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Classifications of Rearrangement Mechanisms by Means of Double Cosets and Counting Formulas for the Numbers of Classes

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Rearrangements of ligands attached at given sites of a certain skeleton may be classified according to two principles: symmetry equivalence, where the same permutation of objects is related to symmetry equivalent sites and rotational equivalence, where the resulting isomers differ just by their orientation. The combination of both these principles leads to a classification wanted by experimentalists. This latter classification is shown to be correlated to double cosets, which easily allow to find the rearrangements belonging to a class in a formal way and to enumerate the distinguishable classes for any given problem.

Umordnungen von Liganden, die auf vorgegebene Plätze eines bestimmten Molekülgerüstes verteilt sind, können nach zwei Prinzipien klassifiziert werden: Symmetrieäquivalenz, gekennzeichnet durch dieselbe Permutation von Objekten bezogen auf symmetrieäquivalente Gerüstplätze, und Rotationsäquivalenz, dadurch charakterisiert, daß die entstehenden Isomere sich nur durch ihre Orientierung unterscheiden. Die Kombination dieser beiden Prinzipien führt zu einer Klassifikation, die zur Interpretation von Experimenten benötigt wird. Es wird gezeigt, daß diese Klassifikation auf Doppelnebenklassen führt, mit denen die Umordnungen einer Klasse auf formale Weise leicht zu finden sind und die Anzahl der unterscheidbaren Klassen für jedes vorgegebene Problem bestimmt werden kann.

Double Cosets and Configurations

In a previous paper [1], it has been shown that double cosets of permutation groups are the natural algebraic analogue of configurations of permutational isomers.

The representation of configurations by classes of permutations, and formulas for their enumeration, have been discussed on the basis of the concept "ordered molecule", which implies an artificial distinction between distributions of n numbered ligands on n numbered sites of a rigid molecular skeleton. The set of all ordered molecules can be classified into subsets such that each contains all those ordered molecules which cannot be distinguished if we ignore the numbers assigned to ligands and sites and disregard the orientation and conformation of a molecule. This classification is associated with a classification of ligand permutations acting on a reference ordered molecule. It has been shown [1] that these classes are the so-called double cosets of two subgroups $\mathfrak{A}$ and $\mathfrak{B}$ of the group $\mathfrak{S}_n$ of all permutations, $\mathfrak{A}$ and $\mathfrak{B}$ being chosen according to the special classification one has in mind. $\mathfrak{A}$ contains all permutations representing rotations of the whole molecule and may contain further permutations representing inner rotations or some other rearrangements which one assumes to take place independently of the attached ligands within the characteristic time of the experiment. $\mathfrak{A}$ expresses exclusively properties of the skeleton. $\mathfrak{B}$ contains all permutations of ligands of the same kind or ligands that are not distinguished by the experiment concerned and refers to the sites occupied by like ligands in the reference isomer. $\mathfrak{B}$ expresses exclusively properties of the ligands. Since the concept configuration used in chemistry should be defined by the kind of experiment considered, we may speak of $\mathfrak{A}\mathfrak{B}$-configurations.

A double coset $\mathfrak{A}x_i\mathfrak{B}$ consists of all permutations which can be written as $a x_i b$ where x_i is a given element of $\mathfrak{S}_n$, a and b are any elements respectively of $\mathfrak{A}$ and $\mathfrak{B}$.
The classification of the set $\mathfrak{S}_n$ thus obtained can be expressed as a sum of sets

$$\mathfrak{S}_n = \mathfrak{A}\mathfrak{B} \dot{+} \mathfrak{A}x_2\mathfrak{B} \dot{+} \cdots \dot{+} \mathfrak{A}x_z\mathfrak{B} \tag{1}$$

where $\dot{+}$ means the union of sets having no permutation in common.

$\mathfrak{A}\mathfrak{B}$ consists of all permutations leading from the reference isomer to ordered molecules which cannot be distinguished from the reference isomer by the experiment concerned. The permutations of $\mathfrak{A}x_i\mathfrak{B}$ with $i \neq 1$ lead to experimentally distinguishable classes of mutually non-distinguishable ordered molecules. Therefore the double cosets $\mathfrak{A}x_i\mathfrak{B}$ or representative elements of them, e.g., the x_i with $x_1 = e$ (identity permutation) may be used as symbols for configurations of permutational isomers.

