Finally, the two colored Zn(II)–TX complexes have, undoubtedly, unusual structures. The yellow Zn(II) complex involves bidentate TX ligands (*vide supra*) and may be either polynuclear with bridging TX groups in the chair conformation or monomeric with chelating TX ligands in the boat conformation; distinction between the chair and boat conformation of TX is rather unlikely because of their low basic symmetry ($C_s$).[7] It is, however, noteworthy that in the only yellow Zn(II) complex with DX the ligand is in the boat conformation.[13] A white polymeric analog of this compound, involving bridging DX groups has also been reported.[2a,3] It is, thus, possible that the yellow Zn(II) complex involves a monomeric complex cation involving two chelating TX groups in the boat conformation and two aquo groups and coordination number six for the Zn(II) ion. In the rest of the TX and in the DX complexes reported, the ligands apparently retain the more stable chair conformation. The formation of an intensely red colored complex of Zn(II) with a colorless ligand[36] was quite unexpected. The limited solubility of this complex in nitromethane may be indicative of a polymeric structure. In addition, the fact that the red compound forms colorless solutions in organic solvents demonstrated that the structure responsible for the red color is stable only in the solid state. An analogous case reported in the literature is the red polymeric complex of Sn(IV), formed during reduction of benzene-1,2-disulfonyl chloride with tin and hydrochloric acid.[37] In fact, this polynuclear compound, which involves bridging S ligands, exhibits a visible spectrum similar to that of the red Zn(II) complex (Table III, Figure 3) and forms colorless solutions in the organic solvents in which it is soluble.[37] Further, monomeric Sn(IV) complexes with analogous sulfur ligands are colorless.[37] The assignment of a bi- or polynuclear structure involving both terminal and bridging monodentate TX groups acting exclusively as S ligands (*vide supra*) to the red Zn(II) complex is justified from the above discussion. The yellow Zn(II) compound is, therefore, formulated as $[Zn(TX)_2(OH_2)_2](ClO_4)_2$ and the red complex as $[Zn(TX)_2(OH_2)_2]_n(ClO_4)_{2n}$ ($n = 2$ or higher).

(36) J. Barrett and M. J. Hitch, *Spectrochim. Acta, Part A*, **25**, 407 (1969).

(37) R. C. Poller, *Proc. Chem. Soc.*, 312 (1963), and references therein.

---

CONTRIBUTION FROM THE BELFER GRADUATE SCHOOL OF SCIENCE,
YESHIVA UNIVERSITY, NEW YORK, NEW YORK 10033

# Modes of Intramolecular Rearrangement in Octahedral Complexes

BY JEREMY I. MUSHER

*Received November 1, 1971*

The types or modes of rearrangement of an octahedral complex are examined in detail. The behavior of tris-chelate complexes under each of these modes is considered and recent nmr experiments on $M(AB)_3$ complexes are interpreted in terms of split modes. It is pointed out that the experiments cannot distinguish between a mode of rearrangement which involves racemization and one which does not.

## 1. Introduction

Intramolecular rearrangements in octahedral complexes have been of interest since the time of Werner[1] and recent experiments,[2-12] mainly using nmr, have prompted the analysis of some of the possible mechanisms involved.[1c,13-15] There has, however, been no general description in the literature of *all* the theoretically possible rearrangements[16] so that no unambiguous analysis of the experiments could be carried out.

The present article is concerned with an enumeration of all the physically distinguishable intramolecular rearrangements of an arbitrary octahedral complex in which the nature of the individual ligands is assumed to be of secondary importance. The argument follows precisely the argument given previously[17] for trigonal-bipyramidal molecules and is based on the description of intramolecular rearrangements of molecules with skeletons possessing any symmetry whatsoever in terms of sets of like processes or "modes of rearrangement." A mode of rearrangement refers to a class of stereoisomerizations in which the relative orientation of a certain subset of all the ligands changes. Thus each mode of rearrangement can be defined as a class of rearrangements in which $x$ ligands retain their rela-

(1) (a) A. Werner, *Ber.*, **45**, 3061 (1912). For general discussions see (b) F. Basolo, *Chem. Rev.*, **52**, 459 (1953); (c) J. C. Bailar, Jr., *J. Inorg. Nucl. Chem.*, **8**, 165 (1958); (d) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," Interscience, New York, N. Y., 1966, Chapter 5; (e) J. A. Broomhead, M. Dwyer, and A. Meller, *J. Chem. Educ.*, **45**, 716 (1968); (f) K. Mislow and M. Raban, *Top. Stereochem.*, **1**, 1 (1967).

