Topological Representation of Stereoisomerism.
I. Polytopal Rearrangements

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Abstract: This paper is an attempt to establish principles and definitions that will have general applicability in the area of topological representation of stereoisomerism in molecular species. The present analysis is restricted to polytopal rearrangements. Illustrative examples are taken from inorganic and organometallic chemistry.

This is a first attempt[1] to outline a general approach to topological representations of stereoisomerization processes. Definitions and illustrative examples are developed for a polytopal isomerization process which is defined below. The ultimate objectives are (1) delineation of differences in stereoisomerizations for alternative mechanisms, (2) simple pictorial representations that illustrate subgroups and depict relative energy relationships, and (3) clues to render molecular structures stereochemically more, or less, rigid.[1a]

Polytopal Isomers and Rearrangements

Stereoisomers apply to different spatial arrangements of atoms in molecules or ions of the same constitution.[2] A special class of stereoisomers, critical to the following discussion, is designated as polytopal isomers, G. This class differentiates spatial arrangements for any constitutional form in terms of idealized polygons or polyhedra whose vertices are defined[3] by the ligand atom positions in coordination compounds and by the core and by the peripheral atoms in polyhedral boranes and metal clusters. Examples of polytopal isomers are the tetrahedron and square plane in the four-atom family, and the square antiprism and trigonal dodecahedron in the eight-atom family. The term polytopal isomer will carry *no connotation of lifetime* as in structural and configurational[2] isomers.

A polyhedral rearrangement is defined as a traverse of two or more polytopal forms, *i.e.*, deformation of a specific polytopal form, by thermal or photochemical excitation, to the point that the ligand atoms define a new polytope. The traverse presents the possibility of permutation of ligand atom position and accordingly stereoisomerization within either polytopal form. An example is the racemization of an optically active nickel(II) tetrahedral complex through deformation to a square-planar form.

Many molecular species undergo polyhedral rearrangements, and there is extensive research on stereochemically nonrigid or fluxional molecules. Recent review articles or books cover most of the major areas.[4-11]

In the following section, reference will be made to the "general case." This is a hypothetical stereochemical system of the type ML_x or M_x wherein ligand-atom or core-atom vertex sites are nuclearly distinguishable by labeling. This is done simply to engender high symmetry in the topological approach.

Definitions

A specific x-atom problem is described as a stereochemical family, F, composed of all stereoisomers of all polytopal isomers G_A, G_B, G_C, ... To simplify the analysis, the family will be factored out into classes $\mathcal{S}$ whose members are the stereoisomers of two polytopal sets, G_A–G_B, G_A–G_C, etc.

An operation, O, a specific change in shape parameters, is postulated to alter the spatial arrangement in ML_x or M_x from one idealized polytope (G_A) to a second (G_B). Two sequential operations performed on a stereoisomer of the G_A (or G_B) set will generate a new stereoisomer of this set. The $O \cdot O'$ operations will be referred to as steps, R, or processes. The step order of a specific stereoisomerization is simply the number of steps involved. The product $O \times O^{-1}$ is simply the identity process.

Connectivity, δ, of polytopal forms, referenced to a postulated process, is the number of *new* stereoisomers of G_A (or G_B) generated from a stereoisomer of G_A (or G_B) in one *step*. Connectivities of individual stereoisomers within the G_A (or G_B) set are always identical in a general ML_x or M_x class but may vary in others.

A stereochemical class, $\mathcal{S}$, may be open or closed in a graphical or topological sense. Closure obtains if and only if the operations permit traverse of *all stereoisomers in the two polytopal classes.* Graph theory requires for a closed system the condition that the product of the isomer count and the connectivity of one polytopal set equals that product for the other set, *i.e.*, $I_A\delta_A = I_B\delta_B$. However, *one* polytopal set may be closed for the given operation even though the products are not equal (*vide infra*). A connectivity of one for either set indicates an

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[1] *Cf.* earlier related papers: (a) E. L. Muetterties, *Inorg. Chem.*, **6**, 635 (1967); (b) *J. Am. Chem. Soc.*, **90**, 5097 (1968).

[2] K. Mislow, "Introduction to Stereochemistry," W. A. Benjamin, Inc., New York, N. Y., 1965, p 51.

[3] Definition of idealized polygons and polyhedra by atom positions is applicable to the majority of molecular species. Although this terminology is imprecise in those cases where the atoms are nonidentical, the ligand atom positions do *generally* conform closely to idealized polyhedra. This definition is employed to maximize symmetry and simplify discussions.

[4] E. L. Muetterties and R. A. Schunn, *Quart. Rev.* (London), **20**, 245 (1965).

[5] F. W. Westheimer, *Accounts Chem. Res.*, **1**, 70 (1968).

[6] E. L. Muetterties and C. M. Wright, *Quart. Rev.* (London), **21**, 109 (1967).

[7] W. N. Lipscomb, *Science*, **153**, 373 (1966).

[8] E. L. Muetterties and W. H. Knoth, "Polyhedral Boranes," Marcel Dekker, Inc., New York, N. Y., 1968, Chapter III.

[9] G. Schroeder, *Angew. Chem. Intern. Ed. Engl.*, **4**, 752 (1965).

[10] G. Schroeder and J. F. M. Oth, *ibid.*, **6**, 414 (1967).

[11] F. A. Cotton, *Chem. Brit.*, **4**, 345 (1968).

open system unless the $I \cdot \delta$ product of the other set is equal to I for the former. If isomer connectivities vary within a set, then the sum of the individual products is taken.

The isomer count, I, in the general case for a specific polytope is simply $N!/h_r$, where N is the number of polytopal vertices and h_r is the order of the rotational subgroup of the point group of the polytope. (I am indebted to Professor F. A. Cotton for this explicit expression.)

Topological Analysis

Given the above definitions and the postulation of a stereoisomerization problem, the stereochemical class can be analyzed by graph theory. This analysis is quite straightforward if the number of isomers is not too large (at least up to ML_6 where $I = 20–30$), but only computer analysis is a realistic approach for the more complicated systems.

Several specific elements in the topological analysis are of particular interest for application to mechanistic problems. They are cycles $\mathscr{C}$, subcycles C, and chains c. These elements are defined as follows with their order equal to the number of steps.

