ceptors should decrease the M–M bond strength.[31] Certainly the Mn–Mn bond length in $f_4farsMn_2(CO)_8$ (2.971 (3) Å) is longer than in $Mn_2(CO)_{10}$ (2.923 (3) Å).[17] However, the mechanism of cleavage of $Mn_2(CO)_{10}$ is probably different from that of $Re_2(CO)_{10}$.[30] The iodine complexes $f_4fars[M(CO)_4I]_2$ are unstable and, on heating, give metal carbonyl iodides and the chelate complexes $f_4farsM(CO)_3I$ (M = Mn, Re). This also is an unexpected result in view of the abovementioned reluctance of $f_4$fars to form chelate complexes.[32]

The reactions of $f_4$fos with $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$ produce $f_4fosMn_2(CO)_8$ and $f_4fosRe_2(CO)_8$, respectively. These were identified by elemental analysis and by mass spectrometry. In the case of the rhenium compound the calculated intensities for the parent multiplet, due to the two isotopes of rhenium, agreed very well with the observed spectrum. Since the ^{19}F nmr spectrum of $f_4fosRe_2(CO)_8$ consists of a singlet at 107.8 ppm, we propose a bridged structure similar to that in Figure 1 for it. The ^{19}F nmr spectrum of $f_4fosMn_2(CO)_8$, however, shows two absorptions at 106.5 and 110.1 ppm, indicating that $f_4$fos does not act as a bridging ligand in this case. It is not certain whether it acts as a chelating ligand or it rearranges itself as in Figure 2 with the breaking of a phosphorus–carbon bond, although the former seems more likely.

Acknowledgments.—We thank the National Research Council of Canada for financial assistance and Dr. H. K. Spendjian for discussion on infrared spectra.

[31] C. E. Coffey, J. Lewis, and R. S. Nyholm, *J. Chem. Soc.*, 1741 (1964).

[32] A referee has pointed out that in view of the rather drastic rearrangements of groups involved in these thermal reactions structural assignments based on products of similar degradations may not be reliable. A case in point is the characterization of $Mn_2(CO)_8(o\text{-phen})$ as $(CO)_5MnMn(CO)_3(o\text{-phen})$ because of its photochemical decomposition to $Mn_2(CO)_{10}$ and "$Mn(CO)_3(o\text{-phen})$": W. Hieber and W. Schropp, *Z. Naturforsch. B*, **15**, 271 (1960).

CONTRIBUTION FROM THE MINERALOGICAL INSTITUTE, UNIVERSITY OF MARBURG, MARBURG, GERMANY, AND
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A Nomenclature Symbolism for Chiral and Achiral Isomers of Bridged Inorganic Complexes

BY U. THEWALT,[1a] K. A. JENSEN,*[1b] AND C. E. SCHÄFFER[1b]

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A nomenclature symbolism for bridged inorganic complexes, characterized by an interplay of configurational and conformational chiralities, is described. The complexes are represented by two-dimensional projection formulas containing chirality descriptors (Δ, Λ, δ, λ) which make them three-dimensional as far as their manipulation and symmetry properties are concerned. The symbolism is applied to characterize and enumerate the isomers for dinuclear and tetranuclear skeletons known from X-ray crystallography.

1. Introduction

Many bridged inorganic complexes exist as different isomers caused by different configurations about the central ions combined with different conformations of chelate rings, including those rings involving the bridges. The present paper is concerned with giving account to the different isomers of the above type, in a systematic way, using symmetry considerations, and at the same time proposing a simple nomenclature symbolism, applicable to their classification and the unique specification of individual isomer species.

The number of structures, that one can think of, is immense, and this paper, therefore, does not attempt to cover the subject exhaustively. Rather, it takes as its starting point certain bridged complexes, which have been illucidated by structure analyses, and uses these to illustrate the way of going about the augmentation of the standard nomenclature for their skeletons.[2]

A recent IUPAC publication[2b,3] proposed the symbols Δ and Λ for characterizing configurational chirality and δ and λ for conformational chirality. These proposals have been adhered to without exception.

In the present paper the basic idea is to represent a given complex by a kind of projection formula which is two dimensional, but which, by replacing the chiral components by the relevant Δ, Λ, δ, λ symbols, becomes effectively three dimensional. Or, in other words, these symbols allow one to build a sterically correct model (from wire, *e.g.*) of the complex under consideration. It is important that this extended projection formula exhibits the same three-dimensional symmetry properties as the complex it represents.

2. Illustration of Principles

In order to clarify at the outset the interplay of configurational and conformational chiralities to give rise to diastereoisomerism we consider an example.

The tris(ethylenediamine)chromium(III) ion, which has the point group symmetry D_3-32 (where the Schönfliess and Hermann–Mauguin symbols have been given connected by a hyphen), exists in two configurational isomers, Δ and Λ (Figure 1). In the Δ form the edges covered by a pair of chelating ligands are skew lines defining a right-handed screw. By proper rotations the Δ form remains Δ and the Λ form Λ, but by improper rotations, *e.g.*, by inversion at the site of the

[1] (a) University of Braunschweig. (b) University of Copenhagen.

[2] (a) International Union of Pure and Applied Chemistry, "Nomenclature of Inorganic Chemistry," Butterworths, London, 1959; (b) 2nd ed, London, 1971.

[3] International Union of Pure and Applied Chemistry, Information Bulletin No. 33, 1968; *Inorg. Chem.*, **9**, 1 (1970).

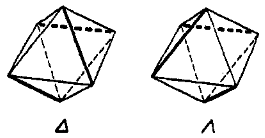

Figure 1.—Δ and Λ configuration of a tris(bidentate) metal complex. The two edges spanned by the two upper chelate rings are directly seen from the figures to form a pair of skew lines, defining a right-handed helix in the Δ form and a left-handed helix in the Λ form. Because of the threefold axis of symmetry any pair of edges spanned by chelate rings will, within the same complex, define the same helicity (see also Figures 2 and 3).

