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ABSTRACT. In contrast to aluminum alkyls, alkyl aluminum halides such as EtAlCl₂ react with crown ethers to form cation-anion pairs which exhibit the liquid clathrate effect. Specifically, [12-C-4·AlCl₂][AlCl₃Et] and [18-C-6·AlCl₂][AlCl₃Et] have been isolated and characterized by X-ray diffraction techniques. The cations show aluminum in an octahedral environment made up of four of the oxygen atoms from the crown and two chlorine atoms. The 12-C-4 derivative crystallizes in the monoclinic space group P2₁/c with cell constants of a = 7.497(4), b = 22.121(8), c = 12.339(5) Å, β = 94.99(3)°, and Z = 4 for ρ = 1.43 g cm⁻³. Least-squares refinement based on 1413 observed reflections led to a final conventional R value of 0.093. The 18-C-6 complex belongs to the triclinic space group P1̄ with a = 8.414(4), b = 12.193(6), c = 12.394(6) Å, α = 73.14(4), β = 86.07(4), γ = 81.52(4)°, and Z = 2 for ρ = 1.45 g cm⁻³. Refinement based on 2605 observed reflections led to R = 0.063. The complex aluminum-containing species are related to a class of compounds called aluminoxanes.

Key words: crown ether, liquid clathrate, aluminum alkyl, aluminoxane.

1. Introduction

In previous contributions we have shown that aluminum alkyls such as AlMe₃ react with crown ethers to form adducts [1,2]. The structural characterization of several of these complexes has showed that the aluminum alkyl has the ability to essentially turn the crown ether inside-out. Even though the Al-O bond is a strong one as measured from the bond length, the complexes quickly undergo reaction with MX species to form compounds in which the M cation is associated with the crown ether and the X anion is bonded to the aluminum alkyl [3]. As we began to expand the range of aluminum alkyls to include halogen-containing molecules, we found two kinds of behavior: (1) simple adducts, and (2) novel reaction products. The subject of this manuscript is the latter.

2. Results and Discussion

Reaction of either 12-C-4 or 18-C-6 (12-C-4 is 12-crown-4; 18-C-6, 18-crown-6) with a toluene solution of EtAlCl_2 occurs quickly at room temperature. The formation of two liquid layers characteristic of the presence of a cation-anion arrangement of a certain type is observed (the liquid clathrate effect) [4]. Slow cooling of the solution to 5°C affords clear, colorless crystals of the air-sensitive crystalline compounds in high yield. Since the formation of liquid clathrates was unexpected, single crystal X-ray diffraction studies were carried out. The structure of the cation $[\text{12-C-4}\cdot\text{AlCl}_2]^+$ is shown in Figure 1, while that of $[\text{18-C-6}\cdot\text{AlCl}_2]^+$ is found in Figure 2.

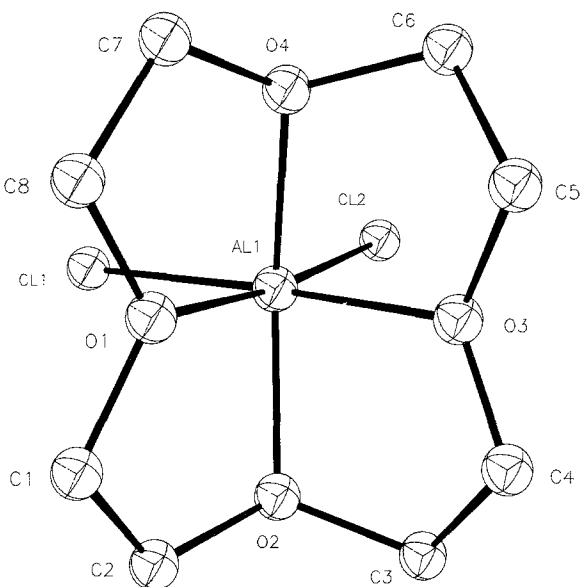


Fig. 1. Structure of the $[\text{12-C-4}\cdot\text{AlCl}_2]^+$ cation. The hydrogen atoms of the crown ether have been omitted for clarity.

