  axis. The chirality polynomial for the (51<sup>2</sup>) ligand partition ( $g = 3$ ) of the framework group  $C_{7v}[7\sigma_v(L)]$  (polarized planar heptagon) is

$$X(s_1, s_2, \dots, s_7) = (s_1 - s_2)^3 + (s_2 - s_3)^3 + (s_3 - s_4)^3 \\ + (s_4 - s_5)^3 + (s_5 - s_6)^3 + (s_6 - s_7)^3 + (s_7 - s_1)^3 . \quad (22)$$

## 5. Four-Site Framework Groups (Table 4)

The transitive shoe-like four-site framework groups are the regular tetrahedron  $T_d[4C_3(L)]$  and the allene skeleton  $D_{2d}[2\sigma_d(L_2)]$  formed by removal of the three-fold symmetry from the regular tetrahedron. Tetrahedral species are well-known to be chiral if and only if all four ligands are non-equivalent in a species of the type  $MABCD$ . Thus the corresponding ligand partition (1<sup>4</sup>) is the only

**Table 4.** Chiral representations for achiral four-site framework groups

Framework group <sup>a</sup>	Site partition	Description	Chiral ligand partitions <sup>a</sup>
$T_d[4C_3(L)]$	(4)	regular tetrahedron	(1 <sup>4</sup> )
$D_{4h}[2C_2(L_2)] \rightarrow C_{4v}[2\sigma_v(L_2)]$	(4)	square planar	(21 <sup>2</sup> )*
$D_{3h}[O(L), 3C_3(L)]$	(31)	trigonal planar + center	
$C_{3v}[C_3(L), 3\sigma_v(L)]$	(31)	trigonal pyramid	(1 <sup>4</sup> ) + (21 <sup>2</sup> )
$D_{2h}[C_2(L_2), C_2'(L_2)]$	(2 <sup>2</sup> )	planar rhombus	
$D_{2h}[\sigma(L_4)] \rightarrow C_{2v}[X(L_4)]$	(4)	planar rectangle	(21 <sup>2</sup> )* + (31)*
$D_{2d}[2\sigma_d(L_2)]$	(4)	allene skeleton	(1 <sup>4</sup> ) + (2 <sup>2</sup> )
$C_{2h}[\sigma_h(L_4)]$	(2 <sup>2</sup> )	planar parallelogram	
$C_{2v}[C_2(L_2), \sigma_v(L_2)]$	(2 <sup>2</sup> )	planar	
$C_{2v}[\sigma_v(L_2), \sigma_v'(L_2)]$	(2 <sup>2</sup> )	butterfly	(1 <sup>4</sup> ) + (21 <sup>2</sup> ) + (2 <sup>2</sup> )
$C_{2v}[\sigma(L_4)]$	(2 <sup>2</sup> )	planar trapezoid	
$C_s[\sigma(L_4)]$	(1 <sup>4</sup> )	planar trapezium	
$C_s[\sigma(L_2), X(L_2)]$	(21 <sup>2</sup> )	non-planar	(1 <sup>4</sup> ) + 2(21 <sup>2</sup> ) + (2 <sup>2</sup> ) + (31)

<sup>a</sup> The notation used is that given by Pople, J. A., J. Am. Chem. Soc. **102**, 4615 (1980). Polarizations are represented by arrows and the chiral ligand partitions corresponding to polarized planar framework groups are starred.

chiral ligand partition for a regular tetrahedron. Distortion of  $T_d[4C_3(L)]$  to  $D_{2d}[2\sigma_d(L_2)]$  also leads to chiral species  $MA_2B_2$  (e.g. chiral allenes) which have the chiral ligand partitions  $(1^4) + (2^2)$ . This has been previously discussed in detail in several places [6, 29].

The transitive potato-like four-site framework groups are the polarized square  $C_{4v}[2\sigma_v(L_2)]$  and the polarized rectangle  $C_{2v}[X(L_4)]$ . Chirality in the polarized square  $C_{4v}[2\sigma_v(L_2)]$  arises only from the  $(21^2)$  ligand partition corresponding to a species  $MA_2BC$  with structure II.



Reduction of the symmetry from  $C_{4v}[2\sigma_v(L_2)]$  (polarized square) to  $C_{2v}[X(L_4)]$  (polarized rectangle) by distorting the  $C_4$  axis to only a  $C_2$  axis introduces chirality in the  $(31)$  ligand partition corresponding to a species  $MA_3B$  with structure III. Note that in the potato-like framework groups  $C_{4v}[2\sigma_v(L_2)]$  and  $C_{2v}[X(L_4)]$  unlike the shoe-like groups the fully unsymmetrical ligand partition  $(1^4)$  is *not* chiral since a less unsymmetrical ligand partition (i.e. one of lower degree), namely  $(21^2)$ , is already sufficient to account for all of the phenomena depending upon chirality for these potato-like framework groups.

