

Values for the spin populations for the three cases are given in Table III.

A correlation diagram for the splitting of the e level is given in Figure 6. Considering just orbital energies, both kinds of distortions lead, of course, to a splitting of the e level of the D_{2d} case. Distortion to C_{2v} leads automatically to a nearly complete localization of the unpaired electron on one of the rings whereas distortion to D_2 symmetry leaves it delocalized (for the calculation only bond lengths have been changed). The distortion to C_{2v} is much more effective in lifting the degeneracy although an unrealistically large torsion angle of 45° has been assumed for the distortion to D_2 . From these crude calculations one would therefore assume a double-minimum potential surface for the complex, where the minima correspond to states with the unpaired electron localized on one chelate ligand. The energy barrier is calculated to be about 0.17 eV. Such a value would lead, of course, to a rapid exchange of the unpaired electron from one ligand to the other, resulting in an apparent identity of the two ligands on the ESR time scale.

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Registry No. Zn(gilir)⁺, 58002-31-6; Zn(gilir)Cl(DMF)₂, 58002-32-7; Zn(gilir)Cl(DME)₂, 58002-33-8; Zn(gilir)Cl₂, 58002-34-9; Zn(gilir)Br(DMF)₂, 58002-35-0; Zn(gilir)Br(DME)₂, 58074-41-2; Zn(gilir)Br₂⁻, 58002-36-1; Zn(gilir)(NCO)(DMF)₂, 58002-37-2;

Zn(gilir)(NCO)₂⁻, 58002-38-3; Zn(gilir)(NCS)(DMF)₂, 58002-39-4; Zn(gilir)(NCS)₂⁻, 36471-83-7; Zn(gilir)(N₃)(DMF)₂, 58002-40-7; Zn(gilir)(N₃)₂⁻, 58002-41-8; Zn(gilir)I(DMF)₂, 58002-42-9; Zn(gilir)en⁺, 58002-43-0; Zn(gilir)($\tau/2$)₂⁺, 58117-15-0; Zn(gilir)₂, 58023-82-8.

Supplementary Material Available: Figures 7–16 showing the ESR spectra of the radical complexes generated electrolytically in DMF (10 pages). Ordering information is given on any current masthead page.

References and Notes

- (1) (a) Part III: P. Clopath and A. v. Zelewsky, *Helv. Chim. Acta*, **56**, 980 (1973). (b) Abstracted in part from the Ph.D. Thesis of S. Richter, University of Fribourg, 1974.
- (2) P. Clopath and A. v. Zelewsky, *Helv. Chim. Acta*, **55**, 52 (1972).
- (3) It is proposed to add the letter r (radical) to the abbreviated name of a ligand which is present in the form of a radical, that is, a ligand carrying one unpaired electron. Charges are only given if necessary.
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- (7) Based on a program by J. P. Heinzer (Dissertation, Eidgenössische Technische Hochschule, No. 4255, 1968) a new program ESOP was written in Fortran IV which operates also in the case where several isotopes of an element contribute to the hyperfine pattern, as in the halide complexes. This program is described in the Ph.D. thesis of C. Daul. It can be obtained from the authors upon request.
- (8) We thank Mr. Seeger, Institut of Physical Chemistry, University of Basle, for the original form of the program.
- (9) M. Wolfsberg and L. Helmholz, *J. Chem. Phys.*, **20**, 837 (1952).
- (10) E. Clementi and D. L. Raimondi, *J. Chem. Phys.*, **38**, 2686 (1963).
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Configurational Rearrangements in $cis\text{-M}(\text{AA})_2\text{X}_2$, $cis\text{-M}(\text{AA})_2\text{XY}$, and $cis\text{-M}(\text{AB})_2\text{X}_2$ Complexes. I. A Permutational Analysis¹

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A permutational analysis is described for the coalescence behavior of ¹H NMR probes in a nuclear magnetic resonance experiment, in which the probes are incorporated in bidentate (e.g., β -diketones, RCOCHR'COR'') and/or monodentate (e.g., $-\text{OCH}(\text{CH}_3)_2$) ligands in stereochemically nonrigid complexes of the type $cis\text{-M}(\text{AA})_2\text{X}_2$, $cis\text{-M}(\text{AA})_2\text{XY}$, and $cis\text{-M}(\text{AB})_2\text{X}_2$. Diastereotopic probes have been considered so as to follow the course of metal-centered configurational rearrangements. Changes in signal multiplicities resulting from averaging sets operating on the above complexes with or without diastereotopic ligands are discussed. Distinctions between averaging sets on the basis of changes in signal multiplicities are given. A correlation table of the various averaging sets derived for the three types of systems is presented, and it is proposed that once a unique averaging set has been determined for one of the above systems, this same averaging set can be correlated with those of another system for which a unique choice is not possible.

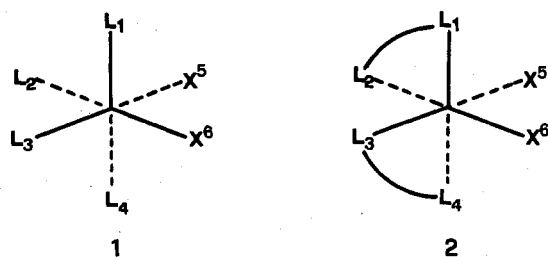
Introduction

Intramolecular exchange processes continue to confront inorganic and organometallic chemists with fascinating problems.² One particularly active area³⁻⁶ deals with intramolecular rearrangement reactions of six-coordinate chelate complexes. Rearrangements may involve diastereomerization and/or enantiomerization, and a classification of metal chelates in terms of their rearrangement rates has introduced the designations "slow" and "fast".⁷ Stereochemically nonrigid or fast complexes exhibit rearrangement rates that are too large to permit isolation of diastereomers and enantiomers but do allow isomer detection and, in some cases, kinetic studies by nuclear magnetic resonance (NMR) line shape analysis.

