versible formation of a purple SO_2 adduct in benzene solution and by catalytic hydrogenation of ethylene in methylene chloride–benzene. Details will be published separately. It seems evident that the synthesis of other A-frame molecules and their use as multifunctional reagents holds great promise.

Acknowledgments. We wish to thank the National Science Foundation (Grant CHE 76-17440) for partial support of this research, Matthey Bishop Co., Inc., for a loan of rhodium salts, and Dr. Alan Balch for a preprint of his studies. C.P.K. gratefully acknowledges a Sherman Clarke Fellowship.

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Clifford P. Kubiak, Richard Eisenberg*
Department of Chemistry, University of Rochester
Rochester, New York 14627
Received May 2, 1977

Configurational Isomerism in Bis(dimethyl metal)-*N,N'*-dialkyloxamides of Aluminum and Gallium

Sir:

We wish to report the discovery by ^1H and ^{13}C NMR and the elucidation by crystal structure analysis of a new type of configurational isomerism in main group metal complexes.

According to a general scheme,[1] trialkyl derivatives of group 3B elements react with *N,N'*-dialkyloxamides to yield covalently bonded products of the general structural formula $(R_2'M)_2(CONR)_2$. Three representative compounds, **1–3,** are shown below; they have been characterized as 2:1 products by elemental analysis, and have been demonstrated to exist in monomeric form.[2]

Table I. Crystallographic Data[a] for the Bis(dimethyl metal)-oxamide Complexes **1–3**

	1	2	3
Space group	$P\bar{1}$	Cm	$P1$
a, Å	5.7438 (9)	11.774 (2)	8.8300 (6)
b, Å	9.466 (1)	5.7068 (6)	11.6355 (5)
c, Å	6.5750 (8)	8.9852 (8)	6.4533 (4)
α, degree	94.78 (1)	90.0	93.74 (1)
β, degree	111.02 (1)	112.00 (1)	99.51 (1)
γ, degree	101.21 (1)	90.0	95.54 (1)
Z	1	2	2
R	0.040	0.040	0.067

[a] Intensity and lattice parameter data were measured with crystals maintained at ca. −150 °C (Syntex LT-1 low temperature device) on a Syntex $P\bar{1}$ autodiffractometer operating in an ω-scan mode. Each data set was collected with one crystal; reference reflections measured periodically during data collection showed neither systematic nor significant variations in their respective intensities.

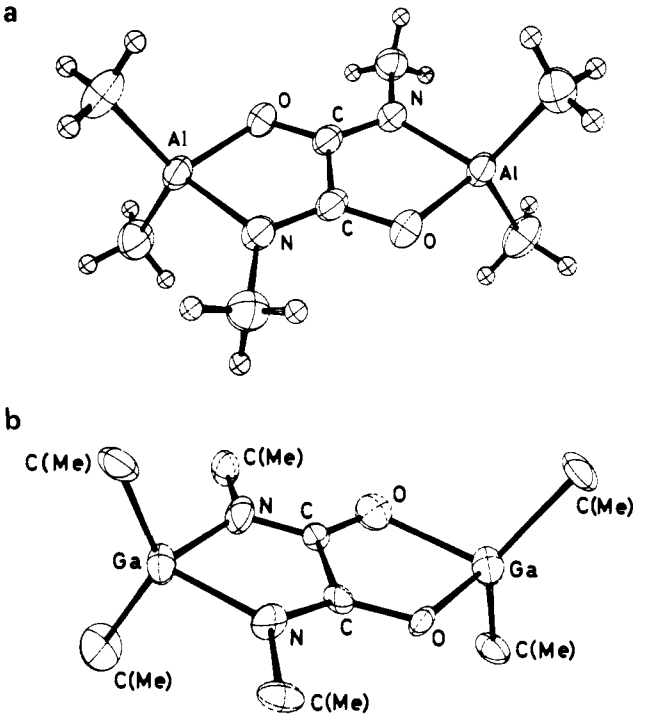


Figure 1. Chemical structure of (a) bis(dimethylaluminum)-*N,N'*-dimethyloxamide (**1**) and (b) bis(dimethylgallium)-*N,N'*-dimethyloxamide (**3**, cis configuration **3B**) (thermal ellipsoids are represented at the 75% probability level).

