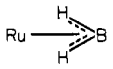
and the BH_4 group may be described as η^2 (Cotton), κ^2 (Sloan and Busch), or a bidentate ligand designated "tetrahydridoborate-*H,H'*" (IUPAC). Should one choose to write the grouping



it becomes η^3 (Cotton), η^3 (Sloan and Busch), or η (IUPAC).

(8) It has been customary to use small Greek letters to denote designators. I have used capital omega because it is unlikely to be confusing and the available small Greek letters are unsatisfactory. Should a small letter be insisted upon, I propose theta (θ).

(9) This does not prevent the informal description of a ligand as Ω^3, Ω^5, etc., as appropriate, however many atoms may compose the ligand part, but unless the usage for nomenclature purposes is severely restricted, considerable difficulties can arise.

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Enumeration of Isomers for Complexes Containing Multiple Elements of Stereoisomerism

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The application of Pólya's counting theorem to determine the number of isomers possible owing to variations in absolute configuration of sites of stereoisomerism is presented. The method described, which is applicable even when different types of stereoisomerism are present, partitions the isomers into classes according to the distributions of absolute configurations among the stereoisomeric sites for a more complete enumeration and permits a determination of whether pseudoasymmetry is possible. Counting functions which allow a facile count of the total isomers possible and a computation of the number of meso structures when only chiral sites have a variable configuration are also presented. The method is illustrated by application to three series of compounds containing multiple sites of dissymmetry—octahedral chelates of bidentate ligands, dihydroxydicarboxylate-bridged binuclear complexes, and trans-octahedral and square-planar complexes of macrocycles.

Introduction

A number of papers have discussed the application of combinatorial methods to the enumeration of permutational isomers by means of Pólya's counting theorem[1-5] or the alternative formulation of Lunn and Senior.[6,7] It has not been recognized, however, that a treatment similar to that used to count permutational isomers can be applied to isomer counting for compounds containing multiple sites of stereoisomerism. In this application, rather than permuting ligands on a molecular skeleton, one permutes absolute configuration designations. In this way, isomerism arising from stereoisomeric elements within the molecular framework itself can be examined.

In this paper, we develop this method and apply it to an enumeration of isomers for three series of complexes containing multiple chiral sites which have been counted in the literature by other, more laborious techniques. Although the present technique is illustrated only for metal ion complexes with dissymmetric sites, it can be used for other systems with other types of stereoisomerism under the restrictions discussed herein.

Procedure

The isomers which may be enumerated by the methods developed here are those which arise owing only to variations in absolute configuration in one or more molecular elements of stereoisomerism.[8] Isomers resulting from other factors such as ligand permutations and skeletal rearrangements must be enumerated separately. We employ the terms "elements of stereoisomerism" and "stereoisomeric sites" interchangeably since the only elements which can be treated by the method described are those which occupy a definite molecular site (though not necessarily a stereoisomeric center[8]). In general, the terms "site" and "element" are restricted to those elements whose absolute configurations are allowed to vary for the isomer enumeration. Invariant elements are included in the skeleton (vide infra). All variable stereoisomeric elements taken into account in one specific step of an isomer enumeration must have the same number (k) of possible configurations. In most cases, and in all examples given here, $k = 2$. The elements must be such that their absolute configurations could be unambiguously specified using either accepted descriptors such as "*R,S*"[9] or "*E,Z*"[10] or any arbitrary but unambiguous designations. An absolute configuration designation for one stereoisomeric site must in no way depend upon the designations of configuration at other sites.

We define the molecular skeleton as the entire molecule whose isomers are to be enumerated with the symmetry it would have if all of the variable-configuration elements were of such a geometry that stereoisomerism were impossible. In the case of chiral elements this is best realized by treating each such element as though it were planar. Skeletons defined in this way are related to the more restrictive two-dimensional projection formulas employed by others to enumerate isomers in some selected bridged chelates.[11] That the skeletal symmetry may change once absolute configurations are assigned (e.g., planar, achiral elements become nonplanar and chiral) is of no more or no less significance than the fact that the symmetry of a molecule for which permutation isomers are counted by standard combinatorial methods[1-5] may change with a permutation of the ligands. Only the initial skeletal symmetry needs to be considered.

Once a skeleton has been chosen, it must remain invariant. Each change involving the absolute configuration of an element of stereoisomerism which has not been included among the variable-configuration elements or involving any change in connectivity of atoms requires that another count be made with the new basic skeleton.

A key point in the enumeration of isomers owing to the presence of elements of stereoisomerism of more than one kind is the following. A descriptive label for absolute configuration can be considered to have meaning only when it is associated with a particular site. Thus, we can label sites as "possibility 1", "possibility 2", ..., "possibility k" and relate these labels, if desired, to more familiar designations once the site associated with each label is considered. This permits us to permute all designations among all sites of stereoisomerism rather than restricting, e.g., *E,Z* descriptors to cis–trans sites. Without this convention, the method presented would be much less useful. We will employ the configuration designations α and β in the examples presented. An extension to (rare) molecular

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systems where all elements of stereoisomerism have k possibilities ($k > 2$) using descriptors α, β, γ, ... is obvious.