This type of behavior for EtAlCl_2 is to our knowledge unprecedented, although the dimeric structure of the compound is known to be a labile one involving the interconversion given below. The



asymmetric split of the bridge leads to the formation of $[\text{AlCl}_2]^+$ and $[\text{AlCl}_2\text{Et}_2]^-$ ions. The anion we observe in the solid state is the

$[\text{AlCl}_3\text{Et}]^-$ one, but this probably just means that it is less soluble in combination with the cation than are the other possibilities. See the Experimental for details. For AlCl_3 itself, there are reports of the apparent generation of AlCl_2^+ , although not in the presence of crown ethers [5]. Two leading references are to the spectroscopic characterization of $[(\text{THF})_4 \cdot \text{AlCl}_2]^+$ [6] and the structural investigation of $[(\text{MeCN})_5 \cdot \text{AlCl}]^+$ [7]. Indeed, this type of behavior

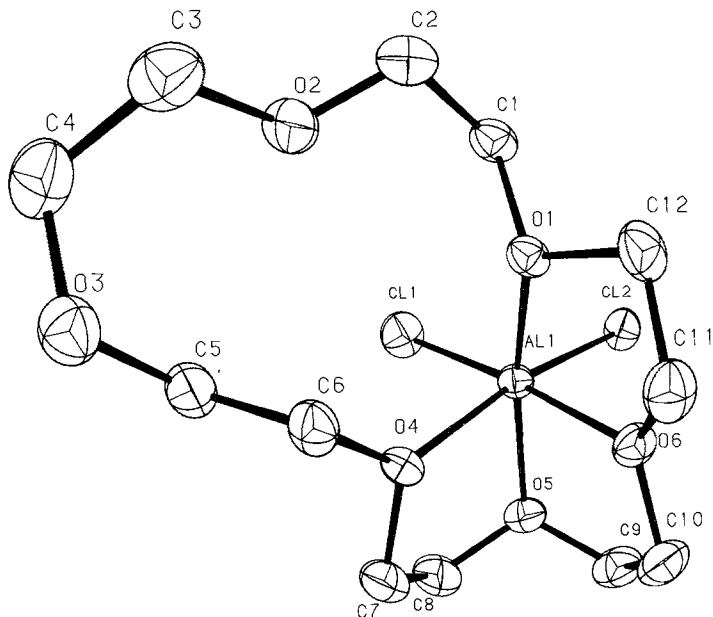


Fig. 2. Structure of the $[\text{18-C-6} \cdot \text{AlCl}_2]^+$ cation.

has considerable generality, as will be reported in future contributions.

Within the cation of the 12-C-4 reaction product, the bond lengths are worthy of notice. The two independent Al-Cl lengths, 2.200(8) and 2.202(5) Å, are substantially longer than those found in the anion, 2.12(1) Å on average, or in neutral four-coordinate Al-containing complexes, 2.13(1) Å in $\text{Cl}_2\text{AlN}(\text{C}_2\text{H}_5)\text{C}_2\text{H}_4\text{N}(\text{CH}_3)_2$ [8]. This is presumably a consequence of the octahedral environment at the Al atom. The Al-O distances average 1.96(2) Å, and are normal for donor-acceptor complexes of aluminum, even those which involve the coordination number four [9]. Important bond lengths and angles are presented in Table I.

The cation of the reaction product of 18-C-6 exhibits an interesting spread of bond lengths. Because the X-ray data was better on this complex, the associated metrical parameters are known with

better precision. The two independent Al-Cl lengths, 2.148(3) and 2.210(2) Å, differ markedly. The Al-O lengths also range from 1.946(5) to 2.065(4) Å. Since we are dealing with a crown ether which has both bonding and nonbonding oxygen atoms with respect to the aluminum atom, the constraints placed on the ring are the likely cause of the observed distortions. Bond lengths and angles are given in Table II.

Table I. Bond lengths (Å) and angles (°) for [12-C-4.AlCl₂][AlCl₃Et].

