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Cationic, Neutral, and Anionic Organoaluminum Species in [$AlMe_2$(18-crown-6)$AlMe_2X$][$AlMeX_3$] (X = Cl, I)

Jerry L. Atwood,* Simon G. Bott, Stephen Harvey, and Peter C. Junk

Department of Chemistry, University of Missouri—Columbia, Columbia, Missouri 65211

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Summary: 18-crown-6 reacts with AlX_3 (X = Cl, **1***, X = I,* **2***) in an excess of $AlMe_3$ in toluene to form the liquid clathrate species [$AlMe_2$(18-crown-6)$AlMe_2X$][$AlMeX_3$]. The $AlMe_2^+$ ion is coordinated to the interior of the macrocycle, while the neutral species is coordinated to the exterior, via an inverted crown oxygen atom.*

Crown ethers are best known for their ability to complex alkali,[1] alkaline-earth,[2] and lanthanide metals.[3,4] In these situations the metal is invariably coordinated through the crown oxygens within the cavity of the crown ether. A few reports have shown that complexes with early transition metals[5−7] or with aluminum[8] exist in which crown ethers function as ligands by placing the oxygen atoms on the exterior of the macrocyclic ring. Indeed, 15-crown-5 is able to use four of its oxygen atoms in this manner in the formation of [(15-crown-5)$(AlMe_3)_4$],[8] while thia crown ethers typically adopt the conformation where the sulfur atoms are exodentate (directed out of the macrocyclic ring).[9,10] Our group has demonstrated the stabilization of unusual coordination chemistry for aluminum complexes bound on the interior of crown ethers.[11,12] One example was the stabilization of $AlMe_2^+$ by coordination to three oxygen atoms of 18-crown-6 and all five oxygen atoms of 15-crown-5.[12] In this contribution we show that the [$AlMe_2^+$(18-crown-6)] cation can further bond a neutral organoaluminum moiety on the outside of the macrocycle. In this fashion, in one compound cationic, neutral, and anionic organoaluminum species are found.

The organoalumium complexes [$AlMe_2$(18-crown-6)-$AlMe_2X$][$AlMeX_3$] (X = Cl, **1**; X = I, **2**) were prepared in moderate yield according to Scheme 1.[13,14] In both cases, a vigorous exothermic reaction occurred upon addition of $AlMe_3$ to the reaction mixture. After the reaction mixture was stirred for approximately 2 h, a pale yellow liquid clathrate[15−17] separated from the solvent layer. Colorless crystals of both complexes deposited from the liquid clathrate layers and were analyzed by X-ray crystallographic techniques.[18]

Scheme 1

$$\mathrm{AlX_3 + 18\text{-}crown\text{-}6 + AlMe_3\ (excess) \xrightarrow{toluene}}$$
$$\mathrm{[AlMe_2(18\text{-}crown\text{-}6)AlMe_2X][AlMeX_3]}$$
$$\mathrm{X = Cl,\ \mathbf{1};\ X = I,\ \mathbf{2}}$$

In the structure of the [$AlMe_2^+$(18-crown-6)] cation the aluminum atom was found to be strongly coordinated to one oxygen at 1.929(5) Å and more weakly to two others at 2.181(5) and 2.435(5) Å.[12] The decision to refer to the last distance as a bond was based in part on the Me−Al−Me bond angle of 140.6(3)°.[19] The three nonbonding Al⋯O separations were 3.09, 3.46, and 3.80 Å.[12] The geometry of the $AlMe_2^+$ group in the title complexes, where the chloride and iodide analogues are

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(1) Fenton, D. E. Alkali Metals and Group IIA Metals. In *Comprehensive Coordination Chemistry*; Wilkinson, G., Gillard, R. D., McCleverty, J. A., Eds.; Pergamon Press: Oxford, U.K., 1987, Vol 3, p 37.

