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Reaction of Trimethylaluminum with Crown Ethers. II. The Synthesis and Crystal Structure of (Dibenzo-18-crown-6)tris(trimethylaluminum) and of (18-Crown-6)tetrakis(trimethylaluminum)

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Abstract. Both title compounds were prepared by adding $AlMe_3$ to a suspension of the appropriate crown ether in toluene, followed by reaction in a sealed tube. Both products were obtained in the form of extremely air-sensitive, colorless crystals. $[AlMe_3]_3$[dibenzo-18-crown-6] crystallizes in space group P$\bar{1}$, with a = 8.898(4), b = 11.848(5), c = 19.060(6) Å, α = 74.86(3), β = 80.73(4), and γ = 67.02(4)°.Refinement led to a final conventional weighted R value of 0.052 for 1800 reflections. $[AlMe_3]_4$[18-crown-6] belongs to space group Pbcn, with a = 18.753(3), b = 12.570(6), and c = 15.095(6) Å. Refinement was taken to R_w = 0.064 for 1320 reflections.

Key words: Crown ethers, trimethylaluminum, crystal structure.

1. Introduction

The use of crown ethers to facilitate reactions (**1**) and (**2**) has been noted previously [1]. Since the 1:2 complexes form the basis for the liquid clathrate effect [2,3], the extension to

$$MX + AlR_3 \longrightarrow M[AlR_3X] \quad (1)$$

$$MX + 2AlR_3 \longrightarrow M[Al_2R_6X] \quad (2)$$

$[M \cdot CE][Al_2R_6X]$ (CE = crown ethers such as 18-crown-6, dibenzo-18-crown-6, or 15-crown-5) was a particularly valuable step. In the course of these investigations, two discrete molecular complexes of $AlMe_3$ with crown ethers were encountered: $[AlMe_3]_2$[dibenzo-18-crown-6], **I**, and $[AlMe_3]_4$[15-crown-5], **II**. For dibenzo-18-crown-6, the plane of the oxygen atoms was found to be distorted into a chair configuration in order to form two strong Al – O linkages. The 15-crown-5 complex exhibited an even greater difference from its normal geometry. The crown was essentially turned inside-out to afford four strong Al – O bonds. In order to understand this unexpected behavior better, additional studies have been undertaken. The results reported herein show that crown ethers have a considerable conformational lability which is doubtless of importance to their host-guest chemistry.

2. Results and Discussion

The typical synthesis of $[M \cdot CE][Al_2Me_6X]$ involves first the formation of a complex of $AlMe_3$ with the crown ether. In the case of dibenzo-18-crown-6, the complex normally

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formulated as $[AlMe_3]_2$[dibenzo-18-crown-6] readily transfers the $AlMe_3$ to the X^- group, while the crown ether encloses the M^+ ion. In view of this facility it was surprising to find that the Al – O bond length, 1.967(3) Å [1], was indicative of a strong interaction (the distance in $[AlMe_3]_2$[dioxane] is 2.02(2) Å [4]). In order to accomplish the strong donor-acceptor bonds, the considerable distortion of the crown shown in Figure 1 was effected. It was believed at the time of publication of Part I of this series [1] that the presence of the benzo-substituents imparted sufficient rigidity to make the adjacent oxygen atoms unavailable for bond formation to an aluminum alkyl unit. Subsequent studies have proved this idea to be incorrect. In Figure 2 the structure of the 3 : 1 adduct, $[AlMe_3]_3$[dibenzo-18-crown-6], **III**, is presented. Important bond lengths and angles are given in Table I. Clearly, the energy of formation of the third Al – O bond is sufficient to cause the further substantial distortion of the crown ether.

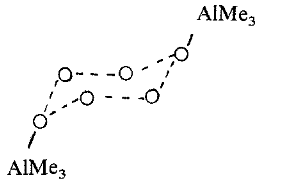


Fig. 1. Geometry of the crown in $[AlMe_3]_2$[dibenzo-18-crown-6], I.