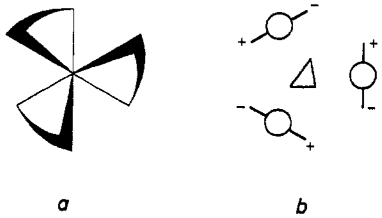

Figure 2.—Δ enantiomer of a tris(bidentate) metal complex: (a) schematic perspective view along the threefold axis of symmetry; (b) our proposed projection formula. + and − at the end of a chelate ring may be used to indicate above and below the plane containing the central ion. One pair of (+, −) is enough to define the configuration. The symbols are superfluous, however, when the configuration Δ is given. The open circles may contain information about the conformations of the chelate rings (Figures 3 and 4).

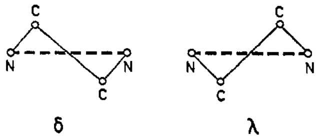

Figure 3.—The line N–N joining the two coordinating atoms (the ligators) and the line C–C joining the two neighboring atoms (of which one has one ligator and the other one the other ligator as their nearest neighbors) forming a pair of skew lines which define the helicity. When the helicity corresponds to that of a right-handed screw, δ is used as a descriptor; when it corresponds to a left-handed screw, λ is used.[3]

central ion, the Δ form is transformed into the Λ form and *vice versa*. In Figure 2 the Δ form is illustrated by a kind of perspective drawing and by the proposed projection formalism. The edges covered by the chelate rings are projected along the threefold axis of the complex onto the plane containing the central atom.

Each ethylenediamine chelate ring is puckered in a chiral way. The line N–N connecting the ligating atoms (the ligators) and the line C–C connecting the neighboring atoms to the ligators are skew and are used to define the conformational chirality, δ or λ (Figure 3). Again δ goes over into δ (and λ into λ) by a proper rotation and δ goes into λ (and λ into δ) by an improper rotation.

When three chiral chelate rings are attached to the central ion to form a tris complex, the configurational chirality is created in addition to the conformational one, resulting in diastereoisomerism.

When the conformations of the chelate rings are different, *e.g.*, two of δ and one of λ conformation, the threefold axis of symmetry vanishes for the complex. However, the configurational chirality and the threefold axis, defined by the edges spanned by the chelate rings, remain unchanged. One may speak of a pseudo threefold axis.

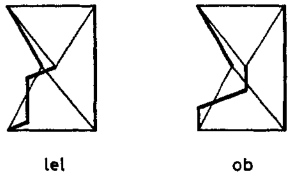

Figure 4.—Diastereoisomeric relationship between configuration and conformation. The (pseudo) threefold axis of the Δ configuration has been indicated by the two triangles. The ethylenediamine molecules are represented by heavy lines. The rear ones are indicated by one line covering the edges spanned by them, and the front one is indicated by a system of lines showing its conformation. When in a Δ configuration the conformation of an ethylenediamine chelate ring is λ, the C–C bond direction is approximately parallel (lel) to the threefold axis of the complex; when it is δ, the C–C bond is oblique (ob) to this axis. The lel and ob symbols refer to relationships which are invariant to proper as well as improper symmetry operations.

The diastereoisomeric relationship which arises when a λ conformation is associated with a Δ configuration is characterized by having the C–C bond direction approximately parallel to the (pseudo) threefold axis (Figure 4). We shall call this relationship lel which is an extension[4] of a nomenclature introduced by Corey and Bailar.[5] When a δ conformation is associated with a Δ configuration, the C–C bond direction is oblique to the threefold axis, and we shall call this relationship ob. So lel is λ(Δ) or δ(Λ), and ob is δ(Δ) or λ(Λ). The lel and ob concepts do not express chirality themselves and the symbols are therefore invariant with respect to proper as well as improper rotations. It is important to realize that the concepts lel and ob are the more interesting as far as energy is concerned. For tris complexes of diamines forming five-membered chelate rings, for example, the lel relationship is in solution the more energetically favored with respect to both enthalpy[6] and free energy.[7,8] However, in solids, lattice forces (*e.g.*, intermolecular hydrogen bonding) may change the issue.[9,10]

In Figure 5 all the isomers of a tris(ethylenediamine) complex have been represented in different ways. An idealized projection of the atoms of the chelate rings along the (pseudo) threefold axis onto the plane of the central ion shows the lel rings as quadrangles and the ob rings as pentagons. Our proposed projection symbols are seen below together with a further simplified version.

Since for a given configuration, Δ say, each of the three chelate rings may adopt the δ or λ conformation independently, there would be $2^3 = 8$ isomers if no symmetry of the configurational site had been present.

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[4] (a) C. E. Schäffer, *Proc. Roy. Soc., Ser. A*, **297**, 96, 98 (1967); (b) P. Andersen, F. Galsbøl, and S. E. Harnung, *Acta Chem. Scand.*, **23**, 3027 (1969).

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

[6] S. E. Harnung, B. S. Sørensen, I. Creaser (nee Olsen), H. Maegaard, U. Pfenninger, and C. E. Schäffer, results on the tris[(±)-*trans*-cyclohexanediamine]cobalt(III) system, to be submitted for publication.

[7] S. E. Harnung, S. Kallesøe, A. M. Sargeson, and C. E. Schäffer, results on the tris[(±)-propylenediamine]cobalt(III) system, to be submitted for publication.

[8] A. M. Sargeson, *Transition Metal Chem.*, **3**, 303 (1966).

[9] K. N. Raymond, P. W. R. Corfield, and J. A. Ibers, *Inorg. Chem.*, **7**, 842 (1968).

[10] U. Thewalt, *Chem. Ber.*, **104**, 2657 (1971).

