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Configurational Rearrangements in *cis*-$M(AA)_2X_2$, *cis*-$M(AA)_2XY$, and *cis*-$M(AB)_2X_2$ Complexes. 2. A Topological and Mechanistic Analysis[1]

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A topological and mechanistic analysis is presented for intramolecular configurational rearrangement processes occurring in the cis diastereomers of $M(AA)_2X_2$, $M(AA)_2XY$, and $M(AB)_2X_2$ complexes. Rearrangements have been considered to occur via two limiting types of mechanisms distinguishable by the effective coordination number of the transition states: namely, the bond rupture pathway proceeding through trigonal bipyramidal (TBP) and square pyramidal (SP) transition states, and twist motions about the four C_3 axes of the octahedral complex. A correlation is also presented which relates the various physical operations to averaging sets from a permutational analysis. It is shown that not all possible averaging sets may be related to conventional mechanistic ideas concerning stereochemically nonrigid chelate complexes. Alternative mechanisms need be thought of should one of these averaging sets be identified from the NMR site interchange pattern(s). One such mechanism is presented for the inversion of configuration in the above complexes but does not involve exchange of terminal AA or AB groups on the chelating ligands.

Introduction

The elucidation of mechanisms of intramolecular rearrangements in nonrigid six-coordinate complexes, within the area of inorganic chelate chemistry, has lately been a matter of some considerable interest.[2-5] Despite such interest, however, the number of systems for which unique rearrangement mechanisms have been unequivocally demonstrated has not as yet been commensurately rewarding. A recent study[1,6] from this laboratory reported on a permutational analysis of the configurational rearrangement processes in *cis*-$M(AA)_2X_2$, *cis*-$M(AA)_2XY$, and *cis*-$M(AB)_2X_2$ systems. Such rearrangements are generally considered to proceed via two limiting types of pathways which are distinguishable by the effective coordination number of the transition state. These pathways have also been differentiated as occurring with or without metal–ligand bond rupture.

One such mechanism, originally proposed by Werner[7] to account for the enantiomerization of the optically active tris(oxalato)cobaltate(III) anion, is the bond rupture mechanism.[2] The geometry of the intermediate is based on polyhedra actually found for five-coordinate complexes;[8,9] it may have either an idealized square-pyramidal (SP) or trigonal-bipyramidal (TBP) geometry with the dangling ligand in an axial (ax) or equatorial (eq) position. Energy differences between the SP and TBP geometries are generally taken to be small,[8] excellent examples being afforded from crystal structure analysis by the pentacyanonickelate ion, $Ni(CN)_5^{3-}$, which crystallizes with the $Cr(en)_3^{3+}$ cation as two different geometries in the same structure,[10] and more recently by the chlorobis(1,2-bis(diphenylphosphino)ethane)cobalt(III) trichlorostannate(II) complex,[11] which exists as a mixture of SP and TBP forms. A SP geometry has also been postulated as the intermediate in the Berry pseudorotation mechanism, a favored process for stereochemically nonrigid five-coordinate TBP compounds.[12-14]

The alternative to the formation of a lower coordination polyhedron during rearrangement is the formation of a polytopal isomer of the six-atom family[15] where the ligating nuclei approximate the vertex positions of a trigonal prism (TP). Such a nonbond rupture path was first described by Ray and Dutt[16] and by Bailar;[17] an "alternative" pathway has more recently been proposed by Springer and Sievers.[18] Differences between the three twist mechanisms[19] appear to arise from differences in chelate ring bond angles during ring motion. However, it has been shown that the Ray and Dutt (rhombic) twist is identical with a Bailar (trigonal) twist about an imaginary C_3 axis,[2,18,20] while the Springer and Sievers twist is identical with a Bailar twist about a real C_3 axis.[2,15]

The two distinct types of mechanisms are physically reasonable because the geometries of the postulated intermediates have been found to occur in other stable transition metal chelates. Five-coordinate complexes in both SP and TBP polytopal forms are plentiful[9] and the number of trigonal prismatic (TP) chelates is constantly increasing[21] or at least distortions toward a TP geometry realized.[22-24] Any physical motion which produces the experimentally observed rearrangement is of course plausible. An example of a topologically equivalent process for the twist mechanism in tris chelates was recently described by Stiefel and Brown.[22] The process is viewed as a simultaneous rotation of the three chelate rings 180° about their C_2 axes via an approximate hexagonal planar transition state and was suggested for highly compressed tris chelates. Unfortunately, the energetics of this digonal twist process would appear to be formidable.

A simple procedure for enumerating allowed rearrangements for a particular complex via a single process is through the use of graph theory (topology).[15,25] The various isomers for a particular coordination polyhedron are represented as corners of a three-dimensional geometric figure, while specific operations that interconvert any two isomers are defined by the line joining the two corners representing these isomers, with the intermediate being located midway along this line. If the process is repeated for all the possible stereoisomers, a complete description of the stereochemical consequences of a particular mechanism is produced. Subsequently, by simple reference to the topological figure it is possible to determine whether or not a certain pathway gives the desired stereochemical interconversions.