The number of different configurations can be found by calculating the number z of double cosets. For this some formulas have been derived [1], which hold independently of the special type of groups we have been discussing for our purpose. We give just the one which we also want to use for the subsequent treatment of another problem.

$$z = \frac{|\mathfrak{S}_n|}{|\mathfrak{A}|\,|\mathfrak{B}|} \sum_{r=1}^{k} \frac{|\mathfrak{A} \cap \mathfrak{C}_r|\,|\mathfrak{B} \cap \mathfrak{C}_r|}{|\mathfrak{C}_r|} \tag{1a}$$

$\mathfrak{C}_r$ is a class of conjugate elements of $\mathfrak{S}_n$. $|\mathfrak{S}_n|$, $|\mathfrak{A}|$, $|\mathfrak{B}|$ and $|\mathfrak{C}_r|$ denote the number of elements of the groups $\mathfrak{S}_n$, $\mathfrak{A}$, $\mathfrak{B}$ and of the class $\mathfrak{C}_r$, and $|\mathfrak{A} \cap \mathfrak{C}_r|$, $|\mathfrak{B} \cap \mathfrak{C}_r|$ designate the number of those elements belonging to the class $\mathfrak{C}_r$ which are contained in $\mathfrak{A}$ and $\mathfrak{B}$ respectively. The sum runs over all classes $\mathfrak{C}_r$.

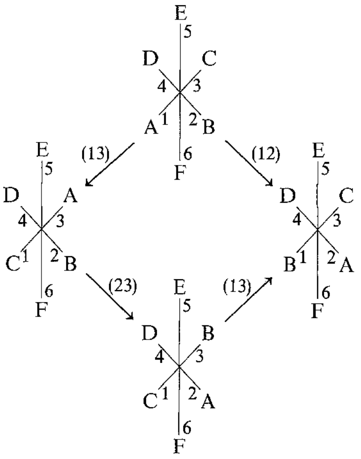
Double Cosets and Modes

A completely different classification problem will be shown to be soluble on a very similar basis also using double cosets. We refer again to rigid molecular skeletons with numbered sites occupied by ligands. A rearrangement of ligands on a given skeleton should be defined with reference to the numbered sites disregarding the nature of the ligands which are rearranged and disregarding the special way in which the rearrangement takes place.

If the skeleton has a certain symmetry, then there are rearrangements which effect different isomerisations but occur under precisely the same influence of the skeleton. They are related to different site numbers in a special way. Their correspondence is such that corresponding site numbers can be mapped into each other by a symmetry operation of the skeleton. Using rearrangements which correspond to symmetry operations of the skeleton we can transform a given rearrangement into a "symmetry equivalent" one. A symmetry-corresponding rearrangement followed by a given rearrangement followed again by the inverse of the first rearrangement leads to a rearrangement that is symmetry equivalent to the given one. Referring to the skeleton symmetry we will speak of the set of all rearrangements which are symmetry equivalent to a given one as of a rearrangement process. A process therefore does not imply the transition from a given molecule to a certain isomer but to a certain set of isomers.

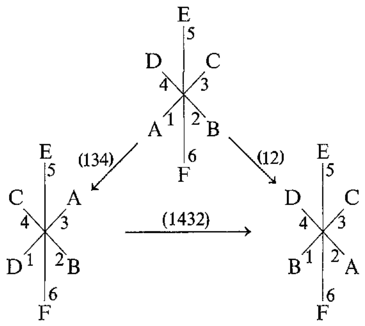
On the other hand, if we differentiate only those rearrangements which lead from a given distribution of ligands to different isomers we have to collect as being nondistinguishable all those rearrangements which can be split into a given rearrangement followed by a rearrangement corresponding to a rotation. Such rearrangements may be called rotationally equivalent. Rotationally equivalent rearrangements lead to the same isomers.

For a demonstration of the concepts introduced above we refer to the tetragonal bipyramid (D_{4h}). The rearrangements corresponding to the permutations (12), (23), (34), (14) are mutually symmetry equivalent while the one associated with (15) is not equivalent to any of these. The rearrangements belonging to (12) and (23) e.g. are related by the reflection (13) according to (13)(23)(13) = (12).



They are however not rotationally equivalent.

On the other hand the rearrangements corresponding to (12) and (134) are not symmetry equivalent, yet they are rotationally equivalent as we have (1432)(134) = (12) where (1432) represents a rotation.



