Symmetry Groups of Nonrigid Tris-Chelate Complexes

S. S. Eaton[1] and G. R. Eaton*[1]

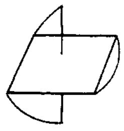
Contribution from the Department of Chemistry,
Massachusetts Institute of Technology, Cambridge, Massachusetts 02139.
Received August 3, 1972

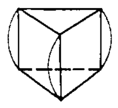
Abstract: Rearrangements of tris-chelate complexes are treated by the method of molecular symmetry groups for nonrigid molecules introduced by Longuet-Higgins. Full details are given for the case of three identical unsymmetrical ligands and for the case of two identical unsymmetrical ligands and a symmetrical ligand. The rearrangements derived include three not previously discussed.

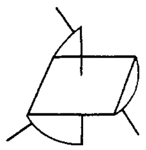
Determination of the mechanisms of intramolecular rearrangement reactions of tris-chelate complexes is a long-standing problem.[2] Although a large amount of kinetic data has been obtained, only in a few recent cases has it been possible to significantly restrict the number of mechanisms[3-10] or to deduce a unique rearrangement mechanism[11] consistent with the experimental results.

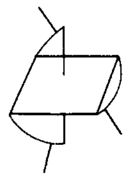
The rearrangement mechanisms which have been discussed for tris-chelate complexes include[12] (a) the Bailar,[13-15] or trigonal,[5] twist about the real threefold molecular axis, (b) the Ray-Dutt,[14-16] or rhombic, twist about the imaginary threefold molecular axis, and (c) bond rupture with a five-coordinate square-pyramidal (SP) or trigonal-bipyramidal (TBP) transition state, with, in each case, dangling axial or equatorial (basal) ligands.[3] Prior analyses of rearrangements of tris chelates in terms of the foregoing mechanisms have been based largely on the apparent physical reasonableness of the postulated intermediates. Thus there is no assurance that every feasible mechanism has been considered. As the measurements become more refined[7-11] it becomes more important to ensure that no feasible rearrangement mechanism has been overlooked. In this paper we report an analysis of all of the rearrangements of tris-chelate complexes, using the molecular symmetry groups for nonrigid molecules introduced by Longuet-Higgins.[17,18]

Symmetry Groups of Nonrigid Molecules. By definition a nonrigid molecule undergoes geometrical changes within the time scale of the measurement technique considered. For example, for a tris-chelate complex the geometry might change from **1** to **2** during the measurement time. Thus the question is raised whether the symmetry should be considered to be D_3 or D_{3h} for the purpose of analyzing the data. As another example, consider that a tris chelate containing three identical unsymmetrical ligands could exist as a mixture of the cis **3** and trans **4** isomers in rapid equilibrium. Should the system be analyzed in terms of C_3 or C_1 symmetry? The answer Longuet-Higgins[17] proposed to this type of seemingly paradoxical question is that the system should not be analyzed in terms of the rigid molecule point group. Rather, nonrigid molecules should be interpreted[17] using a molecular symmetry group which is the set of (a) all feasible permutations, P, of the positions and spins of identical nuclei, including the identity E, and (b) all feasible permutation-inversions, P^*, which simultaneously permute and invert the coordinates of all particles in the center of mass. P^* is the product $PE^* = E^*P$, where E^* is the inversion of all particle positions (E^* is not always among the feasible operations.)[17]


D_3
1


D_{3h}
2


C_3
3


C_1
4

An alternative formulation of the molecular symmetry groups of nonrigid molecules has been proposed,[19] but in its most complete form it affords results identical with those obtained by Longuet-Higgins' method.[19-22]

The method introduced by Longuet-Higgins has been applied to interpretation of vibrational and rotational aspects of the spectra of many nontransition metal