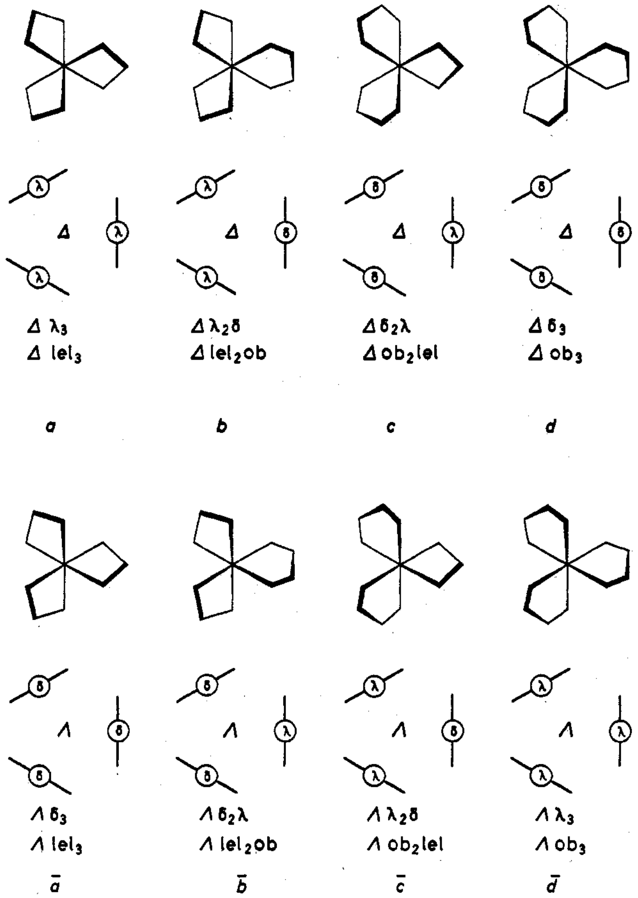


Figure 5.—The eight possible isomers of a tris(ethylenediamine)metal complex. Each configurational isomer, Δ or Λ, contributes four conformational isomers which are distinguishable in solids.[9] Idealized projections are shown, together with our proposed projection symbols and simplified versions of them. For λ(Δ) and δ(Λ) relations the C–C bond direction is approximately parallel (the lel case) to the (pseudo) threefold axis, and the five-membered ethylenediamine ring appears as a quadrangle in the idealized projection. For δ(Δ) and λ(Λ) relations the C–C bond is oblique (the ob case) to the threefold axis and the ring appears as a pentagon in the projection. The symmetries of the isomers are D_3-32 and C_2-2.

However, each of the isomers b and c, for which one conformation is different from the other two, corresponds to three out of the eight isomers. These three are identical because of the invariance of the configurational site with respect to the threefold axis.

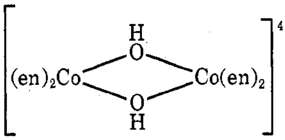
In Figure 5 the isomers a, b, c, d and $\bar{a}$, $\bar{b}$, $\bar{c}$, $\bar{d}$ are pairwise mutually interrelated by a mirror image relationship.[11] The isomers a, $\bar{a}$, d, $\bar{d}$ have the full configurational symmetry D_3-32 and b, $\bar{b}$, c, $\bar{c}$ have the symmetry C_2-2. All eight isomers have been drawn with a horizontal (left–right direction on the paper) twofold axis. Eight isomers analogous to those discussed here occur for the tris[(±)-*trans*-cyclohexanediamine]cobalt(III) system.[6] In this case the (−) and (+) amines form chelate rings of fixed λ and δ conformations, respectively, and the different isomers can be separated and can be had individually in solution. Approximately the same is true for the corresponding (±)-propylenediamine system.[7,8] Here both conformers exist for a given catoptromer of the amine, but the most stable chelate conformations of (−)- and (+)-propylenediamine are λ and δ, in which case the methyl groups are equatorial. Several systems of this kind have been studied by X-ray crystallography.[12]

3. Bridged Complexes. Systems under Consideration

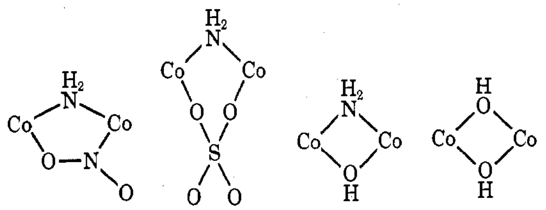
One of the most difficult problems Werner[13] tried to tackle was that of the constitution of the polynuclear complexes. Werner only had classical chemical methods with no help from spectroscopy or X-ray structural methods. Considering this, Werner got very far, as the recent analyses have shown.

We have chosen to consider here two kinds of bridged systems, dinuclear and tetranuclear ones, whose skeletons have been established in recent years by X-ray crystallography. Common to all our systems are their central ions chromium(III) or cobalt(III), which are immaterial for our considerations, and the chelating ligand ethylenediamine, which is important, because its puckered chelate rings give rise to most of the isomeric phenomena with which our nomenclature symbolism is concerned.

3.1. Dinuclear Complexes. 3.1.1. Skeletons under Consideration.—A typical example of such complexes is the di-μ-hydroxo-bis[bis(ethylenediamine)-cobalt(III)]ion



whose bridging skeleton has been established for the corresponding ammonia complex[14,15] and for the chromium(III) complexes[16] containing 2,2′-bipyridine or 1,10-phenanthroline instead of ethylenediamine. We shall consider four different bridging skeletons which are given here in order of increasing symmetry.[17]



A B C D (1)

C_s-m C_2-2 C_{2v}-2mm D_{2h}-mmm

3.1.2. Two-Dimensional Representation of Stereoformulas.—In addition to the IUPAC nomenclature[1] which describes the skeleton by the bridges and by the mononuclear constituents, as exemplified above with the di-μ-hydroxo complex, the configuration about each central ion and the conformation of each chelate

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[11] It has been proposed [D. A. Buckingham, I. E. Maxwell, and A. M. Sargeson, *Chem. Commun.*, 581 (1969)] to use the words catoptromer and catoptric instead of the established words enantiomer and enantiomeric. The new words have been derived from Greek (κάτοπτρον = mirror). In the present paper we shall use both sets of words.

(12) Y. Saito, *Pure Appl. Chem.*, **17**, 21 (1968).

(13) A. Werner, *Justus Liebigs Ann. Chem.*, **375**, 1 (1910).

(14) C. K. Prout, *J. Chem. Soc.*, 4429 (1962).

(15) N.-G. Vannerberg, *Acta Chem. Scand.*, **17**, 85 (1963).

(16) J. Josephsen and C. E. Schäffer, *ibid.*, **24**, 2929 (1970).

(17) For the cases A and B, however, one cannot say that A has a lower symmetry than B. Their symmetry groups are isomorphic, but both are subgroups of C_{2v} which again is a subgroup of D_{2h}.

