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Permutational Isomerism with Bidentate Ligands and Other Constraints

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Abstract: Permutational isomers and isomerization processes are classified and characterized for several cases in which various constraints, such as bidentate ligation, are placed upon the positioning of ligands upon a molecular skeleton. The formulation is group theoretical in nature and identifies double cosets with the various isomers and rearrangement modes. Some illustrative examples of this general approach are presented.

1. Introduction

One of the classical problems in chemistry is the classification and characterization of the various permutational isomers which can arise from the distribution of ligands on a molecular skeleton in different manners.[2] A second but related problem concerns the classification and characterization of the different "modes" of permutational isomerization.

At the outset it is convenient to review briefly the mathematical formulation of these problems. First, let $\mathcal{L}$ denote a set of *N ligands* and let $\mathcal{S}$ represent a set of *N sites* associated with the positions on a molecular (or ionic) skeleton. The assignment of each ligand to a unique site is termed a *bijection* (or bijective mapping) from $\mathcal{L}$ to $\mathcal{S}$. Each such bijection is referred to as a *permutamer* or *arrangement*, and clearly identifies some permutational isomer. In general, because of various site and/or skeletal symmetries, more than one permutamer may identify the same isomer. In the work of Ruch et al.[3] the many-to-one nature of this identification has been described precisely for the case in which there are no constraints upon the skeletal positions which the various ligands can occupy. For a permutational isomerization process one permutamer is rearranged to another, and a partial characterization of such processes is obtained providing they are classified in terms of the sites between which the ligands are moved. Thus we consider bijections, here termed *rearrangements*, from the set $\mathcal{S}$ of skeletal sites back onto $\mathcal{S}$. A classification of these rearrangements has been illustrated[4] and described precisely,[5,6] again for the case in which there are no constraints upon the ligand occupancy of the various skeletal positions.

The primary purpose of the present article is to demonstrate that the previous mathematical descriptions of permutational isomers and isomerization processes can be used also to describe situations with certain physically reasonable constraints which include the following:

(a) Preferential ligand location. This restriction confines a certain subset of ligands to a subset of sites. This situation arises when, e.g., certain skeletal sites will accept only ligands of sufficiently small size or of sufficiently low electronegativity.

(b) Bridging ligands. This implies that a certain subset of sites be occupied by ligands of a particular subset of $\mathcal{L}$.

(c) Bidentate ligands. This restriction requires that specified pairs of ligands must lie on near-neighbor pairs of skeletal sites. [Furthermore, if two bidentate ligands are not to "cross through" one another, this implies the restriction that specified (ordered) quartets of ligands must not lie on certain (ordered) quartets of sites.]

(d) Sterically bulky groups. This restriction requires that specified pairs of ligands do not lie on near-neighbor pairs of sites because of steric congestion.

(e) Tridentate ligands. This requirement implies that specified (ordered) triples of ligands must lie on near-neighbor (ordered) triples of sites.

(f) Quadridentate ligands. Here one has the restriction that specified (ordered) quartets of ligands must lie on near-neighbor (ordered) quartets of sites.

(g) Combinations of two or more of the preceding restrictions.

The constraints described in case a have, in fact, been considered previously.[7,8] However, this case is especially simple (and is described briefly at the end of section 5).

In section 2 of this article the earlier general work[3] describing permutational isomers in the absence of constraints will be reviewed. The inclusion of constraints will be considered in section 3, and it will be demonstrated that the resulting classes of permutamers involve either only permutamers satisfying the constraints or only permutamers not satisfying the constraints. Furthermore, these classes, identifying the various permutational isomers, are grouped together to form, often larger, classes with this same "all-or-none" feature. In section 4 the theory is applied to the particular case of permutational isomer classification which occurs when bidentate chelates are

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present in the coordination sphere. Some explicit examples are given involving trigonal-bipyramidal, octahedral, and icosahedral skeletons. In section 5 the permutational isomerization problem with constraints is mentioned briefly, and in section 6 the bidentate chelate case is considered again. Finally, the relationship of our exhaustive and general (but sometimes tedious) approach to a previously described approach will be discussed. Previous work has been concerned with tris-chelate octahedral complexes[9] and propellar molecules.[10] We argue that this alternative approach is applicable under only rather special circumstances which are discussed and illustrated with examples.

2. Permutational Isomers

In the treatment of Ruch et al.,[3] one considers the symmetric group S_N of permutations on N objects. By convention the superscripts L or S are appended to a permutation to indicate whether it acts on the elements of $\mathcal{L}$ or of $\mathcal{S}$. Thus if $P \in S_N$ sends the integer i to Pi, then $P^L \in S_N{}^L$ and $P^S \in S_N{}^S$ send $\ell_i \in \mathcal{L}$ and $s_i \in \mathcal{S}$ to $P^L\ell_i = \ell_{P_i}$ and $P^S s_i = s_{Pi}$. Now letting φ_1 be a "reference" bijection from $\mathcal{L}$ to $\mathcal{S}$ such that ℓ_i is mapped to $\varphi_1(\ell_i) = s_i$, $i = 1$ to N, any other bijection, say φ_P, which maps ℓ_i to s_{Pi}, may be expressed as

$$\varphi_P = P^S\varphi_1 = \varphi_1 P^L \tag{2.1}$$

In general, several permutamers, each uniquely associated with a permutation in S_N, can identify the same permutational isomer, owing to the occurrence of experimentally indistinguishable ligands or skeletal orientations. This redundancy is accounted for via symmetry groups $\mathcal{L}^L \subseteq S_N{}^L$ and $\mathcal{S}^S \subseteq S_N{}^S$ of permutations acting on $\mathcal{L}$ and $\mathcal{S}$. Typically, $\mathcal{L}^L$ permutes indistinguishable ligands about, and $\mathcal{S}^S$ is the permutation group whose elements relabel the sites in the same manner as effected by conventional point group operations on the molecular skeleton. (It should be noted[3,6] that the definitions of $\mathcal{L}$ and $\mathcal{S}$ depend upon the distinguishability achievable by the experiments under consideration.) Now two permutamers φ_P and φ_Q are associated with the same permutational isomer if[2] there exist $L \in \mathcal{L}$ and $S \in \mathcal{S}$ such that

$$S^S\varphi_P L^L = \varphi_Q \tag{2.2}$$

or equivalently that

$$SPL = Q \tag{2.3}$$

Hence corresponding to a single permutational isomer one has a set of permutations, identified as a single $\mathcal{S},\mathcal{L}$ *double coset*, abbreviated hereinafter to DC. These $\mathcal{S},\mathcal{L}$ DC's disjointly partition S_N, so that they form an equivalence relation on S_N. These DC's possess several additional group-theoretic properties of fundamental use.[5-8,11]

3. General Theory for Permutational Isomers

First mappings of (ordered) n-tuples of ligands into the set of (ordered) n-tuples of sites are introduced

$$\begin{aligned}\varphi_P * (\ell_{i_1}, \ell_{i_2}, \ldots, \ell_{i_n}) &\equiv (\varphi_P\ell_{i_1}, \ldots, \varphi_P\ell_{i_n})\\ &= (s_{Pi_1}, \ldots, s_{Pi_n}),\ \ell_{i_1}, \ell_{i_2}, \ldots, \ell_{i_n} \in \mathcal{L}\end{aligned} \tag{3.1}$$

Next certain subsets $\mathcal{L}^{(j)}$ of n_j-tuples of ligands (in $\mathcal{L}$) are constrained to be mapped into the corresponding subsets $\mathcal{S}^{(j)}$ of n_j-tuples of sites (in $\mathcal{S}$). That is, we term a permutamer φ_P to be *allowed* if

$$\varphi_P * \mathcal{L}^{(j)} \subseteq \mathcal{S}^{(j)} \tag{3.2}$$

for all $j \geq 1$; otherwise φ_P is termed *forbidden*. The general constrained problem to be considered is that of classifying the different allowed permutational isomers (corresponding to some allowed permutamer).