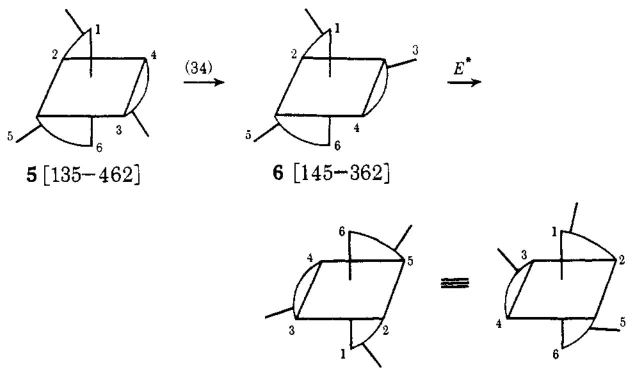
---

[1] Department of Chemistry, University of Denver, Denver, Colo.
[2] For recent reviews see (a) N. Serpone and D. G. Bickley, *Progr. Inorg. Chem.*, in press; (b) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed, Wiley, New York, N. Y., 1967, pp 300–334; (c) J. J. Fortman and R. E. Sievers, *Coord. Chem. Rev.*, 6, 331 (1971).
[3] J. G. Gordon, II, and R. H. Holm, *J. Amer. Chem. Soc.*, **92**, 5319 (1970).
[4] J. R. Hutchison, J. G. Gordon, II, and R. H. Holm, *Inorg. Chem.*, **10**, 1004 (1971).
[5] R. C. Fay and T. S. Piper, *ibid.*, **3**, 348 (1964).
[6] A. Y. Girgis and R. C. Fay, *J. Amer. Chem. Soc.*, **92**, 7061 (1970).
[7] L. H. Pignolet, R. A. Lewis, and R. H. Holm, *ibid.*, **93**, 360 (1971).
[8] L. H. Pignolet, R. A. Lewis, and R. H. Holm, *Inorg. Chem.*, **11**, 99 (1972).
[9] S. S. Eaton and R. H. Holm, *J. Amer. Chem. Soc.*, **93**, 4913 (1971).
[10] M. C. Palazzotto and L. H. Pignolet, *J. Chem. Soc., Chem. Commun.*, 6 (1972).
[11] S. S. Eaton, J. R. Hutchison, R. H. Holm, and E. L. Muetterties, *J. Amer. Chem. Soc.*, **94**, 6411 (1972).
[12] See ref 9 for a detailed discussion.
[13] J. C. Bailar, Jr., *J. Inorg. Nucl. Chem.*, **8**, 165 (1958).
[14] C. S. Springer, Jr., and R. E. Sievers, *Inorg. Chem.*, **6**, 852 (1967).
[15] J. E. Brady, *ibid.*, **8**, 1208 (1969).
[16] P. Ray and N. K. Dutt, *J. Indian Chem. Soc.*, **20**, 81 (1943).
[17] H. C. Longuet-Higgins, *Mol. Phys.*, **6**, 445 (1963).
[18] A summary of some of the results has been reported, ref 11.
[19] S. L. Altman, *Proc. Roy. Soc., Ser. A*, **298**, 184 (1967).
[20] C. M. Woodman, *Mol. Phys.*, **19**, 753 (1970).
[21] J. K. G. Watson, *ibid.*, **21**, 577 (1971).
[22] S. L. Altman, *ibid.*, **21**, 587 (1971).

compounds including ethane,[17] H_3CBF_2,[17,23] *p*-fluorotoluene,[24] cyclobutane,[25] cyclopentane,[26] and methylsilylacetylene.[27] Similar applications have been reported for ferrocene[28] and octahedral metal hexaammine ions.[29] There have been no reported applications of the Longuet-Higgins method to metal chelate complexes or to the nmr spectra of metal complexes.

Tris-Chelate Complexes. Case (1). Three Identical Unsymmetrical Ligands. In the case of tris-chelate complexes containing three identical unsymmetrical ligands, $M(A\text{–}B)_3$, the set of all permutations and permutation-inversions of the ligating nuclei is a group of order 384. This result is obtained by starting with one isomer, such as **5**, and writing down all isomers which can be obtained from **5** by permuting and inverting (through the center of mass) the ligating nuclei, with the restriction that the ligands cannot span trans positions.

The notation is illustrated in **5** for the cis isomer [135-462]. As the complex is viewed down the real-C_3 (or pseudo-C_3) axis with the triangular face including vertex 1 upward, the vertex labels are given clockwise for this face starting with 1, followed by the labels for the lower triangular face starting with the vertex to the right of 1. Square brackets denote isomers and parentheses denote permutations. One end of the ligand is flagged to denote its unsymmetrical nature (*e.g.*, the isopropenyl substituent in α-isopropenyltropolonate). The permutation (34) is illustrated by **5** → **6** and takes cis to trans. Isomer **6** is converted to **7** by E^*, the inversion of all ligands through the center of mass, and the operation which takes **5** to **7** is the permutation-inversion $(34)^*$.