The properties of the intransitive four-site framework groups with site partitions  $(2^2)$  are instructive. Planar groups of this type are the rhombus  $D_{2h}[C_2(L_2), C_2'(L_2)]$ , the parallelogram  $C_{2h}[\sigma_h(L_4)]$ , the framework group  $C_{2v}[C_2(L_2), \sigma_v(L_2)]$ , and the trapezoid  $C_{2v}[\sigma_v(L_4)]$ . Polarization of the parallelogram, the framework group  $C_{2v}[C_2(L_2), \sigma_v(L_2)]$ , and the trapezoid all lead to framework groups of  $C_2$  symmetry. Since these  $C_2$  framework groups have no improper rotation axes, they are chiral for all ligand partitions and therefore are not of interest in the context of this study. Polarization of the rhombus gives the achiral framework group  $C_{2v}[\sigma_v(L_2), \sigma'_v(L_2)]$  which can also have the following origins:

- (1) A two-fold distortion of the allene skeleton  $D_{2d}[2\sigma_d(L_2)]$ .
- (2) A two-fold distortion of the polarized square  $C_{4v}[2\sigma_v(L_2)]$ .
- (3) The automorphism group of the graph IV corresponding to “butterfly-like”



systems. The chiral ligand partitions of  $C_{2v}[\sigma_v(L_2), \sigma'_v(L_2)]$  are  $(1^4) + (2^2)$  reflecting its origin from distortion of the allene skeleton and  $(21^2)$  reflecting its alternate origin from distortion of the polarized square.

The only non-planar four-site framework group with a  $(31)$  site partition is the trigonal pyramid  $C_{3v}[C_3(L), 3\sigma_v(L)]$  which arises by destruction of the  $S_4$  axis in the regular tetrahedron  $T_d[4C_3(L)]$ . The trigonal pyramid  $C_{3v}[C_3(L), 3\sigma_v(L)]$

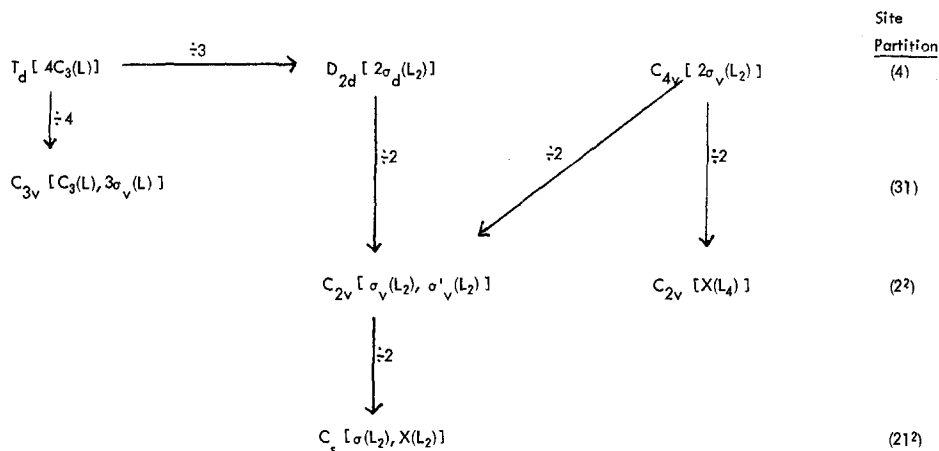


Fig. 1. Relationships between the four-site framework groups. All framework groups with a given site partition are listed in the same row

is chiral if and only if the three ligands in the basal site are non-equivalent: call them *A*, *B*, and *C*. The unique apical site in  $C_{3v}[C_3(L), 3\sigma_v(L)]$  can either contain a ligand which is the same as one of the basal ligands (call the apical ligand *A*) or a ligand different from any of the basal ligands (call the apical ligand *D*). Thus the two chiral ligand partitions of the trigonal pyramid  $C_{3v}[C_3(L), 3\sigma_v(L)]$  are  $(1^4)$  and  $(21^2)$  corresponding to species of the types *MABCD* (*D* in the apical position) and *MA<sub>2</sub>BC* (*A* in the apical position), respectively.

The remaining non-planar achiral four-site framework group is  $C_s[\sigma(L_2), X(L_2)]$  which has a  $(21^2)$  site partition. This framework group becomes chiral if and only if the two ligands outside the single plane of symmetry (i.e.  $X(L_2)$ ) are non-equivalent: call these two ligands *A* and *B*. The ligands in the single plane of symmetry can either be identical or different from each other and from ligands *A* and *B*. This leads to five chiral ligand partitions  $(1^4) + (21^2) + (21^2) + (2^2) + (31)$  corresponding to species  $C_s[\sigma(CD), X(AB)]$ ,  $C_s[\sigma(AC), X(AB)]$ ,  $C_s[\sigma(C_2), X(AB)]$ ,  $C_s[\sigma(AB), X(AB)]$ , and  $C_s[\sigma(A_2), X(AB)]$ , respectively.

The relationships between the non-planar and polarized planar achiral four-site framework groups are depicted in Fig. 1. In this figure all framework groups with a given site partition are listed in the same row. The numbers associated with each arrow indicates the index of the distortion represented by the arrow, i.e.  $|G|/|H|$  where  $|G|$  is the number of elements in the point group of the framework group at the tail of the arrow and  $|H|$  is the number of elements in the point group of the framework group at the head of the arrow.

## 6. Five-Site Framework Groups (Table 5)

The only non-planar *transitive* five-site framework group is the polarized pentagon  $C_{5v}[5\sigma_v(L)]$  which has already been discussed in detail earlier in this paper and therefore will not be discussed further.