A partition $p_d = \{r,s,t,...\}$, where $r + s + t + ... = d$, of the d stereoisomeric sites of a molecule can be used to designate the set of isomers possible when there are r sites of one absolute configuration, s sites of another, t sites of a third, etc. We can then refer to the set of isomers belonging to the partition p_d. Often we will employ the partition $\{r,s,t,...\}$ as though it were unordered since the number of isomers for a particular partition does not depend upon the actual kinds of absolute configurations present but only on the numbers of each type —at least for systems that we can treat by the present method.

Given a set S of mappings, Pólya's counting method permits one to determine the number of equivalence classes with respect to a permutation group G of order $|G|$ and degree d. In the enumeration of permutational isomers, the number of equivalence classes of the set of all mappings of ligands onto skeletal sites is obtained.[1-5] In the enumeration of isomers owing to variations in absolute configurations at stereoisomeric sites, the number of equivalence classes of the set of all mappings of configuration labels onto skeletal elements of stereoisomerism is determined. In either case, one starts with a function $Z(G)$, the cycle index, which is obtained from the cycle structures of the skeletal site permutations corresponding to the symmetry group of the skeleton.[3]

$$Z(G) \equiv Z(G,f_1,f_2,f_3,\dots) = \frac{1}{|G|}\sum_g f_1^{j_1} f_2^{j_2} f_3^{j_3} \dots \qquad (1)$$

Here the sum is over all permutation operations $g \in G$ and the j_i are the number of cycles of length i in each g.

In a count of permutational isomers,[1-5] one sets each $f_i = A^i + B^i + C^i + ...$ in the cycle index to obtain, upon expansion, a counting polynomial $F(G,A,B,C,...)$, where the coefficient of each term $A^rB^sC^t...$ is the number of isomers for a partition $\{r,s,t,...\}$. In the present application, we substitute $f_i = \alpha^i + \beta^i + \gamma^i + ...$ to obtain an analogous counting polynomial $F(G,\alpha,\beta,\gamma,...)$ whose coefficients are the number of isomers $n(G,p_d)$ for various partitions of sites into those of α, β, γ, ... configuration. Here, in contrast to permutational isomer counting, where isomers cannot normally have different ligand partitions, all partitions contribute to the set of all isomers. More information is thereby available concerning the actual types of isomers possible when treating stereoisomers of the type described herein by Pólya's method than when treating permutational isomers. The equivalence relation ⟨"have the same partition"⟩ partitions the stereoisomers into classes.

A fundamental formulation of Pólya's theorem can be used to rapidly sum the stereoisomers for all partitions p_d starting with the cycle index $Z(G,f_1,f_2,f_3,...)$. The total number $N(G)$ of equivalence classes among a set S of mappings of k things (in our application, the k different absolute configurations) with respect to G is given by[12]

$$N(G) = \sum_{p_d} n(G,p_d) = Z(G,k,k,k,\dots) \qquad (2)$$

Thus a count of all isomers can be obtained by setting each $f_i = k$ (usually 2) in the cycle index. Of course, this means that information about the distribution of isomers by partition—which is determined from the counting polynomial $F(G,\alpha,\beta,\gamma,...)$—is not obtained. Equation 2 is of little interest in the enumeration of ligand-permutation isomers where isomers must belong to the same partition.

In an enumeration of isomers resulting from permutations of achiral point ligands, the permutation group used to establish equivalence classes among the set S of ligand → site mappings is the group of all permutations of skeletal sites imposed by the symmetry operations of either the full skeletal point group (giving permutation group G') or its rotational subgroup (giving G''). These permutation groups partition S into classes, each of which contain mappings equivalent under proper rotations only (if G'' is used) or under both proper and improper rotations (G'). Each of the latter classes can contain mappings corresponding to enantiomeric pairs of isomers while the former cannot. Thus utilization of counting polynomials obtained from both $Z(G'')$ and $Z(G')$ allows separate counts of all isomers and geometric isomers only for permutations of point ligands. The difference between the two counts is the number of enantiomeric pairs.

When chiral ligands and chiral designators are permuted among ligand sites and elements of stereoisomerism, respectively, the method just discussed does not give an enumeration of enantiomeric pairs. Although $Z(G'')$ permits a count of all isomers, as in the permutation of point ligands, $Z(G')$ allows only a count of the classes obtained combining isomeric pairs which would be enantiomeric were each chiral ligand or element achiral and distinct from any ligands or elements enantiomeric to it. When chiral ligands are involved, the difference in the counts gives the number of pairs of isomers which have enantiomeric "assemblies of differentiated atoms" as defined by Hirschmann and Hanson.[8] Since a chiral assembly has been proposed as one of the two requirements for pseudoasymmetry,[8] the difference in counts, when doubled, gives the maximum number of isomers which could be pseudoasymmetric. If we can extend the definition of an assembly to include differentiated elements of stereoisomerism, we can use counts with respect to G' and G'' to determine when pseudoasymmetry could be present in systems of the type discussed in this paper.

While Pólya's method in its usual form does not permit a determination of enantiomeric pairs in isomers resulting from either permutations of chiral ligands or variations in absolute configuration at chiral sites (permutations of chiral designators), we have devised a method for carrying out the required enumeration. Isomers resulting from the permutation of chiral ligands will not be discussed any further in this paper, but we give below a method for separately enumerating diastereomeric and enantiomeric isomers in molecules containing multiple dissymmetric elements when each element has only two mirror-image absolute configurations ($k = 2$).

