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James G. Nourse,
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Abstract: A stereoisomerization mode can be defined as a set of symmetry equivalent degenerate rearrangements of a molecular skeleton. The key mathematical constructions in this definition are the double cosets of the skeletal point group in some larger permutation group of identically substituted skeletal sites. This concept is generalized to include the more practical case in which the sites are not identically substituted and in which rearrangements can therefore be degenerate or nondegenerate. A symmetry group, $S_{nL} \times S_{nS}$, is defined which includes all permutations which act on ligand and site labels separately. The generalized stereoisomerization modes are found to be collections of double cosets in this group. It is then shown that the schemes used in some previously solved problems can be viewed as restrictions of this scheme. The methods are also applicable to the site exchange problems often encountered in problems in dynamic stereochemistry.
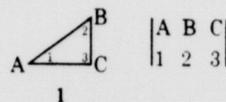
Recently there has been a considerable amount of work making use of permutation group theory to define key symmetry-based concepts in dynamic stereochemistry.[1] Although definitions and terminology vary somewhat the most important concept is probably the stereoisomerization *mode* which is defined by various double coset decompositions of a permutation group by a skeletal site point group.[1b-f] Generally, the existing treatments only consider isomerizations which can be expressed by permutations of nuclei of identical chemical composition. The purpose of this article is to generalize the mode concept by including isomerizations which can be expressed by permutations of nuclei of different chemical composition. This will be done by using a formalism which takes the ligand symmetry (i.e., the number of ligands of identical chemical composition) and site symmetry (e.g., skeletal point group) of the dynamic problem into account simultaneously. The experimental question addressed is this: By changing the number and kind of substituents on a molecule undergoing a skeletally degenerate rearrangement, how many more potentially observable processes are there? Such rearrangements are encountered, for example, in the study of various molecular propellers,[2] pentacoordinate system,[3] and hydrocarbons.[4] In all cases treated here the assumption will be made that the different substituents do not seriously deform the skeleton but may significantly alter the favored rearrangement mechanism. The present treatment does not deal with the case of a skeletally nondegenerate rearrangement.

Ligand-Site Permutation Group

The formulation requires a permutation group which acts on the molecular skeletal site labels and ligand labels separately. The construction of and need for such a group will be shown.

A number of existing treatments make use of the idea of an ordered molecule which is a $2 \times n$ matrix indicating the mapping of a set of n ligands to a set of n molecular sites.[1,5] Each $2 \times n$ matrix corresponds to one of the possible isomers obtained by placing the n ligands on the n sites. For example, consider the simple case of three ligands and three sites. The

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triangular structures used throughout are simply abstract models of molecules.

Structure **1** is described by the $2 \times n$ matrix indicated. Isomerization can now be represented by permutations which act on either the ligand labels or the site labels. However, the same overall change can be effected by either a ligand permutation or site permutation (e.g., the ligand permutation (ABC) and site permutation (132) have the same effect on structure **1**) and these permutations are generally identified.[1e] (The conventions for defining and multiplying permutations are given in the section Notations and Conventions at the end of this paper.) Thus for certain problems it suffices to make use of only one type of permutation; site permutations are usually chosen.[1,6]

In the present formulations the $2 \times n$ matrix represents an *isomerization* rather than an isomer. Consider the examples:
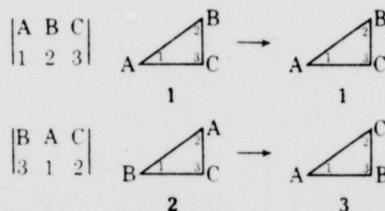
The top row of the matrix gives the position of each ligand on the starting isomer (site labels increase from left to right in the matrix). Thus in the second example above, ligand B starts in site 1, ligand A starts in site 2, and ligand C starts in site 3. The bottom row of the $2 \times n$ matrix gives the site permutation effected by the isomerization. Again in the second example above the permutation is: the ligand in site 1 goes to site 3, the ligand in site 3 goes to site 2, and the ligand in site 2 goes to site 1. The first example above gives the $2 \times n$ matrix for the trivial isomerization of isomer **1** to itself. There will be six such trivial isomerizations since there are six possible isomers. Since each

of the six isomers can go to any of the other six, there are 36 possible isomerizations and therefore 36 possible $2 \times n$ matrices.