(2) R. C. Fay and T. S. Piper, *Inorg. Chem.*, **3**, 348 (1964).

(3) J. J. Fortman and R. E. Sievers, *ibid.*, **6**, 2022 (1967).

(4) J. G. Gordon, II, and R. H. Holm, *J. Amer. Chem. Soc.*, **92**, 5319 (1970).

(5) R. C. Fay, A. Y. Girgis, and U. Klabunde, *ibid.*, **92**, 7056 (1970).

(6) A. Y. Girgis and R. C. Fay, *ibid.*, **92**, 7061 (1970).

(7) L. H. Pignolet, R. A. Lewis, and R. H. Holm, *ibid.*, **93**, 360 (1971).

(8) J. R. Hutchison, J. G. Gordon, II, and R. H. Holm, *Inorg. Chem.*, **10**, 1004 (1971).

(9) B. Jurardo and C. S. Springer, Jr., *J. Chem. Soc., Chem. Commun.*, 85 (1971).

(10) P. Meakin, E. L. Muetterties, F. N. Tebbe, and J. P. Jesson, *J. Amer. Chem. Soc.*, **93**, 4701 (1971).

(11) S. S. Eaton and R. H. Holm, *ibid.*, **93**, 4913 (1971).

(12) M. C. Palazzotto and L. H. Pignolet, *J. Chem. Soc., Chem. Commun.*, 6 (1972).

(13) P. Râу and N. K. Dutt, *J. Indian Chem. Soc.*, **20**, 81 (1943).

(14) C. S. Springer, Jr., and R. E. Sievers, *Inorg. Chem.*, **6**, 852 (1967); see also J. Brady, *ibid.*, **8**, 1208 (1969).

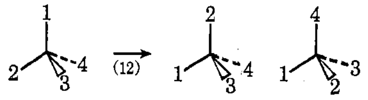
(15) E. L. Muetterties, *J. Amer. Chem. Soc.*, **90**, 5097 (1968); **91**, 1636 (1969).

(16) After this article was completed, we received from Professor M. Gielen a copy of his study which gives such an analysis although it does not discuss any of the experimental results. This analysis has not been referred to in any of the aforementioned experimental analyses. We are grateful to Professor Gielen for his kindness in calling this to our attention and also for having sent a preprint of his review article scheduled to appear in "Graph Theory," A Balaban, Ed., Academic Press, New York, N. Y., 1972. [M. Gielen and N. Vanlauten, *Bull. Soc. Chim. Belg.*, **79**, 679 (1970).]

(17) J. I. Musher, *J. Amer. Chem. Soc.*, **94**, 5662 (1972).

tive configuration (*e.g.*, their relative locations on an octahedral skeleton) while $6 - x$ ligands rearrange in some unique and well-specified manner. The various sigmatropic shifts in organic chemistry taken as classes, each independent of the organic substituents along the chain, are examples of modes of rearrangements in the sense used here.

Perhaps the simplest example of a mode of rearrangement is the racemization which occurs about a tetrahedral carbon atom as there are only two distinguishable isomers of $CR_1R_2R_3R_4$. If the tetrahedral skeleton is considered fixed in space as in **1**, then there are $4! = 24$ unique ways of assigning the ligands to skeletal



**1** **2** **3**

sites and thus 24 "operations" including the identity which can permute these indices and 24 apparent isomers. Of course, these 24 apparent isomers are 12-fold redundant due to the $4 \times 3 = 12$-fold rotational degeneracy of the tetrahedral skeleton. As we are concerned with the *unique* set of (two) chemical isomers, we simply group together all operations which take **1** into itself which we call the identity mode, $M_0$, and group together all operations which take **1** into **2** or into any of its 12 rotationally equivalent structures which we call the racemization mode, $M_1$. We can write this symbolically as

$$M_0(1) = I, l_3{}^8, l_2 \times l_2{}^3$$
$$M_1(1) = l_2{}^6, l_4{}^6$$

where $l_n$ indicates an $n$-cycle (*e.g.*, the permutation (12) which takes **1** into 2 is a 2-cycle), $l_2 \times l_2$ indicates the disjoint product of 2-cycles, I indicates the identity, the superscript indicates the number of times the cycle occurs to give the same rotationally indistinguishable isomer, and the ones in parentheses mean that rearrangement according to each mode gives only one isomer. Thus, for example, the 4-cycle (1234) takes **1** into **3** which is seen to be equivalent to **2** by rotating it about the C–R$_1$ axis.