From the foregoing examples it is obvious that we have to concern ourselves with the group $\mathfrak{S}_n$ of all permutations on the n sites of a given skeleton and two subgroups $\mathfrak{G}$ and $\mathfrak{A}$ of $\mathfrak{S}_n$.

We denote by $\mathfrak{G}$ the group of permutations corresponding to the symmetry operations of the skeleton and by $\mathfrak{A}$ the subgroup of $\mathfrak{G}$ containing all permutations which correspond to proper rotations.

$\mathfrak{A}$ is a subgroup of index two in $\mathfrak{G}$ if the skeleton is achiral and all molecules with n different ligands are chiral. If σ is any permutation of $\mathfrak{G}$ not belonging to $\mathfrak{A}$, i.e. a permutation which represents an improper rotation or a reflection,

$$\mathfrak{G} = \mathfrak{A} \dot{+} \sigma\mathfrak{A} = \mathfrak{A} \dot{+} \mathfrak{A}\sigma$$

is the decomposition of $\mathfrak{G}$ into the subgroup $\mathfrak{A}$ and its coset.

The remaining case $\mathfrak{A} = \mathfrak{G}$ may be regarded as a special situation for which σ does not exist. It designates two types of molecular classes: either the skeleton is chiral and correspondingly all molecules are chiral (chirality order n; cf. [2]) or the skeleton is achiral but reflections are represented by permutations which are also representative for rotations. In this case all molecules are achiral provided the ligands fulfill certain symmetry conditions (chirality order 0, e.g. benzene derivatives).

The definition of symmetry and rotational equivalence reads now:

Two rearrangements x and y are symmetry equivalent if $y = g x g^{-1}$ where g is a permutation of $\mathfrak{G}$.

Two rearrangements x and y are rotationally equivalent if $y = a x$ where a is a permutation of $\mathfrak{A}$.

Rearrangements belonging to the same rearrangement process therefore are of the form $g x g^{-1}$ with a given x and any $g \in \mathfrak{G}$. Such a class of permutations is called a subclass with respect to $\mathfrak{G}$. The group $\mathfrak{S}_n$ decomposes into subclasses with respect to $\mathfrak{G}$. Each of the subclasses represents a rearrangement process.

In addition we note that a subclass with respect to $\mathfrak{G}$, $\{g x g^{-1}\}$ with any $g \in \mathfrak{G}$ can be considered to consist of two subclasses with respect to $\mathfrak{A}$, $\{a x a^{-1}\}$ and $\{a \sigma x \sigma^{-1} a^{-1}\}$ with any $a \in \mathfrak{A}$ which are either identical or disjoint.

Rotationally equivalent rearrangements are of the form $a x$ with a given x and any $a \in \mathfrak{A}$. Such a class of permutations is called a right coset of $\mathfrak{A}$. The group $\mathfrak{S}_n$ decomposes into right cosets of $\mathfrak{A}$. Each of these cosets represents a class of rotationally equivalent rearrangements effecting the same isomerisation.

It is a field of current interest to investigate the occurrence and probability of one-step rearrangement reactions as far as the influence of the skeleton is concerned, i.e. independently of the ligands varying over an appropriate assortment. Correspondingly one does not want to differentiate symmetry equivalent rearrangements. Using experiments which measure the isomerisations effected by such reactions one cannot distinguish rotationally equivalent rearrangements. For these experiments therefore distinguishable sets of rearrangements consist of symmetry equivalent rearrangements and all those rotationally equivalent to them. We call such a set a mode – a word which has been proposed by Musher [3].

Gielen and Vanlautem [4] to our knowledge were the first to give a classification according to the idea of modes for special cases (tetrahedron, square, trigonal bipyramid, octahedron) by writing down properly classified permutations. Essentially the same thing has been done by Musher [3]. But no general concept for this classification has been developed, applicable to more complicated cases. We shall give an algebraic concept of modes that allows one to work out the classification in any case whatever and to calculate the number of distinguishable classes, as we shall see below.

According to the mode concept as developed above we define:

> Two rearrangements x and y are mode equivalent if y is rotationally equivalent to x or to a rearrangement which is symmetry equivalent to x, i.e. if $y = agxg^{-1}$ where a and g are permutations of $\mathfrak{A}$ and $\mathfrak{G}$ respectively.