5 [135–462]

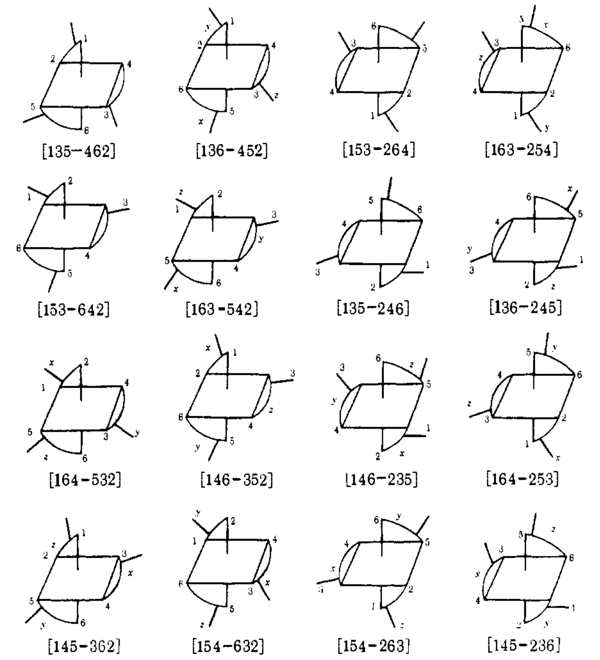
6 [145–362]

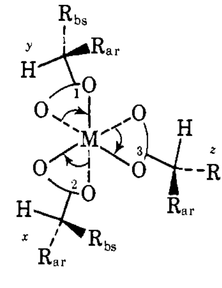
7 [154–263]

By inspection it is found that each isomer can be converted into 15 other isomers which cannot be superimposed on it by rigid-body rotations, but that for each of these 16 isomers there are 23 rearranged forms which can be superimposed on it by rigid body rotations. These rigid body motions are the same for each isomer and have group properties. Furthermore, there are 16 operations which interconvert the isomers within the set of 16 isomers. These 16 operations form an Abelian group. Thus the set of all permutations and permutation-inversions of the ligating nuclei is a group of order 384 which factors into a group of order 16 consisting of the rearrangements and a group of order 24 that can be regarded as consisting of the rigid-body rotations of the molecule. The 16 operations in the group of order 16, which is of primary interest here, constitute the complete group of rearrangements of stereochemically nonrigid tris-chelate complexes. It is important to note that the 16 rearrangements are expressed as permutations, *i.e.*, they merely describe the net change and not the path by which the atoms move from initial to final position.

The 16 isomers are drawn in Table I. The multiplication table for the 16 operations is given in Table II. The effect of each of the 16 operations on the isomer [135-462] is given in Table III. The notation used in these tables to indicate nonequivalent environments is illustrated in **8** for a ligand with a diastereotopic group at one end. The magnetic environments *x*, *y*, and *z* are, in principle, distinguishable for any unsymmetrical ligand whereas the environments r and s apply only to diastereotopic substituents such as the methyl resonances of α-isopropyltropolone or the benzyl CH_2 resonances of *N*-methyl-*N*-benzyldithiocarbamate.

Table I. Isomers of $M(A\text{–}B)_3$ Complexes





8

Since the nmr experiments detect only the net effect on all isomers, permutations which give the same net averaging pattern for the nonequivalent sites are placed

---

(23) P. R. Reed, Jr., and R. W. Lovejoy, *Spectrochim. Acta, Part A*, 26, 1087 (1970).

(24) T. Cvitas and J. M. Hollas, *Mol. Phys.*, 20, 645 (1971).

(25) J. M. R. Stone and I. M. Mills, *ibid.*, 18, 631 (1970).

(26) I. M. Mills, *ibid.*, 20, 127 (1971).

(27) P. R. Bunker, *ibid.*, 9, 257 (1965).

(28) P. R. Bunker, *ibid.*, 8, 81 (1964); *ibid.*, 9, 247 (1965).

(29) A. J. Stone, *J. Chem. Phys.*, 41, 1568 (1964).

together in averaging sets, A_i, although the permutations within each set A may have different effects on a particular isomer. The effect of the eight operations (averaging sets) on the pmr spectra are discussed below for ligands with nondiastereotopic and diastereotopic substituents.