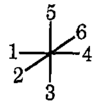
The mathematical structure underlying this analysis is that of double cosets and can be found in the descriptions of Ruch, *et al.*,[18] and of Klein, *et al.*[19] For our problem, in which only six ligands are involved, the nonmathematical "brute force" derivation used here is, however, sufficiently simple to be the most practicable.

In the next section we describe the five different modes of rearrangement for octahedral molecules which are each best remembered in terms of one of their permutations. These modes are thus $M_0(1)$, the identity, $M_1(12)$ a cis exchange, $M_2(1)$ a trans exchange, $M_3(8)$ a trigonal twist, and $M_4(8)$ a concerted triple of cis exchanges. The special case of rearrangements in trischelated complexes, which has provided the most extensive experimental investigations, is examined in the following section where it is pointed out that nmr evidence alone cannot always distinguish the mode unambiguously.

The goal of this type of analysis is to ascertain the exact stereochemistry of an observed rearrangement, for which the discussion of modes of rearrangements is only a preliminary step. When the actual stereochemistry of the rearrangement can be established as has not yet been done in the literature for a single example, it will be necessary to go still further and analyze the possible mechanisms giving rise to the observed stereochemistry.

## 2. Theory

We consider the number of distinguishable ways that the labeled ligands of an octahedral molecule **4** can be rearranged among themselves. These will be divided



**4**

into sets or modes of rearrangements each of which retains the relative configuration among a certain number of the ligands, where of course all rearrangements which give rise to rotationally indistinguishable products are associated with the same mode. We assume for simplicity that the energetics of the motions involved are essentially independent of the nature of the ligands and depend principally on the relative orientations. This is a reasonable hypothesis which serves to define the problem and which is later easily relaxed as in the following sections.

The procedure for constructing all the modes is the following. First we write out the $6! = 720$ permutations of the indices of **4**; second we collect together the 24 permutations which give indistinguishable isomers when rotations of the skeleton are permitted; and third we observe which of the 30 resultant sets of permutations contain individual permutations corresponding to physically similar processes, *e.g.*, trigonal twists,[1c] and call the sets of such sets *modes of rearrangement*. Actually the structure of the results is such that the complete description of the modes can be worked out by hand in 1 hr without having to write out all 720 permutations. Thus, for example, it is easily seen that there are 12 permutations of two ligands cis to each other each of which gives a different, distinguishable isomer. It is therefore necessary to write out only the 24 rotationally indistinguishable isomers of *one* of these rather than the 24 such isomers for all 12 cis-exchange products.

If we denote the permutation of two ligands cis to each other by cc, the permutation of two ligands trans to each other by tt, the permutations of three ligands on the corners of the T-shaped structure formed from two collinear bonds plus a third by cct, etc., then we can specify the resultant five modes, including the identity by the 24 equivalent permutations as

$$M_0(1) = \mathrm{I, eeee^6, tt \times tt^3, con\text{-}ccc \times ccc^8, cc \times cc \times tt^6}$$

$$M_1(12) = \mathrm{cc, cct^2, cc \times tt, ctct, tt \times cct^2, cc \times ccc^4, c_5{}^4, cc \times ccct^4, tt \times ctct, ccccct^4}$$

$$M_2(1) = \mathrm{tt^3, ee \times ee^6, tt \times cccc^6, tt \times tt \times tt, sym\text{-}c_6{}^8}$$

$$M_3(8) = \mathrm{ccc^2, cccc^3, cctct^6, cc \times cct^6, dis\text{-}ccc \times ccc, cc \times cccc^3, cctcct^3}$$

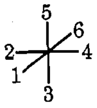
$$M_4(8) = \mathrm{cc \times cc^3, ccct^6, cccct^6, cc \times cc \times cc, cct \times cct^3, ctctct^2, nonsym\text{-}c_6{}^3}$$

---

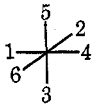
[18] E. Ruch, W. Hasselbarth, and R. Richter, *Theor. Chim. Acta*, **19**, 288 (1970).

[19] D. J. Klein, C. H. Carlisle, and F. A. Matsen, *Advan. Quantum Chem.*, **5**, 219 (1970).