(2) Mertes, K. B.; Lehn, J.-M. Multidentate Macrocyclic and Macropolycyclic Ligands. In *Comprehensive Coordination Chemistry*; Wilkinson, G., Gillard, R. D., McCleverty, J. A., Eds.; Pergamon Press: Oxford, U.K., 1987, Vol 2, p 928.

(3) Hart, F. A. Scandium, Yttrium and the Lanthanides. In *Comprehensive Coordination Chemistry*; Wilkinson, G., Gillard, R. D., McCleverty, J. A., Eds.; Pergamon Press: Oxford, U.K., 1987; Vol. 3, p 1092.

(4) Bunzli, J.-C. G. *Coord. Chem. Rev.* **1984**, *60*, 191.

(5) Bott, S. G.; Kynast, U.; Atwood, J. L. *J. Inclusion Phenom.* **1986**, *4*, 241.

(6) Bott, S. G.; Prinz, H.; Alvanipour, A.; Atwood, J. L. *J. Coord. Chem.* **1987**, *16*, 303.

(7) $ZrCl_4$ in fact reacts with 18-crown-6, leading to the formation of an open-ring macrocyclic coordination complex: Prinz, H.; Bott, S. G.; Atwood, J. L. *J. Am. Chem. Soc.* **1986**, *108*, 2113.

(8) (a) Atwood, J. L.; Hrncir, D. C.; Shakir, R.; Dalton, M. S.; Priester, R. D.; Rogers, R. D. *Organometallics* **1982**, *1*, 1021. (b) Atwood, J. L.; Priester, R. D.; Rogers, R. D.; Canada, L. G. *J. Inclusion Phenom.* **1983**, *1*, 61. (c) Robinson, G. H.; Bott, S. G.; Elgamal, H.; Hunter, W. E.; Atwood, J. L. *J. Inclusion Phenom.* **1985**, *3*, 65. (d) Robinson, G. H.; Hunter, W. E.; Bott, S. G.; Atwood, J. L. *J. Organomet. Chem.* **1987**, *326*, 9. (e) Robinson, G. H. *Coord. Chem. Rev.* **1992**, *112*, 227.

(9) Wolf, R. E., Jr.; Hartman, J. R.; Storey, J. M. E.; Foxman, B. M.; Cooper, S. R. *J. Am. Chem. Soc.* **1987**, *109*, 4328.

(10) Junk, P. C.; Atwood, J. L. *Supramol. Chem.* **1994**, *3*, 241.

(11) Bott, S. G.; Elgamal, H.; Atwood, J. L. *J. Am. Chem. Soc.* **1985**, *107*, 1796.

(12) Bott, S. G.; Alvanipour, A.; Morley, S. D.; Atwood, D. A.; Means, C. M.; Coleman, A. W.; Atwood, J. L. *Angew. Chem.* **1987**, *26*, 485.

(13) Experimental Procedure for **1**: To a stirred slurry of $AlCl_3$ (1.38 g, 10.3 mmol) in toluene (30 mL) was added 18-crown-6 (2.73 g, 10.3 mmol) and $AlMe_3$ (2.76 g, 38.3 mmol) in toluene (10 mL). A vigorous exothermic reaction occurred, yielding initially a brown solid and, after stirring at room temperature for 2 h, a pale yellow liquid clathrate which separated from the solvent layer. Upon standing at ambient temperature, colorless crystals of the title compound deposited from the liquid clathrate layer overnight. These were collected, washed with hexane (20 mL), and dried in vacuo to afford 2.36 g, 42.0% (based on $AlCl_3$) of **1**.

(14) Experimental Procedure for **2**: The procedure used for compound **2** was identical with that for compound **1**, except AlI_3 was used in place of $AlCl_3$; yield 45.4% (based on AlI_3).

(15) Atwood, J. L. In *Inclusion Compounds*; Atwood, J. L., Davies, J. E. D., MacNicol, D. D., Eds.; Academic Press: London, 1984; Vol. 1, pp 375−405.