Cycle $\mathscr{C}$ is a circular path that traverses an isomer **a** and its enantiomer $\bar{\mathbf{a}}$. No isomer is traversed more than once in the circuit of a cycle. The cycle of minimal order is designated $\mathscr{C}_E$.

Subcycle C is a circular path that does not traverse enantiomeric isomers; *i.e.*, it passes through **a**, **b**, **c**, etc., but not $\bar{\mathbf{a}}$, $\bar{\mathbf{b}}$, $\bar{\mathbf{c}}$, etc. A trivial subcycle of order two is generated by the steps $R \cdot R^{-1}$.[12]

Chain c is any noncircular path. There may be unique chains; one of specific stereochemical importance is the chain of c_E, of minimal order for the traverse from **a** to $\bar{\mathbf{a}}$.

Important characteristics of these elements are their degeneracy, *e.g.*, number of $\mathscr{C}_E$ or c_E's per isomer and C's of given order per isomer, and the chirality distinctions among elements.

A stereochemical class may be described by a process table or matrix for either of the two polytopal sets. The matrix explicitly characterizes the minimum number of steps from any isomer to a new isomer (Tables I and II). The matrix, unfortunately, becomes unwieldy if isomer count is large. Some subcycles are not immediately apparent by inspection of the table *but they are derivable*. In any case, the matrix is readily generated and may be the only recourse if the class cannot be described in a projection of a three-dimensional, noninterpenetrating figure (*vide infra*).

Topological illustrations are desirable in two- and three-dimensional representations because all pathways and the degeneracies of $\mathscr{C}$, C, and c elements are immediately apparent. Furthermore, such illustration can be used for energy relationships and, in principle, if energy data are available, for construction of potential energy diagrams. Unfortunately, there are severe limitations. Regular three-dimensional polyhedra are few (five platonic solids and four stellated icosahedra and pentagonal dodecahedra). Even if the isomer count can be accommodated in such regular polyhedra, the subcycle requirements are not always satisfied. Some representations require higher dimensionality and cannot be properly reduced for illustration.[1] For stereochemical classes of high isomer count (in MX_7-D_{5h}, $I = 504$), process matrices, networks, or graphs would be too large, and explicit topological illustration is not feasible. Elements (cycles, etc.) can, however, be obtained by computer analysis and so define the individual systems.

Following is an illustration of this approach and of problems encountered in generating proper representations.

Illustrative Examples

Cyclic Groups. If the connectivity of G_A and G_B is two in a closed class, the operations comprise a cyclic group. The class may be represented simply by a p-gon ($C = \mathscr{S}$), where p is equal to the number of isomers. Many stereochemically labile organometallics meet these conditions. For example, it has been established through nmr studies[11] that a cyclopentadienyl group singly bonded to a metal is nonrigid; the carbon atoms attached to the metal atom are rapidly permuted. Permutation might occur through a 1,2 or 1,3 shift. The cyclic group associated with these operations (rotations) is C_5; the group elements are r^n ($n = 1–5$), where r is a rotation of 72°. Representations of these two possibilities would then be regular pentagons with vertex numbering (labels for carbon atoms bound to the metal) of 1–5 and 1, 3, 5, 2, 4, respectively. Note that for a 1,3 shift the alternative representation (which is not a planar graph) shown in Figure 1 cannot be converted to an energy surface because of the crossover of reaction paths. In the planar graphs, vertices represent G_A isomers and edge midpoints the G_B isomers; the connecting segments are the operations. The graphs can be converted, in principle, to potential energy diagrams by the proper deformation of line segments.

In cyclopentadienylmetalates, permutation of carbon vertices *via* a "sandwich"-type intermediate does not yield a cyclic group since δ for the G_B intermediate or transition state is 5. Here the representation is a tree with the G_B transition state connected to five points representing G_A isomers.

Closed Stereochemical Classes. General Cases. Three-coordinate complexes may have pyramidal or coplanar form. These two polytopal forms are related by a simple MX bending mode. Topologically this class is trivial. The preferred representation is spheroid, either oblate or prolate, depending upon which polytopal form is lower in energy. The *d* and *l* pyramidal isomers are placed at the antipodal positions and the coplanar form is at the equator.[13]

The two idealized polytopal isomers for four-atom systems are the tetrahedron ($I = 4!/12 = 2$) and the square plane ($I = 4!/8 = 3$). Conversion of tetrahedron into a planar form may be visualized as a twisting of two mutually orthogonal planes of the tetrahedron, each

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[12] There always appears to be a subcycle of order one greater than $\mathscr{C}_E/2$. This is simply based on analyses of a number of stereochemical classes.

[13] For a recent discussion of inversion in pyramidal molecules, *cf.* G. W. Koeppl, D. S. Sagatys, G. S. Krishnamurthy, and S. I. Miller, *J. Am. Chem. Soc.*, **89**, 3396 (1967).

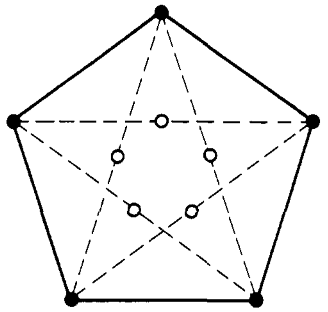

Figure 1. A nonplanar graph for the 1,3 shift process in cyclopentadienylmetalates. Reaction paths are indicated by dotted lines.

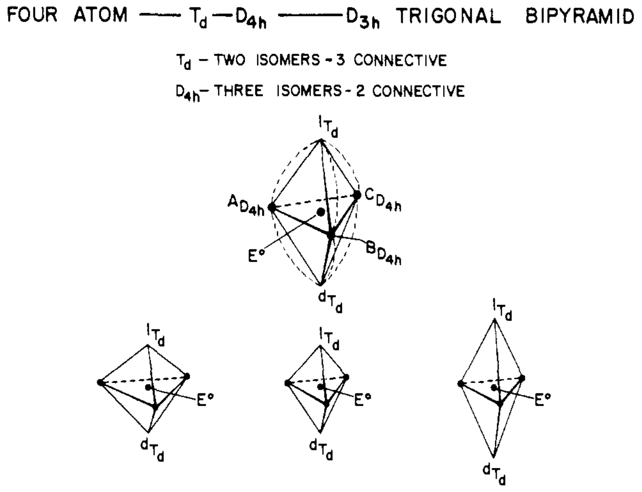

Figure 2. Topological representation of the T_d-D_{4h} class. Polyhedra at the bottom illustrate three possible representations in an energetic sense with the one on the left and the one on the right illustrating T_d and D_{4h} ground states, respectively.