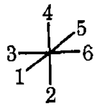
The number of different isomers which can be constructed according to each mode is given in parentheses and the number of identical isomers which can be made from the same process is given as a superscript. The notation $M_1(12)$ indicates that 12 distinct isomers can be made from **4** by a cis exchange, *e.g.*, **5** made by the permutation (12); $M_2(1)$ indicates that a unique isomer can be made from **4** by a trans exchange, *e.g.*, **6** made by (26), equivalent to the results of the other tt processes (14) and (35); $M_3(8)$ indicates that eight distinct isomers can be made from **4** by the eight different disrotatory ccc×ccc processes (note that both the trigonal twist, ccc, and the generalization of the Rây–Dutt twist,[13,14] cccc, do not give unique isomers, there being 16 of the former and 24 of the latter, so that these "mechanisms" are less useful in denumerating isomers), *e.g.*, **7** made by (123)(456); and $M_4(8)$ indicates the eight distinct isomers that can be made from **4** by the eight different concerted triples of cis exchanges, cc×cc×cc, *e.g.*, **8** made by (12)(34)(56). The total number of processes for each mode is 24 (counting, for example, $tt^3$ as three) while the total number of distinguishable isomers is $6!/24 = 30$. The few operations in the listing which would otherwise appear ambiguous are indicated as follows: the four-ligand all-cis permutations are separated into those in which all four ligands are in an equatorial plane, eeee and ee×ee, and those in which they are not, cccc and cc×cc. The con and dis in the two ccc×ccc permutations refer to the conrotatory and disrotatory senses of the two threefold rotations; and the sym and nonsym in the two $c_6$ = cccccc permutations refer to the symmetric and nonsymmetric ordering of the apical pairs, an example of each being (654231) and (563421), respectively, operating on **4**.



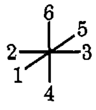
**5**



**6**

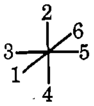


**7**



**8**

The listing of all the processes for a given mode might look like a useless excercise since it contains unnecessary information when molecular rotations are allowed. The listing does, however, serve to provide a series of exactly equivalent rearrangements each of which can be (arbitrarily) used as a model for visualizing the actual physical mechanisms.[17] Thus, for example, the $M_1$ rearrangement which was described as a pairwise cis exchange (12) giving **5** could equally well be described as the five-ligand permutation (12543) giving the rotated identical isomer **9**. If the permutations are visualized as *mechanisms* for the rearrangements, then (12) describes a process which looks to be of higher energy than that of the concerted motions of five ligands described by (12543). Of course, these modes are defined to describe stereochemical changes which are, at least in principle, observable so that they are in a sense *independent of mechanism;* thus they do not distinguish among any of these mechanisms, nor for that matter do they distinguish between bond-rupture and non-bond-rupture intramolecular mechanisms in chelate complexes.



**9**

We should note that this consideration of modes rests on the rather plausible assumption that the steric effects which govern the rearrangement pathways are dominated by the motions of the six arbitrary ligands moving about the central atom. The more specific steric effects due to the nature of the ligands are assumed to be secondary in their contribution except when they are polydentate and absolutely exclude certain isomers. All of our ideas of stereochemistry are in accord with the validity of such a postulate and this permits us to assume some order considering the $(30 \times 29)/2 = 435$ different rearrangements of an octahedral complex with all different ligands which, however, in no way introduces any restrictions to the conclusions to be drawn. The overall situation is simple enough when chelating constraints are involved or when any of the ligands are identical. In the next section all the rearrangements are easily considered explicitly (except for chelate conformations[20]).

We do consider it reasonable to assume that the activation energies for stereospecific rearrangements among isomers of an octahedral complex cluster, to some extent, together according to their modes of rearrangement, and the spread of most of the energies within a mode can often be smaller than the differences in energies between modes. The mode or modes which correspond to the most energetically favorable mechanism may, of course, be different for different metal atoms, oxidation states, chelate ring sizes, etc., as different mechanisms can be relatively favored or hindered depending on the explicit nature of the complex. Furthermore, it should not be forgotten that we *never* make the assumption that two distinct rearrangements belonging to the same mode have the same energetics.

## 3. Tris-Chelated Complexes

The study of tris-chelated complexes is greatly facilitated by having a complete listing of all possible isomerizations and particularly by having such a listing according to modes. Of the 30 possible isomers of an arbitrary octahedral complex, 14 are excluded in tris chelates when trans rings are excluded. The remaining 16 isomers are divided into Δ–Λ pairs[1] according to the helicity of the chelating rings. Rearrangements under each of the modes will affect the molecular asymmetry in a unique way—for example, a Δ or Λ configuration will be retained under $M_4$ rearrangements—and the analysis is presented in Table I.

When the chelating rings are identical nonsymmetric bidentate ligands in structures denoted as $M(AB)_3$, there are only four distinguishable isomers which occur in Δ–Λ and in cis–trans pairs when conformational preferences within the chelating rings themselves[20] are neglected. The behavior of these isomers under a single-step rearrangement belonging to each mode is easily worked out from the description above and the results are summarized in Table I.

