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Reaction of Trimethylaluminum with Crown Ethers. III. The Synthesis and Crystal Structure of (12-Crown-4)bis(trimethylaluminum)

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Abstract. The crown ether 12-crown-4 reacts with trimethylaluminum in toluene to form the complex $[AlMe_3]_2$[12-crown-4]. Attempts to utilize the remaining two oxygen atoms for coordination to $AlMe_3$ molecules were unsuccessful. The 2 : 1 complex crystallizes in the monoclinic space group $P2_1/n$ with a = 11.342(7), b = 12.941(4), c = 6.973(6) Å, and β = 95.48(4)°. Refinement led to a final R value of 0.047 for 925 observed reflections. The molecule resides on a crystallographic center of inversion, and as required by symmetry, the four oxygen atoms are planar. The Al—O bond is strong as revealed by the bond length of 1.977(3) Å.

Key words: crown ether, trimethylaluminum, crystal structure.

Supplementary Data relating to this article are deposited with the British Library as Supplementary Publication No. SUP 82013 (9 pages).

1. Introduction

During our investigation of the reaction of aluminum alkyls with MX (M = alkali metal, X = halide, pseudohalide or related) in the presence of crown ether in aromatic solvents, the formation of AlR_3 · crown ether complexes became apparent. While these 'intermediates' did not hinder the desired reactions, we decided to study the aluminum alkyl-crown ether interaction in detail. In the first two parts of the series the preparation and structure of the following were described: $[AlMe_3]_2$[dibenzo-18-crown-6] [1], $[AlMe_3]_3$[dibenzo-18-crown-6] [2], $[AlMe_3]_4$[18-crown-6] [2], and $[AlMe_3]_4$[15-crown-5] [1]. The most important conclusions were that (1) the Al—O bond is quite strong and (2) the crown ethers have substantial flexibility. Indeed, the 4 : 1 complexes featured crown ethers that had been essentially turned inside-out. In order to test the ability of the smallest commercially available crown ether, 12-crown-4, to behave in a similar fashion, the current study was undertaken. It is worth noting that 12-crown-4 is comparatively little-used because it coordinates effectively only the smaller alkali metal ions Li^+ [3] and Na^+ [4], certain 2^+ species [5], and does not interact with ammonium salts [6]. Much of the theoretical and structural data on 12-crown-4 has been recently reviewed [7].

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2. Results and Discussion

Trimethylaluminum reacts immediately with 12-crown-4 in toluene to give large, colorless, air-sensitive crystals of the title compound. Regardless of the amount of $AlMe_3$ used in excess of the 2 : 1 stoichiometry, no evidence for 3 : 1 or 4 : 1 complexes was found.

The structure, presented in Figure 1, shows that the two coordinated oxygen atoms are found on the outside of the ring. Interestingly, the remaining oxygen atoms are also on the perimeter of the ring, not on the inside as was found in $[AlMe_3]_4$[15-crown-5] and $[AlMe_3]_4$[18-crown-6]. The fact that these donor sites apparently do not coordinate trimethylaluminum atoms may reasonably be ascribed to steric problems (associated with the other $AlMe_3$ groups). No stoichiometry higher than 2 : 1 has been observed.