In general, most isomers or molecules containing multiple dissymmetric elements will be chiral. Achiral (meso) structures result when there are improper rotations which relate enantiomeric sites. This can occur only for partition $\{r,r\}$ isomers and then only when there are one or more improper rotations in the full point group of the skeleton whose corresponding skeletal site permutation operations are composed only of even cycles. This, of course, requires that the skeleton be achiral and that there be an even number of all symmetry-equivalent chiral sites. Even if these conditions are met, however, not every partition $\{r,r\}$ isomer is meso. The following procedure allows a determination of the number of meso structures.

A simple lemma on which Pólya's theorem rests states that the number M of equivalence classes in a set S with respect to G, a group of permutations on S, is equal to the sum of the numbers $w(g)$ of elements of S that remain invariant under each operation $g \in G$ divided by $|G|$.[12]

$$M = \frac{1}{|G|}\sum_g w(g) \qquad (3)$$

This lemma has been used previously to count ligand-permutation isomers[5] and we will employ it here. We take as S the set of all distinguishable absolute configuration → stereoisomeric site mappings (of unknown number) which correspond to meso structures. S is a subset of the $d!/r!r!$ distinguishable mappings possible for $p_d = \{r,r\}$, $r + r = d$. Some of the mappings in S may, of course, be equivalent under the

skeletal symmetry with which G is associated.

Since we have restricted S to the set of mappings corresponding to meso structures, we can employ either G' or G'' in eq 3 and arrive at the same count, there being no enantiomeric pairs to group into the same class under G'.

$$M = \frac{1}{|G'|} \sum_{g'} w(g') = \frac{1}{|G''|} \sum_{g''} w(g'') \tag{4}$$

G' is composed of G'', the group of permutations corresponding to proper rotations, and P, the set of permutations corresponding to improper rotations. If $G' = G''$, $P = 0$ (the empty set) and no meso structures are possible. Otherwise, $|G''| = |P| = {}^1/_2|G'|$. We can therefore rewrite eq 4 as

$$M = \frac{1}{2|G''|} \{ \sum_{g''} w(g'') + \sum_{p} w(p) \} \tag{5}$$

where $p \in P$. One can now easily show that

$$M = \frac{1}{|P|} \sum_{p} w(p) = M(P) \tag{6}$$

We can, therefore, sum the numbers of mappings which are invariant under the set P of permutations corresponding to improper rotations and divide the number obtained by $|P|$ to calculate the number of equivalence classes among the set of all distinguishable mappings corresponding to meso structures. This will give the number of nonequivalent meso isomers.

A configuration of chiral descriptors can be invariant under a permutation $p \in P$ only if all cycles of p are even. For each cycle of such a permutation, regardless of the cycle length, there are two and only two distinguishable assignments of α and β absolute configurations to the sites permuted which can be part of meso structures. For example a cycle of length r (even) of the form $(a_1a_2a_3...a_r)$ on the sites $a_1, a_2, a_3, ..., a_r$ can relate enantiomeric sites only for the two distinguishable partial mappings

$$\begin{bmatrix} \alpha & \beta & \alpha & \dots & \beta \\ a_1 & a_2 & a_3 & \dots & a_r \end{bmatrix} \text{ and } \begin{bmatrix} \beta & \alpha & \beta & \dots & \alpha \\ a_1 & a_2 & a_3 & \dots & a_r \end{bmatrix}$$

If one multiplies together the number of possible assignments (two) for each cycle of the even-cycled operator, one arrives at the total number of mappings which are invariant under that permutation operation. Doing this for each $p \in P$ and dividing the sum by $|P|$, one obtains the total number of meso structures.

To simplify this procedure, we define a function $Z(P)$ of a set P of permutation operations corresponding to the improper rotations of a skeleton such that $Z(P)$ is analogous to the cycle index $Z(G)$ of a permutation group G.

$$Z(P) = \frac{1}{|P|} \sum_{p} f_1^{j_1} f_2^{j_2} f_3^{j_3} \dots \tag{7}$$

where

$$P = G' - G'' \tag{8}$$

Setting $f_i = 2$ or 0 depending on whether i is even or odd, respectively, one obtains from $Z(P)$ a count of all possible meso structures. The difference between this number $M(P)$ and the total number of isomers (given by eq 2) is the number of chiral isomers which are members of enantiomeric pairs. If $G' = G''$ ($P = 0$), the skeleton is chiral and all isomers for all partitions are chiral though their enantiomers are not included in the set of isomers. The method as discussed above can be used only when all sites of stereoisomerism are chiral and only when there are two enantiomeric possibilities for each.

The following section applies the counting methods discussed here to isomer enumerations for some compounds with multiple dissymmetric sites, each of which have only two possible configurations ($k = 2$). We arbitrarily let the symbol α represent "Δ" when associated with an octahedral metal ion,[13] "R" when associated with an asymmetric tetrahedral atom,[9] and "δ" when associated with a chelate ring[13] in these examples. Conversely, β represents "Λ", "S", or "λ".