Rearrangements in $M_3$ provide *all* the mechanisms not involving bond rupture generally considered[14] for octahedral complexes and all involve taking a Δ or a

[20] E. J. Corey and J. C. Bailar, Jr., *J. Amer. Chem. Soc.*, **81**, 2620 (1959).

TABLE I

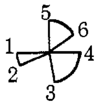
REARRANGEMENTS OF TRIS-CHELATE COMPLEXES

| Mode | Split mode | No. of isomers | Unique description[a] | Chelate asymmetry | $M(AB)_3$ geometrical confign |
|---|---|---|---|---|---|
| $M_1$ | | 6 | cc | Racemate | Cis → trans; trans → [$^2/_3$ trans, $^1/_3$ cis] |
| | $M_1'$ | 3 | cyc-cc | | |
| | $M_1''$ | 3 | noncyc-cc | | |
| $M_2$ | | 1 | tt×tt×tt | Enantiomer | Retained |
| $M_3$ | | 4 | dis-ccc×ccc | Enantiomer | Statistical |
| | $M_3'$(r-$C_3$/p-$C_3$)[b] | 1 | noncyc-ccc | Enantiomer | Retained |
| | $M_3''$(i-$C_3$)[b] | 3 | cyc-cc | Enantiomer | Cis → trans; trans → [$^2/_3$ trans, $^1/_3$ cis] |
| $M_4$ | | 4 | cc×cc×cc | Retained | Statistical |
| | $M_4'$ | 1 | $(\text{cyc-cc})^3$ | Retained | Retained |
| | $M_4''$ | 3 | $(\text{cyc-cc})^1$ | Retained | Cis → trans; trans → [$^2/_3$ trans, $^1/_3$ cis] |

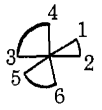
[a] The cyc-cc in the split modes descriptions refers to two cis ligands being in the same cycle. See also the description in the text.
[b] The r-$C_3$/p-$C_3$ and i-$C_3$ refer to the real, pseudo, and imaginary $C_3$ axes of $M(AB)_3$ complexes in the notation of Springer and Sievers.[14]

Λ molecule into its corresponding Λ or Δ diastereomer while taking a pure cis or pure trans isomer into the statistical distribution of trans:cis = 3:1. The rearrangement in $M_2$ also gives the diastereomer with an enantiomeric chelate skeleton (called "enantiomer" for simplicity) but preserves the geometrical configuration. On the other hand, rearrangements in $M_4$ preserve the Δ or Λ configuration of the chelating rings while also giving the statistical trans:cis distribution. $M_1$ also gives the statistical distribution of cis and trans isomers except that this is done in a stereospecific way, *e.g.*, a cis molecule will rearrange solely to a trans molecule, so that the apparent rate of equilibration is not the rate for a single-step process. Similarly, the relative rate of enantiomerization of $M_1$ will be half that of $M_2$ and $M_3$ since it takes a sample of pure optically active dissymmetric molecules into a racemic mixture in one step, half of the products retaining the original helicity and half becoming enantiomers. (By a step we mean a single forward reaction in which only products are obtained while, of course, the actual reaction permits the reactants to be obtained in equal probability. The argument should be easier to follow in the present complicated problem with this definition.)

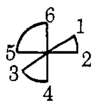
The nature of the constraints imposed by the chelating rings is such that we can classify structure within the modes. Thus, for example, rearrangements in $M_3$ can be divided into two groups which we refer to as submodes or split modes. The first of these, $M_3'$, requires the three ligands in each threefold twist of dis-ccc×ccc to belong to different rings; there is one such twist, the permutation (163)(245), which takes **10** into **11**, and for $M(AB)_3$ systems this corresponds to rotations about real $C_3$ and pseudo $C_3$ axes for the cis and trans isomers in the notation of Springer and Sievers.[14]



**10**



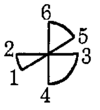
**11**



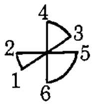
**12**

The second of these, $M_3''$, has two of the ligands in each twist belonging to a single chelate ring; there are three rearrangements of this split model, an example of which is (243)(165) which takes **10** into **12**, and all of these are rotations about imaginary $C_3$ axes.

In the same way, $M_4$ can be divided into split modes, the first of which, $M_4'$, takes all three cc twists of cc×cc×cc to be within individual rings, *i.e.*, (12)(34)(56) which takes **10** into **13** the enantiomer of **11**. The second of these split modes, $M_4''$, has three rearrangements in all of which only one cc twist is within a single ring, *e.g.*, (12)(54)(36) which takes **10** into **14** the enantiomer of **12**. The rearrangements of a *trans*-$M(AB)_3$ complex *via* the two different split modes $M_3'$ and $M_4'$ to enantiomers with retention of the trans configuration is shown in Figure 1 and further details are given in Table I. From the figure it can be appreciated that only nmr experiments which can measure directly changes in molecular chirality are capable of differentiating between the two types of processes.