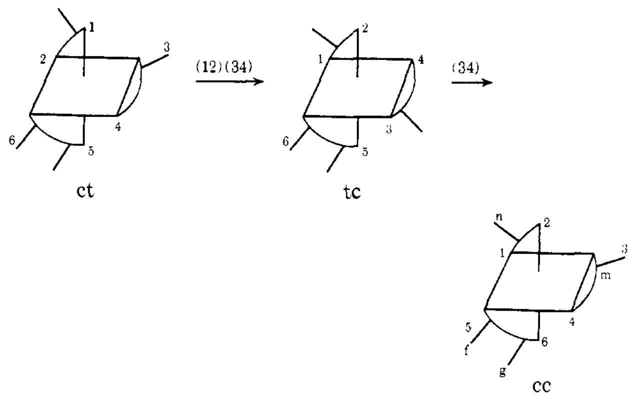
Nondiastereotopic. When the substituents are not diastereotopic, the site averaging does not indicate whether a rearrangement proceeds with inversion or retention of configuration at the metal center. Thus the operations, A_i, are pairwise indistinguishable: (A_1, A_5), (A_2, A_6), (A_3, A_7), (A_4, A_8). (A_1, A_5) has no effect on the pmr spectra. (A_2, A_6) averages two trans sites (yz) reducing the signal multiplicity from four at slow exchange to three at fast exchange. Distinctions between (A_3, A_7) and (A_4, A_8) are more subtle. Both pairs effect cis–trans isomerization and thus average all four signals to one at fast exchange. The two pairs differ in the four matrix elements related to exchange between y and z out of the total of 16 matrix elements in the pmr kinetic exchange matrix.[11]

Diastereotopic. Although the substituents are diastereotopic and thus distinguish between processes which effect inversion and those which do not, the difficulties in assigning observed resonances to absolute magnetic environments precludes distinctions between some operations. A_1, the identity operation, is obviously easily distinguished. A_2 effects two pair-wise exchanges ($yr \rightleftharpoons zr$, $ys \rightleftharpoons zs$), leaving four signals unbroadened and reducing signal multiplicity from eight to six. A_3 and A_4 both interconvert cis and trans without inversion at the metal center, reducing the signal multiplicity from eight to two. However, as in the case of nondiastereotopic nuclei the exchange matrices for A_3 and A_4 are very similar, differing in eight matrix elements out of 64. A_5 and A_6 result in four pair-wise exchanges which are indistinguishable in the absence of unambiguous assignments of the magnetic environments yr, ys, zr, and zs to observed resonances (A_5 averages yr with ys and zr with zs whereas A_6 averages yr with zs and ys with zr). A_7 and A_8 average all eight resonances to a single peak but the differences again are restricted to eight matrix elements which have a relatively small effect on the overall shape of the exchange-broadened spectra.

Comparison of Results for Diastereotopic and Nondiastereotopic Substituents. If the ligand contains both diastereotopic and nondiastereotopic groups, then the combined information allows distinction between the following operations on the basis of changes in signal multiplicity alone: A_1, A_2, (A_3, A_4), A_5, A_6, (A_7, A_8). For example, by observing the nondiastereotopic CH_3 and diastereotopic CH_2 resonances in tris(*N*-methyl-*N*-benzyldithiocarbamato)iron it was concluded that A_6 is the low-temperature process.[30] In principle such a comparison could also be done for the nondiastereotopic α'-H and diastereotopic isopropyl methyls of α-isopropyltropolone. Where it is not feasible to look at diastereotopic and nondiastereotopic nuclei in the same ligand, closely related complexes can be compared, provided the assumption is made that both rearrange by the same mechanism. As is discussed in detail elsewhere,[10,31] this procedure was used to determine that A_6 is the only mechanism which fits the nmr data for the low-temperature processes of both $M(\alpha\text{-}C_3H_5T)_3$ and $M(\alpha\text{-}C_3H_7T)_3$ for M = Co, Al, and Ga.[11,31-33]

Physical Mechanisms. The following correspondences can be made between the various physical mechanisms considered previously[4,6] and the permutations derived here: p-C_3 or r-C_3 twists, A_6; i-C_3 twists, A_8; TBP-axial, A_7; TBP-equatorial, A_3; SP-axial, $A_3 + A_6 + A_8$. Stiefel has also proposed a "distorted hexagonal planar" intermediate.[34] Rotation of the ligands through a planar transition state to positions roughly perpendicular to the original ones gives as a net result A_5. If the rotation is continued through a trigonal twist motion, the net result is A_2. Various physical representations of A_i can be obtained by comparison of a starting isomer with each of the 24 rotated forms of the product isomer to suggest the ring motion necessary to effect the observed site averaging. The magnetic molecular models recently described[35] are useful for this purpose.