The examples a, c, e, and f of section 1 are readily discerned to be included in the present formulation. A very simple case arises if one has a single constraint for a single bidentate chelate: presuming ℓ_i and ℓ_j form this chelate, then $\mathcal{L}^{(1)} = \{(\ell_i,\ell_j), (\ell_j,\ell_i)\}$; furthermore, $\mathcal{S}^{(1)}$ is the set of near-neighbor pairs of sites, and the constraint statement is such that $\varphi_P * \mathcal{L}^{(1)} \subseteq \mathcal{S}^{(1)}$, i.e., that φ_P map ℓ_i and ℓ_j onto a near-neighbor pair of sites. Examples b and d of section 1 are most directly stated in terms of a set $\tilde{\mathcal{L}}^{(j)}$ of n_j-tuples of ligands to be excluded (under mappings as in (3.1)) from a set $\tilde{\mathcal{S}}^{(j)}$ of n_j-tuples of sites; however, such constraints are readily restated in terms of inclusion statements, as in (3.2), if one merely considers $\mathcal{L}^{(j)}$ and $\mathcal{S}^{(j)}$ to be complements of $\tilde{\mathcal{L}}^{(j)}$ and $\tilde{\mathcal{S}}^{(j)}$,

$$\begin{aligned}\mathcal{L}^{(j)} &\equiv \{(\ell_{i_1}, \ell_{i_2}, \ldots, \ell_{i_{n_j}}) \notin \tilde{\mathcal{L}}^{(j)}\}\\ \mathcal{S}^{(j)} &\equiv \{(s_{i_1}, s_{i_2}, \ldots, s_{i_{n_j}}) \notin \tilde{\mathcal{S}}^{(j)}\}\end{aligned} \tag{3.3}$$

Finally, example g of section 1 is included in the present formulation, when j in (3.2) ranges over two or more values.

Now mappings corresponding to each $P \in S_N$ are introduced:

$$\begin{aligned}P^L * (\ell_{i_1}, \ldots, \ell_{i_n}) &\equiv (P^L\ell_{i_1}, \ldots, P^L\ell_{i_n})\\ &= (\ell_{Pi_1}, \ldots, \ell_{Pi_n}),\ \ell_{i_1}, \ldots, \ell_{i_n} \in \mathcal{L}\\ P^S * (s_{i_1}, \ldots, s_{i_n}) &\equiv (P^S s_{i_1}, \ldots, P^S s_{i_n})\\ &= (s_{Pi_1}, \ldots, s_{Pi_n}),\ s_{i_1}, \ldots, s_{i_n} \in \mathcal{S}\end{aligned} \tag{3.4}$$

and the following groups are defined

$$\begin{aligned}\mathcal{L}^{(j)} &\equiv \{P \in S_N;\ \vec{\ell} \in \mathcal{L}^{(j)} \Rightarrow P^L * \vec{\ell} \in \mathcal{L}^{(j)}\}\\ \mathcal{S}^{(j)} &\equiv \{P \in S_N;\ \vec{s} \in \mathcal{S}^{(j)} \Rightarrow P^S * \vec{s} \in \mathcal{S}^{(j)}\} \quad j \geq 1\end{aligned} \tag{3.5}$$

Now if $\vec{s} \in \mathcal{S}^{(j)}$ is an n_j-tuple of sites which may be the result of mapping a $\vec{\ell} \in \mathcal{L}^{(j)}$, then it is anticipated that any point-group equivalent n_j-tuple of sites, say $S^S * \vec{s}$ for $S \in \mathcal{S}$, will be an allowed result also; consequently

$$\mathcal{S} \subseteq \mathcal{S}^{(j)} \qquad j \geq 1 \tag{3.6}$$

Now if $\mathcal{L}^{(0)}$ denotes the group of permutations which permutes like ligands, then $\mathcal{L}^{(0)}$ is a simple product of smaller symmetric groups; however, it is not necessarily a subgroup of the $\mathcal{L}^{(j)}$, $j \geq 1$. Nevertheless, the various $\mathcal{L}^{(j)}$, $j \geq 1$, generally acknowledge physically detectable relations possibly not accounted for by $\mathcal{L}^{(0)}$ (as is seen, for instance, in the examples of section 4 with bidentate chelates); consequently the physically relevant ligand symmetry group is

$$\mathcal{L} \equiv \mathcal{L}^{(0)} \cap \mathcal{L}^{(1)} \cap \mathcal{L}^{(2)} \cap \ldots \tag{3.7}$$

and hence

$$\mathcal{L} \subseteq \mathcal{L}^{(j)} \qquad j \geq 1 \tag{3.8}$$

Thus

$$\begin{aligned}\mathcal{L} &\subseteq \mathcal{L}^{\cap} \equiv \mathcal{L}^{(1)} \cap \mathcal{L}^{(2)} \cap \ldots\\ \mathcal{S} &\subseteq \mathcal{S}^{\cap} \equiv \mathcal{S}^{(1)} \cap \mathcal{S}^{(2)} \cap \ldots\end{aligned} \tag{3.9}$$

results from assumptions of the "physical reasonability" of the constraints.

From definition 3.5 it is seen that the elements of the groups $\mathcal{L}^{(j)}$ and $\mathcal{S}^{(j)}$ leave the sets $\mathcal{L}^{(j)}$ and $\mathcal{S}^{(j)}$ invariant. Then using the constraint conditions of (3.2) also, it follows that

$$\begin{aligned}\varphi_{SPL} * \mathcal{L}^{(j)} &= S^S * (\varphi_P * (L^L * \mathcal{L}^{(j)}))\\ &= S^S * (\varphi_P * \mathcal{L}^{(j)})\ S^S * \mathcal{S}^{(j)} = \mathcal{S}^{(j)}\\ &\text{all } S \in \mathrm{S}^{\cap}, L \in \mathcal{L}^{\cap}\end{aligned} \tag{3.10}$$

for all allowed φ_P. Hence if φ_P is allowed, then so are all φ_Q with Q in the same $\mathcal{S}^{\cap},\mathcal{L}^{\cap}$ DC. Therefore there are *allowed* and *forbidden* $\mathcal{S}^{\cap},\mathcal{L}^{\cap}$ DC's, in which all permutations yield all allowed or all forbidden permutamers, respectively. Further, because of the subgroup condition of (3.9), each $\mathcal{S}^\cap,\mathcal{L}^\cap$ DC breaks up into a union of $\mathcal{S},\mathcal{L}$ DC's, which also are completely allowed or completely forbidden.