Table 5. Chiral representations for achiral five-site frameworks groups

Framework group <sup>a</sup>	Site partition	Description	Chiral ligand partitions <sup>a</sup>
$T_d[O(L), 4C_3(L)]$	(41)	tetrahedron + center	$(1^5) + (21^3)$
$D_{5h}[5C_2(L)] \rightarrow C_{5v}[5\sigma_v(L)]$	(5)	regular planar pentagon	$(31^2)^*$
$D_{4h}[O(L), 2C_2(L_2)]$	(41)	planar square + center	
$C_{4v}[C_4(L), 2\sigma_v(L_2)]$	(41)	square pyramid	$(21^3) + (2^21) + (31^2)$
$D_{3h}[C_3(L_2), 3C_2(L)]$	(32)	trigonal bipyramid	$(1^5) + (21^3) + (2^21)$
$C_{3v}[C_3(L_2), 3\sigma_v(L)]$	$(31^2)$		$(1^5) + 2(21^3) + (2^21) + (31^2)$
$D_{2h}[O(L), C_2(L_2), C_2'(L_2)]$	$(2^21)$	planar rhombus + center	
$D_{2h}[O(L), \sigma(L_4)]$	(41)	planar rectangle + center	
$D_{2d}[O(L), 2\sigma_d(L_2)]$	(41)	centered allene	$(1^5) + (21^3) + (2^21) + (32)$
$C_{2h}[O(L), \sigma_h(L_4)]$	$(2^21)$	parallelogram + center	
$C_{2v}[C_2(L_3), \sigma_v(L_2)]$	$(21^3)$	planar	
$C_{2v}[C_2(L), \sigma_v(L_2), \sigma'_v(L_2)]$	$(2^21)$	rhombus + apex	$(1^5) + 2(21^3) + 2(2^21) + (31^2) + (32)$
$C_{2v}[C_2(L), \sigma_v(L_4)]$	$(2^21)$	planar	
$C_{2v}[C_2(L), X(L_4)]$	(41)	rectangular pyramid	$(21^3) + (2^21) + 2(31^2) + (32) + (41)$
$C_s[\sigma(L_5)]$	$(1^5)$	planar	
$C_s[\sigma'(L_3), X(L_2)]$	$(21^3)$		$(1^5) + 3(21^3) + 3(2^21) + 3(31^2) + 2(32) + (41)$
$C_s[\sigma(L), X(L_4)]$	$(12^2)$		$(1^5) + 2(21^3) + 2(2^21) + 4(31^2) + 2(32) + 2(41)$

<sup>a</sup> The notation used is that given by Pople, J. A., J. Am. Chem. Soc. **102**, 4615 (1980). Polarizations are represented by arrows and the chiral ligand partitions corresponding to the polarized planar framework group  $C_{5v}[5\sigma_v(L)]$  are starred.

Several of the non-planar five-site framework groups have site partitions (41) or  $(2^21)$  and therefore arise from the four-site framework groups discussed above by addition of a unique fifth site. These include the following:

- (1) The centered regular tetrahedron  $T_d[O(L), 4C_3(L)]$  which has a (41) site partition. The chiral ligand partitions are  $(1^5)$  and  $(21^3)$  corresponding to the chiral species  $T_d[O(E), 4C_3(ABCD)]$  and  $T_d[O(A), 4C_3(ABCD)]$ , respectively.
- (2) The square pyramid  $C_{4v}[C_4(L), 2\sigma_v(L_2)]$  which has a (41) site partition. The chiral ligand partitions are  $(21^3)$ ,  $(2^21)$ , and  $(31^2)$  corresponding to the chiral species  $C_{4v}[C_4(D), 2\sigma_v(A_2BC)]$ ,  $C_{4v}[C_4(B), 2\sigma_v(A_2BC)]$ , and  $C_{4v}[C_4(A), 2\sigma_v(A_2BC)]$ , respectively. Note that for all three of these species the four ligands in the square base have the ligand partition  $(21^2)$  and the configuration in structure II corresponding to the single chiral ligand partition of the polarized planar square  $C_{4v}[2\sigma_v(L_2)]$ .
- (3) The framework group  $D_{2d}[O(L), 2\sigma_d(L_2)]$  which has a (41) site partition and corresponds to an allene skeleton with an additional center point. The chiral ligand partitions are  $(1^5)$ ,  $(21^3)$ ,  $(2^21)$ , and  $(32)$  corresponding to the chiral species  $D_{2d}[O(E), 2\sigma_d(ABCD)]$ ,  $D_{2d}[O(A), 2\sigma_d(ABCD)]$ ,  $D_{2d}[O(C), 2\sigma_d(A_2B_2)]$ , and  $D_{2d}[O(A), 2\sigma_d(A_2B_2)]$ , respectively.
- (4) The rectangular pyramid  $C_{2v}[C_2(L), X(L_4)]$  with a (41) site partition. The chiral ligand partitions are  $(21^3)$ ,  $(2^21)$ ,  $(31^2)$ ,  $(31^2)$ ,  $(32)$ , and  $(41)$  corresponding to the chiral species  $C_{2v}[C_2(D), X(A_2BC)]$ ,  $C_{2v}[C_2(B), X(A_2BC)]$ ,  $C_{2v}[C_2(A), X(A_2BC)]$ ,  $C_{2v}[C_2(C), X(A_3B)]$ ,  $C_{2v}[C_2(B), X(A_3B)]$ , and  $C_{2v}[C_2(A), X(A_3B)]$ , respectively.
- (5) The framework group  $C_{2v}[C_2(L), \sigma_v(L_2), \sigma'_v(L_2)]$  with a  $(2^21)$  site partition corresponding to a pyramid with a rhombus as its base. The seven chiral ligand partitions are  $(1^5)$ ,  $(21^3)$ ,  $(21^3)$ ,  $(2^21)$ ,  $(2^21)$ ,  $(31^2)$ , and  $(32)$  corresponding to the chiral species  $C_{2v}[C_2(E), \sigma_v(CD), \sigma'_v(AB)]$ ,  $C_{2v}[C_2(A), \sigma_v(CD), \sigma'_v(AB)]$ ,  $C_{2v}[C_2(D), \sigma_v(AC), \sigma'_v(AB)]$ ,  $C_{2v}[C_2(B), \sigma_v(AC), \sigma'_v(AB)]$ ,  $C_{2v}[C_2(C), \sigma_v(AB), \sigma'_v(AB)]$ ,  $C_{2v}[C_2(A), \sigma_v(AC), \sigma'_v(AB)]$ , and  $C_{2v}[C_2(A), \sigma_v(AB), \sigma'_v(AB)]$ , respectively.

