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THE INTERACTION OF GROUP III METAL ALKYLS WITH CROWN ETHERS. THE SYNTHESIS AND STRUCTURE OF $[Ga(CH_3)_3]_2$[DIBENZO-18-CROWN-6] AND $[Al(CH_3)_3]_2$[DICYCLOHEXANO-18-CROWN-6]

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Summary

$[Ga(CH_3)_3]_2$[dibenzo-18-crown-6] and $[Al(CH_3)_3]_2$[dicyclohexyl-18-crown-6] were prepared by the reaction of $Ga(CH_3)_3$ or $Al(CH_3)_3$ with the appropriate crown ether in toluene. After filtering and cooling, both products were obtained as colorless, air-sensitive, rectangular crystals. The structures of both compounds were determined from single crystal X-ray diffraction data collected on a CAD-4 diffractometer. $[Ga(CH_3)_3]_2$[dibenzo-18-crown-6] belongs to the monoclinic space group $P2_1/c$ with unit cell parameters a 11.460(5), b 18.000(7), c 7.495(4) Å, β 105.65(4)°, and ρ(calc) 1.32 g cm^{-3} for $Z = 2$. Least-squares refinement gave a final R value of 0.061 for 1179 independent observed reflections. The molecule resides on a crystallographic center of inversion. The Ga–O distance of 2.198(8) Å is among the longest yet observed. In order to accommodate the two trialkylgallium units, the crown ether is forced to adopt a chair configuration. $[Al(CH_3)_3]_2$[dicyclohexano-18-crown-6] crystallizes in the space group $P2_1/a$ with cell parameters a 16.423(7), b 9.812(5), c 20.935(8) Å, β 107.41(5)°, and ρ(calc) 1.07 g cm^{-3} for $Z = 4$. Least-squares refinement gave a final R value of 0.079. The greater flexibility of the crown ether in this case allows the bonded oxygen atoms to be positioned on the outside of the crown, with all six oxygen atoms in a near-planar arrangement.

Introduction

The interaction of alkylaluminums with MX species (M = alkali metal, X = halide, pseudohalide, or related) relative to the phenomenon of liquid clathrates has long been studied in our laboratory [1]. Reactions leading to the formation of 1/1 (eq. 1) or 2/1 (eq. 2) compounds have been carried out in aromatic solvents. As the

$$MX + AlR_3 \rightarrow M[AlR_3X] \qquad (1)$$

$$MX + 2\ AlR_3 \rightarrow M[Al_2R_6X] \qquad (2)$$

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range of suitable MX species was extended, the metal ion coordinating ability of crown ethers (CE) [2] was incorporated into the systems. It was later observed that alkylaluminums formed stable "intermediates" with crown ethers, but the complexes readily dissociated in the presence of MX to yield salts according to the general reaction in eq. 3 [2]:

$$n\mathrm{AlR_3} + \mathrm{CE} \xrightarrow{\text{aromatic}} [\mathrm{AlR_3}]_n \cdot \mathrm{CE} \xrightarrow{\mathrm{MX}} [\mathrm{M} \cdot \mathrm{CE}][\mathrm{Al_2R_6X}] \qquad (3)$$

We have since reported the synthesis and X-ray structure of several such compounds: $[Al(CH_3)_3]_2$[dibenzo-18-crown-6] [3], $[Al(CH_3)_3]_3$[dibenzo-18-crown-6] [4], $[Al(CH_3)_3]_4$[18-crown-6] [4], $[Al(CH_3)_3]_4$[15-crown-5] [3], and $[Al(CH_3)_3]_2$[12-crown-4] [5]. We now report the synthesis and structure of $[Ga(CH_3)_3]_2$[dibenzo-18-crown-6] (**1**) and $[Al(CH_3)_3]_2$[dicyclohexano-18-crown-6] (**2**). The reasons for this study are two-fold. First, it is a natural extension of the aluminum work to examine the corresponding gallium-based crown ether complexes. Furthermore, only two other trialkylgallium adducts related to **1** or **2** have been characterized crystallographically [6,7] and this is the first trimethylgallium-crown ether complex. Second, $[Al(CH_3)_3]_2$[dicyclohexano-18-crown-6] is the first alkylaluminum complex of dicyclohexano-18-crown-6 to be isolated. It was therefore of interest to test the flexibility of a crown fused to the cyclohexano group compared to the benzo derivative.