A. Cation

Atoms	Distance	Atoms	Distance
Al(1)-Cl(1)	2.202(5)	Al(1)-Cl(2)	2.200(8)
Al(1)-O(1)	1.97(1)	Al(1)-O(2)	1.97(1)
Al(1)-O(3)	1.99(1)	Al(1)-O(4)	1.92(1)
Atoms	Angle	Atoms	Angle
Cl(2)-Al(1)-Cl(1)	92.2(3)	Cl(1)-Al(1)-O(1)	88.0(3)
Cl(2)-Al(1)-O(1)	176.0(4)	Cl(1)-Al(1)-O(2)	97.9(4)
Cl(2)-Al(1)-O(2)	107.4(5)	Cl(1)-Al(1)-O(3)	172.3(4)
Cl(2)-Al(1)-O(3)	95.5(4)	Cl(1)-Al(1)-O(4)	99.5(4)
Cl(2)-Al(1)-O(4)	99.2(4)	O(1)-Al(1)-O(2)	76.5(5)
O(1)-Al(1)-O(3)	84.3(4)	O(1)-Al(1)-O(4)	76.8(4)
O(2)-Al(1)-O(3)	79.6(5)	O(2)-Al(1)-O(4)	147.5(5)
O(3)-Al(1)-O(4)	79.5(5)		

B. Anion

Atoms	Distance	Atoms	Distance
Al(2)-Cl(3)	2.120(6)	Al(2)-Cl(4)	2.122(6)
Al(2)-Cl(5)	2.115(6)	Al(2)-C(9)	2.23(3)
C(9)-C(10)	1.41(7)		
Atoms	Angle	Atoms	Angle
Cl(3)-Al(2)-Cl(4)	105.0(3)	Cl(3)-Al(2)-Cl(5)	105.8(2)
Cl(4)-Al(2)-Cl(5)	107.0(3)	Cl(3)-Al(2)-C(9)	103.8(7)
Cl(4)-Al(2)-C(9)	121.1(7)	Cl(5)-Al(2)-C(9)	112.8(7)
Al(2)-C(9)-C(10)	105(3)		

Table II. Bond lengths (Å) and angles (°) for $[18-C-6 \cdot AlCl_2][AlCl_3Et]$.

A. Cation

Atoms	Distance	Atoms	Distance
Al(1)-Cl(1)	2.148(3)	Al(1)-Cl(2)	2.210(2)
Al(1)-O(1)	1.946(5)	Al(1)-O(4)	2.065(4)
Al(1)-O(5)	1.961(6)	Al(1)-O(6)	1.976(4)
O(1)-C(1)	1.468(9)	O(1)-C(12)	1.455(8)
O(2)-C(2)	1.403(8)	O(2)-C(3)	1.405(9)
O(3)-C(4)	1.41(1)	O(3)-C(5)	1.43(1)
O(4)-C(6)	1.428(9)	O(4)-C(7)	1.43(1)
O(5)-C(6)	1.450(8)	O(5)-C(9)	1.442(9)
O(6)-C(10)	1.42(1)	O(6)-C(11)	1.42(1)
C(1)-C(2)	1.47(1)	C(3)-C(4)	1.49(1)
C(5)-C(6)	1.48(1)	C(7)-C(8)	1.47(1)
C(9)-C(10)	1.50(1)	C(11)-C(12)	1.48(1)

Atoms	Angle	Atoms	Angle
Cl(1)-Al(1)-Cl(2)	96.8(1)	Cl(1)-Al(1)-O(1)	101.4(2)
Cl(2)-Al(1)-O(1)	96.1(1)	Cl(1)-Al(1)-O(4)	89.4(1)
Cl(2)-Al(1)-O(4)	171.5(2)	O(1)-Al(1)-O(4)	88.3(2)
Cl(1)-Al(1)-O(5)	100.1(2)	Cl(2)-Al(1)-O(5)	94.6(20)
O(1)-Al(1)-O(5)	154.6(2)	O(4)-Al(1)-O(5)	78.5(2)
Cl(1)-Al(1)-O(6)	173.4(2)	Cl(2)-Al(1)-O(6)	89.78(1)
O(1)-Al(1)-O(6)	78.7(2)	O(4)-Al(1)-O(6)	84.0(2)
O(5)-Al(1)-O(6)	78.5(2)		

B. Anion

Atoms	Distance	Atoms	Distance
Al(2)-Cl(3)	2.517(4)	Al(2)-Cl(4)	2.516(3)
Al(2)-Cl(5)	2.163(4)	Al(2)-C(13)	1.93(1)
C(13)-C(14)	1.45(3)		