It is now well recognized⁸ that when a $-\text{CXY}_2$ group is bound to some dissymmetric group, the two Y substituents neither achieve equivalence in any rotational conformation nor achieve it as a result of internal rotation, however rapid. To achieve equivalence, inversion of the dissymmetric moiety must occur. Incorporation of a diastereotopic group within the chelate ring may thus enable enantiomerization processes to

be detected and rates to be measured. This ability to detect enantiomerization processes in nonrigid chelates has enabled significant progress in the elucidation of the mechanism(s) of rearrangement. Physical rearrangement pathways are generally considered to be of two limiting types:^{3,4} (i) twist motions proceeding about axes passing through octahedral faces via an idealized trigonal-prismatic transition state and (ii) bond rupture processes via a five-coordinate trigonal-bipyramidal or square-pyramidal transition state, with, in each case, dangling axial or equatorial (basal) ligands. While these two distinct types of mechanisms are physically reasonable, there is no assurance that every feasible mechanism has been considered.

An inherent problem^{6,9} often faced in dynamic NMR studies is that the NMR experiment does not define the actual configurational changes during the rearrangement but rather defines a particular site interchange pattern. In order to overcome this problem and also to ensure that every feasible mechanism has been considered, permutational analyses have recently been applied¹⁰⁻²⁴ to six-coordinate molecules to



enumerate all of the theoretically possible, physically distinguishable intramolecular rearrangements. This type of analysis yields a mathematical description of all of the possible permutations of ligating nuclei about a particular polytopal form without specifying how atoms move from an initial configuration to a final configuration via a single-step process. Such a description may afford a deduction of NMR-observable site interchanges and actual configurational changes (diastereomerization and/or enantiomerization) from the allowed permutations. However, in molecules possessing some degree of symmetry, not every allowed permutation will be physically distinguishable by NMR methods. Musher^{17,18} has recently emphasized that rearrangement modes or observable processes (averaging sets²⁵) are concerned only with the difference between the initial and the final configuration and contain no connotations concerning the actual physical motions of ligating nuclei. While numerous physical rearrangement mechanisms may be envisaged for a given molecule, there exists only a finite number of averaging sets or rearrangement modes.

As implied earlier, the NMR experiment can only determine the site interchange pattern and hence the averaging set. Once the averaging set has been identified, the most probable physical pathway which generates that particular averaging set may be deduced. This deduction may not be unique and chemical intuition often may play a significant role. Thus, a rearrangement mechanism can only be demonstrated as operating in the sense that it is the most reasonable physical motion which yields the observed averaging set. In addition, in the absence of any information concerning the stereochemistry of the rearrangement process, comments regarding the mechanism of the rearrangement are tenuous.

The determination of the allowed permutations (and thus averaging set) of nuclei surrounding a particular polytopal form has been achieved by several methods. Some of these include graph theory,^{10,11} the mathematical structure of combinatorial analysis,^{12,16} empirical methods,¹⁷⁻²¹ double cosets and counting formulas,^{22,23} and symmetry groups for nonrigid molecules as developed by Longuet-Higgins.^{24,26}

Recent work from this laboratory has focused on the stereochemistry of and configurational rearrangements in complexes of the type $M(AA)_2X_2$, $M(AA)_2XY$, and $M(AB)_2X_2$ for cases in which the chelating ligands are generally β -diketones and $M = Sn(IV)$,²⁷ $Si(IV)$,²⁸ $Ge(IV)$,²⁸ and $Ti(IV)$.²⁹ In the course of these studies complete permutational and mechanistic analyses have been performed for these systems. Diastereotopic probes have also been incorporated into a number of chelate complexes to detect enantiomerization processes. Further, recent communications on dynamic NMR studies of inversion and diketonate R group exchange in some glycolatobis(acetylacetonato)- and dialkoxybis(β -diketonato)titanium(IV) complexes^{30,31} prompt us to report our permutational analyses in related systems as these may aid in the delineation of plausible mechanisms for the rearrangement processes.

This work describes the application of Longuet-Higgins' procedure to determine the allowed averaging sets for the nonrigid six-coordinate bis-chelate complexes $cis-M(AA)_2X_2$, $cis-M(AA)_2XY$,³² and $cis-M(AB)_2X_2$. Only the *cis* diaste-

reomer is considered in the analysis as rearrangements do not involve the *trans* diastereomer. A recent report by Eaton and Eaton²⁴ describes the application of this procedure to nonrigid tris chelates of the type $M(AB)_3$ and $M(AB)_2(CC)$. Musher and Agosta¹⁹ have also recently published an analysis of rearrangement modes in *cis*- M (bidentate phosphine)₂H₂ complexes, while Miller and Caulton²⁰ have analyzed the *cis*- M (diphos)₂HCl case.

Application of Longuet-Higgins' Molecular Symmetry Groups for Nonrigid Molecules to Rearrangements in the *cis*- $M(AA)_2X_2$, *cis*- $M(AA)_2XY$, and *cis*- $M(AB)_2X_2$ Systems

Longuet-Higgins²⁶ proposed that nonrigid molecules be analyzed in terms of molecular symmetry groups which comprise the set (a) of all feasible permutations, P , of the positions and spins of the identical nuclei (including the identity E) and (b) of all feasible permutation inversions, P^* , which simultaneously permute and invert the relative coordinates of all atoms in the center of mass of the molecule. P^* is the product $PE^* = E^*P$, where E^* is the inversion of the positions of all atoms and may not always be among the feasible operations.²⁶

The *cis*- $M(AA)_2X_2$ System. The *cis*- $M(AA)_2X_2$ system is analyzed in detail since the basic set of distinguishable permutamers³⁴ and allowed P and P^* operations is identical with that for the *cis*- $M(AA)_2XY$ and *cis*- $M(AB)_2X_2$ systems, with the appropriate inclusion of different substituents in these latter systems.