In the present general classification scheme with constraints it is seen that each allowed permutational isomer is in unique correspondence with an allowed $\mathcal{S},\mathcal{L}$ DC, all of the permutations of which yield allowed permutamers. The interpretation and properties of these allowed $\mathcal{S},\mathcal{L}$ DC's are similar to those in the unconstrained case. For instance,[6] the group $\mathcal{S} \cap G_z\mathcal{L}G_z^{-1}$, the order of which gives the repetition frequency d_q for the DC $\mathcal{S}G_z\mathcal{L}$, is seen to be the (proper rotational) molecular point group of the qth permutational isomer, in contrast to $\mathcal{L}$ the (proper rotational) molecular point group for the (idealized) skeleton; hence[6] the repetition frequency d_q of $\mathcal{S}G_z\mathcal{L}$ provides a "symmetry number" for the qth permutational isomer. Every allowed $\mathcal{S},\mathcal{L}$ DC is obtained from a usually larger allowed $\mathcal{S}^\cap,\mathcal{L}^\cap$ DC, so that to generate or enumerate the allowed $\mathcal{S},\mathcal{L}$ DC's all that is necessary to do is determine the allowed $\mathcal{S}^\cap,\mathcal{L}^\cap$ DC's and break them up. In the Appendix some general theory is presented for breaking up larger DC's into smaller ones. The determination of the larger allowed $\mathcal{S}^\cap,\mathcal{L}^\cap$ DC's might be pursued by computer via the method such as that of Brown et al.[11] with the checking for allowedness or forbiddenness being simply a check of the conditions of (3.2). Here we consider determining these larger DC's only in the explicit cases of the next section.

4. Bidentate Chelates

Here the classification problem is considered for the case where both unidentate and bidentate ligands are present in the coordination sphere. It is assumed that the bidentate chelates must be coordinated to near-neighbor sites on the molecular skeleton, but that the near-neighbor sites are arranged such that no crossing constraints, as mentioned as a possibility in (c) of section 1, are required. Then there is just a single pair of constraint sets, $\mathcal{L}^{(1)}$ and $\mathcal{S}^{(1)}$, with $\mathcal{S}^{(1)}$ consisting of pairs of near-neighbor sites and $\mathcal{L}^{(1)}$ consisting of pairs of ligands common to a single bidentate chelate. If for n bidentate chelates ligand indexes ℓ_{2i-1} and ℓ_{2i} are chosen to form a pair for a bidentate chelate, $i = 1$ to n, then

$$\mathcal{L}^{(1)} = \{(\ell_{2i-1},\ell_{2i}),\ (\ell_{2i},\ell_{2i-1});\ i = 1 \text{ to } n\}$$

$$\mathcal{L}^{(1)} = S_n{}^{\star} \prod_{i=1}^{n} S_{\{2i-1,2i\}}\, S_{\{2n+1,\ldots,N\}} \qquad (4.1)$$

Here $S_{\{i,j,\ldots\}}$ denotes the symmetric group of permutations on $i, j, \cdots$, and $S_n{}^\star$ (isomorphic to S_n) is generated by the bitranspositions $(2i-1, 2i+1)(2i, 2i+2)$ for $i = 1$ to $n-1$. Verbally $\mathcal{L}^\cap = \mathcal{L}^{(1)}$, or $\mathcal{L}^{\cap L} = \mathcal{L}^{(1)L}$, may be described as the group permuting the unidentate ligands among themselves, interchanging ends of a bidentate chelate, and permuting whole bidentate chelates among themselves. Clearly $\mathcal{L} = \mathcal{L}^{(0)} \cap \mathcal{L}^{(1)}$ is generally not a product of disjoint symmetric groups, in contrast to the case with no constraints. Since point group operations preserve distances, neighbor pairs of sites must remain so when both are transformed by a permutation corresponding to a point group operation, and consequently $\mathcal{S} \subseteq \mathcal{S}^\cap$. Thus the general conditions and assumptions of section 3 are readily verified for the present special type of case.

Now if points are identified with the elements of $\mathcal{S}$ and lines between these points with the appropriate elements of $\mathcal{S}^{(1)}$, then a *site-adjacency graph* is obtained, and $\mathcal{S}^\cap = \mathcal{S}^{(1)}$ is simply the *automorphism* group of this graph. Often this graph may be viewed as an outline of a polytope with $\mathcal{S}^\cap$ its maximum possible point group symmetry (including improper rotations). Similarly, $\mathcal{L}^\cap$ is the maximum possible ligand symmetry group $\mathcal{L}$. Hence the allowed $\mathcal{S}^\cap,\mathcal{L}^\cap$ DC's may often be viewed as the least discriminatory classification which would

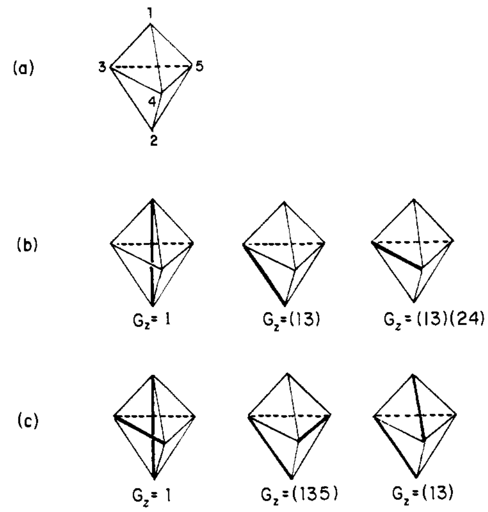

Figure 1. The trigonal-bipyramidal case with the various $\mathcal{S}^\cap,\mathcal{L}^\cap$ DC's that may arise. The G_z given are the associated choices for the DC generators.

sometimes be complete for permutational isomers with a given number, n, of bidentate chelates. We now proceed with a number of examples with particular choices for $\mathcal{L}^\cap$ and $\mathcal{S}^\cap$ and give the various allowed (and sometimes forbidden) $\mathcal{S}^\cap,\mathcal{L}^\cap$ DC's. In these examples the site-adjacency graph is illustrated. The position of the bidentate chelate(s) are also illustrated for a particular bijection associated with the various $\mathcal{S}^\cap,\mathcal{L}^\cap$ DC's, thus identifying these DC's.

For a trigonal-bipyramidal graph with sites as in Figure 1a, we have

$$\mathcal{S}^\cap = S_{\{1,2\}}S_{\{3,4,5\}} \qquad (4.2)$$

When $n = 1$

$$\mathcal{L}^\cap = S_{\{1,2\}}S_{\{3,4,5\}} \qquad (4.3)$$

and there are three $\mathcal{S}^\cap,\mathcal{L}^\cap$ DC's, with generators and corresponding bijections given in Figure 1b; here a broad boldface line represents a chelate position, and the first DC is forbidden while the last two are allowed. When $n = 2$

$$\mathcal{L}^\cap = S_2{}^\star S_{\{1,2\}}S_{\{3,4\}}$$
$$S_2{}^\star = \{1,(13)(24)\} \qquad (4.4)$$

and there are three $\mathcal{S}^\cap,\mathcal{L}^\cap$ DC's, with generators and corresponding bijections given in Figure 1c; here the first DC is forbidden and the last two are allowed. Because of the rather simple symmetric group structure of $\mathcal{S}^\cap$, and of $\mathcal{L}^\cap$, special DC symbol techniques[6] are applicable. The two bidentate ligand case is now specialized, assuming that the two identical chelates possess distinguishable ends, as in Figure 2a. Then

$$\mathcal{L}^{(0)} = \{1,(13),(24),(13)(24)\}$$
$$\mathcal{L} = \mathcal{L}^{(0)} \cap \mathcal{L}^\cap = \{1,(13)(24)\} \qquad (4.5)$$

and as an illustrative example we determine how the third $\mathcal{S}^\cap,\mathcal{L}^\cap$ DC of Figure 1c breaks up. Thus utilizing the methods of Appendix A, we first decompose

$$\mathcal{L}^\cap = \dot{\bigcup_j}\, (G_z{}^{-1}\mathcal{S}G_z \cap \mathcal{L}^\cap)G_j\mathcal{L}$$

$$S_2{}^\star S_{\{1,2\}}S_{\{3,4\}} = \dot{\bigcup_j}\, \{1,(14)(23)\}G_j\{1,(13)(24)\}$$
$$= \{1,(14)(23)\}\mathcal{L} \cup \{1,(14)(23)\}(12)\mathcal{L} \cup \{1,(14)(23)\}(34)\mathcal{L} \qquad (4.6)$$

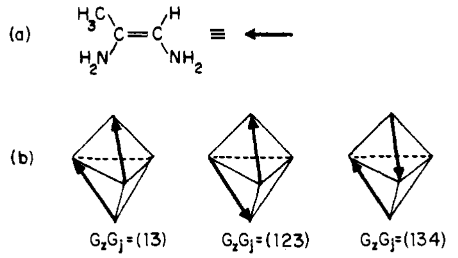

Figure 2. A typical bidentate chelate with distinguishable ends, and the three $\mathcal{S}^{\cap},\mathcal{L}$ DC's of eq 3.7.