(16) Atwood, J. L. In *Chemical Separations*; King, C. J., Navratil, J. D., Eds.; Litarvan: Denver, CO, 1986, pp 335−354.

(17) Atwood, J. L. In *Separation Technology*; Li, N. N., Strathmann, H., Eds.; United Engineering Trustees: New York, 1988, pp 46−56.

(18) Crystal Data for [$AlMe_2$(18-crown-6)$AlMe_2Cl$][$AlMeCl_3$] (**1**): $C_{17}H_{39}Cl_4O_6Al_3$, triclinic, $P\bar{1}$, a = 7.285(2) Å, b = 10.801(2) Å, c = 19.272(3) Å , α = 89.01(1)°, β = 86.24(1)°, γ = 81.23(1)°, V = 1495(2) $Å^3$, and D_c = 1.254 g cm^{-3} for Z = 2. Of 5200 data collected (CAD4, $2\theta_{max}$ = 50°, Mo Kα), 4920 were observed at greater than $3\sigma F_o$. Refinement converged with R = 0.088 and R_w = 0.094. [$AlMe_2$(18-crown-6)$AlMe_2I$][$AlMeI_3$], (**2**): $C_{17}H_{39}I_4O_6Al_3$, triclinic, $P\bar{1}$, a = 7.386(4) Å, b = 11.047(2) Å, c = 19.998(2) Å, α = 90.03(1)°, β = 94.77(3)°, γ = 99.55(3)°, V = 1603(2) $Å^3$, and D_c = 1.93 g cm^{-3} for Z = 2. Of 6084 data collected (CAD4, $2\theta_{max}$ = 50°, Mo Kα), 2760 were observed at greater than $3\sigma F_o$. Refinement converged with R = 0.069 and R_w = 0.069. For compound **1**, all non-hydrogen atoms were refined with anisotropic thermal parameters except the carbon atoms of the crown ether. For compound **2**, all non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed at calculated positions and their parameters were not refined.

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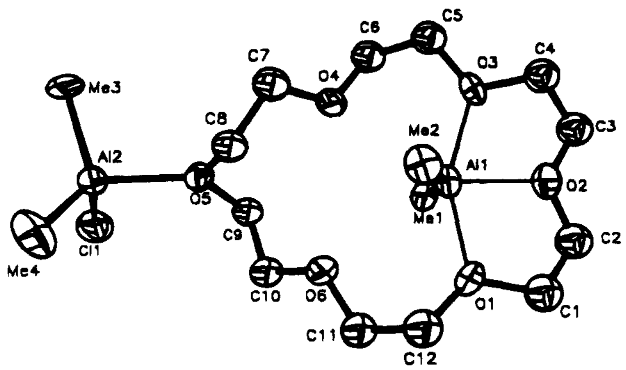

Figure 1. Structure of the [$AlMe_2^+$(18-crown-6)$AlMe_2Cl$] cation in **1**. The iodide species is isostructural. Al—O distances (Å) and angles (deg) are as follows (data for the iodide analogue are given in brackets): Al—O(1), 2.129(9) [2.16(1)]; Al—O(2), 1.966(9) [1.94(1)]; Al—O(3), 2.135(9) [2.13(1)]; Al—O(4), 2.95 [2.97]; Al—O(5), 4.83 [4.82]; Al—O(6), 3.07 [3.08]; Al—Me—Al, 152.1(5) [152.5(6)].