**13**



**14**

It should be noted here that by excluding from consideration the trans-linked chelate rings at the beginning of this section we had already, in effect, split the modes. Thus we might have described Table I as incorporating two levels of mode splitting: the first in which all trans chelates are excluded and the second in which the cycle structure of the cis-chelate rings is taken into account.

We consider now the recent experiments of Holm, Pignolet, and coworkers[7,11,12] on rearrangements in tris-chelated complexes. Temperature-dependent nmr studies have been carried out in organic solvents on the $M(AB)_3$ complexes tris($\alpha$-isopropenyltropolonato)cobalt(III) ($Co(\alpha\text{-}C_3H_5T)_3$),[11] tris($\alpha$-isopropenyltropolonato)aluminum(III),[11] and tris(*N*-methyl-*N*-phenyldithiocarbamato)iron(III) (Fe(Me,Ph-dtc)$_3$).[12] In all of these experiments two rearrangements were observed: a low-temperature process (LTP) which equilibrated two out of the three peaks in the trans isomers while not affecting the single cis-isomer peak and a high-temperature process (HTP) which equilibrated cis and trans isomers. The experiment can be interpreted by associating the LTP with the $M_3'$ rearrangement[11,12] which retains cis and trans configurations and by associating the HTP with the $M_3''$ rearrangements which cause equilibration among cis and trans isomers; it is not unreasonable to suppose that the activation energies for the two $M_3$ processes be relatively similar but not equal. However, as the HTP is not stereospecific, this interpretation is conjectural and merely a possible alternative to the rotation about the

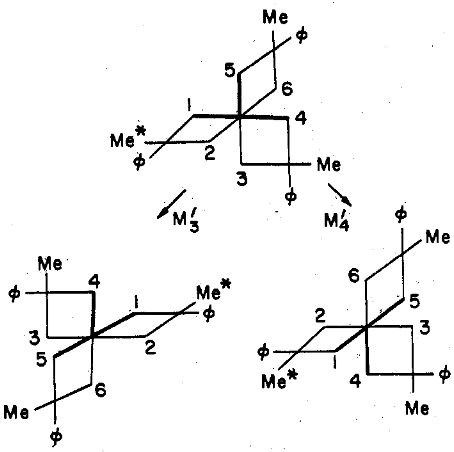


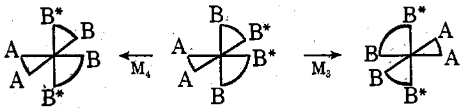
Figure 1.—Rearrangements of *trans*-tris(*N*-methyl-*N*-phenyldithiocarbamato)iron(III) according to split modes $M_3'$ and $M_4'$ to give enantiomers. Notice how both rearrangements preserve the trans orientation of the methyl groups as indicated by the boldface line and keep the starred methyl groups in identical magnetic environments.

C–N bond proposed previously and observed in other systems. The LTP of $M_3'$ is shown in Figure 1 where bold lines indicate the bonds to the three like ligands. It can be seen that the starred methyl group is not equilibrated by the rearrangement in that it remains in a plane perpendicular to the plane of the boldface "T" in both isomers, whereas the other two methyls do equilibrate among themselves. The analogous figure for the cis isomer is not necessary as all the substituents are equivalent in the first place.

It can be seen, however, that all the same experimental data can be interpreted by the analogous split-mode rearrangements in $M_4$ in which enantiomerization of the chelate ring structure does not occur. This can be recognized by examining the split-mode $M_4'$ rearrangement indicated in Figure 1 wherein again the starred methyl remains unique while the other two equilibrate between themselves. The nmr spectra of these planar chelate ring systems *cannot* differentiate between rearrangements according to the two split modes $M_3'$ and $M_4'$ so that there exists an *ambiguity* which only the simultaneous observation of a change in chirality can resolve. A similar ambiguity has already been noted[17] with reference to the nmr spectra of $(CH_3)_2NPF_4$ which are consistent with *two* stereochemically different rearrangements due to the magnetic equivalence of the fluorine atoms in pairs. The same ambiguity occurs in the very recent experiment of Meakin, *et al.*,[10] on the *cis*-$FeH_2[P(OC_2H_5)_3]_4$ complex.