For the skeletal framework of a *cis*- $M(AA)_2X_2$ complex as represented by **1**, for which the X^5 and X^6 ligands are constrained to remain in a mutually *cis* configuration, the number of permutamers of **1** is 48—the product of the number of permutations of L_1 , L_2 , L_3 , and L_4 among themselves and all possible permutations of the two X groups among themselves, that is, $4! \times 2!$. With the additional constraints that L_1L_2 and L_3L_4 represent the ligating nuclei of bidentate ligands and that these ligands cannot span *trans* positions, 16 of the above 48 permutamers are no longer allowed; thus, there remain 32 permutations of the groups in configuration **2**. However, owing to the presence of the C_2 rotation axis, pairwise equivalencies occur within the 32 permutamers and the number of distinguishable permutational isomers for configuration **2** is 16. One permutamer of **2** can be converted into the 15 other permutational isomers (which cannot be superimposed on **2** by proper rotations of the molecule) only by P and P^* operations. The set of all permutamers of a complex of configuration **2** is a group of order 384, which factors into a unique Abelian group of order 16 consisting of distinguishable permutational isomers and a group of order 24 consisting of rearranged forms resulting from rigid-body rotations.³⁶

The notation used to describe the 16 permutamers and an illustration of P and P^* operations are shown in Figure 1. As the complex is viewed down an imaginary threefold ($i-C_3$) axis with the triangular face including position 1 upward, the ligating nuclei are labeled 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. Brackets denote permutational isomers and parentheses represent P and P^* operations. The 16 permutamers for a complex of general configuration **2** are listed in Table I. Enantiomeric permutamers of Table I are related to each other by the numbering sequence by reversing the digits in each subset but keeping label 1 as the first digit—thus, the Δ permutamer of Δ -[163-542] is [136-245]. The 16 P and P^* operations were determined by selecting one of the 16 permutamers and ascertaining what interchanges of nuclei generate the other 15 isomers. The eight P and eight P^* operations which interconvert the isomers within the set of 16 isomers are listed in Table II. Permutations other

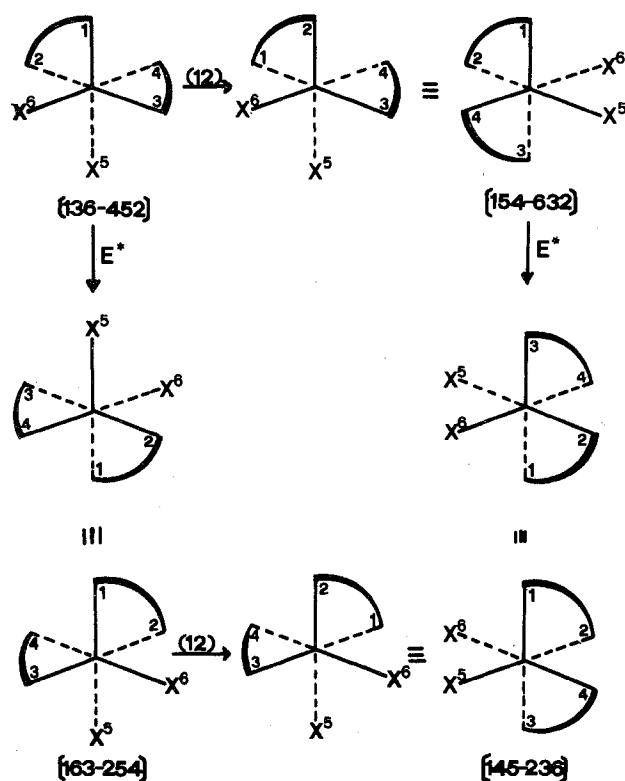


Figure 1. Illustration of notation and P and P^* operations for a $cis\text{-M}(\text{AA})_2\text{X}_2$ complex. This diagram also illustrates the equivalence of the relation $PE^* = E^*P$.

Table I. The 16 Permutational Isomers for a $cis\text{-M}(\text{AA})_2\text{X}_2$ System

| Δ | Λ | Δ | Λ |
|------------------------|-----------|-----------|-----------|
| [135-462] ^a | [153-264] | [145-362] | [154-263] |
| [136-452] | [163-254] | [145-236] | [154-632] |
| [135-246] | [153-642] | [146-235] | [164-532] |
| [136-245] | [163-542] | [146-352] | [164-253] |

^a For a definition of notation used, see text and Figure 1.

Table II. Permutational Analysis of the $cis\text{-M}(\text{AA})_2\text{X}_2$ System

| Operations ^a | Product permutamer | Exchange pattern ^b | Inversion | Averaging set |
|-------------------------|--------------------|-------------------------------|--------------------|---------------|
| E | [163-542] | 1 | | A_1 |
| (56) | [153-642] | | | |
| (12) | [145-362] | | | |
| (12)(56) | [146-352] | 2 | | A_2 |
| (34) | [164-532] | | | |
| (34)(56) | [154-632] | | | |
| (12)(34) | [135-462] | 3 | | A_3 |
| (12)(34)(56) | [136-452] | | | |
| E^* | [136-245] | 1 | $\Delta = \Lambda$ | A_4 |
| (56)* | [135-246] | | | |
| (12)* | [154-263] | | | |
| (12)(56)* | [164-253] | 2 | $\Delta = \Lambda$ | A_5 |
| (34)* | [146-235] | | | |
| (34)(56)* | [145-236] | 3 | $\Delta = \Lambda$ | A_6 |
| (12)(34)* | [153-264] | | | |
| (12)(34)(56)* | [163-254] | | | |

^a Operations performed on the [163-542] permutamer. ^b Exchange patterns are defined in Table III.

than those in Table II either correspond to rigid-body rotations or generate configurations in which one of the bidentate ligands must span the trans positions. The effect of each of the 16 allowed operations on the [163-542] isomer is given in Table II. The complete 16×16 group multiplication table for the group of 16 P and P^* operations may be found elsewhere.²⁴

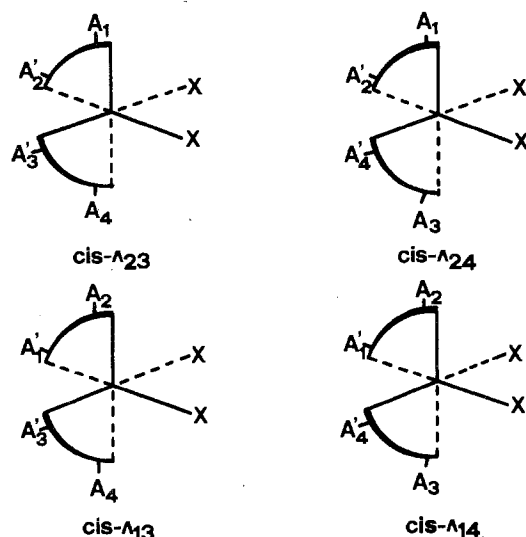


Figure 2. Illustration of the notation used in the analysis of the $cis\text{-M}(\text{AA})_2\text{X}_2$ system in terms of four Δ - Λ pairs. See text for the significance of the primes and subscripts.