Tris-Chelate Complexes. Case (2). One Symmetrical and Two Identical Ligands, M(A–B)$_2$(C–C). If the substituents on the symmetrical ligand can be studied by nmr (^{19}F, ^{1}H,...), the two ends may be distinguishable if they are in magnetically nonequivalent environments. Thus the permutation-inversion group is the set of permutations and permutation-inversions of six distinguishable nuclei connected in pairs of two, just as for M(A–B)$_3$. The 16 isomers for M(A–B)$_2$(C–C) are the same as those in Table I if the ligand **5–6** is regarded as the symmetrical ligand, C–C. There are, then, three geometrical isomers and a total of four magnetic environments for a nondiastereotopic substituent on either the symmetrical ligand or unsymmetrical ligand. The notation for the isomers[7] and magnetic environments is illustrated below. Isomers ct and tc have twofold symmetry so in each there is a single environment for the two ends of the symmetrical ligand and for the two unsymmetrical ligands. However in isomer cc the two ends of the symmetrical ligand are nonequivalent (f, g) as are the two unsymmetrical ligands (m, n). In addition for diastereotopic substituents the arbitrary environments r,s are defined as for M(A–B)$_3$. When the effects of the 16 operations of Table II on all the



---

[30] D. J. Duffy and L. H. Pignolet, *Inorg. Chem.*, 11, 2843 (1972).

[31] S. S. Eaton, Ph.D. Thesis, Massachusetts Institute of Technology, 1972.

[32] S. S. Eaton, G. R. Eaton, R. H. Holm, and E. L. Muetterties, to be submitted for publication.

[33] The following abbreviations are used for ligand anions: α-C_3H_5T, α-isopropenyltropolonate; α-C_3H_7T, α-isopropyltropolonate; RR′-dtc, N,N-disubstituted dithiocarbamate; tfd, 1,2-bis(perfluoromethyldithiolene); mnt, maleonitriledithiolene.

[34] E. I. Stiefel and G. F. Brown, *Inorg. Chem.*, 11, 434 (1972).

[35] S. S. Eaton and G. R. Eaton, to be submitted for publication.

Table II. Multiplication Table

	E	(12)(34)(56)	(12)	(34)	(56)	(12)(34)	(34)(56)	(12)(56)
E	*E*	(12)(34)(56)	(12)	(34)	(56)	(12)(34)	(34)(56)	(12)(56)
(12)(34)(56)	(12)(34)(56)	*E*	(34)(56)	(12)(56)	(12)(34)	(56)	(12)	(34)
(12)	(12)	(34)(56)	*E*	(12)(34)	(12)(56)	(34)	(12)(34)(56)	(56)
(34)	(34)	(12)(56)	(12)(34)	*E*	(34)(56)	(12)	(56)	(12)(34)(56)
(56)	(56)	(12)(34)	(12)(56)	(34)(56)	*E*	(12)(34)(56)	(34)	(12)
(12)(34)	(12)(34)	(56)	(34)	(12)	(12)(34)(56)	*E*	(12)(56)	(34)(56)
(34)(56)	(34)(56)	(12)	(12)(34)(56)	(56)	(34)	(12)(56)	*E*	(12)(34)
(12)(56)	(12)(56)	(34)	(56)	(12)(34)(56)	(12)	(34)(56)	(12)(34)	*E*
*E**	*E**	(12)(34)(56)*	(12)*	(34)*	(56)*	(12)(34)*	(34)(56)*	(12)(56)*
(12)(34)(56)*	(12)(34)(56)*	*E**	(34)(56)*	(12)(56)*	(12)(34)*	(56)*	(12)*	(34)*
(12)*	(12)*	(34)(56)*	*E**	(12)(34)*	(12)(56)*	(34)*	(12)(34)(56)*	(56)*
(34)*	(34)*	(12)(56)*	(12)(34)*	*E**	(34)(56)*	(12)*	(56)*	(12)(34)(56)*
(56)*	(56)*	(12)(34)*	(12)(56)*	(34)(56)*	*E**	(12)(34)(56)*	(34)*	(12)*
(12)(34)*	(12)(34)*	(56)*	(34)*	(12)*	(12)(34)(56)*	*E**	(12)(56)*	(34)(56)*
(34)(56)*	(34)(56)*	(12)*	(12)(34)(56)*	(56)*	(34)*	(12)(56)*	*E**	(12)(34)*
(12)(56)*	(12)(56)*	(34)*	(56)*	(12)(34)(56)*	(12)*	(34)(56)*	(12)(34)*	*E**