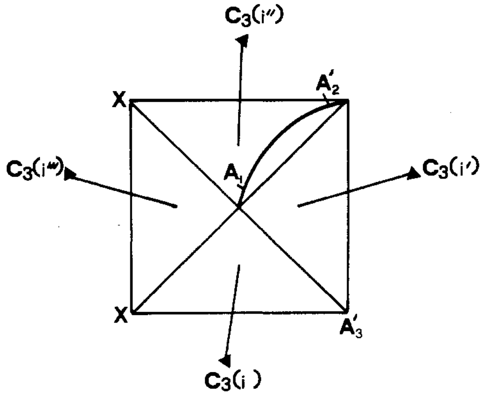
The isomers represented by the vertices of the topological figure may be either real, physically distinguishable diastereomers and/or enantiomers or permutational isomers. The former case is obtained for the *cis*-$M(AB)_2X_2$ system, while the latter situation prevails for *cis*-$M(AA)_2X_2$ complexes.

The purpose of this work is to present the consequences of the various physical mechanisms (bond rupture and twist motions) on the *cis*-$M(AA)_2X_2$, *cis*-$M(AA)_2XY$, and *cis*-$M(AB)_2X_2$ systems. Correlations between the physical processes and the averaging sets of the permutational analysis[1] are also considered in the hope that these may aid in following the steric course of and the delineation of some of the plausible pathways of configurational rearrangements in the type of complexes considered herein.

The *cis*-$M(AA)_2X_2$ System

This system is analyzed in terms of the same four Δ–Λ pairs that were used in the permutational analysis,[1] namely, *cis*-$\Delta(\Lambda)_{23}$, *cis*-$\Delta(\Lambda)_{13}$, *cis*-$\Delta(\Lambda)_{24}$, and *cis*-$\Delta(\Lambda)_{14}$, the subscripts referring to those terminal A groups on $M(AA)_2X_2$ trans to the X groups. These isomers correspond to the 16 permutamers after the removal of those permutational isomers generated by the distinguishability of the two X groups. This analysis could therefore be described as a permutational mechanistic analysis. An analogous procedure has been developed by Springer for the $M(AA)_2(BB)$ system.[26,27]

Labeling of the four imaginary C_3 axes for a *cis*-$M(AA)_2X_2$ complex is indicated below; the twist mechanism about the four *i*-C_3 axes of the *cis*-Δ_{23} form is illustrated elsewhere.[2]



cis-Δ_{23}

Twists about the $C_3(i)$ and $C_3(i'')$ axes result in exchange of both terminal groups with inversion of the molecular configuration (corresponding to averaging set A_6); in addition, rotations about the latter axis provide a path for the conversion of the cis enantiomers to the trans diastereomers, as the bidentate ligands do not span the upper and lower octahedral faces. Twists about the $C_3(i')$ and $C_3(i''')$ axes provide for exchange of only one (but different) set of nonequivalent groups along with optical inversion; these correspond to the averaging set A_5.

The stereochemical consequences upon application of the twist mechanism on all of the four Δ–Λ pairs are summarized in the topological diagram illustrated in Figure 1. Three types of trigonal-prismatic-like transition states are formed; these are represented by squares, open circles, and triangles, with a permutational degeneracy of four, four, and eight, respectively.

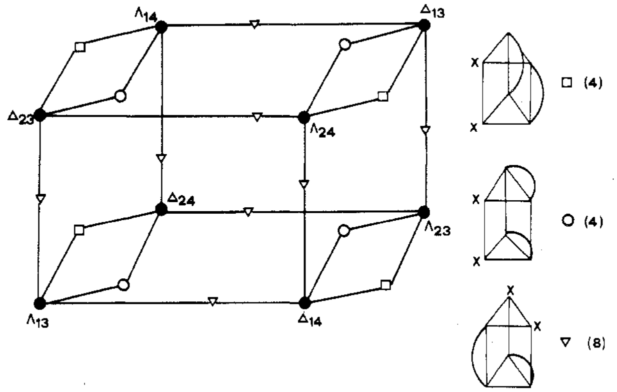


Figure 1. Topological correlation diagram for the stereochemical rearrangements of the four Δ–Λ pairs (solid circles) of a *cis*-$M(AA)_2X_2$ complex via a twist mechanism. The three different types of intermediates are represented as open circles, squares, and triangles, with the permutational degeneracy of each indicated in parentheses.

Transition states represented as squares and circles correspond to averaging set A_6 and predict a ratio of rates of terminal group exchange to enantiomerization of unity; that is, to a $\Delta(\Lambda)_{23} \rightleftharpoons \Lambda(\Delta)_{14}$ or $\Delta(\Lambda)_{13} \rightleftharpoons \Lambda(\Delta)_{24}$ process. Transition states represented by triangles correspond to averaging set A_5 which predicts a ratio of rates of terminal group exchange to enantiomerization of 1:2.[1] In order to obtain exchange of both sets of terminal A groups via triangle-type intermediates, twists must occur about the $C_3(i')$ and $C_3(i''')$ axes with equal probability to produce the reaction

$$\begin{tikzcd}
 & \Lambda(\Delta)_{13} \arrow[dl, shift left] & & & \Lambda(\Delta)_{13} \arrow[dl, shift left] \\
\Delta(\Lambda)_{23} \arrow[ur, shift left] \arrow[dr, shift left] & & \text{or} & \Delta(\Lambda)_{14} \arrow[ur, shift left] \arrow[dr, shift left] & \\
 & \Lambda(\Delta)_{24} \arrow[ul, shift left] & & & \Lambda(\Delta)_{24} \arrow[ul, shift left]
\end{tikzcd}$$