Table III. Scrambling Patterns for Nonequivalent Terminal Groups in Rearrangements of a $cis\text{-M}(\text{AA})_2\text{X}_2$ Complex^a

1. No exchange, e.g., $(\Delta, \Lambda)_{23} = (\Delta, \Lambda)_{23}$, $(\Delta, \Lambda)_{14} = (\Delta, \Lambda)_{14}$
- 2a.^b $(\Delta, \Lambda)_{23} = (\Delta, \Lambda)_{13}$, $(\Delta, \Lambda)_{14} = (\Delta, \Lambda)_{24}$
3. $(\Delta, \Lambda)_{23} = (\Delta, \Lambda)_{14}$, $(\Delta, \Lambda)_{13} = (\Delta, \Lambda)_{24}$

^a Scrambling patterns contain no connotations concerning whether inversion does or does not occur during exchange of the terminal groups. ^b Equivalent scrambling patterns owing to C_2 symmetry.

Rearrangements within the $cis\text{-M}(\text{AA})_2\text{X}_2$ system are analyzed in terms of the four Δ - Λ pairs depicted in Figure 2. The prime indicates that an A end of the ligand is one of the nonequivalent terminal group environments trans to an X group. Each configuration is then labeled according to its absolute configuration with subscripts referring to which A groups are primed. The possible scrambling patterns for the nonequivalent terminal groups on the bidentate ligands are summarized in Table III.

When all 16 operations are performed on the 16 permutational isomers, certain permutations produce equivalent configurational changes and site interchanges. These permutations are placed together in averaging sets, A_i , although the permutations within each set may have different effects on a particular permutamer. This condition arises from the fact that the NMR experiment can detect only the net effect on all permutamers. The configurational changes, site interchanges, averaging sets, and individual permutamers are summarized in Table II for the $cis\text{-M}(\text{AA})_2\text{X}_2$ system.

For this system, the 16 P and P^* operations are classified into six averaging sets, A_i . The changes in signal multiplicities for nondiastereotopic and diastereotopic substituents on either the AA or X ligands, predicted from the averaging sets A_i , are compiled in Table IV. It is noted that in the absence of diastereotopic groups, the site exchange patterns are not indicative as to whether a rearrangement occurs with or without inversion of the configuration at the metal center. Thus, averaging sets (A_1, A_4), (A_2, A_5), and (A_3, A_6) are pairwise indistinguishable.

Considering the distinctions that can be made between averaging sets A_1, A_2 , and A_3 , when all substituents within the complex are nondiastereotopic, it is apparent, on inspection of Table IV, that A_1 is distinct from A_2 and A_3 as A_1 affords no exchange (cf. Table III). Unfortunately, A_2 and A_3 cannot be differentiated on the basis of changes in signal multiplicities.

Table IV. Changes in Signal Multiplicities Resulting from the Averaging Sets A_i Operating on a $cis\text{-}M(\text{AA})_2\text{X}_2$ Complex Containing Diastereotopic and/or Nondiastereotopic Ligands^a

| Averaging set | A-A nondiastereotopic (diastereotopic) | -CR= nondiastereotopic (diastereotopic) | X nondiastereotopic (diastereotopic) |
|---------------|--|---|--------------------------------------|
| A_1 | 2 (4) → 2 (4) | 1 (2) → 1 (2) | 1 (2) → 1 (2) |
| A_2 | 2 (4) → 1 (2) | 1 (2) → 1 (2) | 1 (2) → 1 (2) |
| A_3 | 2 (4) → 1 (2) | 1 (2) → 1 (2) | 1 (2) → 1 (2) |
| A_4 | 2 (4) → 2 (2) | 1 (2) → 1 (1) | 1 (2) → 1 (1) |
| A_5 | 2 (4) → 1 (2) | 1 (2) → 1 (1) | 1 (2) → 1 (1) |
| A_6 | 2 (4) → 1 (2) | 1 (2) → 1 (1) | 1 (2) → 1 (1) |

^a The numbers of predicted resonances refer to groups which are not coupled either to each other or to another group. For example, if the substituent on the ligand(s) was an isopropyl group, the multiplicities given in this table would refer to the number of spin-coupled doublets for the isopropyl methyl groups due to coupling with the geminal methyl proton.

Table V. Changes in Signal Multiplicities Resulting from the Averaging Sets A_i' Operating on a $cis\text{-}M(\text{AA})_2\text{XY}$ Complex Containing Diastereotopic and/or Nondiastereotopic Ligands^a

| Averaging set | A-A nondiastereotopic (diastereotopic) | -CR= nondiastereotopic (diastereotopic) | X (or Y) nondiastereotopic (diastereotopic) |
|---------------|--|---|---|
| A_1' | 4 (8) → 4 (8) | 2 (4) → 2 (4) | 1 (2) → 1 (2) |
| A_2' | 4 (8) → 3 (6) | 2 (4) → 2 (4) | 1 (2) → 1 (2) |
| A_3' | 4 (8) → 3 (6) | 2 (4) → 2 (4) | 1 (2) → 1 (2) |
| A_4' | 4 (8) → 2 (4) | 2 (4) → 1 (2) | 1 (2) → 1 (2) |
| A_5' | 4 (8) → 2 (4) | 2 (4) → 2 (4) | 1 (2) → 1 (2) |
| A_6' | 4 (8) → 1 (2) | 2 (4) → 1 (2) | 1 (2) → 1 (2) |
| A_7' | 4 (8) → 2 (4) | 2 (4) → 1 (2) | 1 (2) → 1 (2) |
| A_8' | 4 (8) → 4 (4) | 2 (4) → 2 (2) | 1 (2) → 1 (1) |
| A_9' | 4 (8) → 3 (4) | 2 (4) → 2 (2) | 1 (2) → 1 (1) |
| A_{10}' | 4 (8) → 3 (4) | 2 (4) → 2 (2) | 1 (2) → 1 (1) |
| A_{11}' | 4 (8) → 2 (4) | 2 (4) → 1 (2) | 1 (2) → 1 (1) |
| A_{12}' | 4 (8) → 2 (4) | 2 (4) → 2 (2) | 1 (2) → 1 (1) |
| A_{13}' | 4 (8) → 1 (2) | 2 (4) → 1 (2) | 1 (2) → 1 (1) |
| A_{14}' | 4 (8) → 2 (4) | 2 (4) → 1 (2) | 1 (2) → 1 (1) |

^a See footnote *a* of Table IV.