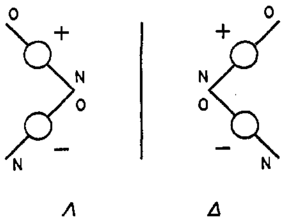


Figure 6.—Projection formula for a dinuclear complex with a planar bridging ring. The projection is along the two parallel fourfold axes of the central ions onto the plane of the bridging ring. The other chelate rings appear in the projection radiating from each central ion, one chelate ring above (+) and the other one below (−) the plane of projection (see also Figure 8). Actually, the + and − information is superfluous since it is contained in the Δ, Λ information. The particular isomer is a di-μ-hydroxo-bis[bis(glycinato)chromium(III)] complex. For both nuclei the nitrogen ligators are cis to each other. The chromium(III) ion to the left has a Λ configuration and that to the right a Δ configuration, so that the symmetry is C_s-m. The particular conformational isomer may be specified in the open circles.

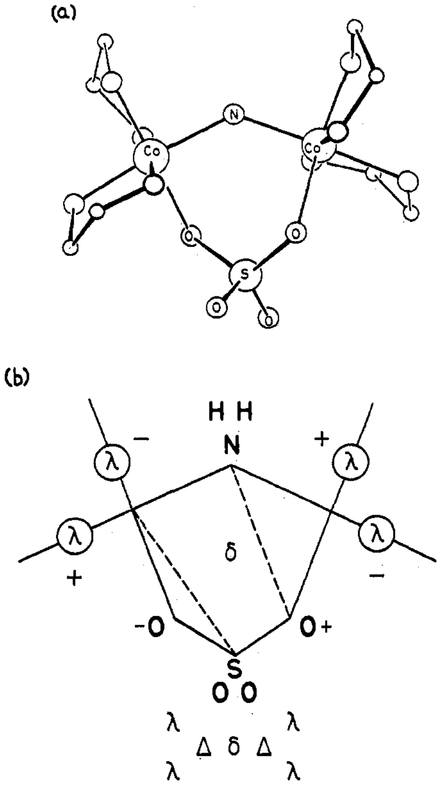


Figure 7.—The μ-amido-μ-sulfato-bis[bis(ethylenediamine)cobalt(III)] ion, one of the catoptromers found in the X-ray structure analysis of its racemic bromide. (a) Projection of one of the cation antipodes in the racemic bromide salt perpendicular to the Co, S, Co plane. (b) Idealized projection formula and its abbreviated form. + and − at an oxygen atom mean above and below the approximate plane formed by the two cobalt(III) ions, the sulfur atom, and the amido nitrogen. + and − at a chelate ring mean essentially above and below the plane mentioned. The conformation of the bridging ring is defined[3] by the helicity of the two dotted lines.

ring must be known in order to specify a particular isomer.

It is convenient to use the kind of projection formulas, analogous to those of Figure 5, to serve this purpose. These involve for the planar (or nearly planar) skeletons A, C, and D, as the direction of projection, their two parallel fourfold axes of the two coordination octahedra of the central atoms (*i.e.*, the axes perpendicular to the central ring). For the skeleton B, these fourfold axes are not parallel and the symbols do, in these cases, not represent proper projections, but this is immaterial for their application provided the skeleton itself, and thereby its symmetry, is included in the symbol.

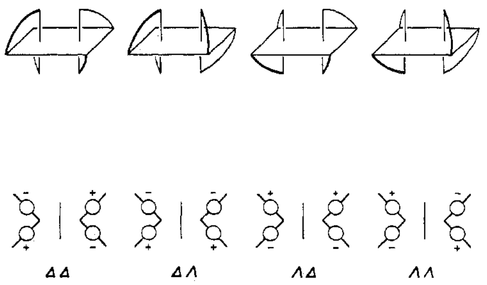


Figure 8.—Configurational isomers for dinuclear complexes (see caption to Figure 6).

The open circles in the projection formulas, in analogy with Figure 5, contain the conformational information lel or ob, or δ or λ. Examples of descriptions of two systems in terms of the projection formalism are given in Figures 6 and 7.

3.1.3. Account of the Isomers.—In the most general case when the skeleton has no nontrivial symmetry properties, there are four classes of configurational isomers

$$\Delta\Delta \qquad \Delta\Lambda \qquad \Lambda\Delta \qquad \Lambda\Lambda \tag{2}$$

as illustrated in Figure 8, by perspective drawings and by our proposed projection formulas. A particular isomer is associated with an ordered pair of configurational assignments, which we write in a row in agreement with the projection formulas.

Furthermore, in each central atom configuration there are two chelate rings whose conformations must be specified, and in agreement with the projection formulas we do this by a column of δ, λ or lel, ob symbols, *e.g.*

$$\begin{matrix}\delta\\ \lambda\end{matrix} \ \text{or}\ \begin{matrix}\text{lel}\\ \text{ob}\end{matrix}$$

There are four classes of conformational columns, which may be given in general as

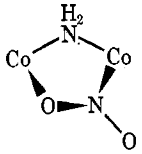
$$\begin{matrix}\delta & \delta & \lambda & \lambda\\ \delta & \lambda & \delta & \lambda\end{matrix} \tag{3}$$

or, alternatively

$$\begin{matrix}\text{lel} & \text{lel} & \text{ob} & \text{ob}\\ \textit{lel} & \text{ob} & \textit{lel} & \textit{ob}\end{matrix} \tag{4}$$

where it may be noted, that the two sets of columns (3) and (4) are identical if they are associated with the configuration Λ. For a given configurational row (2), an ordered pair of conformational columns is required to specify the conformations within a dinuclear complex. We now enumerate the isomers for skeletons of increasing symmetry.

3.1.4. The Skeleton without Symmetry.—An example for the most general case has not been characterized so far. A hypothetical example would be a complex of the following form.



(The actual $\mu(NH_2,NO_2)$ system is planar, however; see section 3.1.5.) In this hypothetical complex each of the four configurational rows (2) are different, and to each of them may be associated any possible combination of ordered pairs of conformational columns. Since there are four such columns, there are 4^2 ordered pairs and accordingly $4^3 = 64$ isomers not including the chiralty of the skeleton. Including this we have altogether 128 isomers.

3.1.5. The Skeleton with a Plane of Symmetry (Type A).—If the skeleton has mirror symmetry as for the Co-μ-(NH_2,NO_2)-Co system,[18] the same considerations are valid as in section 3.1.4 except the final doubling of isomers, so we have in this case 64 isomers. In this salt the skeleton A and the N atoms trans to the bridging atoms lie in a crystallographic mirror plane.