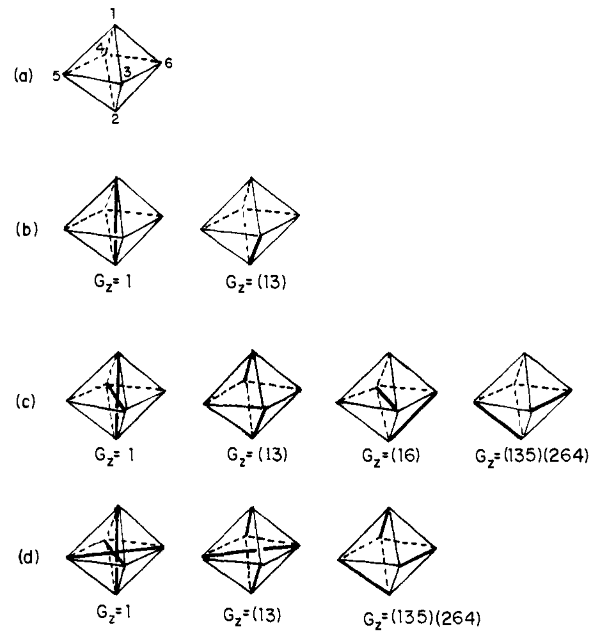

Figure 3. The octahedral case with the various $\mathcal{S}^{\cap},\mathcal{L}^{\cap}$ DC's which may arise. The G_z given are the associated DC generators.

so that

$$\mathcal{S}^{\cap}(13)\mathcal{L}^{\cap} = \mathcal{S}^{\cap}(13)\mathcal{L} \,\dot{\cup}\, \mathcal{S}^{\cap}(13)(12)\mathcal{L} \,\dot{\cup}\, \mathcal{S}^{\cap}(13)(34)\mathcal{L} \tag{4.7}$$

If mirror image chiral structures are presumed to be indistinguishable, then $\mathcal{S} = \mathcal{S}^{\cap}$, and (4.7) is the desired DC decomposition. The structures corresponding to these three $\mathcal{S}^{\cap},\mathcal{L}^{\cap}$ DC's are shown in Figure 2b; in this simple case they are also readily generated by "inspection". If mirror image chiral structures are considered to be distinguishable, then for the trigonal-bipyramidal geometry $\mathcal{S}$ consists of just the even permutations in $\mathcal{S}^{\cap}$. In this case there are six $\mathcal{S},\mathcal{L}$ DC's in $\mathcal{S}^{\cap}(13)\mathcal{L}^{\cap}$ and two in each of the $\mathcal{S}^{\cap},\mathcal{L}$ DC's of eq 4.7 or of Figure 2b; these six $\mathcal{S},\mathcal{L}$ DC's are represented by the three drawings of Figure 2b and their mirror images.

For an octahedral graph with sites as in Figure 3a

$$\mathcal{S}^{\cap} = \mathcal{O}_h = S_3{}^{\star}(\mathcal{S}_{\{1,2\}}S_{\{3,4\}}S_{\{5,6\}})$$

$$S_3{}^{\star} = \{1,(13)(24),(35)(46),(15)(26),(135)(246),(153)(264)\} \tag{4.8}$$

For n = 1, 2, and 3 the groups $\mathcal{L}^{\cap} = \mathcal{L}^{(1)}$ are chosen in accordance with (4.1) and the resulting $\mathcal{S}^{\cap},\mathcal{L}^{\cap}$ DC's are illustrated in Figures 3b, c, and d. For n = 1 there are two DC's, the first of which is forbidden and the second of which is allowed. For n = 2 there are four DC's, the first and third of which are forbidden and the second and fourth of which are allowed. For n = 3 there are three DC's, only the third of which is allowed. Considering this last n = 3 DC of Figure 3d further,

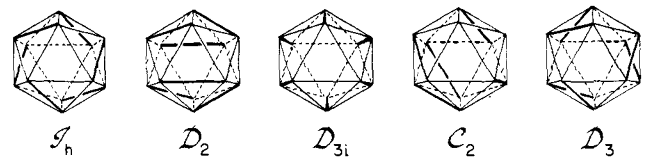

Figure 4. The n = 6 icosahedral case, viewing the icosahedron face-on. Their point group designations $\mathcal{T}_h$, $\mathcal{D}_2$, $\mathcal{D}_{3i}$, $\mathcal{C}_2$, and $\mathcal{D}_3$, respectively.

we find

$$\mathcal{S}^{\cap} \cup G_z\mathcal{L}^{\cap}G_z{}^{-1} = \{1,(135)(246),(153)(264)\}\{1,(23)(56)\} = \mathcal{C}_3\mathcal{C}_2{}' = \mathcal{D}_3 \tag{4.9}$$

so that this DC has repetition frequency $d_z = |\mathcal{D}_3| = 6$, and

$$|\mathcal{S}^{\cap}G_z\mathcal{L}^{\cap}| = \frac{|\mathcal{S}^{\cap}||\mathcal{L}^{\cap}|}{d_z} = 384 \tag{4.10}$$

Thus there are 384 associated bijections. To determine the maximum number of n = 3 permutational isomers which may arise with $\mathcal{S} = \mathcal{O}$, $\mathcal{L} = \{1\}$ is chosen. Note that all the $\mathcal{S},\mathcal{L}$ DC's are simply ordinary right cosets of $\mathcal{O}$ in $\mathcal{S}_6$ all with the same order $|\mathcal{O}| = 24$; the maximum number of n = 3 permutational isomers is, therefore, $|\mathcal{S}^{\cap}G_z\mathcal{L}^{\cap}|/|\mathcal{O}| = 16$.

For an icosahedral graph $\mathcal{S}^{\cap} = \mathcal{S}^{(1)}$ is isomorphic to the icosahedral group $\mathcal{I}_h$, with inversion included. The n = 6 case actually arises for a copper(I) dithiosquarate complex[12] and for crystalline rare-earth double nitrates[13] and five allowed $\mathcal{S}^{\cap},\mathcal{L}^{\cap}$ DC's are found, containing a total of 125 allowed bijections. These allowed DC's are illustrated in Figure 4 along with the point group designations for their symmetry groups $\mathcal{S}^{\cap} \cap G_z\mathcal{L}^{\cap}G_z{}^{-1}$.