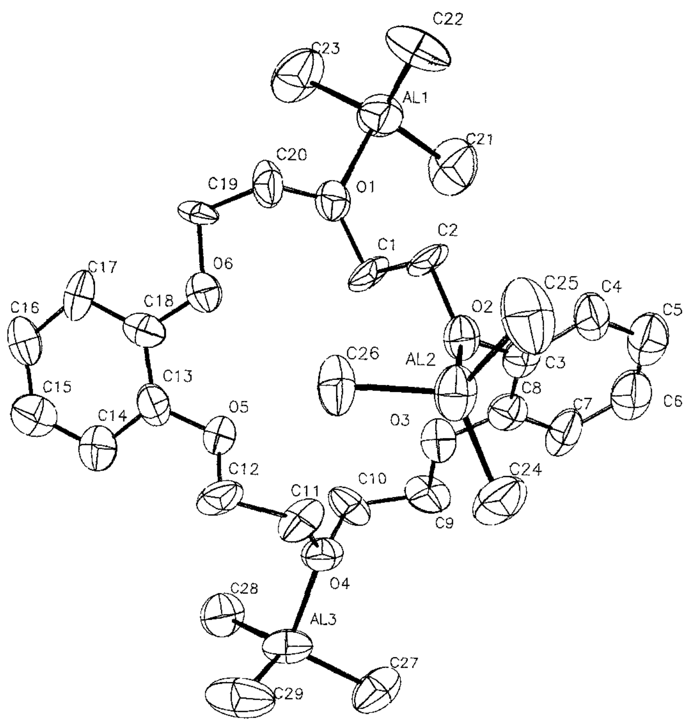
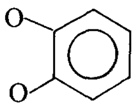


Fig. 2. Molecular structure and atom numbering scheme for $[AlMe_3]_3$[dibenzo-18-crown-6], **III**. The molecule possesses no crystallographic symmetry.

Table I. Bond lengths (Å) and angles (deg) for $[AlMe_3]_3$[dibenzo-18-crown-6], **III**

Atoms	Distance	Atoms	Distance
Al(1) – O(1)	1.982(5)	Al(1) – C(21)	1.952(8)
Al(1) – C(22)	1.972(9)	Al(1) – C(23)	1.983(8)
Al(2) – O(2)	2.024(5)	Al(2) – C(24)	1.927(8)
Al(2) – C(25)	1.969(8)	Al(2) – C(26)	1.972(7)
Al(3) – O(4)	1.972(5)	Al(3) – C(27)	1.969(8)
Al(3) – C(28)	1.997(8)	Al(3) – C(29)	1.953(8)
O(1) – C(1)	1.457(7)	O(1) – C(20)	1.450(7)
O(2) – C(2)	1.463(7)	O(2) – C(3)	1.418(8)
O(3) – C(8)	1.359(9)	O(3) – C(9)	1.437(8)
O(4) – C(10)	1.456(8)	O(4) – C(11)	1.448(7)
O(5) – C(12)	1.413(8)	O(5) – C(13)	1.378(9)
O(6) – C(18)	1.370(8)	O(6) – C(19)	1.413(8)
C(1) – C(2)	1.518(8)	C(3) – C(4)	1.368(9)
C(3) – C(8)	1.40(1)	C(4) – C(5)	1.39(1)
C(5) – C(6)	1.37(1)	C(6) – C(7)	1.38(1)
C(7) – C(8)	1.39(1)	C(9) – C(10)	1.497(9)
C(11) – C(12)	1.490(9)	C(13) – C(14)	1.40(1)
C(13) – C(18)	1.371(9)	C(14) – C(15)	1.40(1)
C(15) – C(16)	1.35(1)	C(16) – C(17)	1.38(1)
C(17) – C(18)	1.40(1)	C(19) – C(20)	1.497(9)