Experimental

All manipulations were carrried out under a nitrogen atmosphere by using Schlenk techniques or in an inert atmosphere glove box. Solvents were dried and degassed in the normal manner. Dibenzo-18-crown-6 and dicyclohexano-18-crown-6 were purchased from Aldrich Chemical Co. Trimethylaluminum was purchased from Alfa Products. Trimethylgallium was generously donated by Texas Alkyls. All reagents were used without further purification.

Synthesis of $[Ga(CH_3)_3]_2$[dibenzo-18-crown-6]

$[Ga(CH_3)_3]_2$[dibenzo-18-crown-6] was prepared by the addition of $Ga(CH_3)_3$ (33.3 mmol) to a slurry of dibenzo-18-crown-6 (5.55 mmol) in toluene (40 ml). Reaction was immediate and very exothermic. It reached completion in ca. 1 hour as evidenced by the disappearance of the crown ether. The solvent was reduced in vacuo and the flask was cooled to 0 °C for 24 hours. Large, colorless, extremely air-sensitive crystals suitable for X-ray analysis resulted. The 2/1 complex was the only product isolated. The yield was nearly quantitative.

Synthesis of $[Al(CH_3)_3]_2$[dicyclohexano-18-crown-6]

To a slurry of dicyclohexano-18-crown-6 (5.37 mmol) and 40 ml of toluene in a 125 ml Schlenk flask, $Al(CH_3)_3$ (32.2 mmol) was slowly added. Again, the resulting reaction was immediate and very exothermic. With reduction of solvent followed by cooling, diffraction-quality, air-sensitive crystals resulted. The yield was quantitative.

In both cases there was a six-fold excess of Group III metal alkyl (relative to the crown-ether) but only the 2/1 complexes were isolated.

X-Ray data collection, structure determination and refinement for $[Ga(CH_3)_3]_2$*[dibenzo-18-crown-6]*

Single crystals of the compound were sealed under N_2 in thin-walled glass capillaries. Final lattice parameters as determined from the least-squares refinement of $(\sin\theta/\lambda)^2$ values for 24 reflections ($\theta \geq 15°$) accurately centered on the diffractometer are given in Table 1. The space group was uniquely defined by systematic absences to be $P2_1/c$.

Data were collected on an Enraf–Nonius CAD-4 diffractometer by the $\theta/2\theta$ scan technique as previously described [14]. A summary of data collection parameters is given in Table 1. The intensities were corrected for Lorentz and polarization effects, but not for absorption.

Calculations were carried out with the SHELX system of computer programs [15]. Neutral atom scattering factors for Ga, O and C were taken from Cromer and Waber [16], and those for H were from "International Tables for X-ray Crystallography" [17]. The scattering by Ga was corrected for the real and imaginary components of anomalous dispersion using the table of Cromer and Liberman [18].

TABLE 1

CRYSTAL DATA, SUMMARY OF INTENSITY DATA COLLECTION AND STRUCTURE REFINEMENT

	$[Al(CH_3)_3]_2$-[dicyclohexano-18-crown-6]	$[Ga(CH_3)_3]_2$-[dibenzo-18-crown-6]
Mol wt.	516.65	592.10
Space group	$P2_1/a$	$P2_1/c$
Cell constants		
a, Å	16.423(7)	11.460(5)
b, Å	9.812(5)	18.000(7)
c, Å	20.935(8)	7.495(4)
α, deg.	–	–
β, deg.	107.41(5)	105.65(4)
γ, deg.	–	–
Cell vol., Å^3	3219.0	1488.8
Molecules/unit cell	4	2
ρ (calcd), g cm^{-3}	1.07	1.32
μ (calcd), cm^{-1}	1.28	1.95
Radiation	Mo-K_α	Mo-K_α
Max crystal dimens, mm	$0.35 \times 0.350 \times 0.25$	$0.30 \times 0.20 \times 0.15$
Scan width, deg.	$0.8 + 0.2 \tan\theta$	$0.8 + 0.2 \tan\theta$
Std. reflections	200, 020, 002	200, 040, 002
Decay of stds.	< 3%	< 3%
Reflections measured	4209	2131
2θ range	2–44	2–40
Obsd. reflections	1474	1179
No. of parameter varied	237	154
GOF	2.79	2.59
R	0.079	0.061
R_w	0.084	0.078