The remaining two non-planar achiral five-site framework groups with greater than  $C_s$  symmetry are the trigonal bipyramid  $D_{3h}[C_3(L_2), 3C_2(L)]$  with a (32) site partition and the framework group  $C_{3v}[C_3(L_2), 3\sigma_v(L)]$  with a  $(31^2)$  site partition. This latter framework group is derived from the trigonal bipyramid by removal of its  $\sigma_h$  symmetry plane thereby making the two axial sites non-equivalent. The trigonal bipyramid has the chiral ligand partitions  $(1^5)$ ,  $(21^3)$ , and  $(2^21)$  corresponding to the chiral species  $D_{3h}[C_3(DE), 3C_2(ABC)]$ ,  $D_{3h}[C_3(AD), 3C_2(ABC)]$ , and  $D_{3h}[C_3(AB), 3C_2(ABC)]$ , respectively. The framework group  $C_{3v}[C_3(L_2), 3\sigma_v(L)]$  has these same three chiral ligand partitions plus the additional two chiral ligand partitions  $(21^3)$  and  $(31^2)$  which correspond to the chiral species  $C_{3v}[C_3(D_2), 3\sigma_v(ABC)]$  and  $C_{3v}[C_3(A_2), 3\sigma_v(ABC)]$ , respectively. These framework groups have the following features of interest:

- (1) In all of the chiral representations of  $D_{3h}[C_3(L_2), 3C_2(L)]$  and

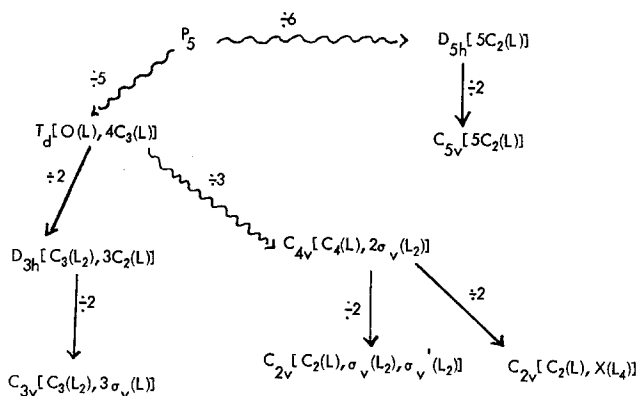


Fig. 2. Relationships between the five-site framework groups. Normal subgroup relationships are indicated by straight arrows; other subgroup relationships are indicated by wavy arrows

$C_{3v}[C_3(L_2), 3\sigma_v(L)]$ , the ligand partition in the equatorial triangle is  $(1^3)$  in accord with the single chiral representation of the polarized triangle  $C_{3v}[3\sigma_v(L)]$ .

(2) The absence of a  $\sigma_h$  symmetry plane in  $C_{3v}[C_3(L_2), 3\sigma_v(L)]$  allows chiral systems to have equivalent ligands in axial sites since the axial sites in  $C_{3v}[C_3(L_2), 3\sigma_v(L)]$  are non-equivalent unlike those in  $D_{3h}[C_3(L_2), 3C_2(L)]$ .

Fig. 2 shows the relationships between these five-site framework groups. Straight arrows indicated normal subgroup relationships [21]. Note that the fully symmetrical permutation group  $P_5$  does not correspond to a framework group in *three* dimensions but represents the symmetries of a four-dimensional simplex (analogue of the tetrahedron) [30]. The two-dimensional projection of the four-dimensional simplex is the non-planar [31]  $K_5$  graph (V). If the four-dimensional simplex is shoe-like like the two- and three-dimensional simplices



(the triangle and tetrahedron, respectively), then its sole chiral ligand partition is  $(1^5)$ . The framework group  $T_d[O(L), 4C_3(L)]$  is the maximum symmetry distortion of the four-dimensional simplex which can be imbedded into three-dimensional space. Distortion of  $P_5$  to  $T_d[O(L), 4C_3(L)]$  adds the  $(21^3)$  chiral ligand representation.