and since the Δ form is converted to the Λ form twice as fast as terminal group exchange, the ratio of rates is thus 1:2. It should also be noted that no single twist process will produce reactions of the type $\Delta(\Lambda)_{23} \rightleftharpoons \Delta(\Lambda)_{x4}$ and $\Delta(\Lambda)_{13} \rightleftharpoons \Delta(\Lambda)_{x4}$ (x = 1 or 2 and corresponding to averaging sets A_1, A_2, and A_3), not unexpected since twist motions lead to inversion; neither are reactions of the type $\Delta_{23} \rightleftharpoons \Lambda_{23}$ possible (averaging set A_4) with a single twist process; sequential, multistep twist motions are necessary.[28]

The topological diagram summarizing the interconversions among the four Δ–Λ pairs is illustrated in Figure 2 for a bond rupture mechanism proceeding via TBP transition states. Trigonal-bipyramidal-axial intermediates are designated α and β. There are eight permutational forms for each type of intermediate, and in the case of α intermediates they may be broken down into four enantiomeric *dl* pairs. TBP-equatorial intermediates, denoted γ, comprise eight enantiomeric permutational pairs.

An important feature revealed by Figure 2 is that there is no single process which will result in simultaneous exchange of both sets of nonequivalent terminal A groups in addition to enantiomerization, that is, in a $\Delta(\Lambda)_{23} \rightleftharpoons \Lambda(\Delta)_{14}$ process (averaging set A_6). Therefore, this mechanism will not produce a ratio of rates of exchange to enantiomerization of unity. Intermediates α always correspond to averaging set A_5 and β correspond to A_4, while γ-type intermediates correspond to averaging set A_2 since a TBP-equatorial transition state *never* results in inversion of the molecular configuration. Moreover, no single path along the three-dimensional structure of Figure 2 will lead to interconversion reactions belonging to averaging set A_3, e.g., $\Delta_{23} \rightleftharpoons \Delta_{14}$.

The stereochemical consequences of a bond rupture mechanism proceeding via SP-axial intermediates are noted in the topological structure of Figure 3, which also illustrates the four SP-axial intermediates a, b, c, and d; the enantiomeric

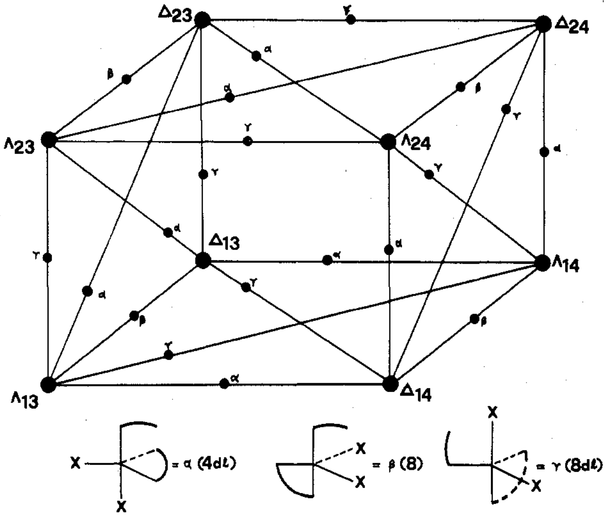


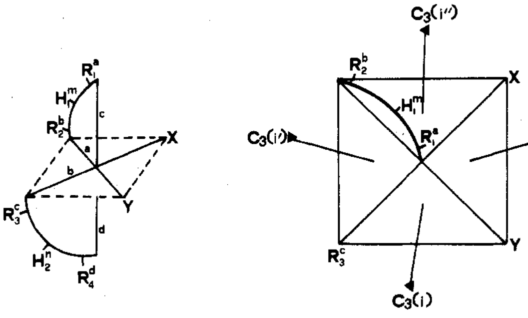
Figure 2. Topological correlation diagram for the interconversions of the four Δ-Λ pairs (solid circles) of a *cis*-M(AA)$_2$X$_2$ complex through trigonal-bipyramidal-axial and -equatorial intermediates. The two types of TBP-axial intermediates are designated α and β, while TBP-equatorial intermediates are labeled γ. Indicated beside each type of intermediate is its permutational degeneracy.

forms of the intermediates are designated $\bar{a}$, $\bar{b}$, $\bar{c}$, and $\bar{d}$. Two microscopically reversible pathways exist for the formation of these SP-axial transition states after the initial bond rupture; these are denoted as primary (p) and secondary (s) processes.[29,30]

Only the primary process was considered which, on an a priori basis, is much more probable than the secondary process owing to the lesser degree of ligand motion involved in the former, both in the formation of the transition states and in their decay to products. In the construction of Figure 3, transition states and products were obtained exclusively from primary processes. All the feasible direct interconversions are possible except those corresponding to averaging sets A$_3$ and A$_4$, for example, $\Delta(\Lambda)_{23} \rightleftharpoons \Delta(\Lambda)_{14}$ and $\Delta(\Lambda)_{23} \rightleftharpoons \Lambda(\Delta)_{23}$, respectively.