Atoms	Angle	Atoms	Angle
Cl(3)-Al(2)-Cl(4)	107.7(1)	Cl(3)-Al(2)-Cl(5)	105.1(2)
Cl(4)-Al(2)-Cl(5)	106.4(1)	Cl(3)-Al(2)-C(13)	112.2(5)
Cl(4)-Al(2)-C(13)	112.5(5)	Cl(5)-Al(2)-C(13)	112.5(4)
Al(2)-C(13)-C(14)	109(1)		

By the reactions discussed in this manuscript, it is possible to build frameworks which contain aluminum in the presence of quite large numbers of oxygen atoms. For the larger crown ethers this method may allow the placement of more than one AlCl_2^+ ion onto the ring. Cations of some size are envisioned. When these are coupled with aluminoxane anions such as $[\text{Al}_7\text{O}_6\text{Me}_{16}]^-$ [10], complexes which have a certain resemblance to zeolites can be foreseen. It remains in later contributions to show that these new compounds can be constructed with shape and size selectivity.

3. Experimental

Synthesis of $[\text{12-C-4}\cdot\text{AlCl}_2][\text{AlCl}_3\text{Et}]$

A toluene solution of EtAlCl_2 (25% by weight, 20 mmol) was added to 12-C-4 (10 mmol) in 5 ml of toluene. The reaction was very exothermic, and two immiscible liquid layers formed immediately. The lower layer began to exhibit crystals in a matter of minutes, and after one hour 90% of the complex in the lower layer had crystallized. The yield of 'cation' was quantitative. The anion clearly varied from crystal to crystal as discussed below.

Synthesis of $[\text{18-C-6}\cdot\text{AlCl}_2][\text{AlCl}_3\text{Et}]$

The molar amounts and reaction conditions were the same as for the reaction with 12-C-4. However, after the formation of the two liquid layers, no solid product was observed for ca. 24 hours.

X-ray Data Collection and Structure Solution for $[\text{12-C-4}\cdot\text{AlCl}_2][\text{AlCl}_3\text{Et}]$

Single crystals were sealed in thin-walled glass capillaries. Final lattice parameters as determined from 20 high-angle reflections centered on an Enraf-Nonius diffractometer 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 given in Table III. The intensities were corrected for Lorentz and polarization effects, but not for absorption.

Structure solution was effected with the aid of the direct methods program MULTAN [12] which revealed the cation and the Al and Cl atoms of the anion. Initially, the anion was assumed to be $[\text{AlCl}_2\text{Et}_2]^-$ because of the overall stoichiometry of the reaction. The ambiguity in the X-ray study was made greater by a combination of high thermal motion and disorder in the anion. Several models were tried, and the best fit is for the anion as given in the title. It is now clear that the anion varies from crystal to crystal, but the noteworthy features of the cation are not affected significantly by the nature of the anion (within the rather narrow limits of our studies). The ethyl group was treated with isotropic thermal parameters and all other nonhydrogen

atoms were refined with anisotropic temperature factors. The hydrogen atoms of the cation were located on a difference Fourier map and were allowed to ride on the bonded carbon atom during the refinement. The reliability indices have been defined previously [1,2], and are given in Table III. The largest parameter shifts in the final cycle of refinement were less than 0.01 of their estimated standard deviations.

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

Compound	[12-C-4·AlCl ₂]- [AlCl ₃ Et]	[18-C-6·AlCl ₂]- [AlCl ₃ Et]
Mol wt	436.5	524.6
Space group	P2 ₁ /c	P $\bar{1}$
Cell constants		
a, Å	7.497(4)	8.414(3)
b, Å	22.121(8)	12.193(4)
c, Å	12.339(5)	12.394(4)
α , deg	-	73.14(3)
β , deg	94.99(4)	86.07(3)
γ , deg	-	81.52(3)
Cell vol, Å ³	2038	1203.1
Molecules/unit cell	4	2
ρ (calc), g cm ⁻³	1.43	1.45
μ (calc), cm ⁻¹	8.0	7.0
Radiation	MoK α	MoK α
Max crystal dimensions, mm	0.50x0.60x0.60	0.25x0.30x0.40
Scan width, deg	0.8 + 0.2 tan θ	0.8 + 0.2 tan θ
Standard reflections	500,0100,006	200,020,002
Variation of standards	$\pm 2\%$	$\pm 2\%$
Reflections measured	2901	2947
2 θ range	1-44	1-44
Reflections considered obs	1678	2605
No. of parameters varied	176	241
GOF	1.76	1.46
R	0.085	0.063
R _w	0.091	0.068

Units weights were used at all stages of refinement. Sources of the scattering factors have been given in [1]. The final values of the positional parameters are given in Table IV [13].