## 7. Six-site Framework Groups (Table 6)

The most symmetrical six-site framework group is the regular octahedron  $O_h[3C_4(L_2)]$ , whose point group contains 48 symmetry operations including  $C_2$ ,  $C_3$ , and  $C_4$  axes [3]. Most of the six-site framework groups of chemical interest can be derived from the octahedron  $O_h[3C_4(L_2)]$  through symmetry reduction (distortion [18]) by removal of various symmetry elements. The relationship

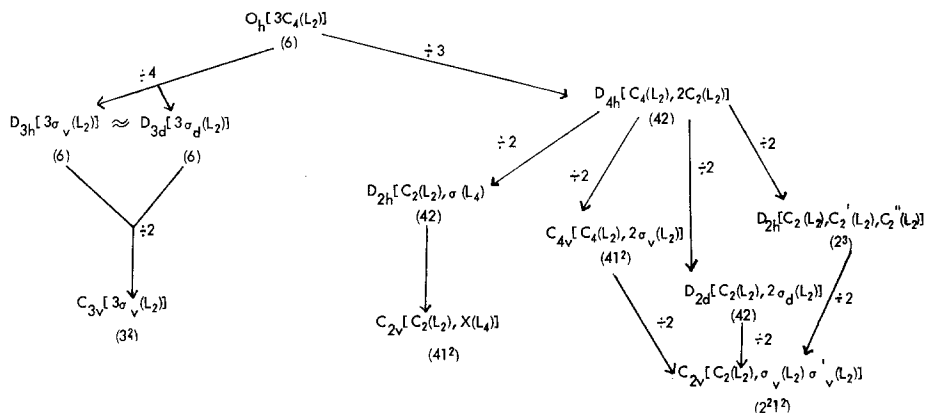
Table 6. Chiral representations for achiral six-site framework groups

Framework group <sup>a</sup>	Site partition	Description	Chiral ligand partitions <sup>b</sup>
$O_h[3C_4(L_2)]$	(6)	regular octahedron	$(2^3) + (31^3)$
$D_{6h}[3C_2(L_2)] \rightarrow$ $C_{6v}[3\sigma_v(L_2)]$	(6)	regular planar hexagon	$(2^2 1^2)^* + (31^3)^* + (321)^* + 2(41^2)^* + (3^2)^*$
$D_{5h}[O(L), 5C_2(L)]$	(51)	planar pentagon + center	$(2^3) + (31^3) + 2(321) + 2(41^2) + (3^2)$
$C_{5v}[C_5(L), 5\sigma_v(L)]$	(51)	pentagonal pyramid	$(21^4) + (2^2 1^2) + (31^3) + (2^3) + (321)$
$D_{4h}[C_4(L_2), 2C_2(L_2)]$	(42)	square bipyramid	$(21^4) + 2(2^2 1^2) + 2(31^3) + (2^3) + 2(321) + (41^2)$
$C_{4v}[C_4(L_2), 2\sigma_v(L_2)]$	(41 <sup>2</sup> )		$(1^6) + 2(21^4) + 2(2^2 1^2) + (31^3) + (2^3) + (321)$
$D_{3h}[O(L), C_3(L_2), 3C_2(L)]$	(321)	trigonal bipyramid + center	
$D_{3h}[3C_2(L_2)]$	(3 <sup>2</sup> )	planar	
$D_{3h}[\sigma_h(L_6)]$	(3 <sup>2</sup> )	planar	
$D_{3h}[3\sigma_v(L_2)]$	(6)	trigonal prism	$2(31^3) + (2^3) + (321) + (41^2) + (42)$
$D_{3d}[3\sigma_d(L_2)]$	(6)	trigonal antiprism	$2(31^3) + (2^3) + (321) + (41^2) + (42)$
$C_{3h}[\sigma_h(L_6)]$	(3 <sup>2</sup> )	planar	
$C_{3v}[C_3(L_3), 3\sigma_v(L)]$	(31 <sup>3</sup> )		$(1^6) + 3(21^4) + 3(2^2 1^2) + 3(31^3) + (2^3) + 2(321) + (41^2)$
$C_{3v}[3\sigma_v(L_2)]$	(3 <sup>2</sup> )		$(2^2 1^2) + 3(31^3) + (2^3) + 2(321) + (3^2) + 3(41^2) + (42)$
$D_{2h}[C_2(L_2), C_2(L_2), C_2(L_2)]$	(2 <sup>3</sup> )	rhombus + 2 apices	$(1^6) + 2(21^4) + 3(2^2 1^2) + (31^3) + (2^3) + 2(321) + (3^2)$
$C_3^i(L_2)]$			
$D_{2h}[C_2(L_4), C_2'(L_2)]$	(2 <sup>3</sup> )	planar	
$D_{2h}[C_2(L_2), \sigma(L_4)]$	(42)	planar	
$D_{2h}[C_2(L_2), \sigma(L_4)]$	(42)	rectangular bipyramid	$(21^4) + (2^2 1^2) + 2(31^3) + (2^3) + 2(321) + (41^2) + (42)$
$D_{2d}[C_2(L_2), 2\sigma_d(L_2)]$	(42)		$2(21^4) + (2^2 1^2) + (31^3) + 2(2^3) + 2(321) + (41^2) + (42)$
$C_{2h}[C_2(L_2), \sigma_h(L_4)]$	(2 <sup>3</sup> )		$(1^6) + 2(21^4) + 4(2^2 1^2) + 2(31^3) + (2^3) + 4(321) + 2(3^2) + 2(41^2) + (42) + (51)$