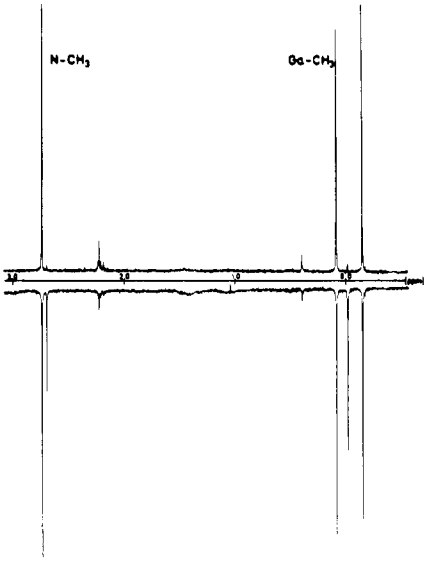
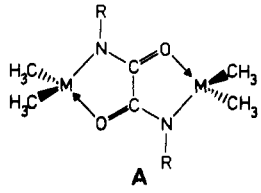


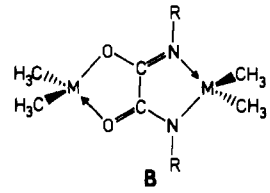
Figure 2. ^1H NMR spectra (C_6D_6 solutions, 30 °C) of a single crystal of **3** (100–200 μg) (top) and a 50-mg random sample of **3** (inverted trace) (bottom).

$$2(CH_3)_3M + (CONHR)_2 \xrightarrow{-2CH_4} (CH_3)_2M(CONR)_2M(CH_3)_2$$

1, M = Al; R = CH_3
2, M = Ga; R = H
3, M = Ga; R = CH_3

A fused five-membered-ring structure has been established for the corresponding bis(dimethylgallium) oxalate;[3] the same structural principle has now been verified for the *N*-methylaluminum derivative **1.** The crystalline complex, utilizing a crystallographic center of symmetry, displays the oxamide ligand in the trans configuration **1A,** Figure 1a, which provides


A


B

the expected identical environment for the two Al atoms (the pertinent crystallographic data are presented in Table I). IR/Raman and $^1H/^{13}C$ NMR data in solution are in accord with the crystal structure (Figure 1a). The gallium complexes **2** and **3**, on the other hand, display *two* complete sets of $^1H/^{13}C$ resonances, one with a widely spaced *double* Ga-CH_3 signal (see Figure 2, lower trace). This spectral pattern, indicating the presence of two isomeric forms, proved peculiar to a whole series of oxamide complexes of dialkylgallium and -indium.[4] As vibration spectral evidence seemed to demand a centrosymmetric molecular geometry,[5] a nonplanar bicyclic structure with conformational isomerism was first proposed;[2] this explanation was in conflict, though, with both chemical experience and other NMR findings.[4,6] To resolve the problem, we extended our crystal structure analyses to the *N*-H and *N*-CH_3 gallium complexes.

The space group of **2** proved not to be uniquely determinable on the basis of the proposed chemical structure, Laue symmetry, and systematic extinctions, the ambiguities being *Cm*, *C*2, and *C*2/*m*. Crystal structure analysis subsequently established the space group as *Cm* and molecular symmetry as C_s, with the mirror symmetry plane, unexpectedly, *perpendicular* to the oxamide C-C bond. The high resolution of the data set and the magnitude of the partially refined thermal parameters strongly indicated that the crystal which we investigated was well ordered; thus, only the cis configuration, **2B**, for the diamide ligand was consistent with both the crystallographic symmetry and its position in the unit cell. To date, the amide hydrogen atoms have not been located by difference Fourier techniques; the necessity for such additional confirmation of structure **2B** was obviated, though, by the subsequent sucessful crystal structure determination for the *N*-methyl compound **3** initiated earlier.

