cycles formed, may lead to the stabilization of some of the intermediates proposed in the above reaction schemes.

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Supplementary Material Available: Table III, thermal parameters, Table IV, a listing of parameters for the non-hydridic hydrogen atoms, and Table V, a listing of $10|F_o|$ andd $10|F_c|$ (23 pages). Ordering information is given on any current masthead page.

Decomposition of High-Oxygen Content Organoaluminum Compounds. The Formation and Structure of the $[Al_7O_6Me_{16}]^-$ Anion

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The unusual anion $[Al_7O_6Me_{16}]^-$ has been encountered in the decomposition pathways of two different high-oxygen content organoaluminum compounds, $K[Al_2Me_6O_2]$ and presumably $Cs_2[Al_2Me_6O]$. It is likely that these two compounds pass through the same intermediate and that the $[Al_7O_6Me_{16}]^-$ ion is a thermodynamic sink. In both cases crystalline material has been isolated, and X-ray structural determinations have been carried out. $K[Al_7O_6Me_{16}]\cdot C_6H_6$ crystalizes in the triclinic space group $P\bar{1}$ with lattice parameters $a = 12.095$ (5) Å, $b = 12.222$ (5) Å, $c = 13.893$ (5) Å, $\alpha = 105.56$ (3)°, $\beta = 94.52$ (2)°, $\gamma = 83.98$ (2)°, and $\rho_{calcd} = 1.09$ g cm^{-3} for $Z = 2$. Least-squares refinement gave a final R value of 0.042 for 2509 independent observed reflections. $Cs[Al_7O_6Me_{16}]\cdot 3C_6H_5Me$ belongs to the cubic space group $P2_13$ with $a = 17.512$ (8) Å and $\rho_{calcd} = 1.16$ g cm^{-3} for $Z = 4$. Refinement based on 460 observed reflections gave a final R of 0.075. The anion for the cesium salt lies on a crystallographic threefold axis. The structure consists of an open Al_6O_6 cage capped by the seventh Al atom which is bonded to three alternate O atoms in the cage. The six Al atoms are bonded to two terminal methyl groups each, while the unique Al is bonded to only one methyl group. Each O atom is three coordinate: the ones on the exterior (not bonded to the unique Al atom) bridge two Al atoms and are also bonded to one methyl group each.

Introduction

In the course of numerous investigations of the reaction of aluminum alkyls with alkali-metal halides and related MX compounds, several high-oxygen content anions have been explored. Compounds such as $K[Al_2Me_6NO_3]$,[1] $K[AlMe_3NO_3]$,[1] [K·dibenzo-18-crown-6]$[Al_2Me_6O_2]$,[2] $[NMe_4][Al_2Me_6(MeCOO)]$,[3] and $K_2[Al_4Me_{12}SO_4]$[4] have resulted. The reactions leading to the formation of the substances are surprisingly mild. For example, KNO_3 reacts smoothly with $AlMe_3$ in refluxing toluene to form $K[Al_2Me_6NO_3]$, and the resulting liquid clathrate[5] $K[Al_2Me_6NO_3]\cdot nC_6H_5Me$ is stable indefinitely at 80 °C in a nitrogen atmosphere. One would expect a much more vigorous result, given the relative Al–C and Al–O bond strengths. Indeed, $K[Al_2Me_6NO_3]$ is violently air sensitive and has been found to detonate photolytically in the $K[Al_2Me_6NO_3]\cdot nC_6H_6$ form.[6] All the substances listed above may be classified as high-energy content compounds which are apparently stabilized by kinetic not thermodynamic factors. Under what conditions do such compounds decompose, and what species may be encountered upon rearrangement? In this contribution we demonstrate the presence of the unexpected $[Al_7O_6Me_{16}]^-$ anion in the decomposition pathway of two different high-oxygen content parent compounds.