TABLE 2. FINAL FRACTIONAL COORDINATES FOR [Ga(CH$_3$)$_3$]$_2$[dibenzo-18-crown-6]

Atom	x/a	y/b	z/c
Ga	0.1238(1)	−0.13814(9)	−0.0725(2)
O(1)	0.3846(8)	0.0609(5)	−0.234(1)
O(2)	0.2176(7)	−0.0346(5)	0.038(1)
O(3)	0.4262(8)	−0.0597(5)	0.340(1)
C(1)	0.280(1)	0.0518(7)	−0.168(2)
C(2)	0.316(1)	−0.0132(7)	−0.036(2)
C(3)	0.230(1)	−0.0118(7)	0.225(2)
C(4)	0.308(1)	−0.0637(7)	0.369(2)
C(5)	0.514(1)	−0.1061(7)	0.440(2)
C(6)	0.506(1)	−0.1482(8)	0.589(2)
C(7)	0.605(2)	−0.1923(8)	0.679(2)
C(8)	0.709(2)	−0.1934(8)	0.620(2)
C(9)	0.719(1)	−0.1513(7)	0.469(2)
C(10)	0.620(1)	−0.1058(7)	0.382(2)
C(11)	0.004(1)	−0.1415(9)	0.077(2)
C(12)	0.066(1)	−0.1092(9)	−0.339(2)
C(13)	0.264(2)	−0.2094(8)	−0.010(2)

TABLE 3. FINAL FRACTIONAL COORDINATES FOR [Al(CH$_3$)$_3$]$_2$[dicyclohexano-18-crown-6]

Atom	x/a	y/b	z/c
Al(1)A	0.3178(3)	0.1707(4)	0.1554(2)
O(1)A	0.5508(5)	−0.2180(9)	0.0155(4)
C(1)A	0.5379(8)	−0.301(1)	0.0676(6)
C(2)A	0.4500(9)	−0.359(1)	0.0431(6)
C(3)A	0.433(1)	−0.449(2)	0.0960(8)
C(4)A	0.447(1)	−0.373(2)	0.1627(8)
C(5)A	0.535(1)	−0.315(2)	0.1851(6)
C(6)A	0.5532(8)	−0.225(1)	0.1328(6)
O(2)A	0.4982(5)	−0.1082(9)	0.1177(4)
C(7)A	0.5182(9)	−0.002(1)	0.1626(7)
C(8)A	0.4883(7)	0.130(1)	0.1308(6)
O(3)A	0.3959(5)	0.1412(8)	0.1019(3)
C(9)A	0.3612(8)	0.091(1)	0.0348(6)
C(10)A	0.3658(8)	0.195(1)	−0.0166(6)
C(11)A	0.3963(8)	0.226(1)	0.2444(6)
C(12)A	0.2397(9)	0.319(2)	0.1070(7)
C(13)A	0.2608(9)	−0.012(2)	0.1493(7)
Al(1)B	0.6752(3)	0.2030(5)	0.3774(2)
O(1)B	0.5181(5)	0.4603(9)	0.6164(4)
C(1)B	0.5704(8)	0.354(1)	0.6501(6)
C(2)B	0.6607(9)	0.406(1)	0.6716(7)
C(3)B	0.7251(9)	0.299(2)	0.7079(7)
C(4)B	0.718(1)	0.174(2)	0.6651(8)
C(5)B	0.627(1)	0.118(1)	0.6438(7)
C(6)B	0.5616(8)	0.226(1)	0.6079(6)
O(2)B	0.5776(5)	0.2667(9)	0.5469(4)
C(7)B	0.5439(9)	0.185(2)	0.4946(7)
C(8)B	0.5243(7)	0.250(1)	0.4274(5)
O(3)B	0.5999(5)	0.3066(8)	0.4146(4)
C(9)B	0.6182(8)	0.447(1)	0.4333(6)
C(10)B	0.5654(8)	0.547(1)	0.3836(6)
C(11)B	0.7897(9)	0.237(2)	0.4435(7)
C(12)B	0.6609(9)	0.287(2)	0.2878(7)
C(13)B	0.6288(9)	0.013(2)	0.3731(7)