The *cis*-M(AA)$_2$XY System

The permutational isomers are named according to the nomenclature described earlier in the permutational analysis.[1] The various nonequivalent sites and rupturable metal–ligand bonds are depicted below for the [163–542] = *cis*-Λ(abcd;m) permutamer.



cis-Λ(abcd;m)= [163–542]

The consequences of twist motions about the four imaginary C_3 axes[6] are summarized in Table Ia which also correlates averaging sets to the various twist operations. There are a total of four trigonal-prismatic-like transition states, of which one is an enantiomeric *dl* pair and two are achiral. As noted in Table Ia, all twist motions result in inversion of the molecular configuration and generate the A$_{12}'$, A$_{13}'$, and A$_{14}'$ averaging sets.

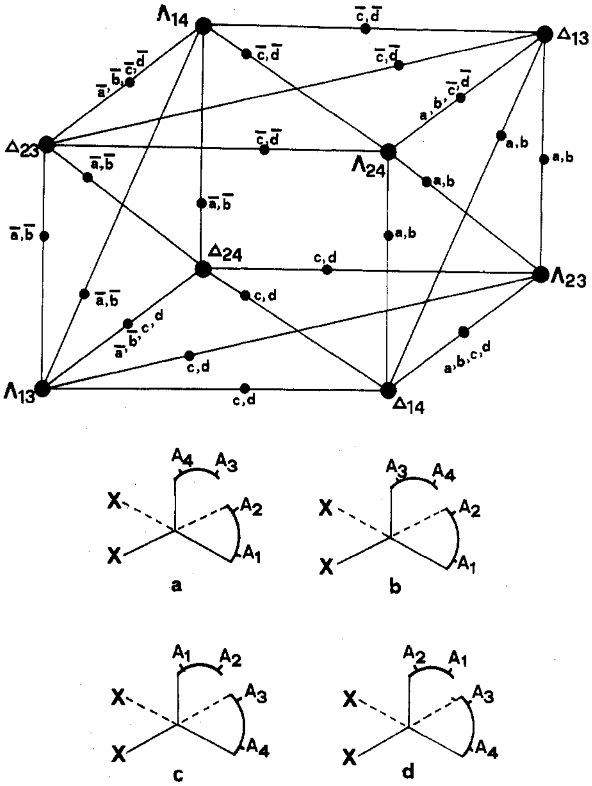


Figure 3. Topological correlation diagram (top) for the interconversion of the four Δ-Λ pairs (solid circles) of a *cis*-M(AA)$_2$X$_2$ complex proceeding via square-pyramidal-axial transition states which are formed and decay to products by the primary process alone. Also illustrated are the four enantiomeric pairs (bottom) of SP-axial intermediates, denoted a, b, c, and d (their enantiomers are denoted $\bar{a}$, $\bar{b}$, $\bar{c}$, and $\bar{d}$).

Metal–ligand bond rupture may result in the formation of TBP or SP intermediates.[6] There are four TBP-axial intermediates that include one enantiomeric *dl* pair. Allowed TBP-equatorial intermediates consist of two enantiomeric pairs, while a single enantiomeric SP-axial *dl* pair is obtained. An illustration of the bond rupture mechanism via TBP-axial, TBP-equatorial, and SP-axial intermediates is provided elsewhere.[6] Stereochemical consequences of bond rupture pathways involving these three types of intermediates are listed in Tables Ib and Ic.

Considering TBP-axial intermediates and consulting Table I reveal that this process always leads to optical inversion and can generate averaging sets A$_9'$, A$_{10}'$, or A$_{11}'$. On the other hand, TBP-equatorial intermediates are inconsequential with regard to enantiomerization while generating either averaging set A$_2'$ or A$_3'$. Thus, if enantiomerization can be demonstrated as occurring during a rearrangement, this mechanism can be unequivocally ruled out as the sole primary physical pathway. Also, SP-axial intermediates formed by and decaying via primary processes result in an equal balance of inversion and retention of configuration; they generate averaging sets A$_1'$, A$_2'$, A$_3'$, A$_{13}'$, and A$_{14}'$.

A final feature of Table I is worth noting. There are five averaging sets which correspond to none of the physical processes considered in Table I; these are A$_4'$, A$_5'$, A$_6'$, A$_7'$, and A$_8'$. Should one of these sets be indicated from the NMR experiment as the one consistent with the NMR site interchange pattern, some thought should then be given to the determination of new, alternative mechanistic pathways (see Conclusions).

In a recent study of the stereochemistry and environmental averaging processes on the related systems RClSn(acac)$_2$ (acac = CH$_3$COCHCOCH$_3^-$ and R = C$_6$H$_5$ or CH$_3$), Serpone and

Table I. Intermediates and the Fate of the *cis*-Λ(Δ)(abcd;m) Permutamer of a *cis*-$M(AA)_2XY$ Complex on Application of Various Physical Rearrangement Mechanisms and Assignment of Averaging Sets to Physical Processes[a]

(a) Twist Mechanism

Rotation axis[b]	TP intermediate	Product permutamer	Averaging set[c]
i	1 (1)	c-Δ(Λ)(cdab;n)	A_{14}'
i'	2d (2l)	c-Δ(Λ)(cdba;n)	A_{13}'
i''	3 (3)	c-Δ(Λ)(badc;m)	A_{12}'
i'''	2l (2d)	c-Δ(Λ)(dcab;n)	A_{13}'