3.1.6. The Skeleton with a Twofold Axis of Symmetry (Type B).—When one of the central ions is taken over into the other by a pure rotation (which leaves Δ and Λ invariant) the two configurational rows ΔΛ and ΛΔ fall into the same class. So in this case we only have three configurational rows [type B in (1)].

When the rows are ΔΔ or ΛΛ, the twofold axis remains and for such a case the order of the pair of conformational columns is no longer distinguishable. So for these cases the four columns of, for example, (4), give rise to only 10 independent pairs, as illustrated in Table I. The ΔΛ row still gives rise to $4^2 = 16$ conformational isomers, so we have $2 \times 10 + 16 = 36$ isomers, not including the chirality of the skeleton, or 72 isomers when including this.

For the particular case of the μ-amido-μ-sulfato skeleton it was found by the structural analysis of the salt $[(en)_2Co\text{-}\mu\text{-}(NH_2,SO_4)\text{-}Co(en)_2]Br_3$[19] that the amido nitrogen atom and the sulfato sulfur atom together with the two cobalt(III) ions form approximately a plane with one of the bridging oxygens above and one below this plane. This is illustrated in Figure 7a (a schematic drawing of the cation is given in Figure 7b) together with the choice of skew lines which according to the IUPAC proposal[2] are used to specify the chirality of the conformation of the bridging ring.

It is of interest to note that the 72 isomers that we have been enumerating consist of 36 enantiomeric pairs. When the central ring has the conformation δ, we have 10 ΔδΔ isomers (a–k of Table I) which are enantiomeric to 10 ΛλΛ isomers (a–k). We further have 10 ΛδΛ isomers and their 10 ΔλΔ enantiomers, and 16 ΔδΛ isomers and their 16 ΛλΔ isomers. For the first 4 ΔΛ isomers (a′–d′) the only difference between the enantiomers lies in the bridging ring. But the enantiomer to

$$e' = \begin{matrix}\text{lel}\\ \text{lel}\end{matrix}\,\Delta\delta\Lambda\,\begin{matrix}\text{lel}\\ \text{ob}\end{matrix} \quad \text{is} \quad \begin{matrix}\text{lel}\\ \text{lel}\end{matrix}\,\Lambda\lambda\Delta\,\begin{matrix}\text{lel}\\ \text{ob}\end{matrix} = \begin{matrix}\text{lel}\\ \text{ob}\end{matrix}\,\Delta\lambda\Lambda\,\begin{matrix}\text{lel}\\ \text{lel}\end{matrix} \qquad (5)$$

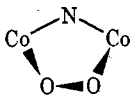
for which the order of conformational columns has been reversed.

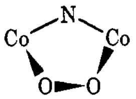
Table I[a]

ΔΔ				ΔΛ	
D_2-222	a	lel lel	lel lel	a′	C_{2h}-2/*m*
C_2-2	b	lel ob	lel ob	b′	*m*
C_2-2	c	ob lel	ob lel	c′	*m*
D_2-222	d	ob ob	ob ob	d′	C_{2h}-2/*m*
C_1-1	e	lel lel	lel ob	e′	C_1-1
C_1-1	f	lel lel	ob lel	f′	C_1-1
C_2-2	g	lel lel	ob ob	g′	C_2-2
C_2-2	h	lel ob	ob lel	h′	C_i-1
C_1-1	i	lel ob	ob ob	i′	C_1-1
C_1-1	k	ob lel	ob ob	k′	C_1-1

[a] Pairs of conformational colums of (4) and their symmetries when associated with the ΔΔ and ΔΛ configurational rows of (2). a–d may be taken to correspond to the diagonal elements of a 4 × 4 matrix and e–k to half its nondiagonal elements. In the general case each of those six last pairs of columns will appear also in reversed order giving altogether 4^2 ordered conformational pairs. It should be noted that whenever the conformation lel is associated with Δ (Λ) it means the same as λ (δ) and whenever the conformation ob is associated with Δ (Λ) it means the same as δ (λ).

Another example of a complex with a skeleton of C_2 symmetry is the μ-amido-μ-peroxo-bis[bis(ethylenediamine)cobalt(III)] cation. An X-ray analysis of the racemic trithiocyanate salt has shown[20] that the central rings of the cations are puckered this way





The complete stereo symbols for the two enantiomers are

$$\begin{matrix}\text{lel}\\ \text{lel}\end{matrix}\,\Delta\delta\Delta\,\begin{matrix}\text{lel}\\ \text{lel}\end{matrix} \quad \text{and} \quad \begin{matrix}\text{lel}\\ \text{lel}\end{matrix}\,\Lambda\lambda\Lambda\,\begin{matrix}\text{lel}\\ \text{lel}\end{matrix}$$

or

$$\begin{matrix}\lambda\\ \lambda\end{matrix}\,\Delta\delta\Delta\,\begin{matrix}\lambda\\ \lambda\end{matrix} \quad \text{and} \quad \begin{matrix}\delta\\ \delta\end{matrix}\,\Lambda\lambda\Lambda\,\begin{matrix}\delta\\ \delta\end{matrix}$$

(Two of the en rings per cation actually exhibit conformational disorder which is not taken into account in the stereo symbols.)

3.1.7. The Skeleton with a C_{2v}-2*mm* Symmetry (Type C).—The skeleton of type C of (1) has an additional set of planes of symmetry with the consequence that the bridging chelate ring cannot be chiral. Therefore the number of isomers in this case can be enumerated in exactly the same way as in the previous case except for the last doubling of their number. We have 10 ΔΔ isomers, 10 ΛΛ isomers, and 16 ΔΛ isomers, making up altogether 36 isomers. The 10 ΔΔ isomers are catoptromers of the 10 ΛΛ ones and the 16 ΔΛ iso-

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(18) The planarity of the skeleton A has been proven by an X-ray analysis of the salt $[(NH_3)_4Co\text{-}\mu\text{-}(NH_2,NO_2)\text{-}Co(NH_3)_4]Cl_4\cdot 4H_2O$: U. Thewalt and R. E. Marsh, *Inorg. Chem.*, **9**, 1604 (1970).

(19) U. Thewalt, *Acta Crystallogr., Sect. B*, **27**, 1744 (1971).

(20) U. Thewalt, *Z. Naturforsch. B*, **25**, 569 (1970), and unpublished results.

mers consist of 4 isomers which are equal to their own catoptromers (a′–d′ in Table I) and 6 pairs of catoptromers (e′–k′ of Table I).