through an angle of 45°. Operationally, the tetrahedron has a connectivity of three and the square plane two. The $I \cdot \delta$ products are identical. A topological representation is a trigonal bipyramid of D_{3h} symmetry (Figure 2). Edges connecting equatorial vertices are disallowed reaction paths. There are no subcycles in this class. The chain c_E for the tetrahedral form is first order, one *step* for *d* to *l* conversion. Relative placement of the T_d and D_{4h} energy levels is achieved as shown at the bottom of Figure 2 by compression or elongation of the bipyramid along the threefold axis. The elongated form is representative of heavy-atom d^8 complexes, the intermediate form of some cobalt and nickel(II) complexes, and the compressed form of most chemical systems. An alternative topological representation, derived from a torus, is depicted in Figure 3. The related T_d–D_{2h} class is also closed, and a hexagonal-bipyramidal representation is given in Figure 4.

Dihedral Groups. Two idealized polytopal isomers in the six-atom family are the octahedron and the trigonal prism which may be interconverted by counter face rotation on a threefold axis. In the general chelate class M(chel)$_3$, there are two possible operations: one a twist on a real threefold axis and one on an imaginary threefold axis (Figure 5). These operations form a dihedral group. The two kinds of operations yield two different types of trigonal prismatic isomers designated Bailar and Rây and Dutt as shown in Figure 5. A *trans* span of a square face is not allowed. For this class, the $I \cdot \delta$ products are 16 × 4 and 32 × 2 for the octahedron and trigonal prism, respectively. An explicit topological representation is the cell-first reduction of the γ_4 (tesseract) polytope (Figure 6) with the octahedral isomers at vertices, the Rây and Dutt type intermediates at edge midpoints of the two interconnected cubes, and the Bailar intermediates at the midpoints of the lines con-

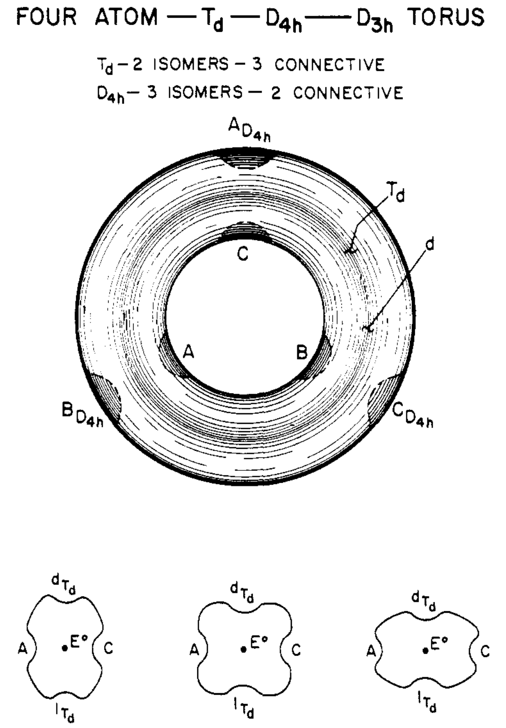

Figure 3. "Toral" representation of the T_d-D_{4h} class. The three figures at the bottom are cross sections to illustrate relative energy relationships as in Figure 2.

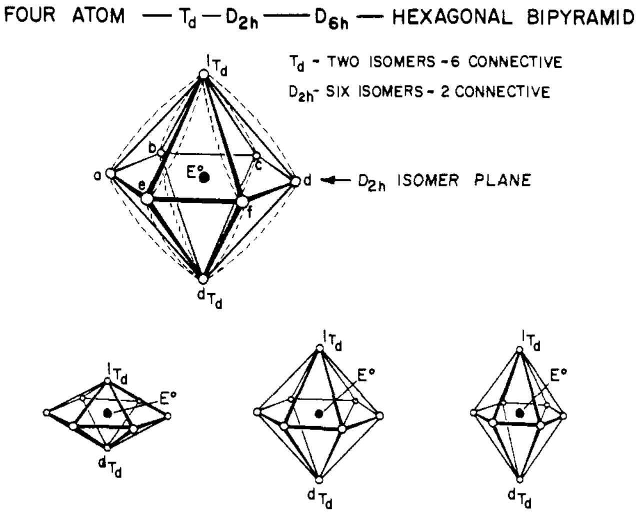

Figure 4. Topological representation of the T_d-D_{2h} class.

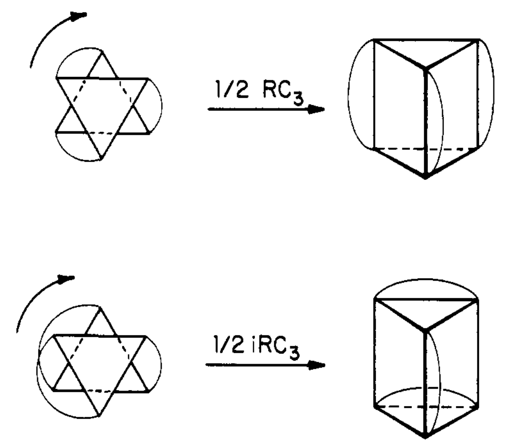

Figure 5. Operations for the M(chel)$_3$ class. At the top and bottom right are the Bailar and the Rây and Dutt intermediates, respectively.[1b]

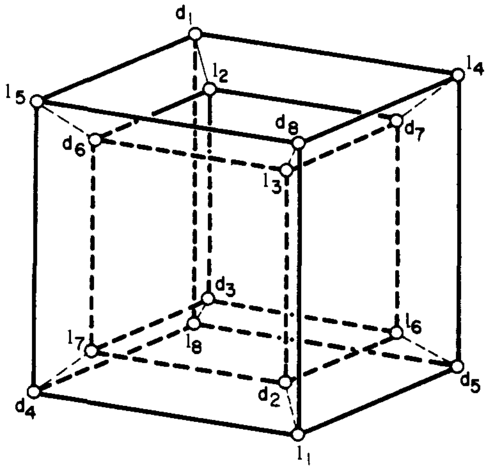

Figure 6. Topological representation of the dihedral stereoisomeric group M(chel)$_3$.

necting the two cubes. Elimination of the RC$_3$ process leaves two isolated subsets which are cubes. In these groups racemization is allowed. Elimination of the iRC$_3$ process leaves eight isolated chains of order one.