Results and Discussion

Potassium superoxide reacts with trimethylaluminum in toluene in the presence of dibenzo-18-crown-6[7] to form a liquid clathrate of composition [K·dibenzo-18-crown-6]$[Al_2Me_6O_2]\cdot nC_6H_5Me$. This liquid can be heated for days at 80 °C with no evidence of decomposition. The crystal structure of the compound from a benzene liquid clathrate has been reported.[2] However, without the crown ether different results are obtained. No liquid layering (liquid clathrate) is observed if KO_2 and $AlMe_3$ (in a 1·2 ratio) are placed in refluxing benzene. Instead, a slow reaction ensues, and large, colorless crystals are deposited on the walls of the flask. X-ray diffraction studies have shown the product to be $K[Al_7O_6Me_{16}]\cdot C_6H_6$. The structure of this surprising anion is shown in Figure 1. Equally surprising, $[Al_7O_6Me_{16}]^-$ is not an isolated crystallographic curiosity.

In parallel with superoxide studies, we have investigated alkali-metal oxides. Cesium oxide reacts smoothly with trimethylaluminum at room temperature in toluene to yield a liquid clathrate, presumably of composition $Cs_2[Al_2Me_6O]\cdot nC_6H_5Me$. Slow cooling to −10 °C affords colorless, air-sensitive needles in ca. 15% yield. X-ray

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0276-7333/83/2302-0985$01.50/0

Table I. Bond Lengths (Å) and Angles (deg) for K[$Al_7O_6Me_{16}$]·C_6H_6

Bond Distances

Al(1)-O(1)	1.808 (3)	Al(1)-O(3)	1.792 (3)
Al(1)-O(5)	1.807 (3)	Al(1)-O(1)	1.936 (6)
Al(2)-O(1)	1.813 (3)	Al(2)-O(2)	1.831 (4)
Al(2)-C(2)	1.945 (6)	Al(2)-C(3)	1.960 (6)
Al(3)-O(2)	1.843 (4)	Al(3)-O(3)	1.812 (3)
Al(3)-C(4)	1.958 (6)	Al(3)-C(5)	1.937 (7)
Al(4)-O(3)	1.822 (3)	Al(4)-O(4)	1.853 (4)
Al(4)-C(6)	1.928 (7)	Al(4)-C(7)	1.934 (6)
Al(5)-O(4)	1.838 (4)	Al(5)-O(5)	1.818 (3)
Al(5)-C(8)	1.957 (6)	Al(5)-C(9)	1.959 (6)
Al(6)-O(5)	1.795 (3)	Al(6)-O(6)	1.839 (4)
Al(6)-C(10)	1.952 (6)	Al(6)-C(11)	1.955 (6)
Al(7)-O(1)	1.805 (3)	Al(7)-O(6)	1.843 (4)
Al(7)-C(12)	1.951 (6)	Al(7)-C(13)	1.954 (6)
O(2)-C(14)	1.425 (7)	O(4)-C(15)	1.446 (6)
O(6)-C(16)	1.398 (7)	C(17)-C(18)	1.36 (1)
C(17)-C(22)	1.34 (1)	C(18)-C(19)	1.39 (1)
C(19)-C(20)	1.39 (1)	C(20)-C(21)	1.35 (1)
C(21)-C(22)	1.36 (1)	K-C(3)[a]	3.144 (6)
K-C(4)[a]	3.280 (6)	K-C(8)	3.288 (5)
K-C(11)[c]	3.179 (6)	K-C(13)[b]	3.370 (7)
K-C(17)[d]	3.29 (1)	K-C(18)[d]	3.27 (1)
K-C(19)[d]	3.31 (1)	K-C(20)[d]	3.36 (1)
K-C(21)[d]	3.39 (2)	K-C(22)[d]	3.35 (1)