Table IV. Final Fractional Coordinates for [12-C-4·AlCl₂][AlCl₃Et]

Atom	x/a	y/b	z/c
Al(1)	0.0992(5)	0.1091(2)	0.1523(3)
Al(2)	0.7003(6)	0.1393(2)	0.5827(3)
Cl(1)	0.3102(5)	0.0421(2)	0.1296(3)
Cl(2)	0.163(1)	0.1607(4)	0.0084(7)
Cl(3)	0.6785(5)	0.0664(2)	0.4710(3)
Cl(4)	0.9790(6)	0.1481(2)	0.6278(3)
Cl(5)	0.6198(6)	0.2172(2)	0.4919(4)
O(1)	0.029(1)	0.0596(4)	0.2746(8)
O(2)	0.217(1)	0.1502(6)	0.2811(9)
O(3)	-0.098(2)	0.1633(6)	0.1904(9)
O(4)	-0.106(1)	0.0651(6)	0.0896(6)
C(1)	0.140(3)	0.066(1)	0.377(2)
C(2)	0.222(3)	0.111(2)	0.369(2)
C(3)	0.135(3)	0.206(1)	0.289(2)
C(4)	-0.060(3)	0.2023(9)	0.278(2)
C(5)	-0.273(3)	0.1436(9)	0.155(2)
C(6)	-0.252(3)	0.1033(9)	0.063(1)
C(7)	-0.147(3)	0.011(1)	0.147(1)
C(8)	-0.075(4)	0.0120(9)	0.246(2)
C(9)	0.510(4)	0.115(1)	0.705(2)
C(10)	0.546(8)	0.156(3)	0.792(5)

X-ray Data Collection and Structure Solution for
[18-C-6·AlCl₂][AlCl₃Et]

The compound was manipulated and data collected in the same manner as for the 12-C-4 reaction product. Final positional parameters are listed in Table V [13].

Table V. Final fractional coordinates for [18-C-6·AlCl₂][AlCl₃Et]

Atom	x/a	y/b	z/c
Al(1)	0.7191(2)	0.1896(2)	0.8706(2)
Al(2)	0.8953(3)	0.3051(2)	0.2955(2)
Cl(1)	0.4705(3)	0.2321(2)	0.9133(2)
Cl(2)	0.7863(2)	0.0612(2)	1.0334(1)
Cl(3)	0.9146(3)	0.4345(2)	0.3795(2)
Cl(4)	0.8855(4)	0.1428(2)	0.4234(2)
Cl(5)	1.1221(3)	0.2877(2)	0.2045(2)

O(1)	0.7059(5)	0.0778(3)	0.7881(3)
O(2)	0.4140(6)	0.1168(4)	0.6618(4)
O(3)	0.4101(6)	0.3516(5)	0.4976(4)
O(4)	0.6904(5)	0.3186(3)	0.7200(4)
O(5)	0.8103(6)	0.3145(4)	0.9048(4)
O(6)	0.9437(5)	0.1652(4)	0.8152(4)
C(1)	0.5789(8)	0.0029(6)	0.8093(6)
C(2)	0.504(1)	0.0077(6)	0.7042(7)
C(3)	0.377(1)	0.1472(8)	0.5471(6)
C(4)	0.303(1)	0.2702(8)	0.5070(7)
C(5)	0.4582(9)	0.3628(6)	0.6017(6)
C(6)	0.6312(8)	0.3166(6)	0.6154(6)
C(7)	0.730(1)	0.4288(7)	0.7187(8)
C(8)	0.742(1)	0.4276(7)	0.8368(8)
C(9)	0.983(1)	0.2940(8)	0.9123(7)
C(10)	1.0511(9)	0.2433(7)	0.8193(7)
C(11)	0.9728(9)	0.1072(7)	0.7299(6)
C(12)	0.8602(9)	0.0202(6)	0.7596(7)
C(13)	0.714(2)	0.347(1)	0.197(1)
C(14)	0.727(3)	0.457(2)	0.115(2)

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