(b) Bond Rupture, TBP Intermediates

Bond broken[b]	TBP-axial intermediate	Product permutamer	Averaging set[c]
a	1d (1l)	c-Δ(Λ)(dcba;n)	A_{11}'
b	1l (1d)	c-Δ(Λ)(dcba;n)	A_{11}'
c	3 (3)	c-Δ(Λ)(abdc;m)	A_{10}'
d	2 (2)	c-Δ(Λ)(bacd;m)	A_9'
	TBP-equatorial intermediate		
a	5d (5l)	c-Λ(Δ)(bacd;m)	A_2'
b	4d (4l)	c-Λ(Δ)(abdc;m)	A_3'
c	5d (5l)	c-Λ(Δ)(bacd;m)	A_2'
d	4d (4l)	c-Λ(Δ)(abdc;m)	A_3'

(c) Bond Rupture, SP-Axial Intermediates (Primary Process)

Bond broken[b]	SP-axial intermediate	Product permutamer	Averaging set[c]
a	6d (6l)	c-Λ(Δ)(abcd;m)	A_1'
		c-Δ(Λ)(dcab;n)	A_{13}'
		c-Λ(Δ)(bacd;m)	A_2'
		c-Δ(Λ)(cdab;n)	A_{14}'
b	6l (6d)	c-Λ(Δ)(abcd;m)	A_1'
		c-Δ(Λ)(cdba;n)	A_{13}'
		c-Λ(Δ)(abdc;m)	A_3'
		c-Δ(Λ)(cdab;n)	A_{14}'
c	6d (6l)	c-Λ(Δ)(bacd;m)	A_2'
		c-Δ(Λ)(cdab;n)	A_{14}'
		c-Λ(Δ)(abcd;m)	A_1'
		c-Δ(Λ)(dcab;n)	A_{13}'
d	6l (6d)	c-Λ(Δ)(abdc;m)	A_3'
		c-Δ(Λ)(cdab;n)	A_{14}'
		c-Λ(Δ)(abcd;m)	A_1'
		c-Δ(Λ)(cdba;n)	A_{13}'

[a] For specification of intermediates and illustration of the mechanism, see ref 6. [b] For definition of bonds broken and rotation axes, see text. [c] Averaging sets are defined in ref 1.

Hersh[31] have reported NMR evidence which imposed[6] certain constraints on the mechanism(s) of the rearrangement process. From these it was deduced that if rearrangements occur via a sole reaction pathway, it is done through averaging sets A_{13}' (and/or possibly A_{14}'). On the basis of the evidence presented and the constraints, Bickley and Serpone[6] concluded that configurational rearrangements in these systems most probably occur via twist motions about the $C_3(i')$ and/or $C_3(i''')$ axes (nearly equivalent stereochemically). Unfortunately, linear combinations of averaging sets that can accomplish —CH= and CH_3 exchange and Δ ⇌ Λ conversion (for example, multistep twists about all four threefold axes) could not be unequivocally ruled out.

The *cis*-$M(AB)_2X_2$ System

This system was analyzed in terms of the three diastereomers having *cis*-X_2 groups illustrated below. In addition, two diastereomers having *trans*-X_2 groups exist.[28] Pathways which can potentially cause *cis*-X_2 → *trans*-X_2 isomerization are noted in Tables II and III; however, attention is herein focused on *cis*-X_2 → *cis*-X_2 rearrangements.

Throughout, subscripts attached to the label of the rearranged complex refer to scrambling patterns[1] for *cis,cis,cis*-Δ ⇌ *cis,cis,cis*-Δ(Λ) rearrangements. The nonequivalent sites were defined earlier and the nonequivalent metal–ligand bonds are indicated above.

Table II. Transition States and Diastereomer Distributions Obtained by a Twist Mechanism for a *cis*-$M(AB)_2X_2$ Complex and Assignment of Averaging Sets to Physical Processes

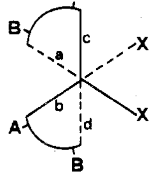
Initial isomer[a]	Rotation axis[b]	Transition state[b]	Product	Averaging set[c]
c,c,c-Λ(Δ)	i	5 (5)	c,c,c-$\Delta_2(\Lambda_2)$[c]	A_7''[f] (A_5''')[g]
	i'	4d (4l)	c,c,t-Δ(Λ)	A_9'' (A_6''')
	i''[d]	6 (6)	c,c,c-$\Delta_4(\Lambda_4)$	A_{10}'' (A_5''')
	i'''	2d (2l)	c,t,c-Δ(Λ)	A_9'' (A_6''')
c,c,t-Λ(Δ)	i	1l (1d)	c,t,c-Δ(Λ)	A_7'' (A_5''')
	i'	4l (4d)	c,c,c-Δ(Λ)	A_9'' (A_6''')
	i''[e]	3d (3l)	c,t,c-Δ(Λ)	A_{10}'' (A_5''')
	i'''	4l (4d)	c,c,c-Δ(Λ)	A_9'' (A_6''')
c,t,c-Λ(Δ)	i	1d (1l)	c,c,t-Δ(Λ)	A_7'' (A_5''')
	i'	2l (2d)	c,c,c-Δ(Λ)	A_9'' (A_6''')
	i''[e]	3l (3d)	c,c,t-Δ(Λ)	A_{10}'' (A_5''')
	i'''	2l (2d)	c,c,c-Δ(Λ)	A_9'' (A_6''')