Isomer Enumerations

Octahedral Chelates of Bidentate Ligands. In a recent note,[14] R.E.T. pointed out that the number of possible isomers for the ion $[Co(stien)_3]^{3+}$ (stien = stilbenediamine) had been reported incorrectly in the literature. Using diagrammatic methods,[15,16] which can lead to error if not applied carefully,[17] we determined that there are 32 isomers for this system. Here we demonstrate the application of Pólya's theorem to this and related problems.

The ligand stilbenediamine contains two chiral centers and exists in three forms: RR (or $\alpha\alpha$), SS ($\beta\beta$), and RS ($\alpha\beta$). We choose the skeleton to be that shown schematically at the top of Table I (skeleton 1) with six numbered chiral sites to which α and β configurations must be assigned. A skeleton of absolute configuration Δ[13] is treated here. The Λ skeleton poses a separate problem.

Since the skeletal symmetry is D_3, the skeleton is chiral ($P = 0$) and no meso structures are possible. The operator $E \in D_3$ is associated with a permutation of skeletal chiral sites of cycle structure 1,1,1,1,1,1 (where the length of each cycle is given); C_3 and C_3^2 with permutations of structure 3,3; and the three C_2 operators with permutations of structure 2,2,2. The resulting cycle index, $Z(D_3)$, is given in the table. The total number of isomers is found by setting each $f_i = 2$ (eq 2).

$$N(D_3) = {}^1/_6(2^6 + 2 \cdot 2^2 + 3 \cdot 2^3) = 16 \tag{9}$$

A counting polynomial obtained by setting each $f_i = \alpha^i + \beta^i$ allows an enumeration by partition.

$$F(D_3,\alpha,\beta) = \alpha^6 + \alpha^5\beta + 4\alpha^4\beta^2 + 4\alpha^3\beta^3 + 4\alpha^2\beta^4 + \alpha\beta^5 + \beta^6 \tag{10}$$

The various terms represent the different partitions of α and β (here R and S). For example, there are four isomers for the partition $p_d = \{3,3\}(n(D_3,p_d) = 4)$. These are the two stereoisomers each of $[Co(RR\text{-stien})(SS\text{-stien})(RS\text{-stien})]^{3+}$ and of $[Co(RS\text{-stien})_3]^{3+}$.[14] The sum of the coefficients of the counting polynomial, 16, gives the total number of rotationally nonequivalent ways that one can assign R and S labels to the numbered sites of the molecular skeleton. An analogous set of 16 isomers is obtained for the Λ skeleton giving a total of 32 isomers, in agreement with the earlier count.[14] The isomers are illustrated in Figure 1. The table gives the number for each partition.

Other chiral elements can be included in this calculation. Inclusion of the chiral metal center (skeleton 2, Table I) and both the chiral metal center and chelate ring δ,λ dissymmetries (skeleton 3) gives, respectively, 32 and 208 isomers. Of course, as more chiral elements are included among the variable-configuration sites, less useful information is obtained from the distribution of isomers by partition. For a problem involving many different types of stereoisomeric elements, it is useful to enumerate the isomers by determining isomer counts for various skeletons as different elements are deleted from the set of elements of variable configuration.

In some cases, one may need to consider more than one skeleton to count all of the isomers. We have already seen an example of this in the problem of skeleton 1. Another instance is the enumeration of the isomers of the 1,2-propylenediamine complex Δ-$[Co(pn)_3]^{3+}$, where both the facial and meridional forms must be considered (skeletons 4a and 4b).

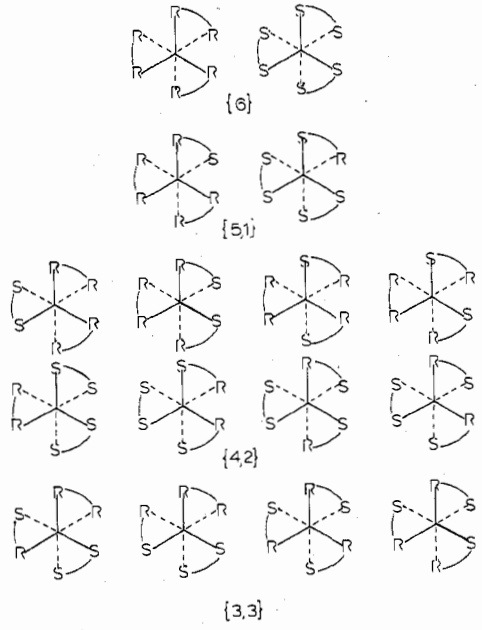


Figure 1. Isomers of Δ-$[Co(stien)_3]^{3+}$.

Thus far, in all of the examples discussed, no meso structures nor chiral assemblies of differentiated elements occur. This is not the case for the example given by skeleton 5 where there is a trans bis chelate containing bidentate ligands with two constitutionally equivalent chiral centers and two different axial groups as in *trans*-$[Co(stien)_2(H_2O)Cl]^{2+}$. Here different isomer counts are obtained depending on whether the full point group G' or the rotational subgroup G'' is used. The difference of 3 in the count shows that there are three pairs of enantiomeric assemblies of differentiated elements. Upon inspection we find six such isomers (Figure 2) and these meet both Hirschmann and Hanson's criteria for pseudoasymmetry[8] and Nourse's criteria for pseudochirality.[18] This is the only example in Table I where the counts obtained with G' and G'' are different and, therefore, has the only table entry where $Z(G')$ is given.