Atoms	Angle	Atoms	Angle
O(1) – Al(1) – C(21)	101.2(3)	O(1) – Al(1) – C(22)	102.5(3)
C(21) – Al(1) – C(22)	115.3(4)	O(1) – Al(1) – C(23)	101.9(3)
C(21) – Al(1) – C(23)	118.1(4)	C(22) – Al(1) – C(23)	114.3(4)
O(2) – Al(2) – C(24)	101.7(3)	O(2) – Al(2) – C(25)	102.5(3)
C(24) – Al(2) – C(25)	116.8(4)	O(2) – Al(2) – C(26)	99.7(3)
C(24) – Al(2) – C(26)	116.0(4)	C(25) – Al(2) – C(26)	115.9(4)
O(4) – Al(3) – C(27)	101.0(3)	O(4) – Al(3) – C(28)	102.6(3)
C(27) – Al(3) – C(28)	117.1(3)	O(4) – Al(3) – C(29)	104.8(3)
C(27) – Al(3) – C(29)	114.2(4)	C(28) – Al(3) – C(29)	114.5(4)
Al(1) – O(1) – C(1)	124.0(4)	Al(1) – O(1) – C(20)	117.9(4)
C(1) – O(1) – C(20)	115.2(5)	Al(2) – O(2) – C(2)	118.0(4)
Al(2) – O(2) – C(3)	120.6(4)	C(2) – O(2) – C(3)	116.4(5)
C(8) – O(3) – C(9)	116.8(6)	Al(3) – O(4) – C(10)	116.7(4)
Al(3) – O(4) – C(11)	124.1(4)	C(10) – O(4) – C(11)	115.7(5)
C(12) – O(5) – C(13)	115.7(6)	C(18) – O(6) – C(19)	118.1(6)
O(1) – C(1) – C(2)	107.9(5)	O(2) – C(2) – C(1)	107.8(5)
O(2) – C(3) – C(4)	119.2(9)	O(2) – C(3) – C(8)	118.1(9)
C(4) – C(3) – C(8)	122.7(8)	C(3) – C(4) – C(5)	118.8(8)
C(4) – C(5) – C(6)	119.4(8)	C(5) – C(6) – C(7)	121.6(9)
C(6) – C(7) – C(8)	119.9(8)	O(3) – C(8) – C(3)	116.4(9)
O(3) – C(8) – C(7)	126(1)	C(3) – C(8) – C(7)	117.5(9)
O(3) – C(9) – C(10)	107.9(6)	O(4) – C(10) – C(9)	113.3(6)
O(4) – C(11) – C(12)	113.0(6)	O(5) – C(12) – C(11)	107.9(6)
O(5) – C(13) – C(14)	122.4(9)	O(5) – C(13) – C(18)	118.2(8)
C(14) – C(13) – C(18)	119.3(9)	C(13) – C(14) – C(15)	119.7(8)
C(14) – C(15) – C(16)	120.6(8)	C(15) – C(16) – C(17)	120.5(8)
C(16) – C(17) – C(18)	119.4(7)	O(6) – C(18) – C(13)	115.2(8)
O(6) – C(18) – C(17)	124.3(9)	C(13) – C(18) – C(17)	120.5(8)
O(6) – C(19) – C(20)	107.8(6)	O(1) – C(20) – C(19)	112.8(6)

The most meaningful comparison of the geometries of **I** and **III** is related to the orientation of the  (*o*-catechol) units. In **I** they are essentially coplanar, while in **III** they exhibit an angle of twist of 47°. (Each individual *o*-catechol unit is planar to within 0.04 Å.) Another way of describing the configuration of **III** is to relate the aluminum-bonded oxygen atoms to the plane of the other three oxygen atoms. The deviations are −0.19, 1.69, and 0.19 Å for O(1), O(2), and O(4), respectively.

The bond of the $AlMe_3$ group to the most hindered oxygen atom produces the longest of the three Al − O distances, 2.024(5) Å (compared to 1.972(5) and 1.982(5) Å). Although 2.02 Å is at the high end of the range of known Al − O bonds, it must be regarded as indicative of a strong interaction.