The class $\mathfrak{M}(x)$ of rearrangements which are mode equivalent to x is the mode to which x belongs. It can be given as follows:

$$\mathfrak{M}(x) = \{agxg^{-1}\} \qquad \text{with any } a \in \mathfrak{A} \text{ and any } g \in \mathfrak{G}\,.$$

$\mathfrak{M}(x)$ is composed of two double cosets

$$\begin{aligned} \mathfrak{A}x\mathfrak{A} &= \{axa'\} && \text{with any} \quad a, a' \in \mathfrak{A} \\ \mathfrak{A}\sigma x\sigma^{-1}\mathfrak{A} &= \{a\sigma x\sigma^{-1}a'\} && \text{with any} \quad a, a' \in \mathfrak{A} \end{aligned}$$

which are either disjoint or identical. Therefore $\mathfrak{M}(x)$ can be expressed as

$$\mathfrak{M}(x) = \mathfrak{A}x\mathfrak{A} \cup \mathfrak{A}\sigma x\sigma^{-1}\mathfrak{A}$$

where $\cup$ denotes the set theoretic union. If σ does not exist, $\mathfrak{M}(x)$ reduces to

$$\mathfrak{M}(x) = \mathfrak{A}x\mathfrak{A}\,.$$

Two modes $\mathfrak{M}(x)$ and $\mathfrak{M}(y)$ are either identical – if the rearrangements x and y are mode equivalent – or disjoint – if x and y are mode inequivalent. Therefore the set of all rearrangements, $\mathfrak{S}_n$, decomposes into modes $\mathfrak{M}_i = \mathfrak{M}(x_i)$:

$$\mathfrak{S}_n = \mathfrak{A} \dot{+} (\mathfrak{A}x_2\mathfrak{A} \cup \mathfrak{A}\sigma x_2\sigma^{-1}\mathfrak{A}) \dot{+} \cdots \dot{+} (\mathfrak{A}x_z\mathfrak{A} \cup \mathfrak{A}\sigma x_z\sigma^{-1}\mathfrak{A}) \tag{2}$$

where $\mathfrak{M}_1 = \mathfrak{M}(e) = \mathfrak{A}$ is the mode of the identity rearrangement consisting of all rotations. The identity permutation e and $x_2, \ldots, x_z$ are representative permutations of the classes $\mathfrak{M}_1, \mathfrak{M}_2, \ldots, \mathfrak{M}_z$. They can be used to characterize distinct modes.

It should be explained that

1. $\mathfrak{A}x_i\mathfrak{A}$ and $\mathfrak{A}\sigma x_i\sigma^{-1}\mathfrak{A}$ may be identical or disjoint. Therefore it can happen that each class $\mathfrak{M}_i$ reduces to a double coset $\mathfrak{A}x_i\mathfrak{A}$ (trigonal bipyramid).
2. The sets $\mathfrak{A}x_i\mathfrak{A}\cup\mathfrak{A}\sigma x_i\sigma^{-1}\mathfrak{A}$ and $\mathfrak{A}x_i^{-1}\mathfrak{A}\cup\mathfrak{A}\sigma x_i^{-1}\sigma^{-1}\mathfrak{A}$ likewise are either identical or disjoint. Because they consist of mutually inverse elements, either these two classes are selfinverse or each of them contains the inverse elements of the other one. Sometimes e.g. for the trigonal bipyramid and the octahedron all classes $\mathfrak{M}_i$ are selfinverse, but generally this is not true.
3. The sets $\mathfrak{A}x_i\mathfrak{A}\cup\mathfrak{A}\sigma x_i\sigma^{-1}\mathfrak{A}$ and $\mathfrak{A}\sigma x_i\mathfrak{A}\cup\mathfrak{A}x_i\sigma^{-1}\mathfrak{A}$ are also either identical or disjoint. If they are disjoint they may be called enantiomeric modes because their rearrangements lead from a given molecule to sets of isomers which are related to each other by enantiomerism.

For experiments which do not distinguish enantiomers e.g. NMR-measurements, enantiomeric modes must be regarded as belonging to one class which we shall call a racemic mode. A classification of rearrangements given by Meakin, Muetterties *et al.* [5] for the octahedron is in agreement with the idea of racemic modes.