[a] The symbols c and t refer to cis and trans, respectively. [b] For definition of rotation axes and specification of transition states, see ref 2. [c] Scrambling patterns for c,c,c-Δ ⇌ c,c,c-Δ(Λ) rearrangements and averaging sets A_i'' and A_i''' are defined in ref 1. [d] Rotation about this axis, only, provides a path for the formation of the t,t,t diastereomer. [e] Rotation about this axis, only, provides a path for the formation of the t,c,c diastereomer. [f] Case where X functions as a NMR probe (see ref 1). [g] Case where X does not function as a NMR probe (see ref 1).

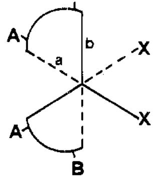
Table III. Intermediates and Fates of the Diastereomers of a *cis*-$M(AB)_2X_2$ Complex Undergoing Rearrangement via a Bond Rupture Mechanism through Trigonal-Bipyramidal-Axial and -Equatorial Intermediates and Assignment of Averaging Sets to Physical Processes

Initial isomer[a]	Rupture of bond[b]	Intermediate[c]	Product	Averaging set[d]
		(a) TBP Axial		
c,c,c-Λ(Δ)	a	4 (4)	c,c,c-$\Delta_3(\Lambda_3)$[d]	A_8'' (A_4''')
	b	8 (8)	c,c,c-$\Delta_3(\Lambda_3)$	A_8'' (A_4''')
	c	6l (6d)	c,t,c-Δ(Λ)	A_9'' (A_6''')
	d	3d (3l)	c,c,t-Δ(Λ)	A_9'' (A_6''')
c,t,c-Λ(Δ)	a	5 (5)	c,t,c-Δ(Λ)	A_8'' (A_4''')
	b	6d (6l)	c,c,c-Δ(Λ)	A_9'' (A_6''')
c,c,t-Λ(Δ)	a	7 (7)	c,c,t-Δ(Λ)	A_8'' (A_4''')
	b	3l (3d)	c,c,c-Δ(Λ)	A_9'' (A_6''')
		(b) TBP Equatorial		
c,c,c-Λ(Δ)	a	12d (12l)	c,c,t-Λ(Δ)	A_4'' (A_3''')
	b	15d (15l)	c,t,c-Λ(Δ)	A_4'' (A_3''')
	c	14d (14l)	c,c,t-Λ(Δ)	A_4'' (A_3''')
	d	13d (13l)	c,t,c-Λ(Δ)	A_4'' (A_3''')
c,t,c-Λ(Δ)	a	13d (13l)	c,c,c-Λ(Δ)	A_4'' (A_3''')
	b	15d (15l)	c,c,c-Λ(Δ)	A_4'' (A_3''')
c,c,t-Λ(Δ)	a	14d (14l)	c,c,c-Λ(Δ)	A_4'' (A_3''')
	b	12d (12l)	c,c,c-Λ(Δ)	A_4'' (A_3''')

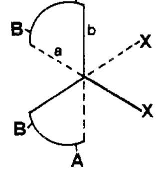
[a] The symbols c and t refer to cis and trans, respectively. [b] Nonequivalent metal–ligand bonds are defined in the text. [c] Intermediates are shown in ref 2. [d] Scrambling patterns and averaging sets are defined in ref 1; A_i'' refer to cases where X is an NMR probe, while A_i''' refer to cases where X does not function as an NMR probe.



cis(X),cis(A),cis(B)-Λ



cis(X),cis(A),trans(B)-Λ



cis(X),trans(A),cis(B)-Λ

Description of the four *i*-C_3 axes for a *cis*-M(AB)$_2$X$_2$ complex and illustration of the twist mechanism operating on the cis,cis,cis diastereomer have been presented elsewhere.[2] A total of ten transition states are produced of which two are achiral and four are enantiomeric *dl* pairs. These intermediates are analogous to those of M(AA′)$_2$(BB) except that BB is replaced by two X groups.[2] The consequences of the twist mechanism operating on the three *cis*-X$_2$ diastereomers are noted in Table II (see also the topological correlation diagram[32] of Figure 40a of ref 2). For each *cis*-X$_2$ isomer, rotation about the $C_3(i'')$ axis after the initial product is formed provides a path for the formation of *trans*-X$_2$ diastereomers. This axis is unique in this regard. It is also noteworthy that twist processes do not lead to direct Δ–Λ interconversion for the cis,cis,trans and cis,trans,cis diastereomers and that the achiral TP intermediates lead to enantiomerization in the cis,cis,cis diastereomer. Further, as noted in Table II, equivalent *i*-C_3 axes in the three *cis*-X$_2$ diastereomers correlate to equivalent averaging sets. Thus, for example, rotations about the $C_3(i')$ and $C_3(i''')$ axes in all three diastereomers produce averaging set A_9'' (A_6''').