Complex **III** was synthesized under mild conditions: the heatmg of a toluene solution of $AlMe_3$ with the appropriate mole ratio of dibenzo-18-crown-6 at 60° for several hours. **III** therefore may well play a role in reactions such as (2). Studies which involve the isolation of **III**, followed by reaction of certain MX species are currently in progress.

The isolation of $[AlMe_3]_4$[15-crown-5], **II**, prompted the investigation of 18-crown-6 in an excess of $AlMe_3$ (mole ratio less than 1 : 6). Two questions of interest were under consideration. First, to what extent could the 18-membered crown be turned inside-out? Second, what effect upon the facilitation of reactions (1) and (2) would the greater flexibility of 18-crown-6 (compared to dibenzo-18-crown-6) exhibit?

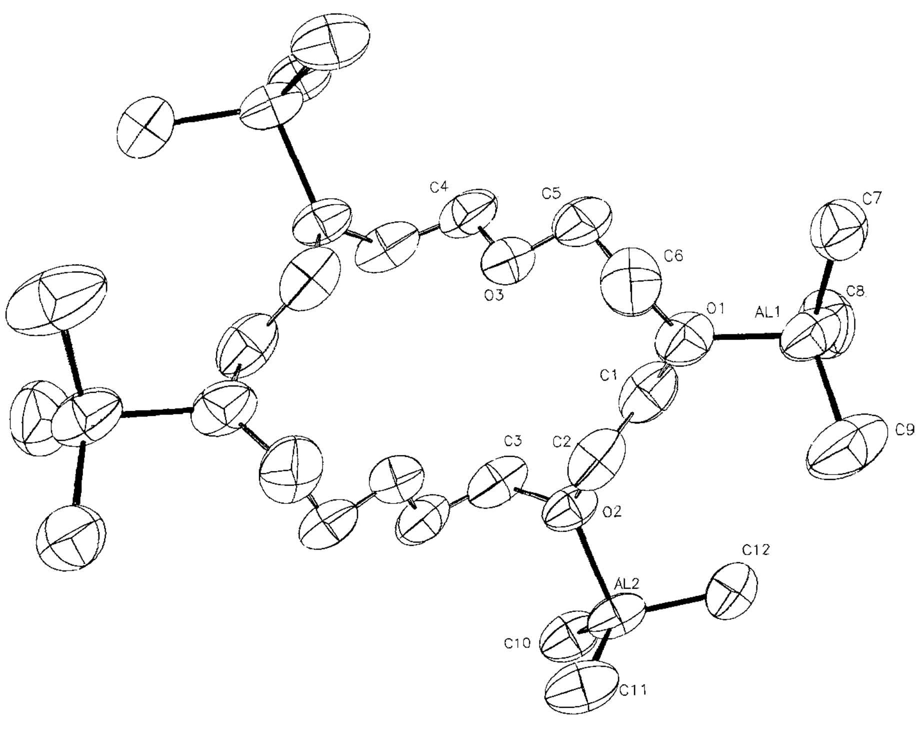


Fig. 3. Molecular structure and atom numbering scheme for $[AlMe_3]_4$[18-crown-6], **IV**. The molecule exhibits a crystallographic two-fold axis normal to the average plane of the crown ether.

The only solid material thus far isolated and characterized from the reaction of 18-crown-6 with $AlMe_3$ in aromatic solvents is $[AlMe_3]_4$[18-crown-6], **IV**. The molecular structure and atom numbering scheme are shown in Figure 3. Table II gives the bond lengths and angles. The view is along the crystallographic two-fold axis which is perpendicular to the average plane of the crown ether.