The set of rearrangements belonging to a racemic mode $\mathfrak{M}^r(x)$ is by definition the set theoretic union

$$\mathfrak{A}x\mathfrak{A}\cup\mathfrak{A}\sigma x\sigma^{-1}\mathfrak{A}\cup\mathfrak{A}\sigma x\mathfrak{A}\cup\mathfrak{A}x\sigma^{-1}\mathfrak{A}.$$

Recalling the decomposition of $\mathfrak{G}$ into the subgroup $\mathfrak{A}$ and its coset we see that the $\mathfrak{M}^r(x)$ are simply double cosets:

$$\mathfrak{M}^r(x)=\mathfrak{G}x\mathfrak{G}.$$

The set of all rearrangements, $\mathfrak{S}_n$, decomposes into racemic modes according to

$$\mathfrak{S}_n=\mathfrak{G}\dotplus\mathfrak{G}x_2\mathfrak{G}\dotplus\cdots\dotplus\mathfrak{G}x_{z^{(r)}}\mathfrak{G}. \tag{3}$$

The Number of Modes

Having given a well defined group theoretic class concept we turn to the problem of enumerating these classes without the need of elaborating them.

We use formula (1a) for the number of double cosets $\mathfrak{A}x\mathfrak{A}$, $\mathfrak{A}x\mathfrak{G}$, $\mathfrak{G}x\mathfrak{A}$ and $\mathfrak{G}x\mathfrak{G}$ in the corresponding decompositions

$$\mathfrak{S}_n=\mathfrak{A}\dotplus\mathfrak{A}x_2'\mathfrak{A}\dotplus\cdots\dotplus\mathfrak{A}x_{z_1}'\mathfrak{A}, \tag{A}$$

$$\mathfrak{S}_n=\mathfrak{A}\mathfrak{G}\dotplus\mathfrak{A}x_2''\mathfrak{G}\dotplus\cdots\dotplus\mathfrak{A}x_{z_2}''\mathfrak{G}, \tag{B}$$

$$\mathfrak{S}_n=\mathfrak{G}\mathfrak{A}\dotplus\mathfrak{G}x_2'''\mathfrak{A}\dotplus\cdots\dotplus\mathfrak{G}x_{z_3}'''\mathfrak{A}, \tag{C}$$

$$\mathfrak{S}_n=\mathfrak{G}\dotplus\mathfrak{G}x_2''''\mathfrak{G}\dotplus\cdots\dotplus\mathfrak{G}x_{z_4}''''\mathfrak{G}, \tag{D}$$

$$z_1=\frac{|\mathfrak{S}_n|}{|\mathfrak{A}|^2}\sum_{r=1}^{k}\frac{|\mathfrak{C}_r\cap\mathfrak{A}|^2}{|\mathfrak{C}_r|}$$

$$z_2=z_3=\frac{|\mathfrak{S}_n|}{|\mathfrak{A}|\,|\mathfrak{G}|}\sum_{r=1}^{k}\frac{|\mathfrak{C}_r\cap\mathfrak{A}|\,|\mathfrak{C}_r\cap\mathfrak{G}|}{|\mathfrak{C}_r|}$$

$$z_4=\frac{|\mathfrak{S}_n|}{|\mathfrak{G}|^2}\sum_{r=1}^{k}\frac{|\mathfrak{C}_r\cap\mathfrak{G}|^2}{|\mathfrak{C}_r|}.$$

Using the decomposition $\mathfrak{G} = \mathfrak{A} \dotplus \sigma\mathfrak{A}$ and noting that $\sigma\mathfrak{A} = \mathfrak{A}\sigma = \mathfrak{A}\sigma^{-1} = \sigma^{-1}\mathfrak{A}$ we can write

$$\begin{aligned}
&\mathfrak{A}\mathfrak{x}\mathfrak{G} = \mathfrak{A}\mathfrak{x}\mathfrak{A} \cup \mathfrak{A}\mathfrak{x}\sigma^{-1}\mathfrak{A}\,,\\
&\mathfrak{G}\mathfrak{x}\mathfrak{A} = \mathfrak{A}\mathfrak{x}\mathfrak{A} \cup \mathfrak{A}\sigma\mathfrak{x}\mathfrak{A}\,,\\
&\mathfrak{G}\mathfrak{x}\mathfrak{G} = \mathfrak{A}\mathfrak{x}\mathfrak{A} \cup \mathfrak{A}\sigma\mathfrak{x}\mathfrak{A} \cup \mathfrak{A}\mathfrak{x}\sigma^{-1}\mathfrak{A} \cup \mathfrak{A}\sigma\mathfrak{x}\sigma^{-1}\mathfrak{A}\,.
\end{aligned}$$