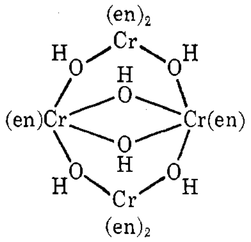
A crystal structure determination of the racemic salt $[(en)_2Co\text{-}\mu\text{-}(NH_2,OH)\text{-}Co(en)_2](NO_3)_4\cdot H_2O$ has indicated that the cations in this salt correspond to the stereoformulas[21]

$$\substack{\lambda\\\lambda}\,\Delta\,\substack{N\\O}\,\Delta\,\substack{\lambda\\\lambda} \quad\text{and}\quad \substack{\delta\\\delta}\,\Lambda\,\substack{N\\O}\,\Lambda\,\substack{\delta\\\delta}$$

These isomers contain a twofold axis of rotation.

3.1.8. The Skeleton with Holohedric Orthorhombic Symmetry (Type D).—In the case of type D of (1) the additional twofold axis through the two central ion nuclei makes *up* and *down* indistinguishable in each pair of conformational columns [(3) and (4)]. This means that among the isomers in Table I, b = c, e = f, and i = k, and the equalities hold for the corresponding primed isomers. The equalities thus reduce the number of isomers of ΔΔ and ΛΛ types from 10 to 7. The 16 isomers of ΔΛ type are similarly reduced to 10 in the following way: b′ = c′ means a reduction by one isomer, e′ = f′ a reduction by two (because the ΔΛ and the ΛΔ forms are different), i′ = k′ is similarly a reduction by two, and finally h′ gives a reduction by only one, because it is identical with its enantiomer. So even for this skeleton of holohedric orthorhombic symmetry the number of isomers amounts to as much as 24. So far no structural details are known for an actual cobalt complex of this series.

3.2. Tetranuclear Complexes. 3.2.1. Systems under Consideration.—Tetranuclear complex cations of the composition $[M_4(OH)_6(en)_6]^{6+}$ have for more than two generations been known to exist for the central ions M being either chromium(III), giving a red complex[22] (rhodoso), or cobalt(III), giving a brown complex.[23] The complexes in which the six ethylenediamine molecules have been replaced by 12 ammonia molecules[24,25] are also known. Werner, mainly on the basis of chemical cleavage experiments of the same types as those of Jørgensen,[26] proposed the cobalt complex to be a tris[*cis*-di-μ-hydroxo-bis(ethylenediamine)cobalt(III)]cobalt(III) ion, and this was recently established by X-ray structure analysis.[10] Pfeiffer[22] proposed the same structure for the chromium complex but it was later realized[27] that this could not be true because there are dissimilarities in ligand field spectra and because chemical cleavage reactions showed the rhodoso ammonia complex to consist of diammine and tetraammine units. The actual structure could probably never have been established by purely chemical means, but it was done recently by an X-ray analysis on both the ammonia complex[28] and the ethylenediamine complex,[29] which was found to be the bis-μ-[*cis*-dihydroxobis(ethylenediamine)chromium(III)]-di-μ-hydroxo-bis[ethylenediaminechromium(III)] ion in an extended version of the IUPAC 1957 nomenclature,[2,30] in which *cis*-$[Cr(en)_2(OH)_2]^+$ has been considered a bridging group



Here we want to give an account of the isomers associated with these two skeletons and again we do this by introducing suitable projection formulas.

3.2.2. The Chromium Complexes.—Here it was found[28,29] that four chromium atoms lie in a plane and are connected by hydroxo bridges to form an eight-membered ring. Further, one of the pairs of the chromium ions, lying opposite to one another, are connected by two hydroxo bridges to form a four-membered ring. We chose a projection perpendicular to the plane of the chromium ions and Figure 9 shows the centrosymmetric isomer found in the crystal. It may be noted that only the two chromium atoms, to which two ethylenediamine molecules are bound, are chiral configurational centroids.

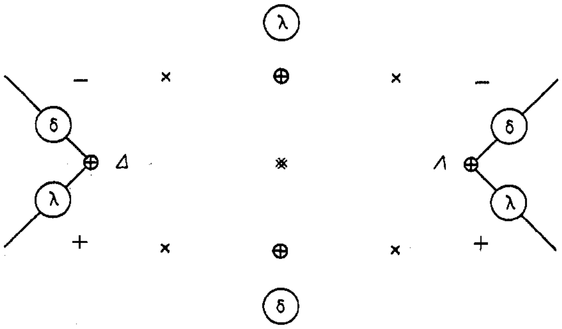


Figure 9.—Projection of the "rhodoso" complex onto the plane of the four chromium(III) ions: ⊕, chromium(III) ion; ×, bridging in-plane hydroxo groups; ⋇, two bridging hydroxo groups, one above and one below the plane of projection.

An account of the different isomers can therefore be obtained by comparisons with the dinuclear complexes. The conformations of the solitary ethylenediamine chelate rings are characterized by a column of δ, λ symbols. For the column $\substack{\delta\\\delta}$ we have the same isomer situation as with the dinuclear skeleton D giving 24 isomers, and the same holds true for the $\substack{\lambda\\\lambda}$ column. For the column $\substack{\delta\\\lambda}$ the situation corresponds to that of skeleton C giving 36 isomers so that altogether the chromium skeleton gives rise to 2 × 24 + 36 = 84 isomers.

3.2.3. The Cobalt Complexes.—It was again found[10]

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[21] U. Thewalt and R. E. Marsh, *Inorg. Chem.*, **10**, 1789 (1971). In the synopsis to this paper one of the stereo formulas has erroneously been written as

$$\substack{\delta\\\delta}\,\Delta\Delta\,\substack{\delta\\\delta} \quad\text{instead of}\quad \substack{\delta\\\delta}\,\Lambda\Lambda\,\substack{\delta\\\delta}$$

[22] P. Pfeiffer, W. Vorster, and R. Stern, *Z. Anorg. Chem.*, **58**, 272 (1908).

[23] A. Werner, *Chem. Ber.*, **40**, 2103 (1907).

[24] (a) S. M. Jørgensen, *J. Prakt. Chem.*, [2] **30**, 1 (1884); (b) S. M. Jørgensen, *ibid.*, [2] **45**, 260 (1892).