In the icosahedra discussed above the skeletal symmetries are actually slightly less than icosahedral; for instance, in the copper complex a cube of copper(I) ions is centered inside the icosahedron, thereby giving rise to a cubic crystal field.[12] It is therefore necessary to consider the $\mathcal{T}_h,\mathcal{L}^{\cap}$ DC's which are obtained from the breakup of the allowed $\mathcal{I}_h,\mathcal{L}^{\cap}$ DC's. The number of $\mathcal{T}_h,\mathcal{L}^{\cap}$ DC's arising from a DC $\mathcal{I}_hG_z\mathcal{L}^{\cap}$ is, by eq A.10 of Appendix A,

$$\xi_z = \frac{|\mathcal{I}_h|}{|\mathcal{T}_h|d_z}\sum_{\rho}\frac{|\mathcal{C}_\rho \cap \mathcal{T}_h|}{|\mathcal{C}_\rho|}|\mathcal{C}_\rho \cap G_z\mathcal{L}^{\cap}G_z{}^{-1}| \tag{4.11}$$

where $\mathcal{H} = \mathcal{I}_h$, $\hat{\mathcal{H}} = \mathcal{T}_h$, and $\mathcal{K} = \hat{\mathcal{K}} = \mathcal{L}^{\cap}$ have also been identified. Next, introducing the definition

$$\mathcal{G}_z = G_z\mathcal{L}^{\cap}G_z{}^{-1} \cap \mathcal{I}_h \tag{4.12}$$

for the DC symmetry group, it follows that

$$\begin{aligned}\xi_z &= \frac{5}{d_z}\sum_{\rho}\frac{|\mathcal{C}_\rho \cap \mathcal{T}_h|}{|\mathcal{C}_\rho|}|\mathcal{C}_\rho \cap \mathcal{G}_z| \\ &= \frac{5}{d_z}\Big\{|\mathcal{C}_1 \cap \mathcal{G}_z| + |\mathcal{C}_{\bar{1}} \cap \mathcal{G}_z| + \frac{1}{5}|\mathcal{C}_2 \cap \mathcal{G}_z| \\ &\quad + \frac{1}{5}|\mathcal{C}_{\bar{2}} \cap \mathcal{G}_z| + \frac{2}{5}|\mathcal{C}_3 \cap \mathcal{G}_z| \\ &\quad + \frac{2}{5}|\mathcal{C}_{\bar{3}} \cap \mathcal{G}_z|\Big\}\end{aligned} \tag{4.13}$$

The following notation was utilized in (4.13): j = 1 for the identity class of $\mathcal{I}_h$, $j = \bar{1}$ for the inversion class, j = 2 for the class of twofold rotations, $j = \bar{2}$ for the class of reflections, j = 3 for the class of threefold rotations, and $j = \bar{3}$ for the class of sixfold improper rotations. From this formula one then readily finds that $\xi_z = 2$ except for the case with $\mathcal{G}_z = \mathcal{C}_2$ in which case $\xi_z = 3$. Of course, if the cube of copper(I) ions rotates around sufficiently rapidly (compared to the time scale of a relevant experiment), these different isomers for this lower symmetry would not be identifiable.

In the case of an icosahedral skeleton with identical bidentate chelates but distinguishable ends, $\mathcal{L} = S_6{}^{\star}$, and it is of interest to break up $\mathcal{I}_h.\ \mathcal{L}^{\cap}$ DC's into $\mathcal{I}_h.\ \mathcal{S}_6{}^{\star}$ DC's. The number of $\mathcal{I}_h.\ \mathcal{S}_6{}^{\star}$ DC's arising from a DC $\mathcal{I}_h G_z \mathcal{L}^{\cap}$ is given by eq A.9 of Appendix A as

$$\xi_z = \frac{|\mathcal{L}^{\cap}|}{d_z|S_6{}^{\star}|}\sum_{\sigma}\frac{|\mathcal{S}_6{}^{\star} \cap \mathcal{C}_\sigma|}{|\mathcal{C}_\sigma|}|\mathcal{G}_{\bar{z}} \cap \mathcal{C}_\sigma| \qquad (4.14)$$

where $\mathcal{H} = \bar{\mathcal{H}} = \mathcal{I}_h = \mathcal{K} = \mathcal{L}^{\cap}$, $\bar{\mathcal{K}} = \mathcal{S}_6{}^{\star}$, and $\mathcal{G}_{\bar{z}} \equiv G_z{}^{-1}\mathcal{I}_h G_z \cap \mathcal{L}^{\cap}$. Using the class specification of Appendix B for the classes of $\mathcal{L}^{\cap}$, it follows that

$$\xi_z = \frac{2^6}{d_z}\sum_{\vec{b}}\frac{|S_6 \cap \mathcal{C}_{\vec{b}}|}{|\mathcal{C}_{\vec{b}}|}|\mathcal{G}_{\bar{z}} \cap \mathcal{C}_{\vec{b}}|$$

$$= \frac{1}{d_z}\sum_{\vec{b}} 2^{b_1+b_2+b_3+b_4+b_5+b_6}|\mathcal{G}_{\bar{z}} \cap \mathcal{C}_{\vec{b}}| \qquad (4.15)$$

where the $\vec{b} = (b_1,b_2,b_3,b_4,b_5,b_6)$ with $\Sigma_{i=1}^{6} ib_i = 6$ identify the classes for which $|S_6{}^{\star} \cap \mathcal{C}_\sigma| \neq 0$. From this formula one then finds that $\xi_z = 8, 22, 13, 36$, and 16 for the five $\mathcal{I}_h.\ \mathcal{L}^{\cap}$ DC's of Figure 4.

5. Permutational Isomerization and Rearrangement Modes

Here a partial characterization of permutational isomerization reactions is effected by classifying the sites between which the ligands are moved (note, however, that in general the particular ligands involved are important also). Formally, the rearrangement bijections from $\mathcal{S}$ onto $\mathcal{S}$ are studied. Because of skeletal symmetry different rearrangements are described[4-6] as *equivalent* with the associated equivalence classes of rearrangements being termed *modes*. A mode $\mathcal{M}_m$ is given[5] in terms of $\mathcal{S},\mathcal{S}$ DC's

$$\mathcal{M}_m = \mathcal{S}G_m\mathcal{S} \cup \mathcal{S}\sigma G_m\sigma^{-1}\mathcal{S} \qquad (5.1)$$

where $\mathcal{S}$ is the proper rotational portion of the full skeletal point group, σ is any improper rotation in the full skeletal point group, and G_m is any (representative) element in $\mathcal{M}_m$. Also of interest are kinetic modes[6,14]

$$\mathcal{M}_m{}^{(k)} = \mathcal{M}_m \cup \mathcal{M}_{\bar{m}} \qquad (5.2)$$

where $\mathcal{M}_{\bar{m}}$ is the mode generated by $G_{\bar{m}} \equiv G_m{}^{-1}$.

We now introduce the notation that if $\mathcal{A}$ is a set, then $\Sigma\{\mathcal{A}\}$ denotes the (uniform) sum over all elements of $\mathcal{A}$. The ith isomer may, therefore, be identified by $\Sigma\{\mathcal{S}^s\varphi_{G_i}\mathcal{L}^L\}$ or $\Sigma\{\mathcal{S}G_i\mathcal{L}\}$ and more generally a linear combination

$$\sum_i c_i\ \Sigma\{\mathcal{S}G_i\mathcal{L}\} \qquad c_i \geq 0 \qquad (5.3)$$

denotes a mixture of isomers, the ith with (relative) concentration c_i. Similarly, $\Sigma\{\mathcal{M}_m\}$ identifies a particular type of isomerization process. Then if the ith isomer is subjected to the mth mode of rearrangements, the relative concentrations of the resulting products are (when there are no constraints) given by

$$\Sigma\{\mathcal{M}_m\}\Sigma\{\mathcal{S}G_i\mathcal{L}\} = \sum_{i'}\langle i'|m_i\rangle\Sigma\{\mathcal{S}G_{i'}\mathcal{L}\} \qquad (5.4)$$

with the positive integers $\langle i'|m_i\rangle$ related simply to those of a DC algebra.[6] Now for the present constrained problems, even if i is an allowed isomer, both allowed and forbidden i' generally result (with nonzero $\langle i'|m_i\rangle$) in this equation (5.4). A way to incorporate constraints into such descriptions would be to define "renormalized" coefficients the same as the $\langle i'|m_i\rangle$ except in the case when i' is forbidden and the renormalized coefficient is taken as zero. This continued viability of the mode concept suggests the use of constrained cases in extracting mode rate constants (the k_P of ref 6) from experimental data. That the mode concept becomes modified only on applying the rearrangement modes to an isomer is clearly expected since the modes are concerned only with the idealized molecular skeleton and are independent of the ligands.