The C_{2v} point group contains two reflection operations which, for skeleton 5, are associated with permutations of cycle structure 2,2. This gives

$$Z(P) = {}^1/_2(2f_2{}^2) \tag{11}$$

Setting $f_2 = 2$, we obtain $M(P)$, the number of meso isomers (eq 6).

$$M(P) = {}^1/_2(2\cdot 2^2) = 4 \tag{12}$$

All four of the isomers corresponding to the partition {4,4} are meso. The remaining six isomers must exist as three enantiomeric pairs.

As a final example in this section, we present a count for the bridged complex $[Co_4(OH)_6(en)_6]^{6+}$ (en = ethylenediamine), skeleton 6, whose isomers have been enumerated by a much more laborious method.[11] Skeleton 6 has symmetry D_{3h} when all chiral elements are considered planar. Permuting absolute configurations among the four chiral metal ions and the six chiral chelate rings, we determine that there are 208 isomers total in agreement with the number reported.[11] No meso isomers are possible since no $p \in P$ has only even cycles. Isomer counts by our method on all other bridged systems discussed in the paper cited[11] are in agreement with those reported.

In all the examples which follow, $Z(P)$ is (fortuitously) identical in form with $Z(G'')$ and will, therefore, not be given. However, the counts of meso isomers determined from $Z(P)$ will be listed in the table.

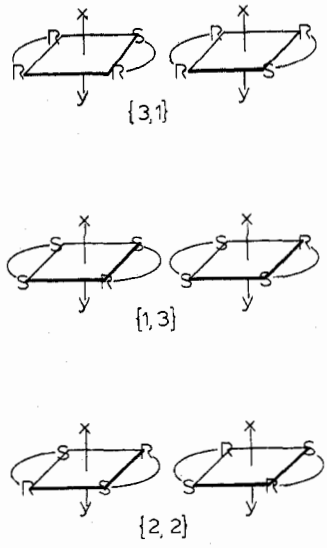
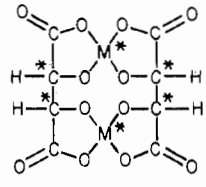


Figure 2. Pseudoasymmetric isomers of *trans*-$[Co(stien)_2xy]^{n+}$.

Dihydroxydicarboxylate-Bridged Binuclear Complexes. A recent paper[19] enumerates the isomers possible for tartrate-bridged binuclear complexes (**1**) using a direct counting



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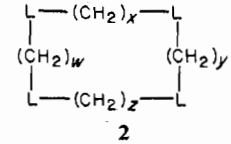
permutation approach. These complexes contain two metal ions, which may be chiral, and two bridging ligands, each of which contain two chiral centers. This gives four to six chiral sites in the structure. Here we confirm the earlier enumerations using Pólya's method and extend the count to related, more complex systems.

Counts given in Table I for simple tartrate-bridged binuclear complexes with both achiral (skeleton 7) and chiral (8) metal ions—as found in the vanadyl(IV)[19] and bipyridylchromium(III)[20] tartrates, respectively—agree with those reported elsewhere.[19] The 7 and 24 isomers for the two cases are illustrated diagrammatically in Figure 3. The addition of a nonhydrogen substituent at one of the aliphatic sites of tartaric acid gives an unsymmetrically substituted ligand such as monomethyltartaric acid (mmt), for which binuclear bridged complexes are known.[21,22] With such ligands, two different bridged-complex skeletons are possible for both achiral (skeletons 9a and 9b) and chiral (10a and 10b) metal ions since the substituents may be cis or trans. The resulting totals of 20 and 76 isomers for the achiral and chiral metal ions are in agreement with totals we calculate by direct enumeration.

Trans-Octahedral and Square-Planar Complexes of Macrocycles. The last section of Table I presents counts for some selected complexes containing tetradentate macrocyclic ligands (**2**, L = S, O, N, or P) in a planar coordination. Upon co-



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ordination (in the case of phosphorus where inversion is usually slow—before coordination), the ligators become centers of stereoisomerism. When the four chains linking the ligators are not all equivalent, R and S absolute configurations can

Table I. Isomer Counts for Selected Complexes Containing Multiple Sites of Dissymmetry