From Figure 6 it can be seen that cycles, $\mathscr{C}_E$, are of order six and of two types, *e.g.*, $d_1 \xrightarrow{-} l_5 \xrightarrow{+} d_4 \xrightarrow{-} l_1 \xrightarrow{+} d_5 \xrightarrow{-} l_4 \xrightarrow{+} d_1$ and $d_1 \xrightarrow{-} l_5 \xrightarrow{+} d_8 \xrightarrow{-} l_1 \xrightarrow{+} d_4 \xrightarrow{-} l_8 \xrightarrow{+} d_1$. The *d* and *l* designations are arbitrary in that they do not specifically refer to dextro and levo forms. There are also cycles of order eight as in $l_1 \rightarrow d_2 \rightarrow l_6 \rightarrow d_3 \rightarrow l_2 \rightarrow d_1 \rightarrow l_5 \rightarrow d_8 \rightarrow l_1$ and of order ten as in $l_1 \rightarrow d_5 \rightarrow l_6 \rightarrow d_7 \rightarrow l_4 \rightarrow d_1 \rightarrow l_5 \rightarrow d_6 \rightarrow l_7 \rightarrow d_4 \rightarrow l_1$ (note the pervasive alternation in chirality for all operations of these stereoisomeric elements). Subcycles are all tetragons but there are two types. One element of 12-fold degeneracy is represented by cube faces (all steps of $+ - + -$ sequence, and all involve C$_{2v}$ trigonal prismatic intermediates; *i.e.*, all steps are iRC$_3$ as in $l_5 \rightarrow d_8 \rightarrow l_1 \rightarrow d_4 \rightarrow l_5$). The second element (*e.g.*, $l_5 \xrightarrow{+} d_6 \xrightarrow{-} l_7 \xrightarrow{+} d_4 \xrightarrow{-} l_5$) has 12-fold degeneracy and has the same chirality alternations as the other subcycle, but trigonal prismatic pathways alternate between D$_{3h}$ and C$_{2v}$ forms. Chains, c_E, are of order three, *i.e.*, traverse four isomers and comprise three steps ($+ - +$ or $- + -$) —and are only six degenerate with respect to each enantiomeric set.[14]

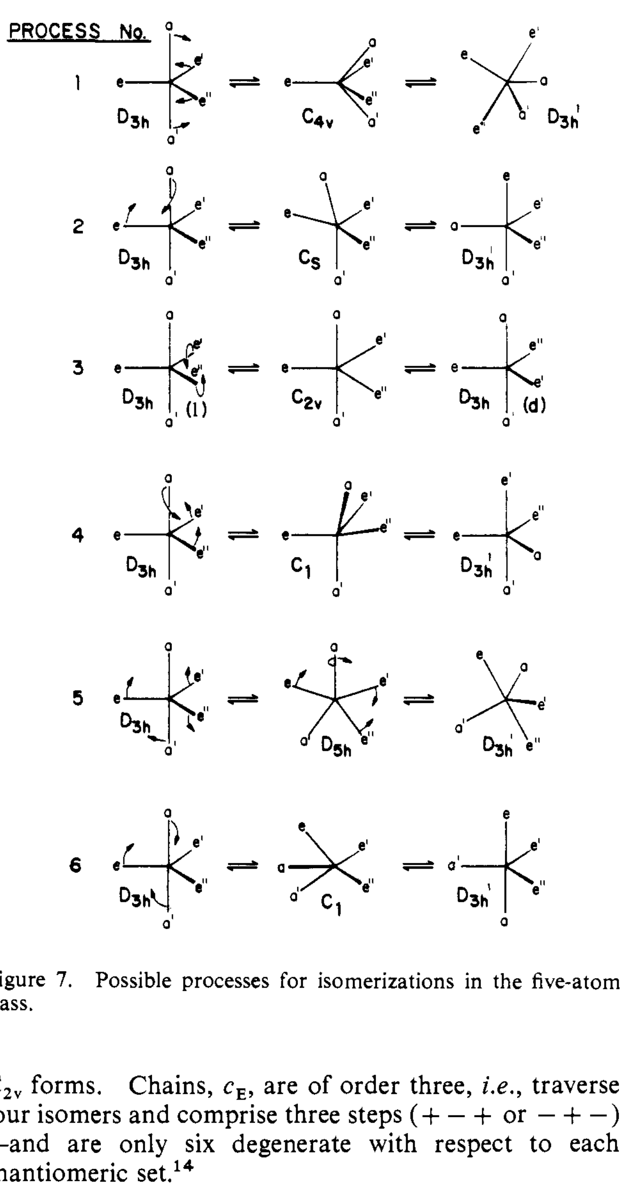

Figure 7. Possible processes for isomerizations in the five-atom class.

Representation Difficulties. Stereochemical Matrices

The trigonal bipyramid and the square pyramid are the prevailing polytopal isomers in the five-atom family. A mode for interconversion of these forms, first proposed by Berry,[15] is process 1 of Figure 7. The $I \cdot \delta$ products are 20 × 3 and 30 × 2 for the D$_{3h}$ and C$_{4v}$ forms, respectively; the stereochemical class is closed. Class elements are the cycle $\mathscr{C}_E$ of order ten, the subcycle of order six with threefold degeneracy, and the chain c_E of order five with 12-fold degeneracy. The regular pentagonal dodecahedron with D$_{3h}$ isomers at the 20 vertices and C$_{4v}$ isomers at the 30 edge midpoints is not a solution. One obvious deficiency is the absence of hexagons for the subcycle requirement. This can be resolved with a double group representation and quasi-RC$_5$ operations,[1b] but this does not yield a conceptually simple model. No three-dimensional representation can

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[14] Compare with the c_E of order three and degeneracy of 24 in ML$_6$[1b] (the reduction in degeneracy is due to the chelate constraints; only one direction of "twist" in the iRC$_3$ operations is allowed); this chelate constraint also accounts for the loss of the subcycle or order 3.

[15] S. Berry, *J. Chem. Phys.*, **32**, 923 (1960).