The gallium position was found using standard heavy atom techniques, and subsequent difference maps revealed the positions of all the non-hydrogen atoms. Refinement with isotropic thermal parameters converged at $R = \Sigma || F_o | - | F_c || / \Sigma | F_o | = 0.11$. Hydrogen atoms were located from a difference map, but their parameters were not refined. (They were subsequently allowed to "ride" on the bonded carbon atoms.) Refinement of the nonhydrogen atoms with anisotropic thermal parameters and inclusion of the hydrogen atom contributions gave final values of $R = 0.061$ and $R_w = 0.078$. A final difference Fourier map showed no feature greater than 0.3 e/Å^3. The positional parameters are given in Table 2, and the temperature factors are available elsewhere.

X-Ray data collection, structure determination and refinement for $[Al(CH_3)_3]_2$*[dicyclohexano-18-crown-6]*

The compound was manipulated and data collected in the same manner as for $[Ga(CH_3)_3]_2$[dibenzo-18-crown-6]. Refinement was carried out as above and converged at $R = 0.079$, and $R_w = 0.084$. Final lattice constants and positional parameters are found in Tables 1 and 3, respectively.

Results and discussion

Studies of liquid inclusion compounds have dwelled on those based on alkyl aluminums since the initial discoveries were made in this area. There have been only two instances of such compounds based on gallium [6,7]. The synthesis and structure of $[Ga(CH_3)_3]_2$[dibenzo-18-crown-6] is notable in that it provides a direct

TABLE 4

COMPARISON OF GALLIUM–CARBON AND GALLIUM–OXYGEN DISTANCES (Å) IN ADDUCTS RELATED TO THE TITLE COMPOUND

Compound	Ga–C	Ga–O	Ref.
$Rb[Ga(CH_3)_6CH_3COO]$	2.00(1)	2.068(8) 2.070(8)	7
$CH_3Ga(CH_3COO)_2$	1.946(3)	1.873(3) 2.086(3)	8
$[(CH_3)_2NCH_2CH_2OGaH_2]_2$		1.911(3) 2.053(3)	9
$[(CH_3)_2NCH_2CH_2OGa(CH_3)_2]_2$	1.961(4)	1.913(3) 2.078(3)	10
$[C_7H_5O_2\cdot Ga(CH_3)_2]_2$	1.939(1)	1.927(3) 2.120(3)	10
$Ga(CH_3COO)_3$		1.941(7) 1.964(6)	11
$[CH_3N(CH_2CH_2O)_2GaH]_2$		1.960(8) 2.018(2)	12
$[(CH_3)_2Ga]_2C_2O_4$	1.941(5)	2.051(7) 2.124(9)	13
[Dibenzo-18-crown-6]$[Ga(CH_3)_3]_2$	2.00(1) 1.99(1) 2.01(1)	2.198(8)	This study