The analogous situation pertains in attempting to distinguish averaging sets A_4 , A_5 , and A_6 . It is instructive, however, to regard A_2 and A_5 as the linear combination of two subsets ($A_{2a} + A_{2b}$) and ($A_{5a} + A_{5b}$) for the purpose of distinguishing these from A_3 and A_6 , respectively. In principle, for example, A_5

Table VI. Distinctions between Averaging Sets A_i' for a $cis\text{-}M(\text{AA})_2\text{XY}$ Complex on the Basis of Changes in Signal Multiplicities

| a | | b | | c | | d | |
|--|--|---|--|---|--|---|--|
| A-A nondiastereotopic -CR= nondiastereotopic X (or Y) nondiastereotopic | | A-A nondiastereotopic -CR= nondiastereotopic X (or Y) diastereotopic | | A-A nondiastereotopic -CR= diastereotopic X (or Y) nondiastereotopic | | A-A nondiastereotopic -CR= diastereotopic X (or Y) diastereotopic | |
| (A ₁ ', A ₂ ') (A ₂ ', A ₃ ', A ₉ ', A ₁₀ ') (A ₄ ', A ₇ ', A ₁₁ ', A ₁₄ ') (A ₅ ', A ₁₂ ') (A ₆ ', A ₁₃) | | A ₁ ' (A ₂ ', A ₃ ') (A ₄ ', A ₇ ') A ₅ ' A ₆ ' A ₈ ' (A ₉ ', A ₁₀ ') (A ₁₁ ', A ₁₄ ') A ₁₂ ' A ₁₃ | | A ₁ ' (A ₂ ', A ₃ ') (A ₄ ', A ₇ ', A ₁₁ ', A ₁₂ ', A ₁₄ ') A ₅ ' (A ₆ ', A ₁₃ ') A ₈ ' (A ₉ ', A ₁₀ ') | | A ₁ ' (A ₂ ', A ₃ ') (A ₄ ', A ₇ ') A ₅ ' A ₆ ' A ₈ ' (A ₉ ', A ₁₀ ') (A ₁₁ ', A ₁₂ ', A ₁₄ ') A ₁₃ | |
| e | | f | | g | | h | |
| A-A diastereotopic -CR= nondiastereotopic X (or Y) nondiastereotopic | | A-A diastereotopic -CR= nondiastereotopic X (or Y) diastereotopic | | A-A diastereotopic -CR= diastereotopic X (or Y) nondiastereotopic | | A-A diastereotopic -CR= diastereotopic X (or Y) diastereotopic | |
| A ₁ ' (A ₂ ', A ₃ ') (A ₄ ', A ₇ ', A ₁₁ ', A ₁₄ ') (A ₅ ', A ₈ ', A ₉ ', A ₁₀ ', A ₁₂ ') (A ₆ ', A ₁₃) | | A ₁ ' (A ₂ ', A ₃ ') (A ₄ ', A ₇ ') A ₅ ' A ₆ ' (A ₈ ', A ₉ ', A ₁₀ ', A ₁₂ ') (A ₁₁ ', A ₁₄ ') A ₁₃ | | A ₁ ' (A ₂ ', A ₃ ') (A ₄ ', A ₇ ', A ₈ ', A ₉ ', A ₁₀ ', A ₁₁ ', A ₁₂ ', A ₁₄ ') A ₅ ' (A ₆ ', A ₁₃ ') | | A ₁ ' (A ₂ ', A ₃ ') (A ₄ ', A ₇ ') A ₅ ' A ₆ ' (A ₈ ', A ₉ ', A ₁₀ ', A ₁₁ ', A ₁₂ ', A ₁₄ ') A ₁₃ | |

may be taken to describe a reaction of type 1, and A_6 , to define



type 2. In the former case, averaging set A_5 would predict



a ratio of the rate of enantiomerization to the rate of terminal group exchange to be 2:1, while A_6 predicts a ratio of rates of unity. On this basis, therefore, A_5 and A_6 can be distinguished from the relative rates of the inversion and exchange processes. When the terminal group degeneracy in $cis\text{-}M(\text{AA})_2\text{X}_2$ is removed on progressing to a $cis\text{-}M(\text{AA})_2\text{XY}$ complex, the macroscopic degeneracy of the operations within A_{5a} and A_{5b} (and A_{2a} and A_{2b}) is lifted, and the difficulty in distinguishing averaging sets is lessened (vide infra).

The $cis\text{-}M(\text{AA})_2\text{XY}$ System. In a $cis\text{-}M(\text{AA})_2\text{XY}$ complex, all four terminal groups are nonequivalent; in the specific case where AA represents a β -diketonate ligand, the two $-\text{CH}=\text{}$ protons (or $-\text{CR}=\text{}$ groups) are also in nonequivalent environments. An illustration of the geometry and labeling of nonequivalent sites within the [163-542] permutamer is provided elsewhere.³³

The same basic set of 16 permutational isomers applies to the $cis\text{-}M(\text{AA})_2\text{XY}$ system (Y is number 6 and X is number 5). The effect of performing the eight P and eight P* operations on the [163-542] = $cis\text{-}\Lambda(\text{abcd}; \text{m})$ isomer has been presented earlier.³³ Those permutations resulting in the same net exchange pattern after all 16 operations are performed on the 16 permutamers are grouped in the same averaging sets, A_i' ; these are listed elsewhere.³³

The various permutations were classified into 14 averaging sets.^{33,37} Changes in signal multiplicities for diastereotopic and nondiastereotopic substituents on the AA and X (or Y) ligands predicted by the A_i' averaging sets are summarized in Table V. The distinctions between averaging sets A_i' on the basis of changes in signal multiplicities for the eight possible combinations of diastereotopic and nondiastereotopic ligands are compiled in Table VI. In the absence of diastereotopic substituents it is difficult to ascertain whether a rearrangement occurs with or without inversion at the metal