Table I. ML_5—Process 1

R_1	12	23	34	45	13	14	15	24	25	35	$\overline{12}$	$\overline{23}$	$\overline{34}$	$\overline{45}$	$\overline{13}$	$\overline{14}$	$\overline{15}$	$\overline{24}$	$\overline{25}$	$\overline{35}$
12	E	2	4	4	3	2	3	3	2	1	5	3	1	1	2	3	2	2	3	4
23	2	E	2	4	3	4	1	3	2	3	3	5	3	1	2	1	4	2	3	2
34	4	2	E	2	3	2	1	3	4	3	1	3	5	3	2	3	4	2	1	2
45	4	4	2	E	1	2	3	3	2	3	1	1	3	5	4	3	2	2	3	2
13	3	3	3	1	E	3	2	4	1	2	2	2	2	4	5	2	3	1	4	3
14	2	4	2	2	3	E	3	3	4	1	3	1	3	3	2	5	2	2	1	4
15	3	1	1	3	2	3	E	4	3	2	2	4	4	2	3	2	5	1	2	3
24	3	3	3	3	4	3	4	E	3	4	2	2	2	2	1	2	1	5	2	1
25	2	2	4	2	1	4	3	3	E	3	3	3	1	3	4	1	2	2	5	2
35	1	3	3	3	2	1	2	4	3	E	4	2	2	2	3	4	3	1	2	5
$\overline{12}$	5	3	1	1	2	3	2	2	3	4	E	2	4	4	3	2	3	3	2	1
$\overline{23}$	3	5	3	1	2	1	4	2	3	2	2	E	2	4	3	4	1	3	2	3
$\overline{34}$	1	3	5	3	2	3	4	2	1	2	4	2	E	2	3	2	1	3	4	3
$\overline{45}$	1	1	3	5	4	3	2	2	3	2	4	4	2	E	1	2	3	3	2	3
$\overline{13}$	2	2	2	4	5	2	3	1	4	3	3	3	3	1	E	3	2	4	1	2
$\overline{14}$	3	1	3	3	2	5	2	2	1	4	2	4	2	2	3	E	3	3	4	1
$\overline{15}$	2	4	4	2	3	2	5	1	2	3	3	1	1	3	2	3	E	4	3	2
$\overline{24}$	2	2	2	2	1	2	1	5	2	1	3	3	3	3	4	3	4	E	3	4
$\overline{25}$	3	3	1	3	4	1	2	2	5	2	2	2	4	2	1	4	3	3	E	3
$\overline{35}$	4	2	2	2	3	4	3	1	2	5	1	3	3	3	2	1	2	4	3	E

be derived to satisfy all of the requirements without recourse to an interpenetrating figure. In this instance, a stereochemical matrix is preferred for simplicity. The matrix for the trigonal-bipyramid group is given in Table I with the entries representing the number of steps (R) to go from an isomer in the vertical column to one in the horizontal column. Specific isomers are designated by the axial substituents, *e.g.*, 12 and its enantiomer $\overline{12}$. All cycles, subcycles, and chains are readily obtained from the matrix. This type of presentation is recommended also for the general ML_6 class; above six the order is too large for matrices to be reasonably employed.

A distinction in mechanisms is immediately apparent by comparing the matrix for the Berry process with that for process 4 of Figure 7. This latter process has $I \cdot \delta$ products of 20 × 6 and 120 × 2 for D_{3h} and C_1, respectively; the class is open. The class consists of two disjoint and isomorphic (enantiomeric) groups. The stereochemical matrix for one of the groups is given in Table II. Note that racemization cannot occur by this mechanism, and that there are many subcycles of order three, four, and five. Processes 4 and 6 are identical. Process 2 yields an open class but *is closed for the trigonal-bipyramid set* (Table III). A detailed discussion of isomerization mechanisms in five-coordination is deferred to paper II of this series.

Stereoisomerization. Differentiation of Mechanisms

Eight-Atom Family. Polytopal isomerism is quite complicated for the eight-atom family in that there is a large number of possible isomers. Of the depicted isomers in Figure 8, only the D_{3h} isomer has not been reported for a molecular species. In coordination compounds and polyhedral boranes, the square antiprism (D_{4d}) and trigonal dodecahedron (D_{2d}) appear to be nearly equivalent in energy.[6] Possible operations for interconversions of some of these forms are illustrated in Figures 9–12. Isomer counts for O_h, D_{4d}, D_{2d}, and C_{2v} are 1680, 5040, 10,080, and 20,160, respectively.

Table II. ML_6—Process 4

R_4	12	25	$\overline{15}$	$\overline{24}$	$\overline{13}$	23	14	$\overline{35}$	45	34
12	E	1	1	1	1	1	1	2	2	2
25	1	E	1	1	2	1	2	1	1	2
$\overline{15}$	1	1	E	2	1	2	1	1	1	2
$\overline{24}$	1	1	2	E	2	1	1	2	1	1
$\overline{13}$	1	2	1	2	E	1	1	1	2	1
23	1	1	2	1	1	E	2	1	2	1
14	1	2	1	1	1	2	E	2	1	1
$\overline{35}$	2	1	1	2	1	1	2	E	1	1
45	2	1	1	1	2	2	1	1	E	1
34	2	2	2	1	1	1	1	1	1	E

Based on the illustrated operations, the connectivities are

$$\begin{array}{ll} O_h(\rightarrow D_{4d}) = 6 & D_{4d}(\rightarrow O_h) = 2 \\ O_h(\rightarrow D_{2d}) = 6 & D_{4d}(\rightarrow D_{2d}) = 4 \\ & D_{4d}(\rightarrow C_{2v}) = 4 \\ D_{2d}(\rightarrow O_h) = 1 & \\ D_{2d}(\rightarrow D_{4d}) = 2 & C_{2v}(\rightarrow D_{4d}) = 1 \end{array}$$

The connectivities of one for D_{2d} in $D_{2d} \rightleftarrows O_h$ interconversion and for C_{2v} in $D_{4d} \rightleftarrows C_{2v}$ show the openness of these classes; they may be treated as isolated subsets represented by 1680 octahedra (D_{2d} isomers at vertices and an O_h at the center) and by 5040 tetrahedra, respectively. Racemization cannot occur in either class. The $O_h \rightleftarrows D_{4d}$ and $D_{4d} \rightleftarrows O_h$ classes are closed. In the former, the racemization chain c_E is of order six with one $(+)^1/_2RC_4$ and eleven $(-)^1/_2RC_4$, or one $(-)^1/_2RC_4$ and eleven $(+)^1/_2RC_4$ operations. One of the subcycles is seventh order. For the $D_{4d} \rightleftarrows D_{2d}$ system c_E is 13, and there are subcycles of order $2n$ with $n = 3$–7.[16]

Twelve-Atom Family. For the 12-atom family the prevailing ground-state form is the icosahedron (I_h) in coordination compounds and in polyhedral boranes. An operation[6,8] on the icosahedron that ultimately leads to isomerization is a stretching of three orthogonal sets

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(16) I am indebted to Dr. J. P. Jesson for writing the computer program for this permutation problem.