In some special cases the modes can be classified into allowed and forbidden classes. For instance, consider the cases a or b of section 1, with the ligands of $\mathcal{L}^{(1)} \equiv \{\ell_1,\ell_2,\ldots\ell_m\}$ constrained to lie on the sites of $\mathcal{S}^{(1)} \equiv \{s_1,s_2,\ldots,s_n\}$. Then

$$\mathcal{S}^{\cap} = \mathcal{S}^{(1)} = S_{\{1,2,\ldots,n\}}\ S_{\{n+1,n+2,\ldots,N\}}$$

$$\mathcal{L}^{\cap} = \mathcal{L}^{(1)} = S_{\{1,2,\ldots,m\}}\ S_{\{m+1,m+2,\ldots,N\}} \qquad (5.5)$$

When one site s_i is an allowed site for the occupancy of the ligands in $\mathcal{L}^{(1)}$ (i.e., $s_i \in \mathcal{S}^{(1)}$), it follows that the other point group equivalent sites are also allowed; hence $\mathcal{S}^{(1)}$ is invariant under $\mathcal{S}$ and $\mathcal{S} \subseteq \mathcal{S}^{\cap}$. The $\mathcal{S}^{\cap},\mathcal{L}^{\cap}$ DC's may be identified by DC symbols,[6] and it is readily recognized that only the identity $\mathcal{S}^{\cap},\mathcal{L}^{\cap}$ DC is allowed, thus allowing permutational isomers to be identified immediately. Clearly, all the modes occurring in

$$\mathcal{S}^{\cap}G_m\mathcal{S}^{\cap} \cup \mathcal{S}^{\cap}\sigma G_m\sigma^{-1}\mathcal{S}^{\cap} = \mathcal{S}^{\cap} \qquad G_m = 1 \quad (5.6)$$

are entirely allowed since when applying $\Sigma\{\mathcal{S}^{\cap}\}$ to any of the allowed $\mathcal{L},\mathcal{S}$ DC sums, as $\Sigma\{\mathcal{S}G_i\mathcal{L}\}$ with $\mathcal{S}G_i\mathcal{L} \subseteq \mathcal{S}^{\cap}\mathcal{L}^{\cap}$, only allowed $\mathcal{L},\mathcal{S}$ DC sums are obtained. However, for $G_m \notin \mathcal{S}^{\cap}$ the sets of (5.6) generally give rise to modes which when applied to an allowed isomer give back both allowed and forbidden isomers. If in addition to (5.5) one chooses[7,8] $m = n$, so that $\mathcal{S}^{\cap} = \mathcal{L}^{\cap}$, then all the sets of (5.6) with $G_m \notin \mathcal{S}^{\cap}$ will be entirely forbidden. Rather similar results still apply if there are several different constraints of the types a or b given in section 1.

6. An Alternative Approach

In the preceding sections the approach to the constrained problem has relied on individually and exhaustively examining $\mathcal{S}^{\cap},\mathcal{L}^{\cap}$ DC's to determine whether each one is allowed or forbidden. Another approach to the constrained problem has been described[9,10] such that, for a few special cases, exactly all the allowed permutational isomers are generated. In a general formulation of this alternate approach one considers certain bijections from the set $\{\varphi_P;P \in \mathcal{S}_N\}$ of permutamers back onto itself. These certain bijections are those of the group $S_N{}^S \otimes S_N{}^L$, with a group action defined by

$$(P^S,Q^L) \circ \varphi_R \equiv P^S\varphi_R Q^{L-1}$$
$$= \varphi_{PRQ^{-1}},(P^S,Q^L) \in S_N{}^S \otimes S_N{}^L \quad (6.1)$$

Then one seeks a *generating* subgroup

$$\mathcal{Q} \subseteq S_N{}^S \otimes S_N{}^L \qquad (6.2)$$

such that if φ_R is allowed, then the set

$$\mathcal{Q} \circ \varphi_R \equiv \{(P^S,Q^L) \circ \varphi_R;\ (P^S,Q^L) \in \mathcal{Q}\} \qquad (6.3)$$

comprises exactly all allowed permutamers.

It is desirable for $\mathcal{Q}$ to generate all the allowed permutamers since in general they are all needed to identify all the allowed permutational isomers. (When $\mathcal{L} = \mathcal{S} = \{1\}$ each permutamer uniquely identifies a permutational isomer.) Hence the number, M, of allowed permutamers should be a divisor of the order $|\mathcal{Q}|$ of the generating group $\mathcal{Q}$, if it exists. Since $|\mathcal{Q}|$ in turn should be a divisor of $|S_N{}^S \otimes S_N{}^L| = (N!)^2$, M should also be a divisor of $(N!)^2$. This condition is not met for the cases of Figures 1b, 1c, 3c, and 4; therefore there exists no such generating group $\mathcal{Q}$ for these cases. It seems likely that the nonexistence of such generating groups might be a fairly general occurrence. Indeed, although there is[15] a rather simple way to characterize all subgroups of $S_N{}^S \otimes S_N{}^L$ in terms of the subgroup structure of S_N, the only cases for which a generating group $\mathcal{Q}$ has been identified are instances with

$$\mathcal{Q} = \mathcal{S}^{\cap S} \otimes \mathcal{L}^{\cap L} \tag{6.4}$$

Since this choice for $\mathcal{Q}$ generates only a single $\mathcal{S}^{\cap},\mathcal{L}^{\cap}$ DC, the approach of this section seems restricted in application to those (few) cases where there is a single allowed $\mathcal{S}^{\cap},\mathcal{L}^{\cap}$ DC. Of course, even if there are several allowed $\mathcal{S}^{\cap},\mathcal{L}^{\cap}$ DC's the group of (6.4) could still be utilized to generate those isomers in each of these $\mathcal{S}^{\cap},\mathcal{L}^{\cap}$ DC's from any single member of the same $\mathcal{S}^{\cap},\mathcal{L}^{\cap}$ DC.