One can easily verify that for each quadruple $\mathfrak{A}\mathfrak{x}\mathfrak{A}$, $\mathfrak{A}\sigma\mathfrak{x}\mathfrak{A}$, $\mathfrak{A}\mathfrak{x}\sigma^{-1}\mathfrak{A}$, $\mathfrak{A}\sigma\mathfrak{x}\sigma^{-1}\mathfrak{A}$ one of the following five conditions is fullfilled

α) $\mathfrak{A}\mathfrak{x}\mathfrak{A}$, $\mathfrak{A}\sigma\mathfrak{x}\mathfrak{A}$, $\mathfrak{A}\mathfrak{x}\sigma^{-1}\mathfrak{A}$ and $\mathfrak{A}\sigma\mathfrak{x}\sigma^{-1}\mathfrak{A}$ are all identical.
β) $\mathfrak{A}\mathfrak{x}\mathfrak{A}$ and $\mathfrak{A}\sigma\mathfrak{x}\sigma^{-1}\mathfrak{A}$ as well as $\mathfrak{A}\sigma\mathfrak{x}\mathfrak{A}$ and $\mathfrak{A}\mathfrak{x}\sigma^{-1}\mathfrak{A}$ are identical.
γ) $\mathfrak{A}\mathfrak{x}\mathfrak{A}$ and $\mathfrak{A}\sigma\mathfrak{x}\mathfrak{A}$ as well as $\mathfrak{A}\mathfrak{x}\sigma^{-1}\mathfrak{A}$ and $\mathfrak{A}\sigma\mathfrak{x}\sigma^{-1}\mathfrak{A}$ are identical.
δ) $\mathfrak{A}\mathfrak{x}\mathfrak{A}$ and $\mathfrak{A}\mathfrak{x}\sigma^{-1}\mathfrak{A}$ as well as $\mathfrak{A}\sigma\mathfrak{x}\mathfrak{A}$ and $\mathfrak{A}\sigma\mathfrak{x}\sigma^{-1}\mathfrak{A}$ are identical.
ε) $\mathfrak{A}\mathfrak{x}\mathfrak{A}$, $\mathfrak{A}\sigma\mathfrak{x}\mathfrak{A}$, $\mathfrak{A}\mathfrak{x}\sigma^{-1}\mathfrak{A}$ and $\mathfrak{A}\sigma\mathfrak{x}\sigma^{-1}\mathfrak{A}$ are pairwise disjoint.

Assuming that in the decomposition (A) there occur z_α quadruples of type α, z_β of type β, z_γ of type γ, z_δ of type δ and z_ε of type ε, we can infer from the decompositions (B), (C), (D) and (2) the equations

$$\begin{aligned}
z &= z_\alpha + 2z_\beta + z_\gamma + z_\delta + 2z_\varepsilon\\
z_1 &= z_\alpha + 2z_\beta + 2z_\gamma + 2z_\delta + 4z_\varepsilon\\
z_2 &= z_\alpha + z_\beta + z_\gamma + 2z_\delta + 2z_\varepsilon\\
z_3 &= z_\alpha + z_\beta + 2z_\gamma + z_\delta + 2z_\varepsilon\\
z_4 &= z_\alpha + z_\beta + z_\gamma + z_\delta + z_\varepsilon
\end{aligned}$$

which are solved to give

$$z = z_1 + 2z_4 - z_2 - z_3\,.$$

Using formula (1a) for z_1, z_4 and $z_2 = z_3$ we get the counting formula for z

$$z = \frac{|\mathfrak{S}_n|}{|\mathfrak{A}|\,|\mathfrak{G}|} \sum_{r=1}^{k} \frac{|\mathfrak{C}_r \cap \mathfrak{A}|^2 + |\mathfrak{C}_r \cap \sigma\mathfrak{A}|^2}{|\mathfrak{C}_r|}\,. \tag{2a}$$

For the use of formula (2a) it should be mentioned that if permutations are written in the form of products of disjoint cycles it is very simple to find the numbers $|\mathfrak{C}_r \cap \mathfrak{A}|$ and $|\mathfrak{C}_r \cap \sigma\mathfrak{A}|$ by inspection, while the orders $|\mathfrak{C}_r|$ are given by

$$|\mathfrak{C}_r| = \frac{n!}{1^{r_1} r_1!\, 2^{r_2} r_2! \ldots n^{r_n} r_n!}$$

where $r_1, \ldots, r_n$ denote the numbers of cycles of length $1, 2, \ldots, n$.