Table III. ML_5—Process 2

R_2	12	23	34	45	13	14	15	24	25	35	$\bar{1}\bar{2}$	$\bar{2}\bar{3}$	$\bar{3}\bar{4}$	$\bar{4}\bar{5}$	$\bar{1}\bar{3}$	$\bar{1}\bar{4}$	$\bar{1}\bar{5}$	$\bar{2}\bar{4}$	$\bar{2}\bar{5}$	$\bar{3}\bar{5}$
12	E	2	2	2	1	2	1	1	2	3	3	1	3	3	2	1	2	2	1	2
23	2	E	2	2	1	2	3	1	2	1	1	3	1	3	2	3	2	2	1	2
34	2	2	E	2	1	2	3	1	2	1	3	1	3	1	2	1	2	2	3	2
45	2	2	2	E	3	2	1	1	2	1	3	3	1	3	2	1	2	2	1	2
13	1	1	1	3	E	1	2	2	3	2	2	2	2	2	3	2	1	3	2	1
14	2	2	2	2	1	E	1	1	2	3	1	2	1	1	2	3	2	3	3	2
15	1	3	3	1	2	1	E	2	1	2	2	2	2	2	1	2	3	3	2	1
24	1	1	1	1	2	1	2	E	1	2	2	2	2	2	3	2	3	3	2	3
25	2	2	2	2	3	2	1	1	E	1	1	1	3	1	2	3	2	2	3	2
35	3	1	1	1	2	3	2	2	1	E	2	2	2	2	1	2	1	3	2	3
$\bar{1}\bar{2}$	3	1	3	3	2	1	2	2	1	2	E	2	2	2	1	2	1	1	2	3
$\bar{2}\bar{3}$	1	3	1	3	2	2	2	2	1	2	2	E	2	2	1	2	3	1	2	1
$\bar{3}\bar{4}$	3	1	3	1	2	1	2	2	3	2	2	2	E	2	1	2	3	1	2	1
$\bar{4}\bar{5}$	3	3	1	3	2	1	2	2	1	2	2	2	2	E	3	2	1	1	2	1
$\bar{1}\bar{3}$	2	2	2	2	3	2	1	3	2	1	1	1	1	3	E	1	2	2	3	2
$\bar{1}\bar{4}$	1	3	1	1	2	3	2	2	3	2	2	2	2	2	1	E	1	1	2	3
$\bar{1}\bar{5}$	2	2	2	2	1	2	3	3	2	1	1	3	3	1	2	1	E	2	1	2
$\bar{2}\bar{4}$	2	2	2	2	3	3	3	3	2	3	1	1	1	1	2	1	2	E	1	2
$\bar{2}\bar{5}$	1	1	3	1	2	3	2	2	3	2	2	2	2	2	3	2	1	1	E	1
$\bar{3}\bar{5}$	2	2	2	2	1	2	1	3	2	3	3	1	1	1	2	3	2	2	1	E

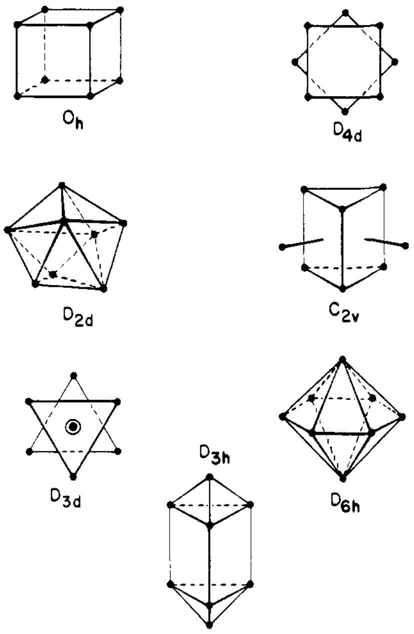

Figure 8. Idealized polytopes in the ML_8 or M_8 family.

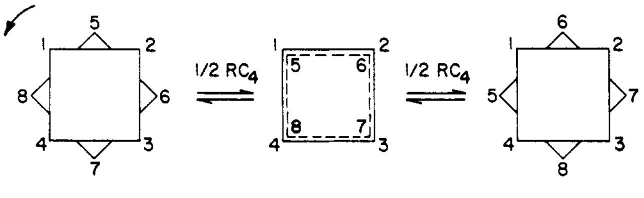

Figure 9. An operation for traverse of D_{4d} and O_h polytopes in the eight-atom class.

Figure 10. Distortion of the cube to generate the trigonal dodecahedron.

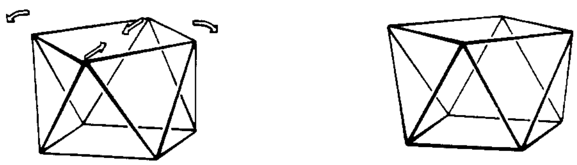

Figure 11. Operation for square antiprism to C_{2v}-bicapped trigonal prism traverse.