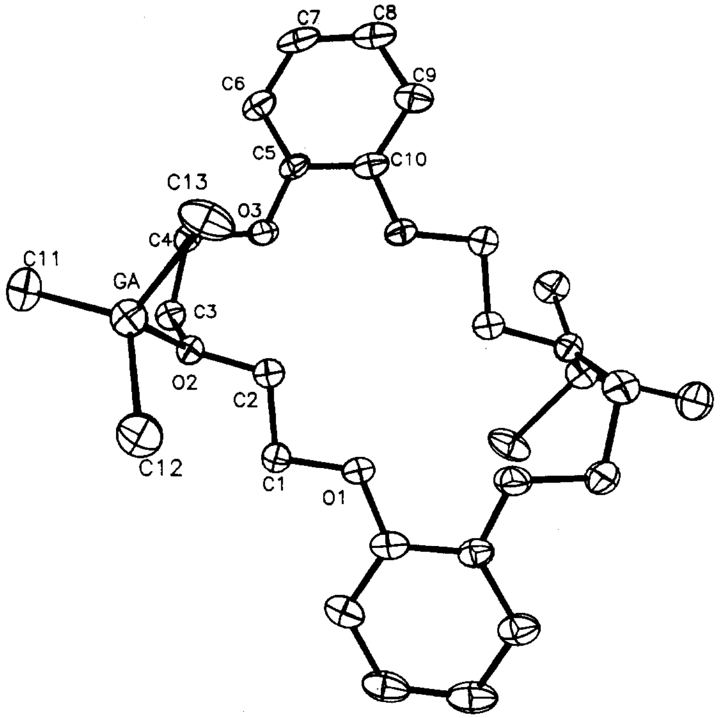

Fig. 1. Molecular structure of $[Ga(CH_3)_3]_2$[dibenzo-18-crown-6]. The Ga–O length is 2.198(8) Å. The Ga–C distances range from 1.99–2.01 Å, and the C–Ga–C angles, 116–119°.

comparison with the previously reported $Al(CH_3)_3$ compounds. The structure and atom numbering scheme for $[Ga(CH_3)_3]$[dibenzo-18-crown-6] are shown in Fig. 1. As was the case with the isostructural $[Al(CH_3)_3]_2$[dibenzo-18-crown-6] [3], the six oxygen atoms of the crown assume a chair configuration so as to better accommodate the two $Ga(CH_3)_3$ ligands. The molecule resides on a crystallographic center of inversion. The independent Ga–O distance 2.198(8) Å and Ga–C distances of 1.99(1)–2.01(1) Å are compared with related organogallium compounds in Table 4 where it is shown that these are among the longest yet observed. Indeed, as we have previously pointed out [7], one may expect on the basis of covalent radii a lengthening of ca. 0.12 Å as one progresses from Al to Ga. The Ga–O distance is in fact 0.23 Å longer than the Al–O value, while the Ga–C lengths are only about 0.04 Å longer than the Al–C ones.

In addition to changes in metal, it was decided to examine variations in properties of complexes of closely related crown ethers. With regard to dicyclohexano-18-crown-6, the major point of comparison was the relative flexibility of dibenzo-18-crown-6 and dicyclohexano-18-crown-6 as evidenced by complexation with trimethylaluminum.

The space group of $[Al(CH_3)_3]_2$[dicyclohexano-18-crown-6] is $P2_1/a$. With four molecules in the unit cell, it is interesting to note that there are two independent molecules, each residing on a center of inversion. The two molecules of