$C_{2H}[\sigma_H(L_6)]$	$(2^3)$	planar	$(21^4) + 2(2^2 1^2) + 3(31^3) + (2^3) + 4(321) + (3^2) + 3(41^2)$
$C_{2H}[\sigma_H(L_2), X(L_4)]$	$(42)$		$+ 2(42) + (51)$
$C_{2v}[C_2(L_4), \sigma_v(L_2)]$	$(21^4)$	planar	$(21^4) + 2(2^2 1^2) + 3(31^3) + (2^3) + 4(321) + (3^2) + 3(41^2)$
$C_{2v}[C_2(L_2), \sigma_v(L_2), \sigma'_v(L_2)]$	$(2^2 1^2)$		$+ 2(42) + (51)$
$C_{2v}[C_2(L_2), \sigma_v(L_4)]$	$(2^2 1^2)$	planar	$(21^4) + 2(2^2 1^2) + 3(31^3) + (2^3) + 4(321) + (3^2) + 3(41^2)$
$C_{2v}[C_2(L_2), X(L_4)]$	$(41^2)$		$+ 2(42) + (51)$
$C_{2v}[\sigma_v(L_4), \sigma'_v(L_2)]$	$(2^3)$		$2(21^4) + 2(2^2 1^2) + 4(31^3) + 2(2^3) + 4(321) + 2(41^2)$
$C_{2v}[\sigma_v(L_6)]$	$(2^3)$	planar	$(21^4) + 2(2^2 1^2) + 3(31^3) + (2^3) + 4(321) + (3^2) + 3(41^2)$
$C_{2v}[\sigma(L_2), X(L_4)]$	$(42)$		$+ 2(42) + (51)$
$C_i[X(L_6)]$	$(2^3)$		$(1^6) + 2(21^4) + 6(2^2 1^2) + 4(31^3) + (2^3) + 8(321) + 4(3^2)$
$C_3[\sigma(L_6)]$	$(1^6)$	planar	$+ 6(41^2) + 3(42) + 3(51)$
$C_3[\sigma(L_4), X(L_2)]$	$(21^4)$		$(1^6) + 4(21^4) + 6(2^2 1^2) + 6(31^3) + 3(2^3) + 8(321) + 2(3^2)$
$C_3[\sigma(L_2), X(L_4)]$	$(2^2 1^2)$		$+ 4(41^2) + 3(42) + (51)$
$C_3[X(L_6)]$	$(2^3)$		$2(21^4) + 4(2^2 1^2) + 6(31^3) + 2(2^3) + 8(321) + 2(3^2) + 6(41^2)$
			$+ 4(42) + 2(51)$
			$(1^6) + 2(21^4) + 6(2^2 1^2) + 4(31^3) + (2^3) + 8(321) + 4(3^2)$
			$+ 6(41^2) + 3(42) + 3(51)$

<sup>a</sup> The notation used is that given by Pople, J. A., J. Am. Chem. Soc. **102**, 4615 (1980). Polarizations are represented by arrows and the chiral ligand partitions corresponding to the polarized planar framework group  $C_{6v}[3\sigma_v(L_2)]$  are starred.



**Fig. 3.** Subgroups of the six-site framework group  $O_h[3C_4(L_2)]$  corresponding to the regular octahedron

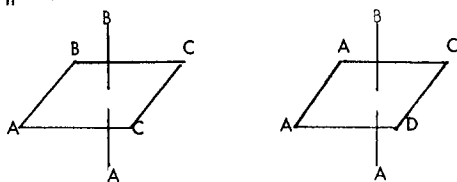
between various six-site framework groups derived from the octahedron is outlined in Fig. 3.

Initial distortion of the octahedron  $O_h[3C_4(L_2)]$  can occur through destruction of either its  $C_4$  symmetry or its  $C_3$  symmetry. Destruction of the  $C_4$  symmetry of  $O_h[3C_4(L_2)]$  retains transitivity to give initially either the trigonal prism  $D_{3h}[3\sigma_v(L_2)]$  or the trigonal antiprism  $D_{3d}[3\sigma_d(L_2)]$ ; these two framework groups correspond to identical permutation groups in which the horizontal symmetry plane ( $\sigma_h$ ) of  $D_{3h}[3\sigma_v(L_2)]$  plays the same role as the inversion center (i) of  $D_{3d}[3\sigma_d(L_2)]$ . Two distinguishable framework groups consisting of identical permutations (i.e. with the same cycle index as defined in Eq. (1)) may be called *isopermutational*. Inspection of Pople's tables [19] reveals the following additional pairs of isopermutational framework groups:

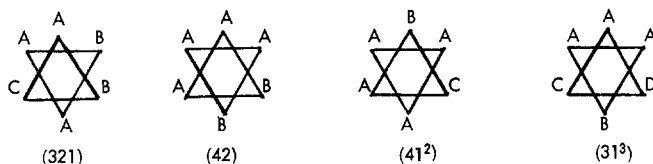
- (1) The planar four-site framework groups  $C_{2v}[\sigma_v(A_4)]$  and  $C_{2h}[\sigma_h(A_4)]$ .
- (2) The six-site framework groups  $C_{2v}[\sigma_v(A_2), X(A_4)]$  and  $C_{2h}[\sigma_h(A_2), X(A_4)]$ .
- (3) The six-site framework groups  $C_{2v}[\sigma_v(A_6)]$  and  $C_{2h}[\sigma_h(A_6)]$ . In all three of these pairs of isopermutational framework groups the  $\sigma_v$  symmetry plane in the one with a  $C_{2v}$  point group plays the same permutational role as the  $\sigma_h$  symmetry plane in the one with a  $C_{2h}$  point group.