The $2 \times n$ matrices now serve as a convenient representation for visualizing the effect of the full permutation group on ligand and site indices. The permutation group in question is the direct product, $S_{nL} \times S_{nS}$, where S_{nL} includes all possible ligand permutations and S_{nS} includes all possible site permutations. The order of (number of elements in) the group is $(n!)^2$. Referring to the $2 \times n$ matrix, the elements of S_{nL} permute the ligand indices in the top row in all possible ways and elements of S_{nS} permute the site indices in the bottom row in all possible ways. Referring to the possible isomerizations the effect of the direct product group can be visualized as follows:

1. Permutations in S_{nL} act on the top row of the $2 \times n$ matrix and change both the starting isomer and the resulting isomer.

2. Permutations in S_{nS} act on the bottom row of the $2 \times n$ matrix thereby changing the isomerization and hence change only the resulting isomer.

Since there are $(n!)^2$ possible isomerizations (equivalences of some of these by symmetry will be discussed shortly), there is a one-to-one correspondence between these isomerizations and the elements of $S_{nL} \times S_{nS}$. This correspondence is most easily visualized by noting the one-to-one correspondence between the elements of $S_{nL} \times S_{nS}$ and the $2 \times n$ matrices and then noting the one-to-one correspondence between the $2 \times n$ matrices and the possible isomerizations discussed above. It should be noted that S_{nL} contains permutations of all ligands being considered irrespective of chemical identity. The ligand permutation group used in some other treatments[1,6] which contains only permutations of chemically identical ligands is a subgroup of S_{nL}.

The need for the full group $S_{nL} \times S_{nS}$ in some problems can be demonstrated by an example.

Consider the isomerization of structures such as:

1
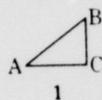
This is an idealized case in which there are three nonequivalent sites and three nonequivalent ligands. It is assumed that the starting isomer and resulting isomer of any isomerization (but nothing in between) can be distinguished. Since there are 6 possible isomers of this idealized structure, there are $6 \times 6 = 36$ possible isomerizations which could in principle occur and be observed. Thus under given conditions isomer **1** may not isomerize but isomer **2** may go to isomer **3**, etc.,
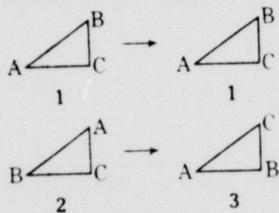
Now consider structure **4** with 3 equivalent sites and 3 equivalent ligands.
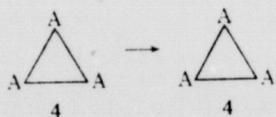
The same isomerization of **4** yields only one possibility, the trivial isomerization **4 → 4**. However by labeling the sites and ligands as in **5** it is still possible to describe 36 isomerizations. The point here is that by increasing ligand and site symmetry


5
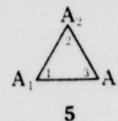
to that in structure **4**, all 36 possible isomerizations have become equivalent. It can be shown that the smallest symmetry group which makes 36 objects equivalent must have 36 elements.[7a] In this case the appropriate group is $S_{3L} \times S_{3S}$ as shown above.[7b] Consideration of only the ligand symmetry group (order 6) or the site symmetry group (order 6) is not sufficient for the problem at hand.

### Generalized Stereoisomerization Modes

By taking into account both ligand and site symmetry within the group $S_{nL} \times S_{nS}$, generalized stereoisomerization modes can be constructed. These generalized modes can be represented by subsets of the set of $(n!)^2$ isomerizations collected by the effect of the ligand and site symmetry groups.

By making use of the representations of $S_{nL} \times S_{nS}$ on isomerizations and $2 \times n$ matrices discussed in the previous section it will be shown that an isomerization is invariant (i.e., unchanged as far as the permutational representation is concerned) to three kinds of operations. Stated differently, each of these operations will change any isomerization into an equivalent isomerization.

1. An isomerization is unchanged if it is preceded by a skeletal rotation coupled to a compensating ligand permutation. As an example consider the isomerization of the isosceles triangle skeletons:


$$\begin{vmatrix} A & B & C \\ 2 & 1 & 3 \end{vmatrix}$$

M1
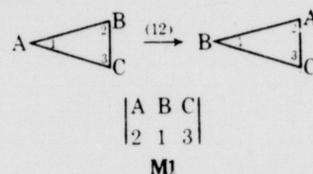
expressed by the $2 \times n$ matrix M1. Since ... 2 and 3 are equivalent by a C_2 rotation through the vertex 1. This isomerization could not be distinguished from the isomerization:


$$\begin{vmatrix} A & C & B \\ 2 & 3 & 1 \end{vmatrix}$$

M2
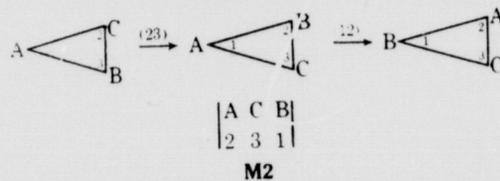
The first step is just a skeletal rotation. Referring to the $2 \times n$ matrices, M2 is obtained from M1 by an interchange of the two columns associated with the symmetry equivalent skeletal sites. This change can be expressed by the ligand-site permutation (23)(BC). In the general case the set of all such permutations from a group isomorphic to the rotation group of the skeletons R_{LS} (skeletal rotation group acting on ligand (L) and site (S) indices).