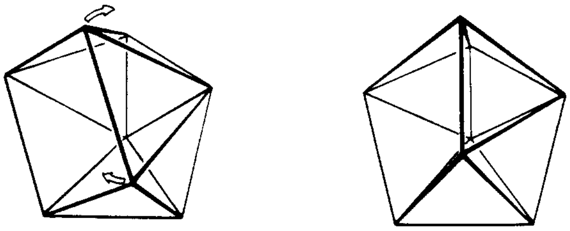

Figure 12. Operation for C_{2v}-bicapped trigonal prism to trigonal dodecahedron traverse.

of two coplanar edges. An *intermediate* state is the patohedron[6,8] which has isosceles triangular faces and T_h symmetry; see Figure 13 for the stretching mode. The icosahedron cannot be isomerized *via* the patohedron because the connectivity of the latter is one. Hence the I_h–T_h class is open and consists of disjoint groups, namely 7,983,360 trees with an I_h isomer connected to five T_h isomers. If the stretching mode outlined in Figure 13 is carried to the point that square faces (six) are generated, cube octahedral geometry (O_h) results

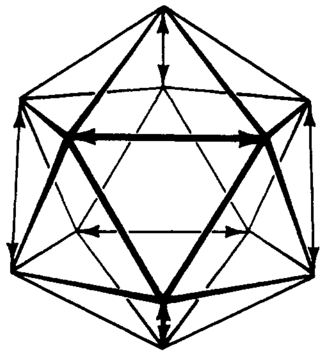

Figure 13. Distortion mode for $I_h \rightarrow T_h$.

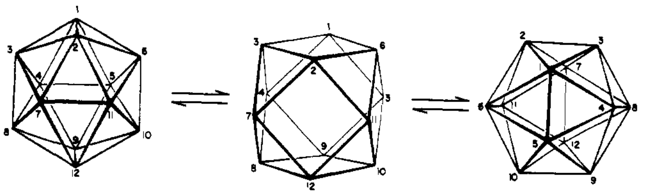

Figure 14. Isomerization of icosahedral ML_{12} or M_{12} species *via* the cube octahedron. Antipodal relations are maintained throughout the process.

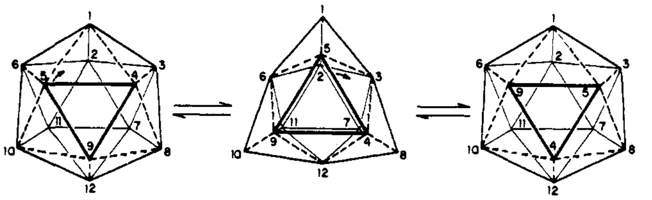

Figure 15. Face rotation mechanism for isomerization in icosahedral ML_{12} or M_{12} species.

(Figure 14). The isomer counts are: $I(I_h) = 12!/60 = 7,983,360$ and $I(O_h) = 12!/24 = 19,958,400$. Connectivities are five and two for I_h and O_h, respectively. The stereoisomeric class is not closed since $I \cdot \delta$ products are not equivalent. This openness is also visually evident from inspection of the process depicted in Figure 14. Antipodal relationships of vertices (1–12, 2–9, etc.) must be maintained in both polytopal forms. Interconversion of enantiomers may occur by this process; the minimum number of steps for this process is seven.

An operation that yields a closed class for the icosahedron is single-face rotation (Figure 15). The intermediate polytopal form has C_3 symmetry, an isomer count of 159,667,220, and a connectivity of two. The connectivity of the icosahedron with respect to this operation is simply twice the number of faces in this polyhedron since the faces can be rotated in either direction. Thus the equality

$$\left.\begin{array}{l} I \cdot \delta(I_h) = 7,983,360 \times 40 \\ I \cdot \delta(C_3) = 159,667,200 \times 2 \end{array}\right\} = 319,334,400$$

is obtained.

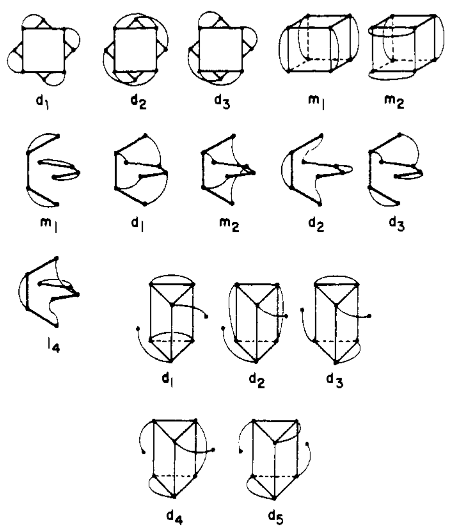

Figure 16. Stereoisomers in three polytopal isomer forms of $M(chel)_4$.

Different Isomer Connectivities

In eight-coordinate chelates of the type $M(chel)_4$, there are two predominating polytopal isomers, the square antiprism ("D_{4d}") and the trigonal dodecahedron ("D_{2d}"). Intermediate between these two polytopal isomers is the bicapped trigonal prismatic ("C_{2v}") form (see Figures 11 and 12). The antiprism–dodecahedron and bicapped trigonal prism–dodecahedron stereochemical classes are closed; individual stereoisomer connectivities vary. The stereoisomers are depicted in Figure 16. First-order operational relationships for these two classes are as follows.

"D_{4d}"	"D_{2d}"
d_1 (l_1)	d_1,l_2 (l_1,d_2)
d_2 (l_2)	l_1,d_3, m_1 (d_1,l_3,m_1)
d_3 (l_3)	d_3,d_4,m_2 (l_3,l_4,m_2)

$$\text{"}D_{4d}\text{"} \ \sum I_i\delta_i = (2 \times 2) + (2 \times 3) + (2 \times 3) = 16$$

$$\text{"}D_{2d}\text{"} \ \sum I_i\delta_i = (1 \times 1) + (1 \times 2) + (2 \times 2) + (2 \times 1) + (2 \times 2) + (2 \times 1) = 16$$

Two specific first-order operations are illustrated in Figure 17.

"C_{2v}"	"D_{2d}"
d_1 (l_1)	m_1,l_3 (m_1,d_3)
d_2 (l_2)	l_1,d_3 (d_1,l_3)
d_3 (l_3)	l_3,l_4 (d_3,d_4)
d_4 (l_4)	m_2,l_4 (m_2,d_4)
d_5 (l_5)	d_1,l_2 (l_1,d_2)

$$\text{"}C_{2v}\text{"} \ \sum I_i\delta_i = (2 \times 2) + (2 \times 2) + (2 \times 2) + (2 \times 2) + (2 \times 2) = 20$$

$$\text{"}D_{2d}\text{"} \ \sum I_i\delta_i = (1 \times 2) + (1 \times 2) + (2 \times 2) + (2 \times 1) + (2 \times 3) + (2 \times 2) = 20$$

In contrast, to the above two classes, neither the D_{4d}–O_h nor the D_{2d}–O_h classes in $M(chel)_4$ are closed, and within the subsets isomer connectivities vary.