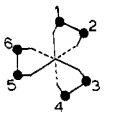
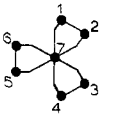
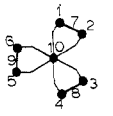
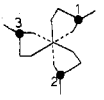
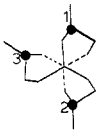
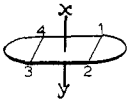
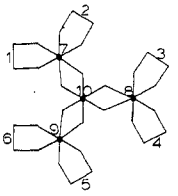
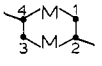
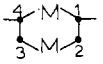
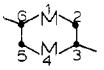
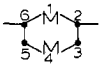
no.	skeleton[a]	G'	$Z(G)$	no. of isomers[b] $N(G)$	$M(P)$	no. of isomers by partition[c] P_d	$n(G, P_d)$
			Octahedral Chelates of Bidentate Ligands				
1		D_3	$Z(D_3) = {}^1/_6(f_1{}^6 + 2f_3{}^2 + 3f_2{}^3)$	16	0	{6}	1 + 1
						{5,1}	1 + 1
						{4,2}	4 + 4
						{3,3}	4
2		D_{3h}	$Z(D_3) = {}^1/_6(f_1{}^7 + 2f_3{}^2f_1 + 3f_2{}^3f_1)$	32	0	{7}	1 + 1
						{6,1}	2 + 2
						{5,2}	5 + 5
						{4,3}	8 + 8
3		D_{3h}	$Z(D_3) = {}^1/_6(f_1{}^{10} + 2f_3{}^3f_1 + 3f_2{}^4f_1{}^2)$	208	0	{10}	1 + 1
						{9,1}	3 + 3
						{8,2}	10 + 10
						{7,3}	25 + 25
						{6,4}	41 + 41
						{5,5}	48
4a		C_3	$Z(C_3) = {}^1/_3(f_1{}^3 + 2f_3)$	4	0	{3}	1 + 1
						{2,1}	1 + 1
4b		C_1	$Z(C_1) = f_1{}^3$	8	0	{3}	1 + 1
						{2,1}	3 + 3
5		C_{2v}	$Z(C_2) = {}^1/_2(f_1{}^4 + f_2{}^2)$	10	4	{4}	1 + 1
						{3,1}	2 + 2
						{2,2}	4
			$Z(C_{2v}) = {}^1/_4(f_1{}^4 + 3f_2{}^2)$	7		{4}	1 + 1
						{3,1}	1 + 1
						{2,2}	3
6		D_{3h}	$Z(D_3) = {}^1/_6(f_1{}^{10} + 2f_3{}^3f_1 + 3f_2{}^4f_1{}^2)$	208	0	{10}	1 + 1
						{9,1}	3 + 3
						{8,2}	10 + 10
						{7,3}	25 + 25
						{6,4}	41 + 41
						{5,5}	48
			Dihydroxydicarboxylate-Bridged Binuclear Complexes				
7		D_{2h}	$Z(D_2) = {}^1/_4(f_1{}^4 + 3f_2{}^2)$	7	3	{4}	1 + 1
						{3,1}	1 + 1
						{2,2}	3
8		D_{2h}	$Z(D_2) = {}^1/_4(f_1{}^6 + f_1{}^2f_2{}^2 + 2f_2{}^3)$	24	4	{6}	1 + 1
						{5,1}	2 + 2
						{4,2}	6 + 6
						{3,3}	6
9a		C_{2h}	$Z(C_2) = {}^1/_2(f_1{}^4 + f_2{}^2)$	10	2	{4}	1 + 1
						{3,1}	2 + 2
						{2,2}	4
9b		C_{2v}	$Z(C_2) = {}^1/_2(f_1{}^4 + f_2{}^2)$	10	2	{4}	1 + 1
						{3,1}	2 + 2
						{2,2}	4
10a		C_{2h}	$Z(C_2) = {}^1/_2(f_1{}^6 + f_2{}^3)$	36	4	{6}	1 + 1
						{5,1}	3 + 3
						{4,2}	9 + 9
						{3,3}	10
10b		C_{2v}	$Z(C_2) = {}^1/_2(f_1{}^6 + f_1{}^2f_2{}^2)$	40	0	{6}	1 + 1
						{5,1}	4 + 4
						{4,2}	9 + 9
						{3,3}	12

Table I (*Continued*)

		Trans-Octahedral and Square-Planar Complexes of Macrocycles					
11		C_{2v}	$Z(C_2) = 1/2(f_1^4 + f_2^2)$	10	2	{4} {3,1} {2,2}	1 + 1 2 + 2 4
12		D_{2h}	$Z(D_2) = 1/4(f_1^4 + 3f_2^2)$	7	3	{4} {3,1} {2,2}	1 + 1 1 + 1 3
13		C_{2v}	$Z(C_2) = 1/2(f_1^4 + f_2 f_1^2)$	12	0	{4} {3,1} {2,2}	1 + 1 3 + 3 4
14		C_{2h}	$Z(C_2) = 1/2(f_1^6 + f_2^3)$	36	4	{6} {5,1} {4,2} {3,3}	1 + 1 3 +3 9 + 9 10

[a] A schematic of the skeleton is given. Example complexes for each skeleton are the following: 1, Δ-$[Co(stien)_3]^{3+}$; 2, 3, $[Co(stien)_3]^{3+}$; 4a, *fac*-Δ-$[Co(pn)_3]^{3+}$; 4b, *mer*-Δ-$[Co(pn)_3]^{3+}$; 5, *trans*-$[Co(stien)_2(H_2O)(Cl)]^{2+}$; 6, $[Co_4(OH)_6(en)_6]^{6+}$; 7, $[(VO)_2(tart)_2]^{4-}$; 8, $[Cr_2(bpy)_2(tart)_2]$; 9, $[(VO)_2(mmt)_2]^{4-}$; 10, $[Cr_2(bpy)_2(mmt)_2]$; 11, $[Pt(13\text{-ane-}S_4)]^{2+}$; 12, $[Pt(14\text{-ane-}S_4)]^{2+}$; 13, $[Pt(14\text{-ane-}S_4)]^{2+}$; 14, $[Ni(1,7\text{-CTH})]^{2+}$. [b] $N(G)$ and $M(P)$ give, respectively, the total number of isomers and the number of meso isomers. [c] Two (equal) numbers of isomers are given for all partitions of the type $\{r,s\}$, $r \neq s$, which can represent two different combinations of absolute configuration designators.