2. An isomerization is unchanged if acted on by any permutation of constitutionally equivalent ligands. Such a permutation acts on ligand indices and has the effect of changing both the starting and resulting isomers of the isomerization. Consider the isomerization of scalene triangle skeletons symbolized by M3:

$$\begin{vmatrix} A & B & A' \\ 2 & 1 & 3 \end{vmatrix}$$

M3
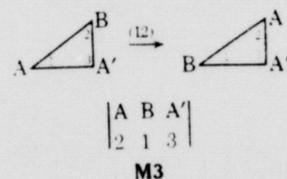
Ligands A and A' are constitutionally equivalent and are dis-

tinguished only by the superscript. This isomerization would not be distinguishable from:

$$\begin{vmatrix} A' & B & A \\ 2 & 1 & 3 \end{vmatrix}$$
M4
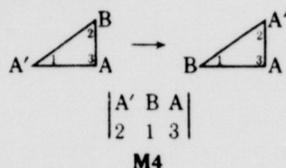
The starting and final isomers of isomerization **M3** are equivalent to those of **M4** if the arbitrary superscript is eliminated. Matrices **M3** and **M4** are related by the ligand permutation (AA'). The set of all such permutations in the general case will be a group which is a direct product of symmetric groups and will be symbolized L_L (acts on ligand indices only). These ligand permutations must *follow* the permutations of R_{LS} since permutations in L_L can exchange ligands between nonequivalent sites and therefore the permutational description of a rotation. Consider the sequences:
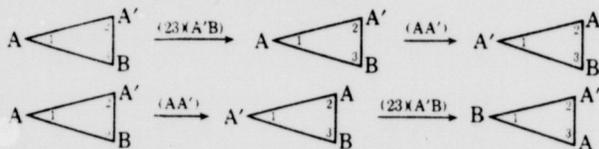
In the first sequence, (23)(A'B) (which is an element in R_{LS} for this structure) followed by (AA') (an element of L_L), the rotation precedes the ligand exchange and an identical isomer is obtained. In the second sequences, (AA') followed by (23)(A'B), a different isomer is obtained. Thus an isomerization is invariant to the combined permutations in R_{LS} and L_L only if the permutation of R_{LS} precedes that of L_L.

3. An isomerization is unchanged when followed by an overall skeletal rotation assuming the molecule is free to move (i.e., in solution). These rotations are represented by permutations which act on the site indices only. Thus the isomerizations symbolized by **M1** and **M5** are not distinguishable.

$$\begin{vmatrix} A & B & C \\ 2 & 1 & 3 \end{vmatrix}$$
M1

$$\begin{vmatrix} A & B & C \\ 3 & 1 & 2 \end{vmatrix}$$
M5
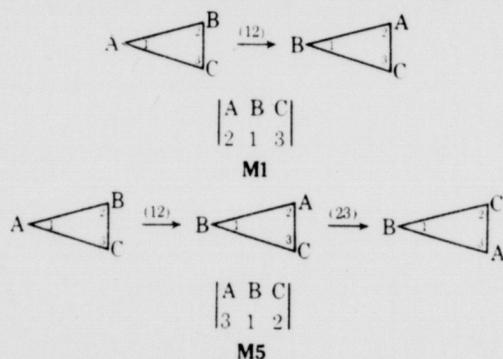
The site permutation (23) has the effect of a skeletal rotation. All such permutations will form a group, symbolized by R_S, isomorphic to the skeletal rotation group acting on the site indices only.