Table II. Bond lengths (Å) and angles (deg) for $[AlMe_3]_4$[18-crown-6], **IV**

Atoms	Distance	Atoms	Distance
Al(1) – O(1)	1.985(6)	Al(1) – C(7)	1.957(8)
Al(1) – C(8)	1.933(9)	Al(1) – C(9)	1.954(8)
Al(2) – C(2)	1.984(4)	Al(2) – C(10)	1.958(7)
Al(2) – C(11)	1.971(8)	Al(2) – C(12)	1.966(9)
O(1) – C(1)	1.471(9)	O(1) – C(6)	1.430(8)
O(2) – C(2)	1.478(8)	O(2) – C(3)	1.458(8)
O(3) – C(4)	1.432(9)	O(3) – C(5)	1.42(1)
C(1) – C(2)	1.48(1)	O(3) – C(4)′	1.48(1)
C(5) – C(6)	1.50(1)		

Atoms	Angle	Atoms	Angle
O(1) – Al(1) – C(7)	102.7(3)	O(1) – Al(1) – C(8)	101.8(3)
C(7) – Al(1)–C(8)	116.1(4)	O(1) – Al(1) – C(9)	103.7(4)
C(7) – Al(1)–C(9)	113.7(4)	C(8) – Al(1) – C(9)	116.0(4)
O(2) – Al(2)–C(10)	101.4(3)	O(2) – Al(2) – C(11)	102.3(3)
C(10) – Al(2)–C(11)	118.5(4)	O(2) – Al(2) – C(12)	102.1(3)
C(10) – Al(2)–C(12)	114.4(4)	C(11) – Al(2) – C(12)	114.6(4)
Al(1) – O(1) – C(1)	115.2(5)	Al(1) –O(1) – C(6)	123.7(5)
C(1) – O(1) – C(6)	120.5(6)	Al(2) –O(2) – C(2)	119.3(4)
Al(2) – O(2) – C(3)	122.4(4)	C(2) –O(2) – C(3)	116.2(5)
C(4) – O(3) – C(5)	113.8(7)	O(2) –C(2) – C(2)	108.5(6)
O(2) – O(2) – C(1)	105.1(6)	O(2) –C(3) – C(4)′	112.0(6)
O(3)′ – C(4)′ – C(3)	110.1(7)	O(3) –C(5) – C(6)	110.9(8)
O(1) – C(6) – C(5)	112.3(7)		

The configuration of **IV** is quite similar to that observed for **II**: O(3) and O(3)′ remain on the interior of the ring, while the other four oxygen atoms are bonded to aluminum atoms and are thus on the exterior. The two sets of oxygen atoms related by the two-fold axis are arranged in a boat-like configuration. The angle made by the normals to the planes of O(1), O(2), O(3) and O(1)′, O(2)′, O(3)′ is 114°. The two unique Al – O bond lengths, 1.984(4) and 1.985(6) Å, lie between the values reported for **I**, 1.967(3) Å, and **II**, 2.000(9) Å [1]. From an overall consideration of the geometry, it would seem possible to form $[AlMe_3]_5$[18-crown-6], if not $[AlMe_3]_6$[18-crown-6].

Qualitatively, reactions (1) and (2) do not appear as rapid for 18-crown-6 as for dibenzo-18-crown-6. (Although the former is certainly effective: it has afforded the well-characterized [K · 18-crown-6] $[GaMe_3NCS]$ [5].) This may be attributed to the energy needed to break the Al – O bonds and regain the normal 18-crown-6 configuration from **IV** compared to a similar situation in **I**. However, this is again qualitative: no rate data are available.

As was stated initially, the use of crown ethers in conjunction with reactions (1) and (2) has provided a wealth of compounds. Quite a number of X-ray structures have resulted

[6 – 10]. It was seen, however, that the intermediate formation of the aluminum alkyl-crown complex is not as simple as first envisioned. Further studies in this series will involve more detailed studies of 18-crown-6, dibenzo-18-crown-6, and 15-crown-5, as well as an expansion to other crown ether systems.