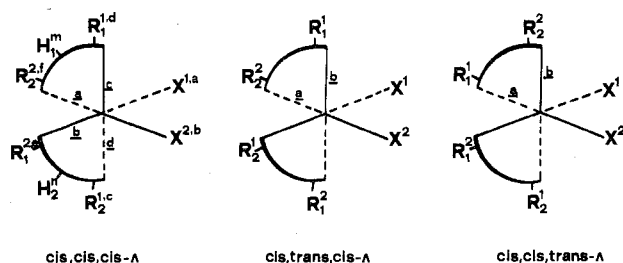


Figure 3. The three diastereomers containing mutually *cis* X groups for a *cis*-M(AB)₂X₂ complex. The numerical superscripts label the terminal, ring proton, and X groups; letter superscripts label the nonequivalent environments. Letter subscripts label the two types of R groups on the A-B ligand. The letters a, b, c, and d define the four nonequivalent metal-chelate bonds in the three diastereomers.

center, and the averaging sets³⁹ (A₁['], A₈[']), (A₂['], A₉[']), (A₃['], A₁₀[']), (A₄['], A₁₁[']), (A₅['], A₁₂[']), (A₆['], A₁₃[']), and (A₇['], A₁₄[']) are pairwise indistinguishable (Table VIa). As noted in Table VIb, the maximum number of distinct averaging sets originates from incorporating monodentate diastereotopic ligands in the complex. It is also noteworthy that the presence of a diastereotopic group in the complex, as on the bidentate AA ligand, will not necessarily afford detection of Δ-Λ interconversion (cf. Table VIe).

Distinctions between averaging sets in Table VI are based solely on the predicted signal multiplicities for the various substituents in the fast-exchange limit. It is also assumed that all resonances are well resolved in the slow-exchange region and that no chemical shift degeneracies occur in either the fast- or the slow-exchange regions. For example, in case a of Table VI, averaging sets A₆['] and A₇['] could generate identical spectra in the fast-exchange limit for a particular complex with a unique set of chemical shifts and thus be indistinguishable, even though Table VIa indicates otherwise. This particular case has been observed for the *cis*-(CH₃)ClSn(acac)₂ complex.^{33,39}

The *cis*-M(AB)₂X₂ System. Complexes of the type *cis*-M(AB)₂X₂ may exist in three diastereomeric forms in which the X groups are mutually *cis*.⁴⁰ As depicted in Figure 3, the *cis,cis,cis*⁴¹ isomer has C₁ symmetry and consequently possesses four nonequivalent terminal R groups, two nonequivalent -CH= (or -CR= groups) protons, and two nonequivalent X groups. The nonequivalent sites are defined as follows. Sites a and b refer to X groups, site a being *trans* to R₁ and site b *trans* to R₂. Sites c, d, e, and f refer to the terminal R groups. The site *trans* to a is always e; the one *trans* to site b is labeled f. Sites c and e are always connected with the same ring; a similar case applies to d and f. Thus, if R₁¹ is in site d, then R₂² is in site f. Site m for the -CH= ring proton (or group) on the R₁¹-R₂² ring is surrounded by terminal groups in the f and d sites; if the terminal groups on the ring associated with the ring proton (or group) are in sites c and e, the ring proton is then in site n.

Both the *cis,cis,trans* and *cis,trans,cis* diastereomers possess twofold symmetry, and thus both isomers have only one environment for each of the R₁, R₂, -CH= (or -CR=), and X groups.

Scrambling patterns for the various nonequivalent environments within the *cis,cis,cis* diastereomer are listed in Table VII.

The same basic set of 16 permutational isomers obtained for the *cis*-M(AA)₂X₂ system pertains to the present system (X¹ is number 5 and X² is number 6).

Permutations resulting in the same net exchange pattern on carrying out all 16 operations on the 16 permutamers of Table I have been included in the same averaging set A_i['] and are listed in Table VIII.

Table VII. Scrambling Patterns for Nonequivalent Environments in the *cis,cis,cis*-Δ → *cis,cis,cis*-Δ(A) Rearrangements of a *cis*-M(AB)₂X₂ Complex

- [ijkl; a; m]^a ⇌ [ijkl; a; m] No exchange
- [ijkl; a; m] ⇌ [jilk; a; n] R₁, R₂, and -CH= exchange
- [ijkl; a; m] ⇌ [ijkl; b; m] X exchange
- [ijkl; a; m] ⇌ [jilk; b; n] R₁, R₂, -CH=, and X exchange

^a The sites in brackets refer to the various nonequivalent groups within the *cis,cis,cis* isomer in the order R₁¹, R₁², R₂¹, R₂²; X²; -CH=, and they are defined in Figure 3 and the text. The letters used in this table simply define a general case for each type of scrambling pattern.

Table VIII. Permutational Analysis of the *cis*-M(AB)₂X₂ System

| Permutation ^a | Isomerization | Inversion | Scrambling pattern in <i>cis,cis,cis</i> isomer ^b | Averaging set |
|--------------------------|-----------------------|-----------|--|------------------------------|
| E | | | 1 | A ₁ ['] |
| (12)(34)(56) | c,c,t ⇌ c,t,c | | 2 | A ₂ ['] |
| (56) | | | 3 | A ₃ ['] |
| (12) | c,c,t ⇌ c,c,c ⇌ c,t,c | | | A ₄ ['] |
| (34) | | | | |
| (12)(56) | | | | |
| (34)(56) | | | | |
| (12)(34) | c,c,t ⇌ c,t,c | | 4 | A ₅ ['] |
| E* | | Δ ⇌ Λ | 1 | A ₆ ['] |
| (12)(34)(56)* | c,c,t ⇌ c,t,c | Δ ⇌ Λ | 2 | A ₇ ['] |
| (56)* | | Δ ⇌ Λ | 3 | A ₈ ['] |
| (12)* | c,c,t ⇌ c,c,c ⇌ c,t,c | Δ ⇌ Λ | | A ₉ ['] |
| (34)* | | | | |
| (12)(56)* | | | | |
| (34)(56)* | | | | |
| (12)(34)* | c,c,t ⇌ c,t,c | Δ ⇌ Λ | 4 | A ₁₀ ['] |

^a See footnote a of Table II. ^b Scrambling patterns defined in Table VII.