The key construction in the definition of generalized stereoisomerization modes is the double coset decomposition of the group $S_{nL} \times S_{nS}$ by the symmetry groups R_{LS}, L_L, R_S:

$$R_{LS}|S_{nL} \times S_{nS}|L_L \times R_S \qquad (1)$$

This construction is generated by the three symmetry criteria listed above. A *generalized stereoisomerization mode* will be a collection of one or more of the double cosets obtained from (1). Note that since multiplication of group elements proceeds from left to right, the rotations in R_{LS} precede the ligand permutations in L_L and the rotations in R_S follow the permutations in S_{nS} as required. To illustrate this construction consider the possible isomerizations of an isosceles triangle skeleton with two identical ligands

The group $S_{3L} \times S_{3S}$ acts on the ligand and site indices as described in the previous sections. The three symmetry groups are:
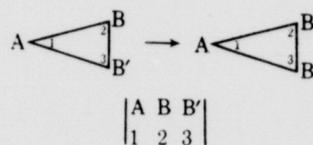
$$R_{LS} = \{e,(23)(BB')\} \cong C_{2LS}$$
$$L_L = \{e,(BB')\} \cong S_{2L}$$
$$R_S = \{e,(23)\} \cong C_{2S}$$

The desired double cosets therefore are:

$$C_{2LS}|S_{3L} \times S_{3S}|S_{2L} \times C_{2S}$$

There are five of these and they are indicated in Table I. Double coset 1 is the trivial isomerization of the symmetric (C_2) isomer (only one member of the double coset is shown):
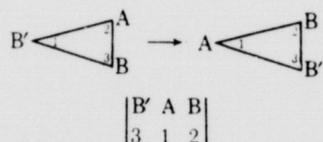

$$\begin{vmatrix} A & B & B' \\ 1 & 2 & 3 \end{vmatrix}$$

Double coset 2 is the trivial isomerization of the nonsymmetric isomer:

$$\begin{vmatrix} B & A & B' \\ 1 & 2 & 3 \end{vmatrix}$$
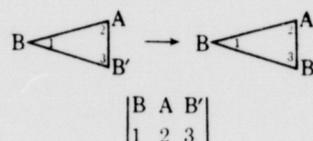
Double coset 3 is the nondegenerate isomerization:

$$\begin{vmatrix} A & B & B' \\ 2 & 3 & 1 \end{vmatrix}$$
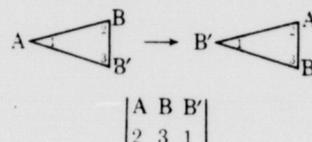
Double coset 4 is the nondegenerate isomerization (the reverse of 3):

$$\begin{vmatrix} B' & A & B \\ 3 & 1 & 2 \end{vmatrix}$$

and double coset 5 is the degenerate isomerization in which the B ligands exchange sites:

$$\begin{vmatrix} B' & A & B \\ 3 & 2 & 1 \end{vmatrix}$$
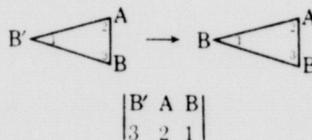
Each of these double cosets represents an isomerization which is in principle distinguishable under appropriate experimental conditions. The order of (number of elements in) each double coset is related to the statistical likelihood of the isomerization apart from energetics.

In a more complicated general case the number of double cosets, N_{DC}, can be determined by a hand calculation while the full treatment would probably be best handled by computer.[8] The appropriate combinatorial formula 2 is easily obtained from that given by Ruch[1d] for the enumeration of the double cosets in an arbitrary group.

$$N_{DC} = \frac{|S_{nL} \times S_{nS}|}{|R_{LS}||L_1||R_S|}$$

$$\times \sum_{r=1}^{k} \frac{|R_{LS} \wedge C_r||(L_L \times R_S) \wedge C_r|}{|C_r|} \quad (2)$$

The summation is over the k conjugacy classes of $S_{nL} \times S_{nS}$. For the example just presented the formula (2) gives:

$$\frac{36}{2 \cdot 2 \cdot 2}\left(1 + \frac{1 \cdot 1}{9}\right) = 5$$

as required. If all the sites were equivalent and achiral ($R_{LS} \simeq R_L \simeq C_{3r}$) and if all the ligands were different ($L_L \simeq S_1$) there would be:

$$\frac{36}{6 \cdot 1 \cdot 6}(1) = 1$$

double coset. There would only be one trivial isomerization in this case. If all the sites were inequivalent ($R_{LS} \simeq R_L \simeq C_1$) and if all the ligands were identical ($L_L \simeq S_3$) there would be:

$$\frac{36}{1 \cdot 6 \cdot 1}(1) = 6$$

double cosets and therefore a maximum of six potentially observable processes. For more difficult cases ($n > 3$) the conjugacy classes of $S_{nL} \times S_{nS}$ are most easily obtained from tables of the conjugacy classes of S_n.[9] The conjugacy classes in $S_{nL} \times S_{nS}$ will be products of those for S_n alone. Furthermore only those classes of $S_{nL} \times S_{nS}$ in which both components are of the same cyclic type will make any nonzero contribution. As an example consider the problem of the isomerization of 6.