Unfortunately all the experiments in which enantiomerization of the chelate skeleton is observed directly, *i.e.*, on tris(5-methylhexane-2,4-dionato)cobalt(III)[4] and on the tris(acetylacetonates) of Co(III), Cr(III), Ru(III), and Rh(III),[5] involve much slower processes that are best interpreted in terms of nonstereospecific bond-rupture mechanisms so that the observed enantiomerizations do not bear useful analogy to the non-bond-breaking rearrangements studied by nmr. The much faster rates observed for the intramolecular rearrangements in $Co(\alpha\text{-}C_3H_5T)_3$ and $Fe(Me,Ph\text{-}dtc)_3$ could be due to the relative favoring of entirely different mechanisms. For example, certain mechanisms to intramolecular rearrangement without bond breaking might have prohibitively high barriers in the six-membered rings which could be reduced to the observed ~15 kcal/mol in the four- and five-membered rings by the strain involved.

The experiments of Fortman and Sievers[3] on the equilibrations of $Al(AA)(BB)_2$ compounds, with AA, BB = 2,2,6,6-tetramethyl-3,5-heptanedione and 2,4-pentanedione, are also subject to the same ambiguity. Molecule **15** can rearrange to **16** *via* $M_3$ which exchanges B and B* proton resonances while racemizing, but it can also rearrange to **17** *via* $M_4$ which exchanges B and B* without racemizing. The same argument applies to the studies of LaMar[21] on (4,7-dimethyl-1,10-phenanthroline)bis(acetylacetonato)cobalt(II), to those of Hutchison, *et al.*,[8] on tris(1-phenyl-5-methylhexane-2,4-dionato)aluminum(III) and -gallium(III), and to those of Muetterties and Alegranti[22] on tris(α-isopropyltroponato)aluminum(III).[23] Furthermore, we have not even demonstrated the stereochemistry-retaining character of the $M(AB)_3$ rearrangements; they can also occur *via* mode $M_1$ which exchanges B and B* directly.



**17** **15** **16**

The studies of Jurado and Springer,[9] on the other hand, do prove racemization as the compound $Al(acac)_2$(dibm), with dibm = 2,6-dimethylheptane-3,5-dionato, contains two diastereotopic methyl groups on each of the isopropyl functionalities. These can then equilibrate only in a process involving enantiomerization. However, again here we know nothing of the stereochemistry-retaining character of the rearrangement; any of the modes $M_1$, $M_2$, and $M_3$ which give racemization could be involved.

This discussion should serve to emphasize the unique character of the trans-$M(AB)_3$ chelates studied whose LTP equilibration provides a demonstration of stereospecificity which is otherwise highly elusive when spinless nuclei such as $^{16}O$ and $^{32}S$ are directly bonded to the metal atom. Clearly the proper type of system to study would combine the *trans*-$M(AB)_3$ system with the diastereotopic isopropyl groups of Jurado and Springer, an example of which for four-membered chelating rings is tris(*N*-α-deuterioisopropyl-*N*-phenyldithiocarbamato)iron(III).[23,24] It is worth noting that it is not trivial to design the analogous experiment to establish definitively the mode of rearrangement in trigonal-bipyramidal molecules[17] since, in the absence of a highly doped $^{13}C$ species, the phosphoranes are either achiral or, due to small $^3J_{PH}$'s, effectively achiral.

The understanding of the behavior of the rearrangements indicated in Table I can, however, serve to ex-

---

[21] G. N. LaMar, *J. Amer. Chem. Soc.*, **92**, 1806 (1970).

[22] E. L. Muetterties and C. W. Alegranti, *ibid.*, **91**, 4420 (1969).

[23] The tris(α-isopropyltroponato)aluminum(III) of ref 22 has been restudied by Holm and Muetterties (personal communication from R. H. Holm) and their results are in accord with the original assumption that enantiomerization occurs during the rearrangement. Thus the rearrangement occurs *via* $M_3'$, and not *via* the configuration-retaining $M_4'$, which could not be excluded experimentally by the earlier data.

[24] NOTE ADDED IN PROOF.—A related compound, although of iron(IV), has been studied recently by D. H. Duffy and L. H. Pignolet (to be published). This shows the rearrangment to take place *via* $M_3'$ in the case of the positive ion. The author is grateful to Dr. Pignolet for having sent him a preprint of this work.

plain the observation of an apparent lower activation energy for "enantiomerization" in the last two of these compounds[9,22] that is observed for the cis–trans isomerization. A set of unsplit or weakly split $M_3$ or $M_4$ processes will give statistical isomers in one step, but will equilibrate the two A sites (*i.e.*, racemize in $M_3$) in half a step, so that the apparent rates can differ by a factor of 2. However, further studies are required on these systems to ascertain if there is really any stereospecific character to justify such an interpretation.