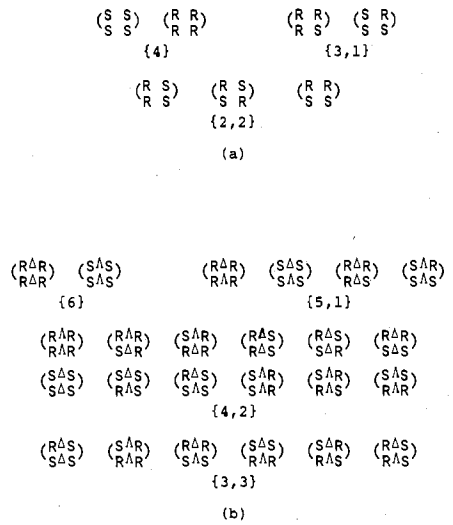
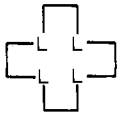


Figure 3. Isomers of tartrate-bridged complexes containing achiral (a) and chiral (b) metal ions.

be associated with the donor atoms and the isomers can be enumerated as described previously. Isomer counts are given in Table I for complexes of three typical[22,23] macrocyclic ligands (skeletons 11–13) and the isomers for the first enumeration are shown schematically in Figure 4. It is interesting that our enumeration shows seven isomers for a planar coordination of 14-ane-L_4 (e.g., cyclam; skeleton 12) while Bosnich and co-workers report a count of five.[25] They, however, have apparently chosen to ignore the possibility of enantiomeric pairs for the partitions {4} and {3,1}. Likewise, a recent paper lists six isomers for trans-octahedral complexes of 15-ane-N_4. This ligand has the same symmetry as 13-ane-L_4 (skeleton 11, Figure 4) for whose planar complexes we count ten isomers. Again, optical isomers have been neglected.

When the chains linking four identical ligators in these macrocycles are equivalent, it is not possible to assign unambiguous absolute configuration labels. Hence for highly symmetric tetradentate macrocycles, such as **3**, isomers of



12-ane-L_4

3

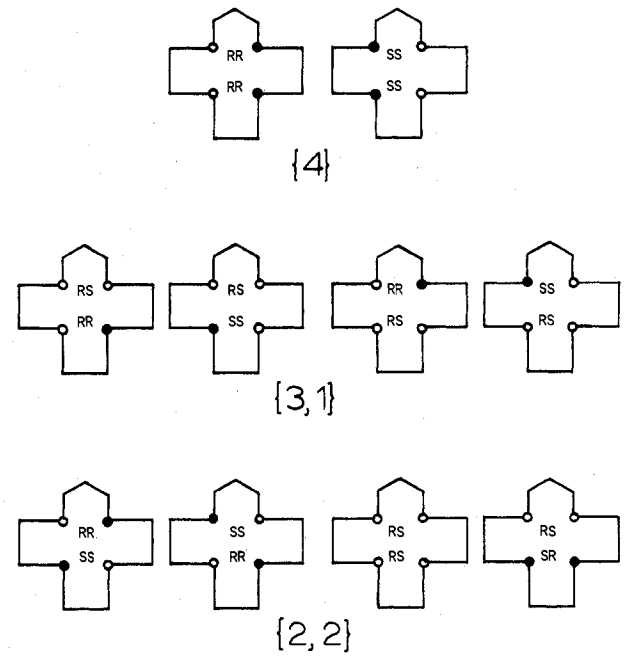


Figure 4. Isomers of square-planar complexes of 13-ane-L_4. Filled circles indicate that a lone pair (L = S or O) or a hydrogen (L = N or P) is directed upward.

complexes cannot be counted by the method discussed here.

A final example (skeleton 14) is given for complexes of a macrocyclic ligand containing four chiral ligators and two chiral carbon atoms: 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetrazacyclotetradecane (1,7-CTH). Our count of 4 meso and 32 chiral isomers (the latter consisting of 16 enantiomeric pairs) agrees with that reported previously for square-planar $[Ni(1,7\text{-CTH})]^{2+}$.[27]

Acknowledgment. We thank the National Institutes of Health for funding of research in isomerism of metal ion complexes of biological interest (Grant GM22435) and Dr. Thomas Jones for helpful discussions concerning isomerism in complexes of macrocyclic ligands.