The regular octahedron  $O_h[3C_4(L_2)]$  has two chiral ligand partitions ( $2^3$ ) and  $(31^3)$  which lead to the chiral systems depicted in the first row of Fig. 4. Destruction of the  $C_4$  symmetry of  $O_h[3C_4(L_2)]$  to give the isopermutational framework group pair  $D_{3h}[3\sigma_v(L_2)]$  and  $D_{3d}[3\sigma_d(L_2)]$  leads to four *new* chiral ligand partitions which are depicted in the second row of Fig. 4 for the trigonal antiprism  $D_{3d}[3\sigma_d(L_2)]$ . Note that the single  $(31^3)$  chiral ligand partition in the regular octahedron  $O_h[3C_4(L_2)]$  is split into two distinct  $(31^3)$  ligand partitions in  $D_{3h}[3\sigma_v(L_2)]$  or  $D_{3d}[3\sigma_d(L_2)]$ . The reason for this can be most easily visualized in the case of  $D_{3d}[3\sigma_d(L_2)]$  which has two triangular faces of one type (which must be equilateral triangles because of the  $C_3$  axis) and six triangular faces of

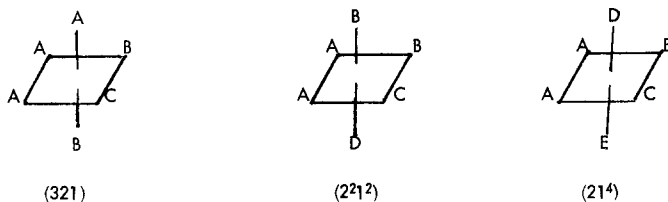
Octahedron:  $O_h[3C_4(L_2)]$



Trigonal prism  $D_{3h}[3\sigma_v(L_2)]$  or trigonal antiprism  $D_{3d}[3\sigma_d(L_2)]$ : additional chiral ligand partitions



Square bipyramid  $D_{4h}[C_4(L_2), 2C_2(L_2)]$ : chiral ligand partitions not found in  $O_h[3C_4(L_2)]$



**Fig. 4.** Schematic drawings of the chiral ligand partitions of the octahedron (top row), trigonal antiprism (top and middle rows), and square bipyramid (top and bottom rows)

a second type (which need only be isocetes). Thus in the regular octahedron  $O_h[3C_4(L_2)]$  in which all eight triangular faces are equivalent equilateral triangles there is only one type of triangular face to accommodate the three equivalent ligands of the  $(31^3)$  ligand partition. However, in  $D_{3d}[3\sigma_d(L_2)]$  the two different types of triangular faces for the three equivalent ligands of a  $(31^3)$  chiral ligand partition lead to two distinguishable  $(31^3)$  chiral ligand partitions.

Further distortion of the isopermutational framework group pair  $D_{3h}[3\sigma_v(L_2)]$  and  $D_{3d}[3\sigma_d(L_2)]$  can occur by destruction of the horizontal symmetry plane ( $\sigma_h$ ) in  $D_{3h}[3\sigma_v(L_2)]$  or the permutationally equivalent inversion center (i) in  $D_{3d}[3\sigma_d(L_2)]$ . In either case the result is the same, namely the framework group  $C_{3v}[3\sigma_v(L_2)]$  with a  $(3^2)$  site partition and no less than 12 distinguishable chiral ligand partitions.

Distortion of the original octahedron  $O_h[3C_4(L_2)]$  by removal of its  $C_3$  symmetry immediately destroys its transitivity to give the square bipyramid

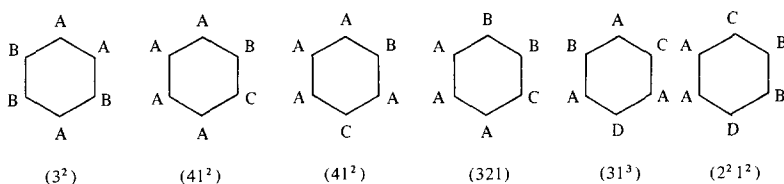
$D_{4h}[C_4(L_2), 2C_2(L_2)]$  with a  $(42)$  site partition. This distortion leads to three chiral ligand partitions not found in  $O_h[3C_4(L_2)]$ ; these are depicted in the third row of Fig. 4. Note that in the framework group  $D_{4h}[C_4(L_2), 2C_2(L_2)]$  the intransitivity implied by the  $(42)$  site partition means that ligand assignments in the two axial sites are independent of those in the four equatorial sites. Thus in all five chiral ligand partitions of  $D_{4h}[C_4(L_2), 2C_2(L_2)]$ , the ligand partition for the four equivalent equatorial sites is  $(21^2)$ , namely the single chiral ligand partition of the polarized square  $C_{4v}[2\sigma_v(L_2)]$  (see Sect. 5) which is the geometry of the equatorial ligand orbit. The difference between the different chiral representations of  $D_{4h}[C_4(L_2), 2C_2(L_2)]$  arises from which (if any) of the two axial ligands are equivalent to which of the  $(21^2)$  partitioned equatorial ligands.