Some special cases to which the present approach does apply include those with site-adjacency graph and number n of bidentate chelates given as: (a) a regular polygon or polyhedron with $n = 1$, (b) a cubo-octahedron or dodeco-icosahedron with $n = 1$, (c) a $2M$-sided polygon with $n = M$, (d) a $(2M - 1)$-sided polygon with $n = M$, (e) a $(2M - 1)$-agonal pyramid with $n = M$, (f) an octahedron with $n = 3$, (g) a pentalene graph with $n = 4$. Other examples (with just a single allowed $\mathcal{S}^{\cap},\mathcal{L}^{\cap}$ DC) can be found. When the desired $\mathcal{Q}$ exists, it might generate (from an allowed φ_R) each allowed permutamer a repeated number of times, whence sometimes one can identify a subgroup $\mathcal{Q}' \subseteq \mathcal{Q}$ generating each allowed permutamer just once. A case where this idea may be illustrated involves $n = 3$ bidentate chelates and an octahedral site-adjacency graph,

$$\mathcal{S}^{\cap} = \mathcal{O}_h$$
$$\mathcal{L}^{\cap} = S_3{}^{\star}(S_{\{1,2\}}\, S_{\{3,4\}}\, S_{\{5,6\}}) \tag{6.5}$$

If the skeletal group $\mathcal{S}$ is the octahedral group $\mathcal{O}$ of proper rotations and the three bidentate chelates are identical, then

$$\mathcal{Q}' = \mathcal{C}_i{}^{s} \otimes (S_{\{1,2\}}\, S_{\{3,4\}}\, S_{\{5,6\}})^{L} \tag{6.6}$$

which is the case described by Eaton and Eaton.[9] If $\mathcal{S}$ is still $\mathcal{O}$ but the three bidentate chelates are different, then

$$\mathcal{Q}' = \mathcal{C}_i{}^{s} \otimes \mathcal{L}^{\cap L} \tag{6.7}$$

which is the case discussed by Mislow and co-workers.[10] The identification of $\mathcal{Q}'$ in both cases is in the form

$$\mathcal{Q}' = \mathcal{S}'^{S} \otimes \mathcal{L}'^{L} \tag{6.8}$$

with $\mathcal{S}^{\cap}$ being a semidirect product of $\mathcal{S}$ and $\mathcal{S}'$, and with $\mathcal{L}^{\cap}$ a semidirect product of $\mathcal{L}$ and $\mathcal{L}'$. In general, even if $\mathcal{Q}$ exists, such a $\mathcal{Q}'$ does not necessarily exist, as in the case of the trigonal antiprism with $n = 3$ (and $\mathcal{S} = \mathcal{D}_3$).

7. Conclusions

Earlier group-theoretic classification and characterization of permutational isomers and rearrangement modes has been extended here to take into account a variety of constraints on the positioning of ligands on the molecular skeleton. The general theory and group theoretical tools have been described. For the case of bidentate ligation constraints examples involving the trigonal bipyramid, the octahedron, and the icosahedron have been given. For the cases of steric hindrance or ligand electronegativity constraints (which confine certain ligands to certain sites), the special simplicity of the present techniques has been described. It is believed that the present approach is widely applicable and provides a unifying group-theoretic view of a significant variety of chemically different situations.

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Appendix A. DC's in DC's

Here the general problem of decomposing larger $\mathcal{H},\mathcal{K}$ DC's into smaller $\hat{\mathcal{H}},\hat{\mathcal{K}}$ DC's with $\mathcal{H} \supseteq \hat{\mathcal{H}}$ and $\mathcal{K} \supseteq \hat{\mathcal{K}}$ is considered. Letting a group $\mathcal{G}$ be decomposed

$$\mathcal{G} = \dot{\bigcup_{z}} \mathcal{H}G_z\mathcal{K} \tag{A.1}$$

it is well known that each $\mathcal{H},\mathcal{K}$ DC is a disjoint union of $\hat{\mathcal{H}},\mathcal{K}$ DC's, and

$$\mathcal{H}G_z\mathcal{K} = \dot{\bigcup_{i}} \hat{\mathcal{H}}G_iG_z\mathcal{K} \tag{A.2}$$

where the G_i are DC generators for the DC expansion

$$\mathcal{H} = \dot{\bigcup_{i}} \hat{\mathcal{H}}G_i(\mathcal{H} \cap G_z\mathcal{K}G_z{}^{-1}) \tag{A.3}$$

Next the $\hat{\mathcal{H}},\mathcal{K}$ DC's can be decomposed similarly into

$$\hat{\mathcal{H}}G_iG_z\mathcal{K} = \dot{\bigcup_{j}} \hat{\mathcal{H}}G_iG_zG_j\hat{\mathcal{K}} \tag{A.4}$$

where the G_j are DC generators for the DC expansion

$$\mathcal{K} = \dot{\bigcup_{j}} [(G_iG_z)^{-1}\hat{\mathcal{H}}(G_iG_z) \cap \mathcal{K}]G_j\hat{\mathcal{K}} \tag{A.5}$$

Hence the overall decomposition of $\mathcal{H},\mathcal{K}$ DC's into $\hat{\mathcal{H}},\hat{\mathcal{K}}$ DC's is obtained in a two-step process involving ordinary DC decompositions. The $\mathcal{H},\mathcal{K}$ DC generators are of the form $G_iG_zG_j$. In the special (but frequent) case in which $\hat{\mathcal{H}}$ is normal in $\mathcal{H}$, the DC's on the right in (A.3) are simple left cosets, and the intersection group of (A.5) is independent of the G_i. Further simplifications can arise when $\hat{\mathcal{H}}$ is normal in $\mathcal{H}$, or $\hat{\mathcal{K}}$ is normal in $\mathcal{K}$. Also it should be noted that one can similarly decompose $\mathcal{H},\mathcal{K}$ DC's first to $\mathcal{H},\hat{\mathcal{K}}$ DC's, then these to $\hat{\mathcal{H}},\hat{\mathcal{K}}$ DC's.

To enumerate the $\hat{\mathcal{H}},\hat{\mathcal{K}}$ DC's in an $\mathcal{H},\mathcal{K}$ DC, one could simply enumerate the DC's in the expansions (A.3) and (A.5) via, for instance, the DC enumeration formula of Ruch et al.,[3] which is most convenient if the class structure of the overall group, $\mathcal{H}$ or $\mathcal{K}$ in (A.3) and (A.5), is simply recognizable. Here an alternative formula is developed which, however, follows a similar method of proof. Letting ξ_z be the number sought

$$\xi_z = \sum_{q\in z}\left\{\sum_{G\in\hat{\mathcal{H}}G_q\hat{\mathcal{K}}}\frac{1}{|\hat{\mathcal{H}}G_q\hat{\mathcal{K}}|}\right\} = \sum_{G\in\mathcal{H}G_z\mathcal{K}}\frac{1}{|\hat{\mathcal{H}}G\hat{\mathcal{K}}|} \tag{A.6}$$

where $|\mathcal{A}|$ indicates the order of the set $\mathcal{A}$ and the $q \in z$ sum is a sum over the different $\hat{\mathcal{H}},\hat{\mathcal{K}}$ DC's in $\mathcal{H}G_z\mathcal{K}$. Next using the relation between the order of a DC $\hat{\mathcal{H}}G\hat{\mathcal{K}}$ and its repetition frequency $d_G = |\hat{\mathcal{H}} \cap G\hat{\mathcal{K}}G^{-1}|$, one obtains

$$\xi_z = \sum_{G\in\mathcal{H}G_z\mathcal{K}}\frac{d_G}{|\hat{\mathcal{H}}||\hat{\mathcal{K}}|} = \frac{1}{|\hat{\mathcal{H}}||\hat{\mathcal{K}}|}\sum_{G\in\mathcal{H}G_z\mathcal{K}}|\hat{\mathcal{H}} \cap G\hat{\mathcal{K}}G^{-1}| \tag{A.7}$$