Table III. Permutational Analysis of $M(A{-}B)_3$ Nmr Spectra

Operation	Resulting isomer[a]	Averaging set	Net configurational change	Net site interchanges (trans)
E	[135-462]	A_1	None	None
(12)(34)(56)	[153-642]	A_2	None	(yz)
(12)	[164-532]	A_3	Cis → trans	(xy),(xz)
(34)	[145-362]		Trans → $^1/_3$ cis	
(56)	[136-452]		+ $^2/_3$ trans	
(12)(34)	[163-542]	A_4	Cis → trans	(xzy),(xyz)
(34)(56)	[146-352]		Trans → $^1/_3$ cis	
(12)(56)	[154-632]		+ $^2/_3$ trans	
*E**	[153-264]	A_5	$\Delta \rightleftharpoons \Lambda$	(rs)
(12)(34)(56)*	[135-246]	A_6	$\Delta \rightleftharpoons \Lambda$	(yz),(rs)
(12)*	[146-235]	A_7	$\Delta \rightleftharpoons \Lambda$	(xy),(xz),(rs)
(34)*	[154-263]		Cis → trans	
(56)*	[163-254]		Trans → $^1/_3$ cis	
			+ $^2/_3$ cis	
(12)(34)*	[136-245]	A_8	$\Delta \rightleftharpoons \Lambda$	(xyz),(xzy), (rs)
(34)(56)*	[164-253]		Cis → trans	
(12)(56)*	[145-236]		Trans → $^1/_3$ cis	
			+ $^2/_3$ trans	

[a] Isomers resulting from performing the indicated operations on [135-462] are given as examples. Columns 3, 4, and 5 summarize net effects of operations on all 16 isomers.

Table IV. Permutational Analysis of $M(A{-}B)_2(C{-}C)$ Nmr Spectra

Operation	Averaging set	Net configurational change	Net site interchanges (cc isomer)	$M(A{-}B)_3$ analog
E	A_1'	None	None	A_1
(12)(34)(56)	A_2'	ct $\rightleftharpoons$ tc	(mn)	A_2
(56)	A_3'	None	(fg)	A_3
(12)	A_4'	tc $\rightleftharpoons$ cc $\rightleftharpoons$ ct		A_3
(34)				A_3
(34)(56)				A_4
(12)(56)				A_4
(12)(34)	A_5'	ct $\rightleftharpoons$ tc	(fg), (mn)	A_4
*E**	A_6'	$\Delta \rightleftharpoons \Lambda$	(rs)	A_5
(12)(34)(56)*	A_7'	ct $\rightleftharpoons$ tc, $\Delta \rightleftharpoons \Lambda$	(mn), (rs)	A_6
(56)*	A_8'	$\Delta \rightleftharpoons \Lambda$	(fg), (rs)	A_7
(12)*	A_9'	tc $\rightleftharpoons$ cc $\rightleftharpoons$ ct $\Delta \rightleftharpoons \Lambda$	(rs)	A_7
(34)*				A_7
(34)(56)*				A_8
(12)(56)*				A_8
(12)(34)*	A_{10}'	ct $\rightleftharpoons$ tc, $\Delta \rightleftharpoons \Lambda$	(fg), (mn), (rs)	A_8

Table V. Changes in Signal Multiplicity for Diastereotopic and Nondiastereotopic Ligands