Further distortion of the square bipyramid  $D_{4h}[C_4(L_2), 2C_2(L_2)]$  can occur by processes of one of the following types:

- (1) Reduction of the symmetry of the equatorial square to give a rectangle (i.e.,  $D_{2h}[C_2(L_2), \sigma_h(L_4)]$ ), rhombus (i.e.  $D_{2h}[C_2(L_2), C_2'(L_2), C_2''(L_2)]$ ), or the non-planar four-site  $D_{2d}$  "allene" configuration (i.e.  $D_{2d}[C_2(L_2), 2\sigma_d(L_2)]$ ).
- (2) Removal of the horizontal plane of symmetry ( $\sigma_h$ ) to make the two axial sites non-equivalent thereby giving the framework groups  $C_{4v}[C_4(L_2), 2\sigma_v(L_2)]$ ,  $C_{2v}[C_2(L_2), X(L_4)]$ , and  $C_{2v}[C_2(L_2), \sigma_v(L_2), \sigma'_v(L_2)]$  in which the equatorial ligands are arranged in a square, rectangle, and rhombus, respectively.

These distortions (which are summarized in Fig. 3) lead to framework groups with rather long lists of chiral ligand partitions which will not be depicted in detail here but which can be derived by methods similar to those used for the more symmetrical systems discussed earlier.

The remaining transitive six-site framework group is the planar hexagon, which after polarization goes to  $C_{6v}[3\sigma_v(L_2)]$ . This framework group is *not* a subgroup of the octahedron  $O_h[3C_4(L_2)]$  since in  $C_{6v}[3\sigma_v(L_2)]$  the operations with a  $(6)$  cycle partition derive from a proper rotation axis  $C_6$  whereas in  $O_h[3C_4(L_2)]$  the operations with a  $(6)$  cycle partition derive from an improper rotation axis  $S_6$ . The polarized planar hexagon has six chiral ligand partitions which correspond to the following chiral systems:



The intransitive framework group  $C_{3v}[3\sigma_v(L_2)]$  with a  $(3^2)$  site partition may be derived from  $C_{6v}[3\sigma_v(L_2)]$  by distortion of the  $C_6$  axis. This splits the six

equivalent sites in  $C_{6v}[3\sigma_v(L_2)]$  into two orbits of three equivalent sites each in  $C_{3v}[3\sigma_v(L_2)]$ .

The remaining six-site achiral non-planar framework groups with distinctive symmetry (at least 6 symmetry operations in the point group) may be derived from five-site framework groups by addition of a unique sixth site. These include the following:

- (1) The pentagonal pyramid  $C_{5v}[C_5(L), 5\sigma_v(L)]$  obtained by placing a unique apex above the planar regular pentagon  $D_{5h}[5C_2(L)]$ .
- (2) The centered trigonal bipyramid  $D_{3h}[O(L), C_3(L_2), 3C_2(L)]$  obtained by adding a unique central point to the trigonal bipyramid  $D_{3h}[C_3(L_2), 3C_2(L)]$ .
- (3) The framework group  $C_{3v}[C_3(L_3), 3\sigma_v(L)]$  obtained by distortion of the centered trigonal bipyramid  $D_{3h}[O(L), C_3(L_2), 3C_2(L)]$  to remove the horizontal symmetry plane  $\sigma_h$ . The determination of the chiral ligand partitions of these six-site framework groups presents no new difficulties.

## 8. Summary

The characterization of polyhedral symmetry in the previous paper [18] is additive since higher symmetry leads to more symmetry operations (i.e. more terms in the cycle index polynomial of Eq. (1)). However, the characterization in the present paper of symmetry of polyhedra or their associated framework groups is subtractive since higher symmetry leads to fewer chiral ligand partitions. This relates to the following two alternative approaches to defining symmetry:

- (1) *Framework Groups*. Symmetry is defined in terms of the symmetry operations of the framework group [19] so that more symmetrical species have more symmetry operations.
- (2) *Chiral Ligand Partitions*. Symmetry is defined in terms of the ligand partitions needed to remove all improper rotations (including reflections and inversions) from the skeletal framework group thereby leading to a chiral species. More symmetrical skeletons require a less symmetrical ligand partition (i.e. that corresponding to a Young diagram of higher degree) to give chiral species. These two approaches to symmetry are complementary since they are effectively used to study different phenomena.

The study of chirality by the methods outlined in this paper is useful for both qualitative and quantitative reasons. Qualitatively, the systematics of ligand partitions leading to chirality for a given skeleton (or framework group) is presented. Quantitatively, the underlying mathematics is presented for the determination of useful functions to estimate the magnitudes of pseudoscalar properties; the pseudoscalar polynomials of lowest degree discussed in this paper are the simplest examples of such chirality functions. Finally, the intimate examination of the properties of the framework groups, which is necessary to develop the chirality algebra in this paper, expands greatly our understanding of the relationships between the various framework groups beyond the pioneering work of Pople [19] in this area.

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