Rupture of the nonequivalent bonds in the three *cis*-X$_2$ diastereomers[1] yields 16 TBP intermediates (8 axial and 8 equatorial) including four achiral and six enantiomeric *dl* pairs.[33] Four pairs, the TBP-equatorial intermediates 12*dl*, 13*dl*, 14*dl*, and 15*dl*, are nonfunctional with respect to inversion of the parent diastereomer but do provide for diastereomerization, while four other transition states (4, 5, 7, and 8) are active in enantiomerization but inactive in diastereomerization (cf. Table III). Products obtained by reattachment of the dangling ligand in the equatorial plane are set out in Table III. All the possible interconversions between *cis*-X$_2$ isomers via TBP intermediates are summarized in the topological structure[32] of Figure 38a of ref 2. The interconversion not permitted by the TBP mechanism is:

cis,cis,trans-Δ(Λ) ⇌ *cis,trans,cis*-Λ(Δ)

The TBP-axial intermediates 4, 5, and 8 are also capable of forming *trans*-X$_2$ diastereomers on reattachment of the dangling ligand. Table III also reveals that TBP-equatorial intermediates correlate with averaging set A_4'' (A_3''') only, while TBP-axial intermediates lead to products consistent with A_8'' (A_4''') and A_9'' (A_6''') sets.

Square-pyramidal transition states[2] obtained from the rupture of nonequivalent bonds in the three *cis*-X$_2$ diastereomers consist of two enantiomeric *dl* pairs. Only SP-axial intermediates are considered as SP-basal transition states are kinetically equivalent to those of the TBP-equatorial type. These SP intermediates are formed and decay via the primary process. Table IV lists product distributions for SP-axial transition states resulting from the rupture of nonequivalent bonds in the *cis*-X$_2$ isomers. Interestingly, only averaging sets A_1'' (A_1'''), A_4'' (A_3'''), A_7'' (A_5'''), and A_9'' (A_6''') are produced by reattachment of the "unidentate" ligand in the SP-axial intermediates. Possible interconversions between these *cis*-X$_2$ diastereomers via these intermediates may be found in the topological diagram of Figure 39a (ref 2). The only direct interconversions precluded by this mechanism are:

cis,trans,cis-Δ(Λ) ⇌ *cis,trans,cis*-Λ(Δ)
cis,cis,trans-Δ(Λ) ⇌ *cis,cis,trans*-Λ(Δ)

It is noteworthy that averaging sets A_2'' (A_2'''), A_3'', A_5'' (A_2'''), and A_6'' (A_4''') are directly produced by *neither* of the two pathways referred to in this work.

From studies on the related complexes Ti(bzac)$_2$X$_2$ (X = F, Cl, Br; bzac = C$_6$H$_5$COCHCOCH$_3^-$) Serpone and Fay[28] demonstrated that exchange of nuclei between all four nonequivalent environments in the cis diastereomers cannot be achieved by twisting motions about *any* one of the four C_3 axes of the octahedron. Owing to the possibility of successive twists about different threefold axes, the available data precluded a definitive choice between twisting mechanisms and bond rupture processes. Similarly, a recent investigation[34] on Sn(tibm)$_2$Cl$_2$ (tibm is the anion of 1,1,1-trifluoro-5-methyl-2,4-hexanedione) indicates that the operating averaging set is A_6''' which, unfortunately also, does not afford a choice between twist motions and a bond rupture pathway.

Table IV. Intermediates and Fates of the Diastereomers of a *cis*-M(AB)$_2$X$_2$ Complex Undergoing Rearrangement via a Bond Rupture Pathway through Square-Pyramidal-Axial Intermediates (Primary Process) and Assignment of Averaging Sets to Physical Processes

Initial isomer[a]	Rupture of bond[b]	Intermediate[c]	Product	Averaging set[e]
c,c,c-Λ(Δ)	a	3l (3d)	c,c,c-$\Lambda_1(\Delta_1)$[d]	A_1'' (A_1''')
			c,c,t-Λ(Δ)	A_4'' (A_3''')
			c,c,c-$\Delta_2(\Lambda_2)$	A_7'' (A_5''')
			c,t,c-Δ(Λ)	A_9'' (A_6''')
	b	4d (4l)	c,c,c-$\Lambda_1(\Delta_1)$	A_1'' (A_1''')
			c,t,c-Λ(Δ)	A_4'' (A_3''')
			c,c,c-$\Delta_2(\Lambda_2)$	A_7'' (A_5''')
			c,c,t-Δ(Λ)	A_9'' (A_6''')
	c	4l (4d)	c,c,c-$\Lambda_1(\Delta_1)$	A_1'' (A_1''')
			c,c,t-Λ(Δ)	A_4'' (A_3''')
			c,c,c-$\Delta_2(\Lambda_2)$	A_7'' (A_5''')
			c,t,c-Δ(Λ)	A_9'' (A_6''')
	d	3d (3l)	c,c,c-$\Lambda_1(\Delta_1)$	A_1'' (A_1''')
			c,t,c-Λ(Δ)	A_4'' (A_3''')
			c,c,c-$\Delta_2(\Lambda_2)$	A_7'' (A_5''')
			c,c,t-Δ(Λ)	A_9'' (A_6''')
c,c,t-Λ(Δ)	a	4l (4d)	c,c,t-Λ(Δ)	A_1'' (A_1''')
			c,c,c-Λ(Δ)	A_4'' (A_3''')
			c,t,c-Δ(Λ)	A_7'' (A_5''')
			c,c,c-Δ(Λ)	A_9'' (A_6''')
	b	3l (3d)	c,c,t-Λ(Δ)	A_1'' (A_1''')
			c,c,c-Λ(Δ)	A_4'' (A_3''')
			c,t,c-Δ(Λ)	A_7'' (A_5''')
			c,c,c-Δ(Λ)	A_9'' (A_6''')
c,t,c-Λ(Δ)	a	3d (3l)	c,t,c-Λ(Δ)	A_1'' (A_1''')
			c,c,c-Λ(Δ)	A_4'' (A_3''')
			c,c,t-Δ(Λ)	A_7'' (A_5''')
			c,c,c-Δ(Λ)	A_9'' (A_6''')
	b	4d (4l)	c,t,c-Λ(Δ)	A_1'' (A_1''')
			c,c,c-Λ(Δ)	A_4'' (A_3''')
			c,c,t-Δ(Λ)	A_7'' (A_5''')
			c,c,c-Δ(Λ)	A_9'' (A_6''')