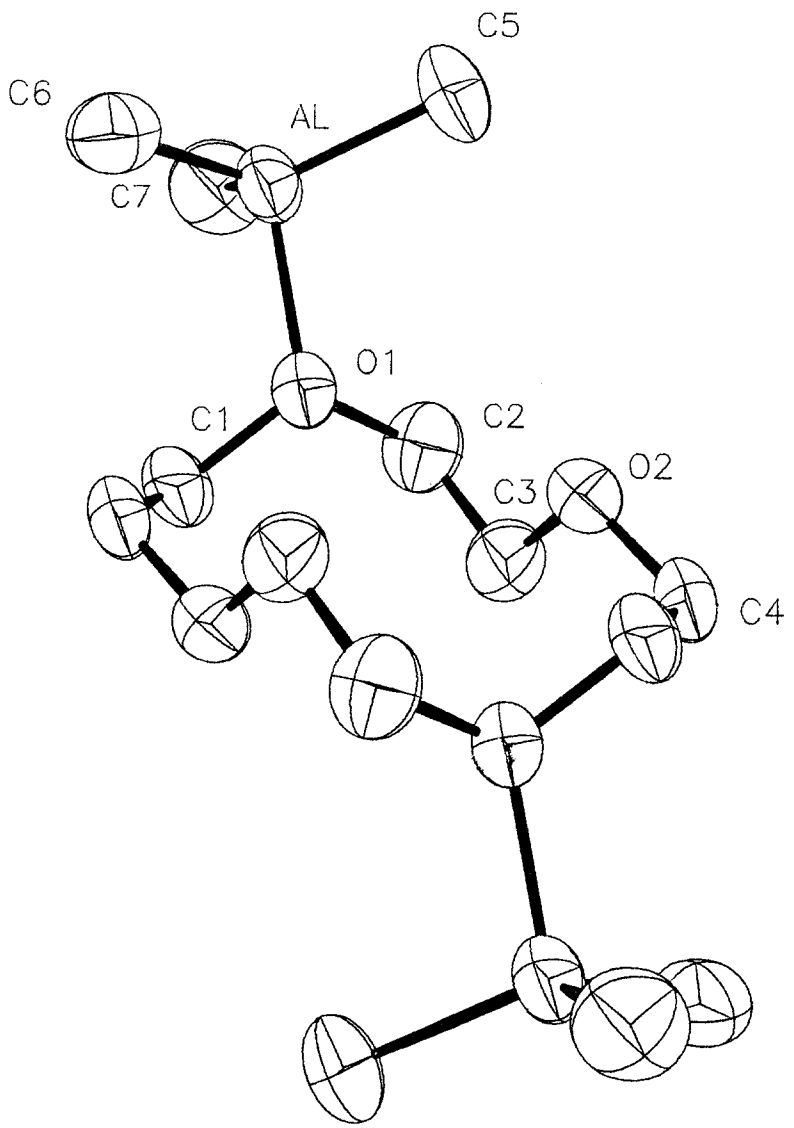

Fig. 1. Structure of $[AlMe_3]_2$[12-crown-4]. The molecule resides on a crystallographic center of inversion.

The molecule resides on a crystallographic center of inversion. As required by summetry, the four oxygen atoms are planar. The independent Al—O length, 1.977(3) Å, is evidence for a strong bond, and may be compared with average values of 1.967(3), 1.984(1), and 2.005(6) Å in $[AlMe_3]_2$[dibenzo-18-crown-6], $[AlMe_3]_4$[18-crown-6], and $[AlMe_3]_4$[15-crown-5], respectively. Other bond distances and angles are given in Table I.

No short intermolecular contacts have been noted.

Table I. Bond lengths (Å) and angles (°) for $[AlMe_3]_2$[12-crown-4]

Atoms	Distance	Atoms	Distance
Al(1)—O(1)	1.977(3)	Al(1)—C(5)	1.969(4)
Al(1)—C(6)	1.958(5)	Al(1)—C(7)	1.958(5)
O(1)—C(1)	1.493(5)	O(1)—C(2)	1.460(5)
O(2)—C(3)	1.423(5)	O(2)—C(4)	1.423(5)
C(2)—C(3)	1.490(6)		
Atoms	**Angle**	**Atoms**	**Angle**
O(1)—Al(1)—C(5)	103.5(2)	O(1)—Al(1)—C(6)	104.2(2)
C(5)—Al(1)—C(6)	114.3(2)	O(1)—Al(1)—C(7)	101.1(2)
C(5)—Al(1)—C(7)	115.8(2)	C(6)—Al(1)—C(7)	115.2(2)
Al(1)—O(1)—C(1)	117.0(2)	Al(1)—O(1)—C(2)	116.1(2)
C(1)—O(1)—C(2)	113.0(3)	C(3)—O(2)—C(4)	112.6(3)
O(1)—C(2)—C(3)	113.2(4)	O(2)—C(3)—C(2)	109.0(4)

Table II. Crystal data and summary of intensity data collection and structure refinement

Compound	$[AlMe_3]_2$[12-crown-4]
Mol wt	320.4
Space group	$P2_1/n$
Cell constants	
a, Å	11.342(7)
b, Å	12.941(4)
c, Å	6.973(6)
β, deg	95.48(4)
Cell vol, Å^3	1018.8
Molecules/unit cell	2
ρ(calc), g cm^{-3}	1.05
μ(calc), cm^{-1}	0.66
Radiation	Mo$K\alpha$
Max crystal dimensions, mm	0.10 × 0.20 × 0.50
Scan width, deg	0.80 + 0.20 tanθ
Standard reflections	(400), (040), (006)
Decay of standards	<1%
Reflections measured	1165
2θ range	1–40
Reflections considered observed	925
No. of parameters varied	91
GOF	0.80
R	0.047
R_w	0.048

3. Experimental

3.1. PREPARATION OF $[AlMe_3]_2$[12-crown-4]

Trimethylaluminum (11.4 mmol) was syringed into a solution of 12-crown-4 (5.7 mmol) in toluene (30 ml). Reaction was immediate and very exothermic. The screw top reaction tube was held at 0°C for 12 h. At the end of this time period a large yield (the reaction is quantitative based on 12-crown-4) of rectangular, air-sensitive crystals had formed.