$$S_{nS} \simeq S_{nL} \simeq S_s$$
$$R_{LS} \sim R_s \simeq D$$
$$L_L \simeq S_3 \times S$$

6
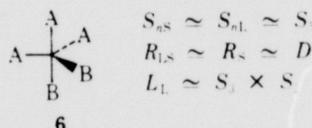
The required double cosets are:

$$D_{3LS}|S_{3L} \times S_{5S}|S_{3L} \times S_{2L} \times D_{3S}$$

Substitution into formula 2 gives:

$$\frac{14400}{6 \cdot 12 \cdot 6}\left(1 \cdot \frac{2 \cdot 4}{400} + \frac{3 \cdot 9}{225}\right) = 38$$

In $S_{3L} \times S_{5S}$ the conjugacy class of cyclic type ($1^2 3 \times 1^2 3$) is of order 400 ($= 20^2$) and the class of cyclic type ($12^2 \times 12^2$) is of order 225 ($= 15^2$). There is therefore a maximum of 38 potentially observable isomerizations for this system (in a chiral environment). This compares with the 6 potentially observable isomerizations for the trigonal bipyramidal skeleton with all ligands identical.[1]

By using different groups in the double coset construction 1, generalized stereoisomerization modes can be defined for a variety of experimental situations. For example, in an achiral situation enantiomers are not differentiated. This situation can be accommodated by substituting the full point group for the rotation group in formula 1 to give the double coset decomposition:

$$P_{LS}|S_{nL} \times S_{nS}|L_L \times P_S \quad (3)$$

where P is the skeletal point group acting on site or ligand indices. It may happen that certain internal motions are fast on the time scale of observation. This can be accommodated by substituting the appropriate nonrigid symmetry group N for R in formula 1:

$$N_{LS}|S_{nL} \times S_{nS}|L_L \times N_S \quad (4)$$

This idea can be generalized by noting that N may in principle be any group in the lattice of subgroups between R and S_n.[10] Finally it may not be necessary to consider all possible skeletal and ligand permutations $S_{nL} \times S_{nS}$ in situations where certain isomerizations are not expected to occur because of prohibitively high energy barriers. This is accommodated by restricting the groups S_{nS} and S_{nL} to subgroups G_S and G_L' which include only those isomerizations which are considered feasible. The appropriate double coset for this most general case is:

$$N_{LS}|G_L' \times G_S|L_L \times N_S$$

(Note that $G_L' \times G_S$ may be isomorphic to each other and that L_L need not be a subgroup of G_L'.)[11]

To justify the term *generalized* stereoisomerization mode it will be shown that some other treatments can be thought of as restrictions of the present scheme. A number of workers[1] have defined stereoisomerization modes for situations in which all ligands are chemically equivalent. In this case the modes are collections of double cosets of the type:

$$R_S|S_{nS}|R_S \quad (5)$$

In the present context the statement that all ligands are chemically equivalent is a statement that L_L is isomorphic to S_{nL} hence the double coset decomposition 1 becomes:

$$R_{LS}|S_{nL} \times S_{nS}|S_{nL} \times R_S$$

This has the effect of "cancelling out" S_{nL} and suppressing the ligand indices to leave only the double coset decomposition 5.

Klemperer[6] has given a double coset construction useful for nondegenerate isomerizations involving different substitutents, e.g.,
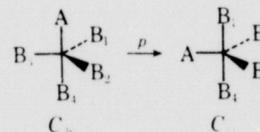

Isomerizations equivalent in a chiral environment to p are of the form:

$$gph \text{ where } \begin{matrix} g \in C_3 \\ h \in C_2 \end{matrix}$$

in which the difference in the rotation symmetry of the initial ($R_i \simeq C_3$) and final ($R_f \simeq C_2$) structures is explicitly taken into account. For the general case the double coset decomposition is:

$$R_i|K|R_f \quad (6)$$

in which $K \equiv S_k \times S_m \times \ldots$ is the direct product of the symmetric group on k ligands of one constitution and the symmetric group on m ligands of another constitution, etc. Thus only ligands of the same chemical type are permutated which gives a subgroup of the group S_{nS} as defined earlier. K is isomorphic to ligand symmetry group L previously defined. In the present treatment an isomerization of this kind is represented by a permutation p_S acting on the common site indices of the two isomers.
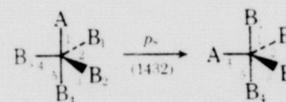
The set of all isomerizations which involve only permutations of constitutionally identical ligands relative to this one are of the form:

$$K_{iS}P_SK_{fS} \quad (7)$$

Where K_{iS} is the appropriate direct product of symmetric groups for the initial isomers and K_{fS} is the group for the final isomers. In the example $K_{iS} \simeq S_4 \times S_1$ in which S_4 acts on sites 2, 3, 4, 5 and S_1 acts on site 1. $K_{fS} \simeq S_4 \times S_1$ in which S_4 acts on sites 1, 2, 3, 5 and S_1 acts on site 4. The groups K_{iS} and K_{fS} are conjugate subgroups of S_{nS} related by:

$$K_{iS} = p_S^{-1} K_{fS} p_S$$

Thus expression 7 becomes:

$$(K_{iS}) p_S p_S^{-1} K_{iS} p_S = K_{iS} p_S$$

so that all the permutations related to p_S by permutation of constitutionally identical ligands form a coset of K_{iS}. A proof that this coset $K_{iS} p_S$ is decomposed by the action of the initial and final skeletal symmetry groups in a manner equivalent to (6) is given in the Appendix. The equivalence class of the isomerization p_S is much larger than the appropriate double coset in (6) because of the many possible orientations of equivalent initial and final isomers.

Finally Ruch[12a] has shown that the possible isomers of a structure with skeletal rotation symmetry R and equivalent ligand symmetry L are in correspondence with double cosets of the form:

$$R|S_n|L$$

In the present treatment this corresponds to suppressing the group S_{nS} and the site labels in double coset decomposition 1 to give:

$$R_L|S_{nL}|L_L$$

Site Exchange

Another problem which can be formulated as a double coset decomposition of $S_{nL} \times S_{nS}$ is the site exchange problem often encountered in the interpretation of first-order NMR spectra. To construct the appropriate representations of $S_{nL} \times S_{nS}$ consider the case of a structure with three nonequivalent skeletal sites and three nonequivalent ligands (i.e., structure 1):
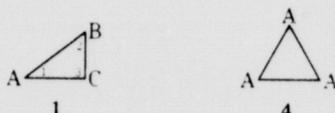
There are 6 isomers of such a structure and a total of 18 inequivalent sites. That is, if the ligands A, B, C all were spin ½ and uncoupled there would be 18 signals for all six isomers. Now for the case with three equivalent sites and ligands (structure 4) there would only be one signal. Thus 18 sites have been made equivalent by the symmetries involved and the associated group must be at least of order 18 and hence larger than the site or ligand symmetry group alone. These 18 sites form the basis for a representation of $S_{3L} \times S_{3S}$ and are in one-one correspondence with the cosets:

$$S_{2LS}|S_{3L} \times S_{3S}$$

where S_{2LS} is a symmetric group acting on two ligand and site indices. There are many conjugate S_{2LS} subgroups of $S_{3L} \times S_{3S}$ and one can be chosen arbitrarily. For example, let S_{2LS} be $\{e,(23)(BC)\}$. This is the group of ligand-site permutations which fix site A in isomer 1.
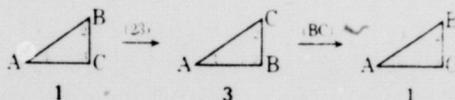
Thus the group $\{e,(23)(BC)\}$ can correspond to site A in isomer 1. Once this association is made the 17 other cosets of the group correspond to the 17 other sites. For example, the coset

Table I. The Five Double Cosets $C_{2LS}|S_{3L} \times S_{3S}|S_{2L} \times C_{2S}$ Represented by Isomerizations ($2 \times n$ Matrices Described in the Text)[a]

	123	132	231	321	213	312
ABB'	1	1	3	3	3	3
AB'B	1	1	3	3	3	3
BB'A	2	2	4	4	5	5
B'BA	2	2	4	4	5	5
BAB'	2	2	5	5	4	4
B'AB	2	2	5	5	4	4

[a] The row headings are the starting isomers, the column headings are the isomerization permutations acting on skeletal sites.