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Syntheses of New Phenylimido- and Sulfido-Tetraphosphorus Ring and Cage Compounds

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Two new tetraphosphorus cage compounds, α-$P_4S_3(NC_6H_5)$ and α-P_4S_4, have been obtained from the reaction of α-$P_4S_3I_2$ with aniline ($C_6H_5NH_2$). Infrared, ^1H NMR, and mass spectral evidence for the presence of $P_4S_3(NHC_6H_5)_2$ as a reaction intermediate has been obtained. On the basis of spectral data and chemical arguments, α-$P_4S_3(NC_6H_5)$ is assigned tentatively a cage structure in which the sulfur atoms maintain the sulfur atom arrangement and the phenylimido moiety (C_6H_5N) occupies what was the opened edge of α-$P_4S_3I_2$. The α-P_4S_4 structure has been established by a single-crystal x-ray study. Crystals of α-P_4S_4 are monoclinic (space group $C2/c$), with a = 9.779 (1) Å, b = 9.055 (1) Å, c = 8.759 (2) Å, β = 102.65°, Z = 4, d_{calcd} = 2.213 g cm^{-3}, and d_{obsd} = 2.26 g cm^{-3} (20 °C, Mo Kα). The crystal structure was solved by direct methods. The P_4S_4 model refined to R_1 = 0.038 and R_2 = 0.048 for 1680 independent observed reflections. Alternate refinement of an S_4P_4 model (atom positions reversed) and application of the Hamilton R-factor test, along with geometrical arguments, allow the S_4P_4 model to be rejected. α-P_4S_4 has approximate D_{2d} symmetry, a structure in which P atoms are pseudotetrahedral and S atoms are in a square plane. The mean P–S and P–P bond distances are 2.111 Å and 2.353 Å, respectively. The three cage bond angles are P–S–P = 98.92°, S–P–S = 95.18°, and S–P–P = 100.42°. Reaction of β-$P_4S_3I_2$ with $C_6H_5NH_2$ yields a diazadiphosphetidine [$P_2S_2(NC_6H_5)_2(NHC_6H_5)_2$], P_4S_3, and β-P_4S_4. Spectral data are presented which support β-P_4S_4 being the second of two possible isomers of an edge-substituted tetraphosphorus–tetrasulfide system. A new type of phosphorus–nitrogen ring compound, $P_4(NHC_6H_5)_4(NC_6H_5)_2$, a 1,4,2,3,5,6-diazatetraphosphorine, has been identified tentatively from the reaction of P_2I_4 with $C_6H_5NH_2$.

Introduction

Tetraphosphorus compounds of formula $P_4E_{0-6}A_{0-4}$, where E and A represent moieties in divalent edge or apical bonding positions on a P_4 tetrahedron (or distorted tetrahedron), comprise a general type of phosphorus cage system. In these, the P_4E_{0-6} unit constitutes a closo-type molecular cage and the A moieties can be regarded as cage substituents (Figure 1).[2] Well-characterized, selected examples of such compounds (classes in parentheses) are P_4S_3[3,4] (P_4E_3); $P_4S_3Mo(CO)_5$[5] (P_4E_3A); P_4S_5[6] (P_4E_4A); P_4S_7[7] ($P_4E_5A_2$); P_4O_6,[8] $P_4(NCH_3)_6$,[9] and $P_4[Ge(CH_3)_2]_6$[10] (P_4E_6); and $P_4O_6Ni(CO)_3$[11] (P_4E_6A). Noteworthy is the fact that all known cages, except perhaps that of the $P_4S_9N^-$ ion,[12] are homo edge-substituted, i.e., contain only one type of E substituent.

Recently, we have undertaken a study of syntheses of hetero edge-substituted $P_4E_xE'_{6-x}$ ($E \neq E'$) and new incompletely edge-substituted (P_4E_{1-5}) cage systems in order to extend our understanding of P_4-cage relative thermodynamic stabilities and chemical reactivities. Routes to phenylimido (>NC_6H_5) and sulfido (–S–) substituted P_4 cages, from reactions of α-$P_4S_3I_2$ (**1**),[13,14] β-$P_4S_3I_2$ (**2**),[15] and P_2I_4 with aniline have been examined. From these reactions, three new tetraphosphorus cage compounds, α-P_4S_4, α-$P_4S_3(NC_6H_5)$, and β-P_4S_4, and a new cyclic phosphorus–nitrogen compound, $P_4(NHC_6H_5)_4(NC_6H_5)_2$, have been obtained. A preliminary account of the independent synthesis and characterization of α- and β-P_4S_4 has appeared very recently, also.[16] The results of our work are described below.

Experimental Section

Apparatus and Materials. All operations were carried out in N_2-flushed glovebags or in evacuated systems.[17] Infrared, ^1H NMR (60.0 MHz), and mass spectra were obtained using Perkin-Elmer 337G, Varian A-60A, and Varian MAT CH-5 spectrometers, respectively. High-resolution mass spectra were obtained using an AEI MS-9 spectrometer. Phosphorus-31 NMR spectra were obtained on JEOL-PFT 100 and Varian HA-100 spectrometers equipped with standard-probe and radio-frequency unit accessories. ^1H and ^{31}P NMR chemical shifts were measured relative to internal $(CH_3)_4Si$ and external H_3PO_4, respectively. Chemical shifts downfield from the standards are given negative values. ^{31}P NMR chemical shifts are given to ±1 ppm. Single-crystal x-ray data were collected at ambient temperature using a Syntex $P\bar{1}$ automated diffractometer.

Tetraphosphorus trisulfide (K and K Laboratories) and aniline (Mallinckrodt Chemical Works) were purified routinely. Carbon disulfide, benzene, and chloroform were distilled from P_4O_{10} prior

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