3.2. X-RAY DATA COLLECTION AND STRUCTURE SOLUTION FOR $[AlMe_3]_2$[12-crown-4]

Single crystals were sealed in thin-walled class capillaries. Final lattice parameters as determined from 25 high-angle reflections ($2\theta > 40°$) carefully centered on an Enraf-Nonius CAD-4 are given in Table II. Intensity data were recorded on the diffractometer in the usual manner [8]. A summary of data collection parameters is also presented in Table II. The intensities were corrected for Lorentz and polarization effects, but not for absorption.

Structure solution was accomplished by means of the direct methods program MULTAN [9], and the subsequent calculation of a difference Fourier map allowed the location of all nonhydrogen atoms. Refinement with isotropic temperature factors led to a reliability index of $R = \Sigma(||F_o| - |F_c||)\Sigma|F_o| = 0.080$. Conversion to anisotropic thermal parameters and further refinement gave $R = 0.060$. The hydrogen atoms of the 12-crown-4 and those on the methyl carbon atoms were located on a difference Fourier map and were not refined.

Table III. Final Fractional Coordinates for $[AlMe_3]_2$[12-crown-4]

Atom	x/a	y/b	z/c	U_{eq}
Al(1)	0.4599(1)	0.1879(1)	0.4824(2)	0.054
O(1)	0.4253(2)	0.3344(2)	0.4198(4)	0.051
O(2)	0.4319(3)	0.4907(2)	0.7284(4)	0.059
C(1)	0.4324(4)	0.3670(4)	0.2159(6)	0.063
C(2)	0.3244(4)	0.3794(4)	0.5050(7)	0.066
C(3)	0.3445(4)	0.4885(4)	0.5679(7)	0.063
C(4)	0.4480(5)	0.5912(4)	0.8095(6)	0.065
C(5)	0.4716(5)	0.1848(4)	0.7658(6)	0.084
C(6)	0.6094(5)	0.1609(4)	0.3723(8)	0.086
C(7)	0.3206(5)	0.1200(4)	0.3507(8)	0.089
H(11)	0.4153	0.2979	0.1284	0.080
H(12)	0.3585	0.4275	0.1694	0.080
H(21)	0.2379	0.3726	0.4166	0.080
H(22)	0.3096	0.3273	0.6230	0.080
H(31)	0.2614	0.5228	0.6005	0.080
H(32)	0.3765	0.5363	0.4598	0.080
H(41)	0.3693	0.6470	0.7512	0.080
H(42)	0.4441	0.5865	0.9552	0.080
H(51)	0.5124	0.1172	0.8349	0.080
H(52)	0.3930	0.1972	0.8314	0.080
H(53)	0.5150	0.2423	0.8202	0.080
H(61)	0.6377	0.0919	0.4058	0.080
H(62)	0.6810	0.2154	0.4191	0.080
H(63)	0.6034	0.1717	0.2424	0.080
H(71)	0.3123	0.0523	0.3522	0.080
H(72)	0.2450	0.1507	0.3522	0.080
H(73)	0.3508	0.1367	0.2181	0.080

Additional cycles of refinement led to final values of $R = 0.047$ and $R_w = \{\Sigma w([|F_o| - |F_c|)^2/\Sigma w(F_o)^2\}^{1/2} = 0.048$. The largest parameter shifts in the final cycle of refinement were less than 0.01 of their estimated standard deviations.

Unit weights were used at all stages; no systematic variation of $w(|F_o| - F_c|)$ vs. $|F_o|$ or $(\sin\theta)/\lambda$ was noted. The function $w(|F_o| - |F_c|)^2$ was minimized [10]. Neutral atom scattering factors were taken from the compilations of Cromer and Waber [11] for Al, O, and C. Scattering factors for H were from [12]. The final values of the positional parameters are given in Table III [13].

Acknowledgement

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