$\{(23),(BC)\}$ corresponds to site A in isomer 3 and the coset $\{(13)(AC),(132)(ACB)\}$ corresponds to site B in isomer 1, etc. In the general case these sites will be in correspondence with the $(n!)^2/(n-1)!$ cosets

$$S_{n-1LS}|S_{nL} \times S_{nS}$$

in which an arbitrary conjugate S_{n-1LS} subgroup is chosen and put in correspondence with an appropriate site on a particular isomer.[13]

These $(n!)^2/(n-1)!$ sites are collected into equivalence sets by ligand, skeletal, and internal symmetries. These equivalence sets are in correspondence with the double cosets:

$$S_{n-1LS}|S_{nL} \times S_{nS}|L_L \times N_S \qquad (8)$$

in which N_S can be the skeletal rotation group, point group, or a group of internal permutations which are fast on the time scale of observation. The number of double cosets from (8) is the number of nonequivalent sites and would correspond to the number of signals in a resolved first-order uncoupled NMR spectrum. The sizes of the double cosets are the statistical weights of the sites and in the unlikely situation of equal isomers populations would correspond to the expected intensities in the NMR spectrum. The number of double cosets from (8) is determined by the formula analogous to (2):

$$N_{DC} = \frac{|S_{nL} \times S_{nS}|}{|S_{n-1LS}||L_L||N_S|}$$
$$\times \sum_{r=1}^{k} \frac{|S_{n-1LS} \wedge C_r||(L_L \times N_S) \wedge C_r|}{|C_r|} \qquad (9)$$

Consider, for example, the case in which two of three sites are equivalent and two of three ligands are equivalent. The number of double cosets from (9) is

$$N_{DC} = \frac{36}{2 \cdot 2 \cdot 2} \left(1 + \frac{1 \cdot 1}{9}\right) = \frac{36}{8} \cdot \frac{10}{9} = 5$$

Thus there are five different sites in the two possible isomers (numbered as shown):
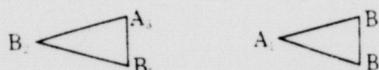
The double coset decomposition is isomorphic to that in Table I and the statistical weights of the five possible sites are 4:8: 8:8:8 which are the orders of the appropriate double cosets. Thus if the two isomers were of equal energy a resolved first-order NMR of an equilibrium mixture would have five lines of relative intensity 1:2:2:2:2.

Further use can be made of double coset decompositions 8 and combinational formula 9 by varying the group N_S with reference to the lattice of subgroups between R_S and S_{nS}.[10] This is the group theoretical analogue of mentally "allowing" a dynamic process and calculating the number of resulting

nonequivalent sites. For example, consider the dynamic process:
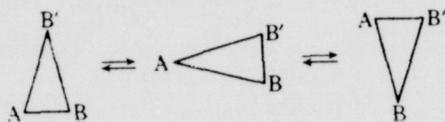
which equates all three sites on the isosceles triangular skeleton. The resulting (nonrigid) permutational symmetry is S_3. The number of nonequivalent sites (double cosets) is now:

$$N_{DC} = \frac{36}{2 \cdot 2 \cdot 6} \left(1 + \frac{3}{9}\right) = 2$$

with relative order 1:2 as expected. Thus the five-line spectrum would become a two-line spectrum if the dynamic process were fast on the NMR time scale.

Extensions of these methods to additional problems are suggested by noting the most general form of the various double coset decompositions:

$$E_{LS}|S_{nL} \times S_{nS}|L_L \times N_S \qquad (10)$$

where E_{LS} is a group acting on site and ligand indices. Thus the generalized stereoisomerization modes 1 are obtained if E_{LS} is the skeletal rotation group R_{LS} and the nonequivalent sites 8 are obtained if E_{LS} is the symmetry group $S_{n-1 LS}$. If E_{LS} were the symmetry group $S_{n-2 LS}$ then the double cosets 10 would be in correspondence with the nonequivalent pairwise ligand interactions for given ligand, L_L, and site, N_S, symmetry. Similarly if E_{LS} were $S_{n-3 LS}$, $S_{n-4 LS}$, ... etc., the double cosets 10 would be nonequivalent three-ligand, four-ligand, etc., interactions.

Overview

An overview of the novel results in this work can perhaps be obtained by considering a combination of two solved problems.

First, there is the static problem of determining the number of isomers possible for a molecular skeleton with a fixed ligand set.[12] As an example consider the problem of determining the number of A_3B_2 trigonal bipyramidal structures. The three possible isomers:
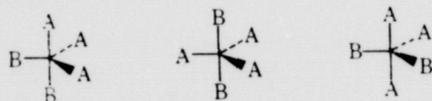
are in correspondence with the three double cosets:

$$D_3|S_5|S_3 \times S_2$$

in which D_3 is the skeletal rotation symmetry and $S_3 \times S_2$ is the ligand symmetry (three ligands of one kind and two of a different kind). In the general case the possible isomers are in correspondence with the double cosets: $R|S_n|L$.