The experiments of Pignolet, Lewis, and Holm[7] on $Fe(Me,Ph(dtc))_2(tfd)$, where tfd = $-S[C_2(CF_3)_2]S-$, can also be interpreted as either of the split-mode processes $M_3'$ or $M_4'$. Similar to the case of the tris chelates discussed above the HTP could be speculatively associated with an intramolecular rearrangement of split modes $M_3''$ or $M_4''$ as an alternative to the C–N bond rotation.

In concluding this section we would note that the present discussion has been limited to a consideration of the modes of rearrangement and to the explicit rearrangement within the modes; individual mechanisms that can produce the various stereochemistries have not been considered at all. The problem of analyzing mechanisms is highly complex as can be seen by the discussion of Holm and coworkers[8] for some mechanisms in $M_3'$ alone. Without extensive further research we could clearly not do justice to the various conceivable mechanisms for the remaining modes. Such an analysis we leave for a future study after which one might be able to make a comparison of the energetics for the most favorable mechanisms which give rise to other stereochemistries for different metal atoms and different types of substituents.

## 4. Conclusions

We have demonstrated here the different modes of rearrangement which an octahedral complex can undergo. The theory has been applied to the special case of tris-chelate complexes and has permitted a complete analysis of the recent experimental results. It would have been most convenient were all octahedral molecules to undergo intramolecular rearrangements according to the same preferred mode or modes, such that the variation in metal atoms or ligands would not significantly change the *ordering* of the energetics of the different preferred pathways which give the stereochemistry of each of the modes. Unfortunately there is no reason to expect that such would be the case, and a comparison of the results of section 3 with those for $H_2ML_4$ complexes[10] which rearrange according to a split $M_1$ mode—although, as mentioned above, these authors are unable to distinguish between *two* stereochemically different arrangements—provides a counter example to such an argument. In the present article we have provided a framework within which all experiments can be analyzed without concern that possible types of processes have been overlooked.

For those who believe in the efficacy of nonempirical or semiempirical molecular calculations it would be a worthwhile task to search the multidimensional configuration space for some six-coordinate complex, or even a metal hexahydride. The unbelievably many possible pathways might be effectively reduced without much loss of information by starting off the rearrangement along the direction of the various different permutations corresponding to any given mode. It is in this sense that the different permutations can serve as aids in visualizing the actual mechanism which gives the rearrangement. It should not be forgotten, of course, that the mechanism may well go through an intermediate or transition state which makes more than one mode possible. The limiting case of this would give all isomers in equal probability and would be a complete scrambler of all relative configurations.

**Acknowledgments.**—This research has been supported in part by the Office of Naval Research, the National Science Foundation, and the North Atlantic Treaty Organization.

---

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
BOWDOIN COLLEGE, BRUNSWICK, MAINE 04011

# Complexes of Bridged Diphosphinothioyl Chelates[1]

BY DAVID A. WHEATLAND,* CHARLES H. CLAPP, AND RICHARD W. WALDRON

*Received February 24, 1972*

A series of bridged diphosphinothioyl bidentate ligands has been synthesized and several have been found to form stable complexes with a number of "class b" metal halides. The infrared spectra indicate that the ligands form six-membered ring chelates by coordination *via* both thiophosphoryl donor sites. The sulfur-bridged ligands undergo cleavage to yield phosphorodithioate complexes.

## Introduction

There has been considerable interest in studying metal complexes with bidentate chelating ligands containing donor thiophosphoryl groups. Tetraalkyldiphosphine disulfides have been reported to form five-membered chelate ring complexes with a variety of metals.[2–8] Complexes with anionic "imidodiphos-

---

[1] Financial support from the Petroleum Research Fund, administered by the American Chemical Society under Grant No. 1363-G3, is gratefully acknowledged.

(2) D. W. Meek and P. Nicpon, *J. Amer. Chem. Soc.*, **87**, 4951 (1965).

(3) H. Teichmann, *Angew. Chem.*, **77**, 809 (1965).

(4) K. Baker and G. W. A. Fowles, *J. Less-Common Metals*, **8**, 47 (1965).

(5) M. Arshad, A. Beg, and K. S. Hussain, *Chem. Ind.* (*London*), 1181 (1966).

(6) M. Arshad, A. Beg, and S. H. Khawaja, *Spectrochim. Acta, Part A*, **24**, 1031 (1968).

(7) V. W. Hieber and K. Kaiser, *Z. Anorg. Allg. Chem.*, **358**, 271 (1968).

(8) V. W. Hieber and K. Kaiser, *ibid.*, **362**, 169 (1968).