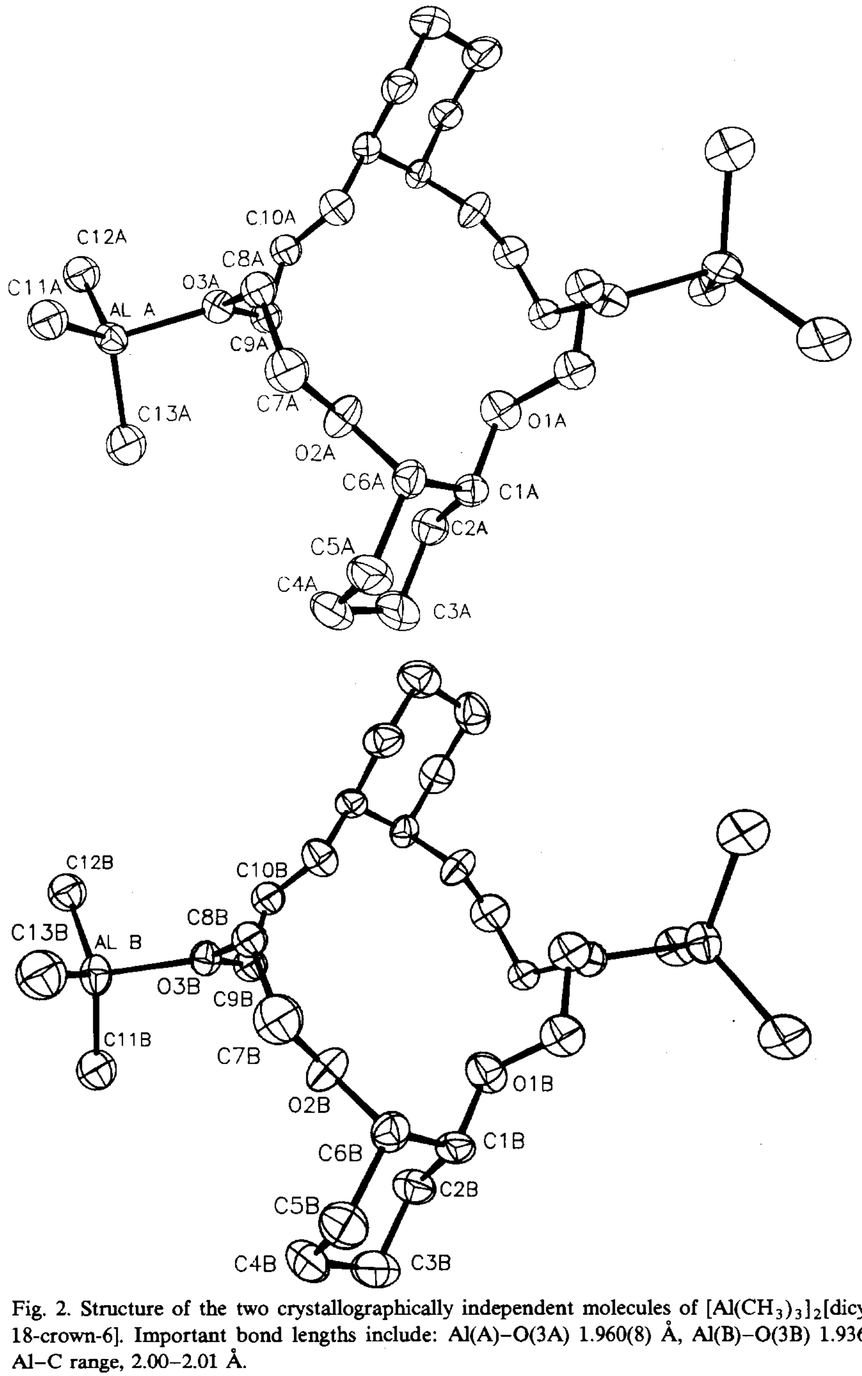

Fig. 2. Structure of the two crystallographically independent molecules of $[Al(CH_3)_3]_2$[dicyclohexano-18-crown-6]. Important bond lengths include: Al(A)–O(3A) 1.960(8) Å, Al(B)–O(3B) 1.936(8) Å, and Al–C range, 2.00–2.01 Å.

$[Al(CH_3)_3]_2$[dicyclohexano-18-crown-6] are virtually identical, as one may see in Fig. 2. The overall configuration of the dicyclohexano and dibenzo derivatives is quite different, even though both contain a center of inversion. The dicyclohexano one contains a nearly planar arrangement of the six oxygen atoms (maximum deviation, 0.19 Å), while the dibenzo moiety exhibits the chair configuration. This is clearly a manifestation of the greater flexibility of dicyclohexano-18-crown-6. The average Al–O bond length, 1.96 Å, is indicative of a strong interaction, and is comparable to that found in other $AlR_3 \cdot$ crown ether complexes *.

The use of crown ethers in conjunction with equations 1, 2, and 3 has produced a number of novel compounds. In these studies the most important conclusions are that (1) the Al–O bond is quite strong and (2) the crown ethers have substantial flexibility.

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* Supplementary material available. Tables of hydrogen atom coordinates, complete bond lengths and angles, thermal parameters, and structure factors for both compounds are available from J.L.A.