Then letting d_z be the repetition frequency for $\mathcal{H}G_z\mathcal{K}$

$$\begin{aligned}\xi_z &= \frac{1}{|\hat{\mathcal{H}}|d_z|\hat{\mathcal{K}}|}\sum_{H\in\mathcal{H}}\sum_{K\in\mathcal{K}}|\hat{\mathcal{H}} \cap HG_zK\hat{\mathcal{K}}K^{-1}G_z{}^{-1}H^{-1}| \\ &= \frac{1}{|\hat{\mathcal{H}}|d_z|\hat{\mathcal{K}}|}\sum_{H\in\mathcal{H}}\sum_{K\in\mathcal{K}}|H\hat{\mathcal{H}}H^{-1} \cap G_z(K\hat{\mathcal{K}}K^{-1})G_z{}^{-1}| \\ &= \frac{|\mathcal{H}||\mathcal{K}|}{|\hat{\mathcal{H}}|hd_zk|\hat{\mathcal{K}}|}\sum_{a}^{h}\sum_{b}^{k}|\hat{\mathcal{H}}_a \cap G_z\hat{\mathcal{K}}_bG_z{}^{-1}|\end{aligned} \tag{A.8}$$

where a labels the h different subgroups $\hat{\mathcal{H}}_a$, $a = 1$ to h, conjugate to $\hat{\mathcal{H}}$; similarly b labels the k subgroups $\hat{\mathcal{K}}_b$ conjugate to $\hat{\mathcal{K}}$. This last result of (A.8) is of some use, but may be further modified if σ is allowed to label the various classes $\mathcal{C}_\sigma$ of $\mathcal{K}$, so that

$$\xi_z = \frac{1}{|\hat{\mathcal{H}}|d_z|\hat{\mathcal{K}}|}\sum_{H\in\mathcal{H}}\sum_{K\in\mathcal{K}}\sum_{\sigma}|G_z{}^{-1}H\hat{\mathcal{H}}H^{-1}G_z \cap K\hat{\mathcal{K}}K^{-1}\cap\mathcal{C}_\sigma| = \frac{1}{|\hat{\mathcal{H}}|d_z|\hat{\mathcal{K}}|}\sum_{\sigma}\sum_{H\in\mathcal{H}} |G_z{}^{-1}H\hat{\mathcal{H}}H^{-1}G_z\cap\mathcal{C}_\sigma||\mathcal{C}_\sigma\cap\hat{\mathcal{K}}|\frac{|\mathcal{K}|}{|\mathcal{C}_\sigma|} = \frac{|\mathcal{H}||\mathcal{K}|}{|\hat{\mathcal{H}}|hd_zk|\hat{\mathcal{K}}|} \sum_{\sigma}\frac{|\hat{\mathcal{K}}\cap\mathcal{C}_\sigma|}{|\mathcal{C}_\sigma|}\sum_{a}^{h}|G_z{}^{-1}\hat{\mathcal{H}}_aG_z\cap\mathcal{C}_\sigma| \quad \text{(A.9)}$$

where it has been noted that if $\hat{K} \in \mathcal{C}_\sigma \cap \hat{\mathcal{K}}$, then as K ranges over the elements of $\mathcal{K}$ in the expression $K\hat{K}K^{-1}$ each element of $\mathcal{C}_\sigma$ is generated exactly $|\mathcal{K}|/|\mathcal{C}_\sigma|$ times. Similarly, if ρ is allowed to label the classes $\mathcal{C}_\rho$ of $\mathcal{H}$, then

$$\xi_z = \frac{|\mathcal{H}||\mathcal{K}|}{|\hat{\mathcal{H}}|d_zk|\hat{\mathcal{K}}|}\sum_{\rho}\frac{|\mathcal{C}_\rho\cap\hat{\mathcal{H}}|}{|\mathcal{C}_\rho|}\sum_{b}^{k}|\mathcal{C}_\rho\cap G_z\hat{\mathcal{K}}_bG_z{}^{-1}| \quad \text{(A.10)}$$

If $\mathcal{K} = \mathcal{G}$ and $\hat{\mathcal{K}} = \mathcal{H}$, then (A.9) yields the previously known[3] formula for the number of $\mathcal{H},\mathcal{K}$ DC's in $\mathcal{G}$.

Appendix B. Concerning Classes of Certain Groups

In order to use the enumeration formula (A.9), the class structure and the orders of the classes of $\mathcal{K}$ should be readily recognizable. To this end we consider the classes for some special types of groups of interest in the applications here.

First, with a symmetric group S_n, the characterization of its classes in terms of cycle structure is well known. Thus if $P \in S_n$ involves c_j cycles of length j, then the sequence $c_1, c_2, \ldots, c_n$ identifies the class containing P and the order of this class is

$$n!\left\{\prod_{i=1}^{n} j^{c_j}(c_j!)\right\}^{-1} \quad \text{(B.1)}$$

Second, consider a group

$$\mathcal{N} = S_n{}^{\star}\prod_{i=1}^{n} S_{\{2i-1,2i\}} \quad \text{(B.2)}$$

termed the *semidirect* (or wreath, or kranz, or composition) product of $\Pi_{i=1}^{n} S_{\{2i-1,2i\}}$ by $S_n{}^{\star}$, as given in (4.1). The particular semidirect product of (B.2) is, in fact, known[16] as the hyperoctahedral group, whose class structure and class orders follow as a special case of a theorem in Kerber.[17] In this case the class to which $P \in \mathcal{N}$ belongs is identified uniquely by a "partially labeled" cycle structure. The development of this identification is aided if it is noted that the elements of $\mathcal{N}$ permute the sets

$$\mathbf{i} \equiv \{2i-1, 2i\} \qquad i = 1 \text{ to } n \quad \text{(B.3)}$$

among themselves. Hence if $P \in \mathcal{N}$ permutes sets $\mathbf{i}_1$ to $\mathbf{i}_2$, $\mathbf{i}_2$ to $\mathbf{i}_3, \ldots$, and $\mathbf{i}_k$ to $\mathbf{i}_1$, then one of two possible types of index-cycles might occur in P giving rise to this cyclic permutation of sets; they are

$$(j_1, j_2, \ldots, j_k, j_1', j_2', \ldots, j_k') \quad \text{(B.4)}$$

and

$$(j_1, j_2, \ldots, j_k)(j_1', j_2', \ldots, j_k') \quad \text{(B.5)}$$

where j_ℓ and j_ℓ' are the two different indices of the set $\mathbf{i}_\ell$, $\ell = 1$ to k. Now any index pair j_ℓ and j_ℓ' can be interchanged in these cycles through conjugation by $(j_\ell, j_\ell') \in \mathcal{N}$. Further, the k different sets involved and their order can be changed around through conjugation by elements of $S_n{}^{\star}$. Hence each class of $\mathcal{N}$ is identified by specifying the set-cycle structure with set-cycles being distinguished as to whether they give rise to index-cycles as in (B.4) or in (B.5). If $P \in \mathcal{N}$ involves a_j and b_j set-cycles of length j with corresponding index-cycles as in (B.4) and (B.5), respectively, then a derivation much like that leading to (B.1) applies; the resulting order for the class containing P is

$$\frac{n!}{\prod_{j=1}^{n} a_j!j^{a_j}\,b_j!j^{b_j}}\prod_{k=1}^{n}(2^{k-1})^{a_k}(2^{k-1})^{b_k} = \frac{n!2^n}{\prod_{j=1}^{n} a_j!b_j!(2j)^{(a_j+b_j)}} \quad \text{(B.6)}$$

Thus, for instance, for $n = 5$ both of the permutations

$$(1,3)(2,4)(5,7,6,8)(9,10) \text{ and } (1,10)(2,9)(3,5,4,6)(7,8) \quad \text{(B.7)}$$

have

$$a_1 = a_2 = b_2 = 1$$
$$b_1 = a_3 = b_3 = a_4 = b_4 = a_5 = b_5 = 0 \quad \text{(B.8)}$$

so that the order of their class is $5! = 120$.

Third, in the case of a direct product of two subgroups, each class of this direct product is a direct product of classes of the two subgroups. Consequently, the class orders are products of orders of classes of the subgroups. Noting that $\mathcal{L}^{\cap}$ of (4.1) is a direct product of subgroups of the first and second types discussed here, it is easy to recognize the class structure and orders for this case.

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