[a] The symbols c and t refer to cis and trans, respectively. [b] Nonequivalent bonds are defined in the text. [c] For specification of intermediates, see ref 36. [d] For scrambling patterns for c,c,c-Δ ⇌ c,c,c-Δ(Λ) rearrangements, see ref 1. [e] Averaging sets have been defined in ref 1; A_i'' refer to cases where X acts as an NMR probe while A_i''' refer to cases where X is not an NMR probe.

Conclusions

Considering both bond rupture and twist processes operating on systems herein discussed, an attempt has been made to correlate the results with averaging sets obtained previously from a permutational analysis,[1] in the hope that such a correlation will aid in the delineation of some plausible mechanisms when these are suggested as sole reaction pathways in configurational rearrangements. Interestingly, neither bond rupture nor twist motions lead to direct interconversions correlating with certain averaging sets. These are (1) A_3 for *cis*-M(AA)$_2$X$_2$, (2) A_4', A_5', A_6', A_7', and A_8' for *cis*-M(AA)$_2$XY,[35] and (3) A_2'', A_3'', A_5'', and A_6'' for *cis*-M(AB)$_2$X$_2$. A topologically equivalent mechanism (except for A_8' and A_6''), though not a probable one owing to unfavorable energetics, is the digonal twist(s) around the C_2 axis of the chelate ring simultaneously about one or more rings, and/or about the XMY fragment. For the A_8' and A_6'' sets, which involve $\Delta \rightleftharpoons \Lambda$ interconversions with no exchange, a topologically equivalent mechanism is one in which when the bis chelate complex is viewed along the C_3 axis of the octahedral framework the six ligating nuclei[36] of the upper and lower triangular faces move toward each other along arcs somewhat parallel to the C_3 axis. The transition state has an hexagonal planar geometry analogous to the one proposed for the digonal twist, noting however that the latter leads to retention of configuration. Continued motion of the ligators about the six arcs leads to the enantiomer. Such a sterically crowded transition state would make this type of mechanism energetically unfavorable also, making it doubtful that the corresponding averaging sets A_8' and A_6'' (or A_4''') would ever be operative, that is, enantiomerization without exchange of terminal groups in *cis*-$M(AA)_2XY$ and *cis*-$M(AB)_2X_2$ systems. In case (2) above, averaging set A_5' may be obtained by pseudorotation of the appropriate TBP-axial transition state, while A_6' and A_7' may by produced by pseudorotation of certain TBP-equatorial intermediates (cf. Table III of ref 6); this pathway is probably of lower energy than the digonal twist(s). Analogous considerations may lead to the discovery of similar, yet energetically more reasonable, pathways.

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(36) Here the two chelate rings would have to span both the upper and lower faces.

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An All-Orders Crystal Field Perturbation Treatment of d–d Optical Activity in Trigonal Transition Metal Complexes

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The crystal field, one-electron perturbation model of d–d optical activity in trigonal transition metal complexes is extended to all orders in the first two noncubic terms of the crystal field interaction operator. As model systems we consider six-coordinate transition metal complexes of nearly octahedral (O_h) but exactly trigonal-dihedral (D_3) symmetry. The crystal field potential at the metal ion is assumed to be octahedral to zeroth order in the perturbation treatment, and the nonoctahedral components of the complete crystal field potential are treated as small perturbations. Chromophoric basis states are constructed from metal 3d, 4p, and 4f orbitals. The perturbation treatment of the chromophoric wave functions is carried to all orders by diagonalizing the Hamiltonian matrix formed by the cubic basis states of the metal ion chromophore and the Hamiltonian operator $\hat{H}$ (trigonal) = $\hat{H}$ (cubic) + $\hat{H}$ (noncubic). The eigenvectors of the diagonalized Hamiltonian are then used to calculate rotatory strengths and from the eigenvalues trigonal splitting energies are obtained. This work is an extension of previous applications of the crystal field, one-electron model of d–d optical activity in which the perturbation treatment was carried only to first or second order in the chiral parts of the crystal field potential.

I. Introduction

Transition metal complexes of trigonal-dihedral (D_3) symmetry have played a central role as model systems in both experimental and theoretical investigations of natural optical activity in coordination compounds. A variety of theoretical models have been proposed for relating the optical activity