3. Experimental

SYNTHESIS OF $[AlMe_3]_3$[Dibenzo-18-crown-6], **III**

Trimethylaluminum (4.0 mmol) was added to a suspension of dibenzo-18-crown-6 (1.0 mmol) in toluene (10 ml). The sealed tube was allowed to stir for 24 h at ambient temperature. During this time, colorless crystals were deposited on the walls of the reaction vessel. The system was then heated to 60° C for 6 h and allowed to cool slowly to room temperature over a 24 h period Colorless, extremely air-sensitive crystals resulted in ca. 20% yield.

SYNTHESIS OF $[AlMe_3]_4$[18-crown-6], **IV**

Trimethylaluminum (6.0 mmol) was added to 18-crown-6 (1.0 mmol) in toluene (10 ml). The sealed tube was heated to 60° C for 24 h and allowed to cool to room temperature over a 24 h period. The only crystalline product was the colorless, extremely air-sensitive **IV** in 80% yield.

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

Compound	$[AlMe_3]_3$[dibenzo-18-crown-6], **III**	$[AlMe_3]_4$[18-crown-6], **IV**
Mol wt	576.7	552.7
Space group	$P\bar{1}$	Pbcn
Cell constants		
a, Å	8.898(4)	18.753(6)
b, Å	11.848(5)	12.570(6)
c, Å	19.060(6)	15.095(6)
α, deg	74.86(3)	–
β, deg	80.73(4)	–
γ, deg	67.02(4)	–
Cell vol, Å^3	1781.8	3560.4
Molecules/unit cell	2	4
ρ(calc), g cm^{-3}	1.08	1.03
μ(calc), cm^{-1}	1.46	1.69
Radiation	MoKα	MoKα
Max crystal dimensions, mm	0.12 × 0.40 × 0.56	0.85 × 0.20 × 0.20
Scan width, deg	0.80 + 0.20 tanθ	0.80 + 0.20 tanθ
Standard reflections	(0014), (060)	(006), (040), (800)
Decay of standards	< 3%	< 4%
Reflections measured	2485	3684
2θ range	36	50
Reflections considered observed	1800	1320
No. of parameters varied	343	154
GOF	1.43	2.25
R	0.045	0.068
R_w	0.052	0.064

X-RAY DATA COLLECTION AND STRUCTURE SOLUTION FOR $[AlMe_3]_3$[Dibenzo-18-crown-6], **III**

Single crystals were sealed in thin-walled glass 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 III. Intensity data were recorded on the diffractometer in the usual manner [11]. A summary of data collection parameters is also presented in Table III. 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 [12], 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

Table IV. Final fractional coordinates for $[AlMe_3]_3$[dibenzo-18-crown-6], **III**

Atom	x/a	y/b	z/c
Al(1)	−0.2223(3)	1.0590(2)	0.3863(1)
Al(2)	−0.4856(3)	0.7147(2)	0.2587(1)
Al(3)	0.2934(3)	0.3391(2)	0.1346(1)
O(1)	−0.1953(5)	0.9880(4)	0.2997(3)
O(2)	−0.3448(5)	0.7297(5)	0.3267(3)
O(3)	−0.0516(7)	0.5463(5)	0.3240(3)
O(4)	0.1375(6)	0.4669(4)	0.1863(3)
O(5)	0.1082(7)	0.7313(5)	0.1334(3)
O(6)	−0.0275(7)	0.9573(5)	0.1579(3)
C(1)	−0.1847(8)	0.8608(6)	0.3033(4)
C(2)	−0.3535(8)	0.8554(7)	0.3270(4)
C(3)	−0.295(1)	0.6363(9)	0.3911(5)
C(4)	−0.398(1)	0.6432(8)	0.4528(7)
C(5)	−0.351(1)	0.548(1)	0.5147(5)
C(6)	−0.205(2)	0.450(1)	0.5123(6)
C(7)	−0.102(1)	0.4430(8)	0.4498(6)
C(8)	−0.144(1)	0.5388(9)	0.3881(5)
C(9)	0.103(1)	0.4447(7)	0.3197(4)
C(10)	0.1941(9)	0.4811(7)	0.2499(4)
C(11)	0.0002(8)	0.5728(7)	0.1536(4)
C(12)	0.0509(9)	0.6673(7)	0.0973(4)
C(13)	0.161(1)	0.823(1)	0.0891(5)
C(14)	0.284(1)	0.7979(8)	0.0337(6)
C(15)	0.338(1)	0.893(1)	−0.0067(5)
C(16)	0.274(1)	1.0089(9)	0.0086(5)
C(17)	0.153(1)	1.0350(8)	0.0638(5)
C(18)	0.95(1)	0.941(1)	0.1037(5)
C(19)	−0.0948(9)	1.0747(7)	0.1781(4)
C(20)	−0.2399(9)	1.0751(7)	0.2304(4)
C(21)	−0.136(1)	0.9065(8)	0.4611(4)
C(22)	−0.461(1)	1.1501(8)	0.3956(5)
C(23)	−0.093(1)	1.1692(8)	0.3537(5)
C(24)	−0.407(1)	0.5355(7)	0.2680(4)
C(25)	−0.7085(9)	0.7944(9)	0.3004(5)
C(26)	−0.4203(9)	0.8116(7)	0.1664(4)
C(27)	0.3081(9)	0.1835(7)	0.2074(5)
C(28)	0.4907(9)	0.3866(7)	0.1151(4)
C(29)	0.186(1)	0.3619(8)	0.0475(5)