	A–B		C–C	
	Nondiastereotopic	Diastereotopic	Nondiastereotopic	Diastereotopic
A_1'	4 → 4	8 → 8	4 → 4	8 → 8
A_2'	4 → 2	8 → 4	4 → 3	8 → 6
A_3'	4 → 4	8 → 8	4 → 3	8 → 6
A_4'	4 → 1	8 → 2	4 → 1	8 → 2
A_5'	4 → 2	8 → 4	4 → 2	8 → 4
A_6'	4 → 4	8 → 4	4 → 4	8 → 4
A_7'	4 → 2	8 → 4	4 → 3	8 → 4
A_8'	4 → 4	8 → 4	4 → 3	8 → 4
A_9'	4 → 1	8 → 2	4 → 1	8 → 2
A_{10}'	4 → 2	8 → 4	4 → 2	8 → 4

Table VI. Distinctions Made between Averaging Sets A_i' due to Changes in Signal Multiplicity

Nondiastereotopic A–B[a] nondiastereotopic C–C	Nondiastereotopic A–B diastereotopic C–C	Diastereotopic A–B nondiastereotopic C–C	Diastereotopic A–B diastereotopic C–C
(A_1', A_6')	A_1'	A_1'	A_1'
(A_2', A_7')	A_2'[b]	(A_2', A_7', A_8')	A_2'
(A_3', A_8'	A_3'	A_3'	A_3'
(A_4', A_9')	(A_4', A_9')	(A_4', A_9')	(A_4', A_9')
(A_5', A_{10}')	(A_5', A_7', A_{10}')	(A_5', A_{10}')	(A_5', A_6', A_7', A_8', A_{10}')
	(A_6', A_8')	A_6'	

[a] The degeneracies in this case are due to the inability to distinguish processes which occur with inversion from those which occur without inversion. [b] A_2' can be distinguished from (A_6', A_8') if the signals due to C–C and A–B, respectively, can be unambiguously identified; the overall multiplicity change is 12 → 8 for all three averaging sets.

isomers are considered, it is found that the operations fall into ten nmr averaging sets, A_i' for $M(A{-}B)_2(C{-}C)$ (*cf.* Table IV). The changes in signal multiplicity which can be deduced from Table IV for diastereotopic and nondiastereotopic ligands A–B and C–C are shown in Table V. Therefore the distinctions which can be made between averaging sets A_i' on the basis of changes in signal multiplicity for the four possible combinations of diastereotopic and nondiastereotopic ligands are shown in Table VI. Thus the maximum information is obtained by comparing the nmr averaging pattern for a complex with nondiastereotopic substituents on both A–B and C–C with a closely related complex containing diastereotopic groups on C–C. With these combined results the following averaging sets are distinguishable: A_1', A_2', A_3', (A_4', A_9'), (A_5', A_{10}'), A_6', A_7', A_8'.

The permutational analysis is simplified at the cost of

*E**	(12)(34)(56)*	(12)*	(34)*	(56)*	(12)(34)*	(34)(56)*	(12)(56)*
*E**	(12)(34)(56)*	(12)*	(34)*	(56)*	(12)(34)*	(34)(56)*	(12)(56)*
(12)(34)(56)*	*E**	(34)(56)*	(12)(56)*	(12)(34)*	(56)*	(12)*	(34)*
(12)*	(34)(56)*	*E**	(12)(34)*	(12)(56)*	(34)*	(12)(34)(56)*	(56)*
(34)*	(12)(56)*	(12)(34)*	*E**	(34)(56)*	(12)*	(56)*	(12)(34)(56)*
(56)*	(12)(34)*	(12)(56)*	(34)(56)*	*E**	(12)(34)(56)*	(34)*	(12)*
(12)(34)*	(56)*	(34)*	(12)*	(12)(34)(56)*	*E**	(12)(56)*	(34)(56)*
(34)(56)*	(12)*	(12)(34)(56)*	(56)*	(34)*	(12)(56)*	*E**	(12)(34)*
(12)(56)*	(34)*	(56)*	(12)(34)(56)*	(12)*	(34)(56)*	(12)(34)*	*E**
E	(12)(34)(56)	(12)	(34)	(56)	(12)(34)	(34)(56)	(12)(56)
(12)(34)(56)	*E*	(34)(56)	(12)(56)	(12)(34)	(56)	(12)	(34)
(12)	(34)(56)	*E*	(12)(34)	(12)(56)	(34)	(12)(34)(56)	(56)
(34)	(12)(56)	(12)(34)	*E*	(34)(56)	(12)	(56)	(12)(34)(56)
(56)	(12)(34)	(12)(56)	(34)(56)	*E*	(12)(34)(56)	(34)	(12)
(12)(34)	(56)	(34)	(12)	(12)(34)(56)	*E*	(12)(56)	(34)(56)
(34)(56)	(12)	(12)(34)(56)	(56)	(34)	(12)(56)	*E*	(12)(34)
(12)(56)	(34)	(56)	(12)(34)(56)	(12)	(34)(56)	(12)(34)	*E*