Formula (1a) for $\mathfrak{A} = \mathfrak{B} = \mathfrak{G}$ gives the number $z^{(r)}$ of racemic modes

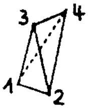
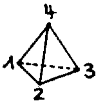
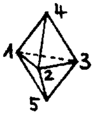
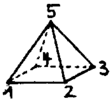
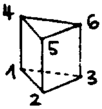
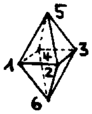
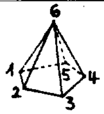
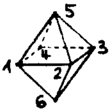
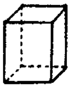
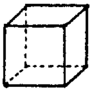
$$z^{(r)} = \frac{|\mathfrak{S}_n|}{|\mathfrak{G}|^2} \sum_{r=1}^{k} \frac{|\mathfrak{C}_r \cap \mathfrak{G}|^2}{|\mathfrak{C}_r|}\,. \tag{3a}$$

A formula for the number $z^{(p)}$ of processes which is equal to the number of subclasses with respect to the group $\mathfrak{G}$ can be given without proof

$$z^{(p)} = \frac{|\mathfrak{S}_n|}{|\mathfrak{G}|} \sum_{r=1}^{k} \frac{|\mathfrak{C}_r \cap \mathfrak{G}|}{|\mathfrak{C}_r|}\,. \tag{4a}$$

Examples

The following table gives the number z of modes for eleven examples

	Skeleton		Number of sites	Symmetry of the skeleton	Number of modes (z)
1		distorted tetrahedron	4	C_{2v}	6
2		trigonal pyramid	4	C_{3v}	4
3		trigonal bipyramid	5	D_{3h}	6
4		tetragonal pyramid	5	C_{4v}	7
5		trigonal prism	6	D_{3h}	20
6		tetragonal bipyramid	6	D_{4h}	13
7		pentagonal pyramid	6	C_{5v}	24
8		octahedron	6	O_h	5
9		tetragonal prism	8	D_{4h}	446
10		cube	8	O_h	78
11		icosahedron	12	J_h	68.384

In the second table we have written down representative permutations for each mode of the first eight skeletons. The numbers in square brackets give the numbers of different isomers arising from any starting isomer through the various rearrangements belonging to any rearrangement process of the corresponding mode, provided the ligands are all different.

1: (1) [1], (12) [1], (13) [4], (123) [4], (13)(24) [1], (1324) [1]

2: (1) [1], (12) [1], (14) [3], (124) [3]

3: (1) [1], (12) [1], (14) [6], (124) [6], (14)(25) [3], (1425) [3]

4: (1) [1], (13) [1], (15) [4], (12) [4], (125) [8], (12)(35) [8], (135) [4]

5: (1) [1], (12)(45) [1], (12) [6], (123) [2], (34) [6], (12)(34) [12], (234) [12], (1432) [6], (1234) [6], (1243) [6], (142) [12], (124) [12], (14) [3], (14)(23) [6], (13)(45) [2], (1254) [6], (15)(34) [6], (1543) [6], (1345) [6], (14)(25) [3]

6: (1) [1], (13) [1], (15) [8], (135) [8], (12) [4], (125) [16], (12)(35) [16], (15)(26) [8], (1526) [8], (15)(263) [8], (15)(236) [8], (15)(36) [2], (1536) [2]

7: (1) [1], (12)(35) [1], (16) [5], (12) [5], (126) [10], (12)(36) [10], (123) [5], (1236) [5], (1263) [10], (1362) [10], (13) [5], (136) [10], (13)(26) [5], (15)(36) [5], (135) [5], (1563) [10], (1365) [10], (1325) [1], (1523) [1], (13256) [5], (16523) [5], (13)(56) [10], (1356) [5], (12)(356) [5]

8: (1) [1], (13) [1], (12) [12], (125) [8], (12)(35) [8]

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