[25] S. M. Jørgensen, *Z. Anorg. Chem.*, **16**, 184 (1898).

[26] S. M. Jørgensen, *J. Prakt. Chem.*, [2] **45**, 274 (1892).

[27] J. Bjerrum, *Quad. Chim., Cons. Naz. Rec. (Italy)*, **1**, 47 (1964).

[28] E. Bang, *Acta Chem. Scand.*, **22**, 2671 (1968).

[29] M. T. Flood, R. E. March, and H. B. Gray, *J. Amer. Chem. Soc.*, **91**, 193 (1969).

[30] In "Nomenclature of Inorganic Chemistry," 2nd ed, Butterworths, London, 1971, a more general system is used. The detailed structures are distinguished in this nomenclature by reference to a drawing using letter locants. This system leads to the name hexakis(ethylenediamine)*efhkmn*-hexa-μ-hydroxo-tetrachromium(III) for the above-mentioned chromium ion and an analogous name for the above-mentioned tetranuclear cobalt complex.

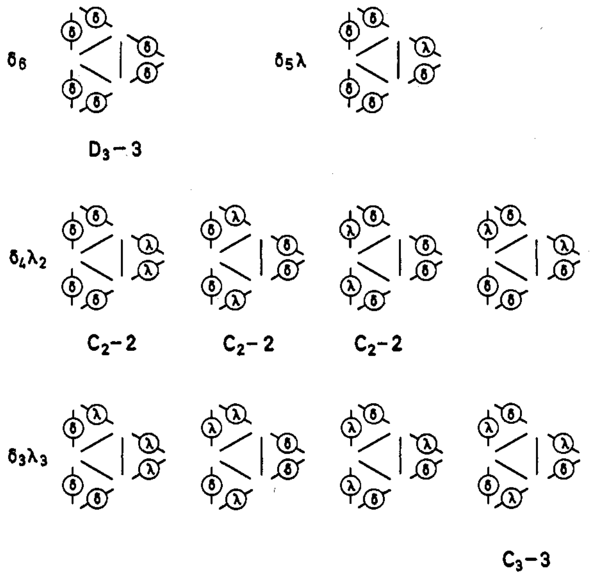

Figure 10.—The types of conformational isomers associated with the Δ(ΛΛΛ) [or Λ(ΔΔΔ)] configuration. For symmetric isomers the symmetry has been given.

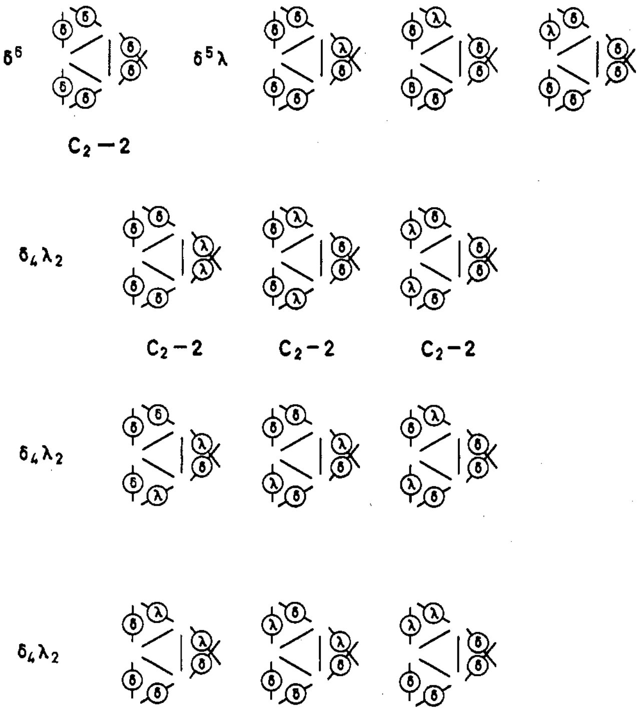

Figure 11.—The conformational isomers of δ_6, $\delta_5\lambda$, and $\delta_4\lambda_2$ types associated with the Δ(ΛΛΔ) [or Λ(ΔΔΛ)] configuration.

that all four cobalt atoms within experimental uncertainty lie in the same plane. But in contradistinction to the chromium case, one of the cobalt atoms is here connected to each of the other three by two hydroxo bridges, so that all four cobalt atoms are chiral configurational centers.

As the line of projection we chose that perpendicular to the plane of the cobalt atoms which always is parallel to the (pseudo) threefold axis of the central cobalt atom, but only when the peripheral cobalt atoms have opposite configurations to that of the central one, is the line of projection also parallel to their (pseudo) threefold axes. In the case where a peripheral cobalt has the same configuration as the central cobalt, one of its ethylenediamine chelate rings lies fully above the plane of the cobalt nuclei and the other one fully below this plane. Therefore two different projection formulas arise for the peripheral cobalt ions.

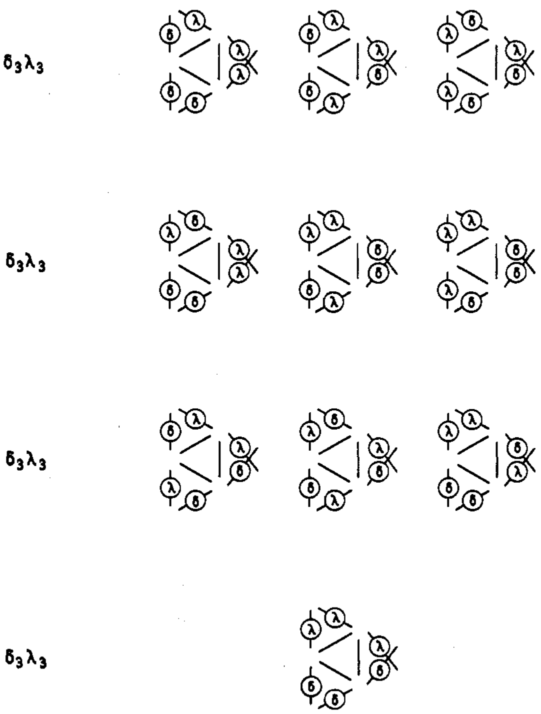

Figure 12.—The conformational isomers of $\delta_3\lambda_3$ type associated with the Δ(ΛΛΔ) [or Λ(ΔΔΛ)] configuration.