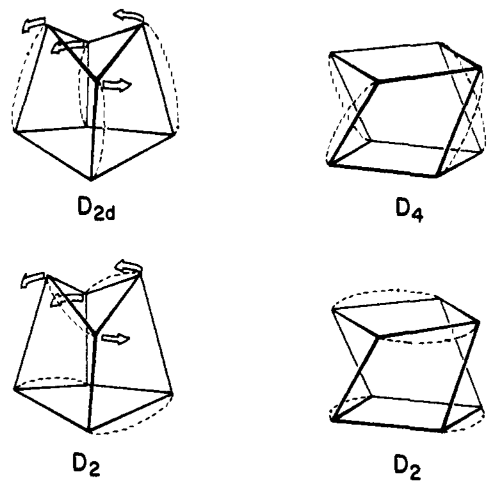

Figure 17. Illustration of dodecahedral to square antiprism operations for specific stereoisomers: (top) D_{2d}("m_1") → D_4("d_1"); (bottom) D_{2d}("d_1") → D_2("d_2").

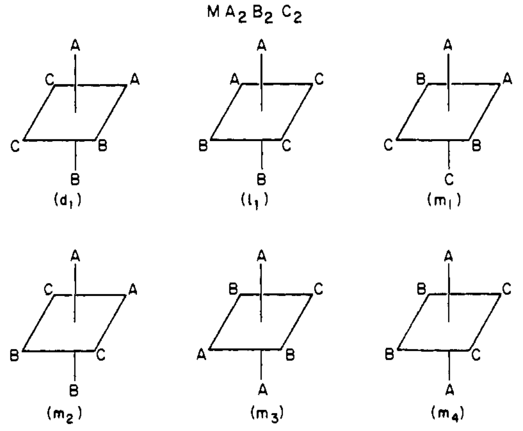

Figure 18. Octahedral stereoisomers in $MA_2B_2C_2$.

Another stereochemical system with isomers of varying connectivity is the six-coordinate $MA_2B_2C_2$ class with octahedral and trigonal prismatic polytopal forms. The processes are RC_3 trigonal twists on C_3 and iC_3 axes. The 6 octahedral and 18 trigonal prismatic isomers are shown in Figures 18 and 19. First-order operational relationships are

"O_h"	"D_{3h}"
d_1	$m_1, m_2, m_3, m_4, d_1, d_2, d_3, d_4$
m_1	$d_4, l_4, d_5, l_5, d_6, l_6$
m_2	$d_3, l_3, d_6, l_6, d_7, l_7$
m_3	d_2, l_2
m_4	$d_1, l_1, d_5, l_5, d_6, l_6$

$$\text{"O}_\text{h}\text{"}\ I\cdot\delta = \textstyle\sum_i I_i\delta_i = (2 \times 8) + (1 \times 6) + (1 \times 6) + (1 \times 2) + (1 \times 6) = 36$$

$$\text{"D}_{3\text{h}}\text{"}\ I\cdot\delta = \textstyle\sum_i I_i\delta_i = 4(1 \times 2) + 7(2 \times 2) = 36$$

The $I\cdot\delta$ products are equivalent and the class is closed. Topologically, a reasonably symmetrical representation is achieved with a compound polytope. Because of the

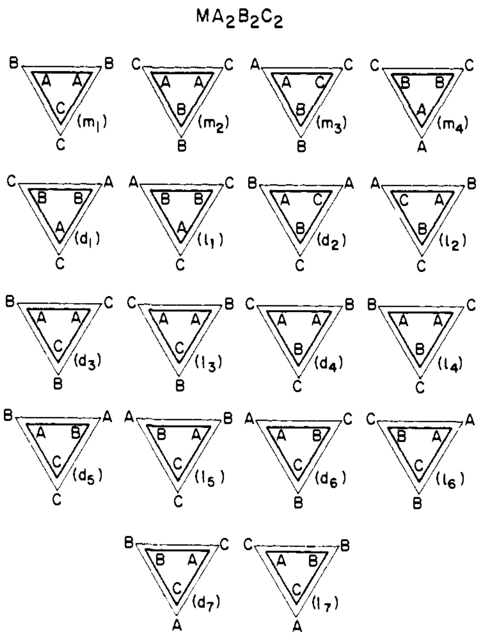

Figure 19. Trigonal prismatic stereoisomers in $MA_2B_2C_2$.

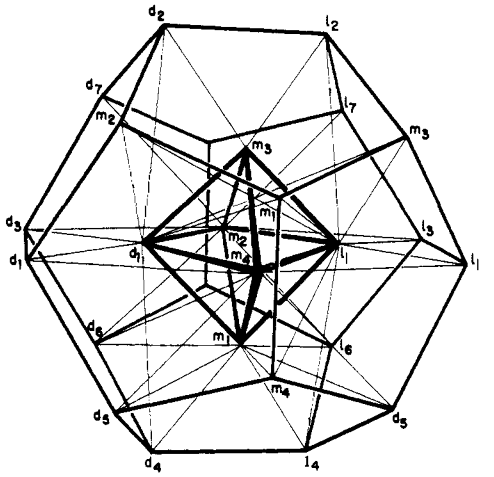

Figure 20. Topological representation of the $MA_2B_2C_2$ class. Octahedral stereoisomers are at the vertices of the enclosed octahedron and trigonal prismatic stereoisomers at 18 of the 20 pentagonal dodecahedral vertices. First-order isomer relationships are shown by line connectors between the octahedron and the pentagonal dodecahedron. The figure is an interpenetrating one.

duality relationship, the octahedron may be placed symmetrically within a pentagonal dodecahedron (Figure 20). The octahedral vertices represent the 6 octahedral isomers, and 18 of the dodecahedral vertices are used for the trigonal prismatic isomers.[17]

Acknowledgment. I am indebted to Mr. Ames Schuck for the drawings and to Professor John Wheeler and Dr. J. P. Jesson for invaluable discussions.

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(17) NOTE ADDED IN PROOF. Closure of a stereochemical class requires the connected graph condition of $I\cdot\delta$ product equality and a rearrangement that is an odd permutation *if* the group of all permutations representing the isomers is even–odd: E. L. Muetterties and A. T. Storr, to be published.