Second, there is the dynamic problem of determining the number of potentially differentiable modes for the degenerate rearrangement of a molecular skeleton with a set of identical ligands.[1] As an example consider the degenerate rearrangement of:
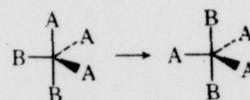
The six possible modes (in a chiral environment) are in correspondence with the double cosets: $D_3|S_5|D_3$. In the general case the possible modes are in correspondence with the double cosets $R|S_n|R$ or collections of these double cosets.

When these two problems are combined a much more complex problem involving degenerate:
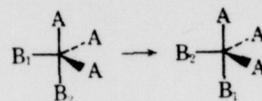
and nondegenerate:

rearrangements is obtained. This problem is solved in the present work by showing that the possible modes in such a system (in a chiral environment) are in correspondence with the double cosets:

$$D_{3LS}|S_{5L} \times S_{5S}|S_{3L} \times S_{2L} \times D_{3S}$$

where the S and L subscripts refer to the action of permutations on site (S) or ligand (L) indices. In the general case the possible generalized stereoisomerization modes are in correspondence with the double cosets:

$$R_{LS}|S_{nL} \times S_{nS}|L_L \times R_S$$

or collections of these double cosets. The two simpler problems can be thought of as special cases of the more general problem.

Notations and Conventions

A permutation acting on site labels (numbers) reads (123): whatever is in site 1 goes to site 2, whatever is in site 2 goes to site 3, etc. A permutation acting on ligand labels (letters) reads (ABC): ligand A is replaced by ligand B, ligand B is replaced by ligand C, etc. Both types of permutations multiply from left to right. Groups with the subscript S act on site labels, groups with the subscript L act on ligand labels, and groups with subscript LS act on both. The symbol $\times$ inserted between two groups signifies the direct product. A double coset decomposition of a group G by subgroups L and R is symbolized:

$$L|G|R = LR \cup Lg_1R \cup Lg_2R \cup \cdots$$

Consistently used group labels: S_n is the symmetric group on n objects (not the point group); R is the skeletal rotation group; P is the skeletal point group; N is a skeletal nonrigid symmetry group which may be restricted to P or R; L is the ligand symmetry group, i.e., all permutations of ligands of identical chemical composition; C_r is the rth conjugacy class of a group; point groups have their usual Schoenflies symbols. An element of a group is symbolized by a lower case letter with the same subscripts as the group, i.e., $p_S \in S_{nS}$, $r_{LS} \in R_{LS}$. The symbols $\wedge$ and $\cup$ mean the intersection and union of the sets or group on either side of them. The identity of a group is symbolized by ϵ.

Appendix

Proof. The group S_{nS} can be expressed as a union of cosets:

$$S_{nS} = K_{iS} \cup K_{iS}p_S \cup K_{iS}p_S' \cup \cdots$$

K_{iS} can be expressed as a union of double cosets

$$K_{iS} = R_S R_{iS}' \cup R_{iS}k_S R_{iS}' \cup R_{iS}k_S' R_{iS}' \cup \cdots$$

where k_S, $k_S' \in K_{iS}$ and where $R_{iS}' = p_S R_{iS}p_S^{-1}$. Thus the

coset $K_{iS}p_S$ can be expressed as:

$$K_{iS}p_S = (R_{iS}k_SR_{fS}' \cup R_{iS}k_S'R_{fS}' \cup \ldots)p_S$$

An arbitrary element of $K_{iS}p_S$ can be written as:

$$r_{iS}k_Sr_{fS}'p_S = (r_{iS})(k_Sp_S)(p_S^{-1}r_{fS}'p_S)$$

$$= (r_{iS}r_{iL})(k_Sp_S)(r_{iL}^{-1})(p_S^{-1}r_{fS}'p_S)$$

$$= (r_{iS}r_{iL})(k_Sp_S)(r_{iL}^{-1})(p_S^{-1}p_Sr_{fS}p_S^{-1}p_S)$$

$$= (r_{iS}r_{iL})(k_Sp_S)(r_{iL}^{-1})(r_{fS})$$

where $r_{iS}r_{iL} = R_{iLS}$, which is the form of an element of the double coset from formula 1. r_{iL}^{-1} will be in L_L since r_{iL} permutes constitutionally equivalent ligands. The final rotation group R_{fS} will be a subgroup of R_S.

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(13) See ref 7a p 5 (Wielandt) and p 55 (Hall) for properties of cosets in permutation groups.