isostructural (Figure 1), exhibits many overall features in common with that in [$AlMe_2^+$(18-crown-6)], but with significant differences. The Al center resides in a highly distorted trigonal bipyramidal environment. The rotation of O(5) to the exterior of the crown has apparently caused a tightening of the bonding of the $AlMe_2^+$ ion to the remaining oxygen atoms. The three bonded oxygen atoms are Al—O(2) (1.966(9) Å), Al—O(3) (2.135(9) Å), and Al—O(1) (2.129(9) Å) for **1** and Al—O(2) (1.94(1) Å), Al—O(3) (2.13(1) Å), and Al—O(1) (2.16(1) Å) for **2**. The nonbonded Al---O separations have also shortened to 2.95 and 3.07 Å for the chloride and 2.97 and 3.08 Å for the iodide derivatives, while the oxygen external to the cavity is 4.83 and 4.82 Å from the cavity-bound aluminum atom in **1** and **2**, respectively. This tightening of the binding of the macrocycle has forced the Me—Al—Me angle to open to 152.1(5) and 152.5(6)° for **1** and **2**, respectively. There is a surprisingly large difference between the Al—Me bond distances for **1** and **2**. In **1** the Al—Me distances are 2.00(1) Å, while in **2** the distances are much shorter at 1.95(1) Å. Torsion angles about the 18-crown-6 moiety are severely distorted from those in 18-crown-6 (see Table 1). These angles exemplify the shift of O(5) from an endodentate conformation to an exodentate conformation to accommodate coordination of the neutral species. They also highlight the conformational mobility of the 18-crown-6 molecule.

Table 1. Torsion Angles (deg) around the Crown in Compounds 1 and 2

angle	1	2	18-crown-6[20]
O1—C2—C3—O2	47	51	74.7
O2—C3—C4—O4	−50	−49	−65.1
O3—C5—C6—O4	65	59	173.7
O4—C7—C8—O5	−73	−78	74.7
O5—C9—C10—O6	−80	−79	−65.1
O6—C11—C12—O1	−66	−66	173.7
C1—C2—O2—C3	172	169	−154.9
C2—O2—C3—C4	−175	−172	165.6
C3—C4—O3—C5	−172	−173	175.2
C4—O3—C5—C6	163	169	172.4
C5—C6—O4—C7	94	104	169.2
C6—O4—C7—C8	−176	−177	−80.3
C7—C8—O5—C9	82	81	−154.9
C8—O5—C9—C10	73	74	165.6
C9—C10—O6—C11	−159	−159	175.2
C10—O6—C11—C12	179	179	172.4
C11—C12—O1—C1	−153	−161	169.2
C12—O1—C1—C2	−178	−178	−80.3

The $AlMe_2X$ unit which is bonded to O(5) at an Al—O distance of 1.922(8) Å in **1** and 1.908(9) Å in **2** resulted from the exchange of methyl and halide groups in the mixture of AlX_3 and $AlMe_3$. Indeed, the existence of the [$AlMe_2^+$(18-crown-6)$AlMe_2X$] cation opens the question as to the range of Lewis acids which can form such a bimetallic cation. The structures of the anions in each species were unexceptional, and there were no cation to anion contacts less than 3.5 Å.

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Supplementary Material Available: Text giving a description of the data collection, structure solution, and refinement and lists of final fractional coordinates, anisotropic thermal parameters, and all bond distances and angles for compounds **1** and **2** (8 pages). Ordering information is given on any current masthead page.

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(19) The Al—O bond in [$AlMe_2^+$(18-crown-6)][$AlMe_2Cl_2$] in ref 12 is very long. The longest formal Al—O bonds reported previously in [$AlCl_2$-(benzo-15-crown-5)][$AlEtCl_3$] in ref 11, where the five Al—O lengths range from 2.03(1) to 2.30(1) Å. There have also been long Mg—O separations reported as bonds in crown ether complexes, e.g. 2.792(1) Å in: Pajerski, A. D.; BergStresser, G. L.; Parvez, M.; Richey, H. G., Jr. *J. Am. Chem. Soc.* **1988**, *110*, 4844.

(20) Maverick, E.; Seiler, P.; Schweizer, W. B.; Dunitz, J. D. *Acta Crystallogr.* **1980**, *B36*, 615.