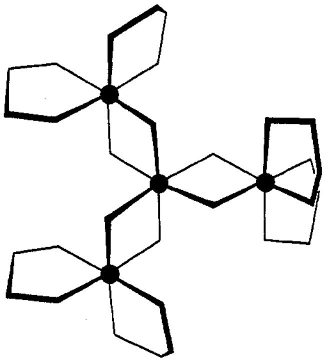

Figure 13.—One catoptromer of the tris[di-μ-hydroxo-bis(ethylenediamine)cobalt(III)]cobalt(III) cation as found in the racemic tris(dithionate) octahydrate salt. A projection perpendicular to the plane of the cobalt atoms is shown.

The diastereoisomerism arising from the mutual configurational chiralities of the central cobalt and the three surrounding ones is completely analogous to that arising in the case of the tris(ethylenediamine) complex of Figure 5 from the configuration of the central ion and the conformation of the three chelate rings. The eight configurational isomers can be characterized by their symmetries which make them fall in either the D_3-32 class or the C_2-2 class (Figure 5 and (6)). For

$$\begin{array}{cccc} {}^{\Lambda}_{\Lambda}\Delta\Lambda & {}^{\Lambda}_{\Lambda}\Delta\Delta & {}^{\Delta}_{\Delta}\Delta\Lambda & {}^{\Delta}_{\Delta}\Delta\Delta \\ \\ {}^{\Delta}_{\Delta}\Lambda\Delta & {}^{\Delta}_{\Delta}\Lambda\Lambda & {}^{\Lambda}_{\Lambda}\Lambda\Delta & {}^{\Lambda}_{\Lambda}\Lambda\Lambda \\ \\ D_3\text{-}32 & C_2\text{-}2 & C_2\text{-}2 & D_3\text{-}32 \end{array} \qquad (6)$$

each member of the classes of D_3-32 symmetry the number of conformational isomers is the same and their enumeration is quite analogous. The same is true for each member of the C_2-2 class.

As an example of the enumeration within the D_3-32 class we take the $\Delta(\Lambda\Lambda\Lambda)$ (or $\Lambda(\Delta\Delta\Delta)$) configuration whose conformational isomers are given in Figure 10. The number of isomers corresponding to the different conformations is

$$\begin{array}{ll} \delta_6 & 1 \text{ isomer} \\ \delta_5\lambda & 1 \text{ isomer} \\ \delta_4\lambda_2 & 4 \text{ isomers} \\ \delta_3\lambda_3 & 4 \text{ isomers} \end{array} \tag{7}$$

with an obvious symmetry about $\delta_3\lambda_3$ so that we altogether get the number of isomers from the three first classes twice and that from the fourth class only once, altogether 16 isomers.

The four possible $\Delta(\Lambda\Lambda\Lambda)\delta_4\lambda_2$ isomers (Figure 10) correspond to the four different distances between a pair of circles containing the conformation descriptors. The three first isomers have C_2-2 symmetry; the last one has no symmetry. The $\Delta(\Lambda\Lambda\Lambda)\delta_3\lambda_3$ isomers correspond to the four possible triangles, having the centers of the descriptor circles as their corners. One of these isomers has C_3-3 symmetry; the others have no symmetry.

As our second example we take $\Delta(\Lambda\Lambda\Delta)$ (or $\Lambda(\Delta\Delta\Lambda)$), belonging to the C_2-2 configurational class. Here the conformational isomers may be enumerated as follows

$$\begin{array}{ll} \delta_6 & 1 \text{ isomer} \\ \delta_5\lambda & 3 \text{ isomers} \\ \delta_4\lambda_2 & 9 \text{ isomers} \\ \delta_3\lambda_3 & 10 \text{ isomers} \end{array}$$

giving in this case 36 isomers. The first 13 isomers are given in Figure 11. Only four of these isomers have the full symmetry of the configuration. The $\delta_4\lambda_2$ isomers fall into three classes, each containing three isomers. The first class has the λ's symmetrically disposed with respect to the twofold axis of the compounded configuration. The second class has the λ's unsymmetrically disposed, one on each side of the twofold axis, and the third has the λ's disposed on the same side of the twofold axis. The $\delta_3\lambda_3$ isomers (Figure 12) consist of six having one pair of λ's disposed symmetrically about the twofold axis, three with one pair of λ's disposed unsymmetrically about the twofold axis, and finally one isomer with all the λ's on the same side of this axis in the projection.

Thus each of the four D_3-32 classes corresponds to 16 isomers and each of the four C_2-2 classes corresponds to 36 isomers giving altogether 208 due to the interplay of configurational and conformational isomerism. Of these 208 isomers 2 catoptromers were found by X-ray analysis on a dithionate of the cation. One of these is shown in Figure 13. It corresponds to the sixth isomer of Figure 11 when this is associated with the compounded configuration

$${}^{\Delta}_{\Delta}\Lambda\Lambda.$$

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Studies in Organometallic Rearrangements. I. Kinetics of the Thermal Isomerization of Trimethylsilylindene. A System of Two Consecutive Reversible First-Order Reactions

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The reversible thermal isomerization of the positional isomers of trimethylsilylindene has been studied in the temperature range 146–201°. The rearrangement proceeds in a stepwise linear manner: 2-isomer ⇄ 1-isomer ⇄ 3-isomer. Rate constants and activation parameters for the forward and reverse reactions are reported. At equilibrium, the mixture contains 31% 2-isomer, 54% 1-isomer, and 15% 3-isomer. A general method is described for the determination of rate constants in a system of two consecutive, reversible, first-order reactions.

The migratory behavior of triorganosilyl groups bound to cyclopentadiene[2-4] and indene[5-7] has been well documented. By contrast the kinetically slower process of hydrogen migration has received much less attention. In the case of trimethylsilylcyclopentadiene, the kinetics[3] and thermodynamic equilibria[4] have been reported. For substituted indenes, base-catalyzed[8] and thermal[9,10] hydrogen migrations have been studied. Only one reference has been made to the thermal isomerization of silylindenes,[7] and no kinetic data were given. We have studied the kinetics of the thermal isomerization of the positional isomers of trimethylsilylindene and determined the activation parameters for the rearrangement process. We also have devised a method for the analysis of systems involving two consecutive reversible first-order reactions.

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