The lattice parameter and Laue symmetry observed for **3** were clearly indicative of a triclinic cell with $Z = 2$, and prompted us to assume $P\bar{1}$ as the space group. In the early stages of analysis the major part of one molecule which had an apparent crystallographic inversion center analogous to that observed for **1** was found. Subsequent difference Fourier maps based on this fragment presented peak distributions not interpretable in terms of a second oxamide complex; furthermore, attempts to refine the initial fragment produced results inconsistent with a correct structural model. The establishment of a noncentrosymmetric chemical structure for **2** raised the strong possibility that the crystal of the *N*-CH_3 derivative contained two symmetry-independent molecules; the associated lower crystallographic symmetry raised the possibility that one molecule each of cis and trans configuration might be present in the crystal. By pursuing the crystal structure in space group *P*1, a successful analysis was readily accomplished; however, both symmetry-independent molecules in the unit cell were demonstrated to display the same chemical structure, that is the *cis*-oxamide configuration, **3B** (Figure 1b).

In establishing this configuration, crystallography satisfactorily accounted for the *double* Ga-CH_3 together with one *N*-CH_3 and C=O NMR signal; the presence of a second set of resonances in the ^1H and ^{13}C spectra indicated that the bulk sample was in fact inhomogeneous. This could subsequently be proven by NMR spectroscopy: the upper trace in Figure 2 represents the proton spectrum of a solution of a single crystal of **3**, a transparent needle of exactly the type selected for crystal structure analysis (100-200 μg in 0.3 mL of C_6D_6); clearly, only one form, **3B**, is present in this crystal, with *two* Ga-CH_3 signals and the lower field *N*-CH_3 resonance. The (inverted) lower trace gives the spectrum of a 50-mg random sample from the same batch of **3** from which the above crystal was selected, and shows the presence also of the second set of NMR signals (ratio 30:70). A pure crystal of the other modification to which we assign the trans configuration, **3A**, on the basis of IR/Raman and NMR spectral data, could so far not be isolated. In each case, sublimation also yielded poorly formed, scale-like crystals containing, however, both isomers in about the same ratio as the whole sample. Quite obviously, in selecting the single crystals for x-ray analysis, only the clear needles with pure cis configuration were picked out for both **2** and **3**.

As preliminary investigations have shown,[4,6] the **A**/**B** isomer ratio is determined primarily by the temperature at which oxamide and gallium alkyl are brought to reaction (e.g., 20:80 at 0 °C, 70:30 at 138 °C). It also depends upon both size and nature of the substituents at the oxamide N and gallium: thus, for the *N*-*tert*-butyldimethylgallium derivative, no cis isomer **B** could be detected by either ^1H or ^{13}C NMR.[4] Attempts at thermal isomerization failed owing to competitive decomposition; however, if benzene solutions of **3A**/**B** with varying isomer ratio are kept at 20 °C for 10-30 days (argon atmosphere), a 1:1 equilibrium state can be obtained from either side. The rate of equilibration is enhanced (though with increasing decomposition) by addition of tertiary amines.[4]

To date, the reasons for the appearance of this unusual configurational isomerism for the gallium compounds are not clearly understood. By a detailed study of the conditions governing the cis/trans ratio, we hope to throw some new light on the complexation behavior of group 3B metals, especially with respect to their use as Friedel-Crafts catalysts.

Acknowledgment. For generous support of this work, we are indebted to the Deutsche Forschungsgemeinschaft.

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Peter Fischer,* Rainer Gräf, John J. Stezowski,* Johann Weidlein
Fachbereich Chemie, Universität Stuttgart Pfaffenwaldring 55, 7000 Stuttgart 80, West Germany
Received March 11, 1977

Application of Deuterium Magnetic Resonance to Biosynthetic Studies. 1. Biosynthesis of Ovalicin

Sir:

In studying the biosynthesis of a given metabolite, one is interested in not only the biogenesis of the carbon skeleton but the metabolic fate of the hydrogens which are attached to that skeleton. The recognition of protonation, deprotonation, and hydride shift processes is essential to the clarification of mechanistic and stereochemical details. When tritium is used as a tracer, alone or in combination with carbon-14, positions and stereochemistry of labeling must be determined by extensive degradations. While ^{13}C NMR techniques are now a viable alternative to experiments with carbon-14 for studying the biosynthesis of a given carbon skeleton, to date no comparably general substitute for tritium has been exploited. The use of deuterium and deuterium magnetic resonance is ap-