Table IX. Changes in Signal Multiplicities Resulting from the Averaging Sets A_i['] and A_j['] Operating on a *cis*-M(AB)₂X₂ Complex Containing Diastereotopic and/or Nondiastereotopic Ligands^a

| Averaging set | A-B nondiastereotopic (diastereotopic) | -CR= nondiastereotopic (diastereotopic) | X nondiastereotopic (diastereotopic) |
|---|--|---|--------------------------------------|
| A ₁ ['] (A ₁ [']) ^b | 4 (8) → 4 (8) | 4 (8) → 4 (8) | 4 (8) → 4 (8) |
| A ₂ ['] | 4 (8) → 2 (4) | 4 (8) → 2 (4) | 4 (8) → 3 (6) |
| A ₃ ['] | 4 (8) → 4 (8) | 4 (8) → 4 (8) | 4 (8) → 3 (6) |
| A ₄ ['] (A ₃ [']) | 4 (8) → 1 (2) | 4 (8) → 1 (2) | 4 (8) → 1 (2) |
| A ₅ ['] (A ₄ [']) | 4 (8) → 2 (4) | 4 (8) → 2 (4) | 4 (8) → 2 (4) |
| A ₆ ['] (A ₄ [']) | 4 (8) → 4 (4) | 4 (8) → 4 (4) | 4 (8) → 4 (4) |
| A ₇ ['] | 4 (8) → 2 (4) | 4 (8) → 2 (4) | 4 (8) → 3 (4) |
| A ₈ ['] | 4 (8) → 4 (4) | 4 (8) → 4 (4) | 4 (8) → 3 (4) |
| A ₉ ['] (A ₆ [']) | 4 (8) → 1 (2) | 4 (8) → 1 (2) | 4 (8) → 1 (2) |
| A ₁₀ ['] (A ₅ [']) | 4 (8) → 2 (4) | 4 (8) → 2 (4) | 4 (8) → 2 (4) |

^a See footnote a of Table IV. ^b Case where X ligands do function as an NMR probe. ^c Case where X ligands do not function as an NMR probe.

In the case where the X ligands in the *cis*-M(AB)₂X₂ complex can act as NMR probes, the permutations are classified into 10 averaging sets (Table VIII). Changes in signal multiplicities for diastereotopic and nondiastereotopic ligands AB and X, predicted by the A_i['] averaging sets, are summarized in Table IX. Distinctions between A_i['], on the basis of changes of signal multiplicities for the different combinations of non- and diastereotopic ligands, are tabulated in Table X.

In the event that the X ligands contain nuclei which are incapable of serving as NMR probes, the permutational analysis is simplified but at the expense of mechanistic information. When the two X groups are chemically equivalent,

Table X. Distinctions between Averaging Sets A_i'' for a $cis\text{-}M(\text{AB})_2\text{X}_2$ Complex on the Basis of Changes in Signal Multiplicities

| a | b | c | d |
|--|---|--|---|
| A-B nondiastereotopic -CR= nondiastereotopic X nondiastereotopic | A-B nondiastereotopic -CR= nondiastereotopic X diastereotopic | A-B diastereotopic -CR= diastereotopic X nondiastereotopic | A-B diastereotopic -CR= nondiastereotopic X diastereotopic |
| (A_1'' , A_6'') (A_2'' , A_7'') (A_3'' , A_8'') (A_4'' , A_9'') (A_5'' , A_{10}'') | A_1'' A_2'' A_3'' (A_4'' , A_9'') (A_5'' , A_7'' , A_{10}'') (A_6'' , A_8'') | A_1'' (A_2'' , A_7'') A_3'' (A_4'' , A_9'') (A_5'' , A_{10}'') A_6'' A_8'' | A_1'' A_2'' A_3'' (A_4'' , A_9'') (A_5'' , A_7'' , A_{10}'') (A_6'' , A_8'') |
| e | f | g | h |
| A-B nondiastereotopic -CR= diastereotopic X nondiastereotopic | A-B nondiastereotopic -CR= diastereotopic X diastereotopic | A-B diastereotopic -CR= diastereotopic X nondiastereotopic | A-B diastereotopic -CR= diastereotopic X diastereotopic |
| A_1'' (A_2'' , A_7'') A_3'' (A_4'' , A_9'') (A_5'' , A_{10}'') A_6'' A_8'' | A_1'' A_2'' A_3'' (A_4'' , A_9'') (A_5'' , A_7'' , A_{10}'') (A_6'' , A_8'') | A_1'' A_2'' A_3'' (A_4'' , A_9'') (A_5'' , A_{10}'') A_6'' (A_7'' , A_8'') | A_1'' A_2'' A_3'' (A_4'' , A_9'') (A_5'' , A_6'' , A_7'' , A_8'' , A_{10}'') |

Table XI. Permutational Analysis of the $cis\text{-}M(\text{AB})_2\text{X}_2$ System When the X Ligand Does Not Function as a Nuclear Magnetic Resonance Probe

| Permutation ^a | Isomerization | Inversion | Scrambling pattern in $cis\text{-}cis$ isomer ^b | Averaging set |
|--------------------------|---|-------------------------------------|--|---------------|
| E | | | 1 | A_1''' |
| (12)(34) | $c, c, t \rightleftharpoons c, t, c$ | | 2 (or 4) | A_2''' |
| (12) } (34) } | $c, c, t \rightleftharpoons c, c, c \rightleftharpoons c, t, c$ | | | A_3''' |
| E^* | | $\Delta \rightleftharpoons \Lambda$ | 1 | A_4''' |
| (12)(34)* | $c, c, t \rightleftharpoons c, t, c$ | $\Delta \rightleftharpoons \Lambda$ | 2 (or 4) | A_5''' |
| (12)* } (34)* } | $c, c, t \rightleftharpoons c, c, c \rightleftharpoons c, t, c$ | $\Delta \rightleftharpoons \Lambda$ | | A_6''' |

^a See footnote *a* of Table II. ^b Scrambling patterns are defined in Table VII with the added restriction that exchange of X groups can no longer be detected.

only eight distinct permutational isomers are found, and eight operations, which form an Abelian group, interconvert the isomers. This is a subset of the group in Table VIII, obtained by eliminating all operations involving the (56) permutation. The NMR averaging sets A_i''' for this case are listed in Table XI. Changes in signal multiplicities that may be deduced from Table XI for cases in which the AB ligand contains diastereotopic and nondiastereotopic groups are noted in Table IX. It is evident, therefore, that the study of complexes of the type $cis\text{-}M(\text{AB})_2\text{X}_2$, in which the X groups are not NMR probes, severely restricts the conclusions that can be made from the NMR experiment.