mechanistic information in the case where the symmetrical ligand does not function as a probe of environment in the experiments performed. When the two ends of C–C become indistinguishable (**5–6** becomes **5–5**), only eight distinct isomers are found and eight operations, which comprise an Abelian group, interconvert the isomers. This is a subset of the group in Table II, found by eliminating all operations which involve permutation (56). This adds the ambiguity that, for example, (12) and (12)(56) become indistinguishable. The nmr averaging sets are given in Table VII.

Table VII. Permutational Analysis of $M(A{-}B)_2(C{-}C)$ Nmr Spectra Where the Ends of C–C are Indistinguishable

Operation	Averaging set	Net configurational change	Net site interchanges (cc isomer)	$M(A{-}B)_3$ analog
E	A_1''	None	None	A_1
(12)(34)	A_2''	ct $\rightleftharpoons$ tc	(mn)	A_2, A_4
(12) (34)	A_3''	ct $\rightleftharpoons$ cc $\rightleftharpoons$ tc		A_3, A_4
*E**	A_4''	$\Delta \rightleftharpoons \Lambda$	(rs)	A_5
(12)(34)*	A_5''	ct $\rightleftharpoons$ tc, $\Delta \rightleftharpoons \Lambda$	(mn), (rs)	A_6, A_8
(12)* (34)*	A_6''	ct $\rightleftharpoons$ cc $\rightleftharpoons$ tc, $\Delta \rightleftharpoons \Lambda$	(rs)	A_7, A_8

For nondiastereotopic substituents on A–B, multiplicity changes distinguish (A_1'', A_4''), (A_2'', A_5''), (A_3'', A_6''). A comparison of diastereotopic and nondiastereotopic substituents could distinguish A_1'', (A_2'', A_5''), (A_3'', A_6''), A_4''. Thus the lack of information from C–C severely restricts the conclusions that can be drawn from the experiment.

Utility. Recent studies of the temperature-dependent nmr spectra of $Fe(RR'\text{-dtc})_2tfd$[7,33] and $Fe(RR'\text{-dtc})_2mnt$[8] illustrate the utility of the above approach. The published results[7] for the nondiastereotopic substituents are consistent with A_2' or A_7' (A_2 or A_6 in the notation for $M(A{-}B)_3$), and not just inversion, as was concluded[7,8] based on what was known at that time. Subsequent to ref 7 and 8 Musher has also recognized the need to consider a rearrangement of type A_2'.[36] As shown above, this ambiguity could be resolved by a study of a complex with a diastereotopic symmetrical ligand. This analysis also explicitly delineates the reasons that the study of $Fe(RR'\text{-dtc})_2mnt$ provided less information than was obtained for $Fe(RR'\text{-dtc})_2tfd$.[7,8]

In addition to the tropolonate complexes mentioned above, an application to $M(A{-}B)_3$ complexes is demonstrated by the trisdithiocarbamates, $M(RR'\text{-dtc})_3$. Originally it was thought that the variable-temperature nmr spectra of *trans*-$Fe(MePh\text{-dtc})_3$ supported a twist mechanism for the low-temperature rearrangement process.[10] Based on the results presented herein, it is recognized that the low-temperature process is consistent with either A_2 or A_6 and that by studying $Fe(MePhCH_2\text{-dtc})_3$, as described above, it can be concluded that A_6 is the low-temperature process.[30]

Acknowledgments. This work was performed in the laboratory of Professor R. H. Holm, whom we thank for support under GP-18978X from the National Science Foundation.

(36) J. I. Musher, *J. Amer. Chem. Soc.*, **94**, 5662 (1972); *Inorg. Chem.*, **11**, 2355 (1972). Musher has approached the problem of a complete set of rearrangements of a tris chelate complex in an alternate fashion. However, the notation for his set of rearrangements fails to distinguish between plausible rearrangements and ones which require a ligand to span trans octahedral positions. Further, although group properties are necessary to prove completeness, his set, as written, is not a group.