further refinement gave $R = 0.055$. The hydrogen atoms of the dibenzo-18-crown-6 were placed at calculated positions 1.00 Å from the bonded carbon atoms and their parameters were not varied. The hydrogen atoms on the methyl carbon atoms were located on a difference Fourier map and were not refined. Additional cycles of refinement led to final values of $R = 0.045$ and $R_w = \{\Sigma w([|F_o| - |F_c|)^2/\Sigma w(F_o)^2\}^{1/2} = 0.052$. 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 [13]. Neutral atom scattering factors were taken from the compilations of Cromer and Waber [14] for Al, O, and C. Scattering factors for H were from [15]. The final values of the positional parameters are given in Table IV [16].

X-RAY DATA COLLECTION AND STRUCTURE SOLUTION FOR $[AlMe_3]_4$[18-crown-6], IV

The compound was manipulated and data collected in the same manner as for **III**. Final positional parameters are listed in Table V [16].

Table V. Final fractional coordinates for $[AlMe_3]_4$[18-crown-6], **IV**

Atom	x/a	y/b	z/c
Al(1)	0.7839(2)	0.0665(2)	0.1575(2)
Al(2)	0.5627(2)	0.2423(2)	− 0.0717(1)
O(1)	0.6861(3)	0.1017(4)	0.1982(3)
O(2)	0.5567(3)	0.2426(4)	0.0597(3)
O(3)	0.5762(3)	0.1911(5)	0.3351(3)
C(1)	0.6518(5)	0.1905(6)	0.1513(6)
C(2)	0.5854(5)	0.1510(6)	0.1098(5)
C(3)	0.5092(6)	0.3135(6)	0.1082(5)
C(4)	0.5655(6)	0.2776(7)	0.3954(5)
C(5)	0.6420(6)	0.1371(9)	0.3473(5)
C(6)	0.6537(5)	0.0563(7)	0.2752(6)
C(7)	0.8200(4)	− 0.0229(6)	0.2537(5)
C(8)	0.8263(5)	0.2059(7)	0.1468(6)
C(9)	0.7683(6)	− 0.0104(8)	0.0466(5)
C(10)	0.5265(5)	0.3844(5)	− 0.1000(5)
C(11)	0.5041(5)	0.1179(6)	− 0.1035(5)
C(12)	0.6654(5)	0.2239(7)	− 0.0919(5)

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16. Tables of thermal parameters, hydrogen atom coordinates, and structures factors for **III** and **IV** are available from the editorial offices.

Supplementary Data relevant to this article have been deposited with the British Library Lending Division, and copies may be ordered from there, quoting Sup. No. 90075.