Correlations among Averaging Sets for the Three Systems. Since the averaging sets for the different molecular systems derived above are all based on the same 16 permutation and permutation-inversion operations of an Abelian molecular symmetry group, it is expected that there will be an interrelation between the A_i , A_i' , A_i'' , and A_i''' averaging sets.

On changing the nature of the bidentate and monodentate ligands, the symmetry of the molecule will be altered and degeneracies within the averaging sets may be lifted. Correlation of the constituent P and P^* operations with the various averaging sets of the $cis\text{-}M(\text{AA})_2\text{X}_2$, $cis\text{-}M(\text{AA})_2\text{XY}$, and $cis\text{-}M(\text{AB})_2\text{X}_2$ systems leads to the correlation of averaging sets presented in Table XII. Thus, it is proposed that once a unique averaging set has been identified for one of the systems in Table XII, this same averaging set may be cor-

Table XII. Correlations between the Averaging Sets for the $cis\text{-}M(\text{AA})_2\text{X}_2$, $cis\text{-}M(\text{AA})_2\text{XY}$, and $cis\text{-}M(\text{AB})_2\text{X}_2$ Systems

| $cis\text{-}M(\text{AB})_2\text{X}_2^a$ | $cis\text{-}M(\text{AB})_2\text{X}_2$ | $cis\text{-}M(\text{AA})_2\text{X}_2^b$ | $cis\text{-}M(\text{AA})_2\text{XY}$ |
|---|---------------------------------------|---|--------------------------------------|
| A_1''' | A_1'' | A_1 | A_1' |
| | A_3'' | | A_4' |
| | | A_2a | A_2' |
| A_3''' | A_4'' | A_2b | A_6' |
| | | A_3 | A_3' |
| A_2''' | A_5'' | | A_5' |
| | A_2'' | | A_7' |
| A_4''' | A_6'' | A_4 | A_8' |
| | A_8'' | | A_{11}' |
| | | A_5a | A_9' |
| A_6''' | A_9'' | A_5b | A_{13}' |
| | | A_6 | A_{10}' |
| | A_7'' | | A_{12}' |
| A_5''' | A_{10}'' | | A_{14}' |

^a Case where the X ligands do not function as NMR probes.
^b See text for the meaning of A_{2a} , A_{2b} , A_{5a} , and A_{5b} .

related with those of another system for which a unique choice is not possible. The correlation may lend support, for example, for the preference of one averaging set over another, despite the fact that they might be NMR indistinguishable.

A tacit assumption involved in the above argument is that differences in the nature and in the various combinations of ligands are not sufficiently great so as sterically or electronically to force a particular member of the series in Table XII to undergo a physical rearrangement process radically different from those of other members of the series.

Topological and mechanistic analyses carried out on the three general systems reported here, as well as the application of the present permutational analysis to environmental averaging processes in complexes of the above types incorporating both diastereotopic and nondiastereotopic probes, will be presented in forthcoming publications.⁴²

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 - (40) Two other diastereomers exist which possess mutually trans X groups.
 - (41) Diastereomers are referred to by three *cis* or *trans* prefixes which specify the relative orientations of the X, R₁, and R₂ groups in that particular sequence.
 - (42) D. G. Bickley and N. Serpone, to be submitted for publication.

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Additions of Alcohols to Simple Nitriles Coordinated to the Cationic Pentachlorophenylnickel(II) Moiety. Isolation of Imidate Complexes

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Cationic pentachlorophenylnickel(II) complexes, *trans*-[C₆Cl₅Ni(P)₂NCR]⁺ClO₄⁻ (P = PPhMe₂, PPh₂Me; R = Me, CH₂Ph, Ph), **2**, prepared from *trans*-C₆Cl₅Ni(P)₂Cl, silver perchlorate, and nitriles in benzene were treated with methanol or ethanol in the presence of triethylamine, to yield the corresponding imidate complexes, *trans*-[C₆Cl₅Ni(P)₂NH=C(R)OR']⁺ClO₄⁻, **3**, identified by ir and ¹H NMR spectra and elemental analyses. The ¹H NMR spectra revealed the products obtained from **2** (P = PPhMe₂) to be mixtures of complexes **3** containing isomeric imidate groups. The major isomer (P = PPhMe₂, R = Ph, R' = Me) was shown by ¹H NMR spectroscopy to be the *cis* adduct. Complex **2** (P = PPhMe₂, R = Me) readily undergoes substitution of the acetonitrile ligand with Br⁻, I⁻, NCS⁻, OOCMe⁻, and P(OMe)₃.

Introduction

In recent years there has been considerable interest in addition of water or of alcohols to a nitrile multiple bond within the coordination sphere of metal ions.¹ The initial step is thought to involve nucleophilic attack of an external or coordinated hydroxide or alkoxide anion on the nitrile carbon atom. Such intermediate imidate complexes have been isolated from reactions of 2-cyanopyridine complexes,² of perfluorobenzonitrile complexes,³ and of *o*-cyanobenzylplatinum

complexes,⁴ but few simple nitrile complexes seem to be known except for rhenium-acetonitrile complexes.⁵ In connection with our current research program concerning the syntheses and reactions of cationic organonickel(II) complexes, we report here the synthesis of simple nitrile complexes and their reactions with alcohols in an attempt to isolate the corresponding imidate complexes.

Results and Discussion

Preparation of Nitrile Complexes, *trans*-[C₆Cl₅Ni-