Bond Angles

O(1)-Al(1)-O(3)	106.2 (2)	O(1)-Al(1)-O(5)	106.3 (2)
O(3)-Al(1)-O(5)	107.7 (2)	O(1)-Al(1)-C(1)	112.3 (2)
O(3)-Al(1)-C(1)	112.2 (2)	O(5)-Al(1)-C(1)	111.8 (2)
O(1)-Al(2)-O(2)	97.0 (2)	O(1)-Al(2)-C(2)	112.7 (2)
O(2)-Al(2)-C(2)	111.3 (2)	O(1)-Al(2)-C(3)	113.5 (2)
O(2)-Al(2)-C(3)	105.8 (2)	C(2)-Al(2)-C(3)	114.9 (3)
O(2)-Al(3)-O(3)	99.1 (2)	O(2)-Al(3)-C(4)	110.0 (2)
O(3)-Al(3)-C(4)	109.5 (2)	O(2)-Al(3)-C(5)	108.8 (2)
O(3)-Al(3)-C(5)	114.6 (2)	C(4)-Al(3)-C(5)	113.8 (3)
O(3)-Al(4)-O(4)	96.9 (2)	O(3)-Al(4)-C(6)	112.3 (2)
O(4)-Al(4)-C(6)	109.2 (2)	O(3)-Al(4)-C(7)	111.3 (2)
O(4)-Al(4)-C(7)	108.4 (2)	C(6)-Al(4)-C(7)	116.8 (3)
O(4)-Al(5)-O(5)	99.2 (2)	O(4)-Al(5)-C(8)	109.9 (2)
O(5)-Al(5)-C(8)	109.0 (2)	O(4)-Al(5)-C(9)	108.4 (2)
O(5)-Al(5)-C(9)	113.8 (2)	C(8)-Al(5)-C(9)	115.3 (3)
O(5)-Al(6)-O(6)	98.5 (2)	O(5)-Al(6)-C(10)	113.5 (2)
O(6)-Al(6)-C(10)	109.2 (2)	O(5)-Al(6)-C(11)	112.6 (2)
O(6)-Al(6)-C(11)	107.0 (2)	C(10)-Al(6)-C(11)	114.6 (3)
O(1)-Al(7)-O(6)	99.4 (2)	O(1)-Al(7)-C(12)	114.7 (2)
O(6)-Al(7)-C(12)	107.2 (2)	O(1)-Al(7)-C(13)	109.9 (2)
O(6)-Al(7)-C(13)	109.8 (2)	C(12)-Al(7)-C(13)	114.6 (3)
Al(1)-O(1)-Al(2)	120.0 (2)	Al(1)-O(1)-Al(7)	120.1 (2)
Al(2)-O(1)-Al(7)	118.4 (2)	Al(2)-O(2)-Al(3)	122.5 (2)
Al(2)-O(2)-C(14)	118.6 (4)	Al(3)-O(2)-C(14)	118.9 (4)
Al(1)-O(3)-Al(3)	118.8 (2)	Al(1)-O(3)-Al(4)	122.3 (2)
Al(3)-O(3)-Al(4)	117.0 (2)	Al(4)-O(4)-Al(5)	121.7 (2)
Al(4)-O(4)-C(15)	120.2 (3)	Al(5)-O(4)-C(15)	116.6 (3)
Al(1)-O(5)-Al(5)	118.7 (2)	Al(1)-O(5)-Al(6)	122.9 (2)
Al(5)-O(5)-Al(6)	117.1 (2)	Al(6)-O(6)-Al(7)	121.6 (2)
Al(6)-O(6)-C(16)	118.7 (4)	Al(7)-O(6)-C(16)	119.6 (4)
C(18)-C(17)-C(22)	121.1 (8)	C(17)-C(18)-C(19)	119.8 (8)
C(18)-C(19)-C(20)	118.2 (8)	C(19)-C(20)-C(21)	120.5 (8)
C(20)-C(21)-C(22)	120.2 (8)	C(17)-C(22)-C(21)	120.2 (8)

[a] Atoms related to those in Table IV by $(1 - x, 1 - y, 1 - z)$. [b] $(x, y, 1 + z)$. [c] $(-x, 1 - y, 1 - z)$. [d] $(-x, 2 - y, 1 - z)$.

diffraction analysis has established the composition to be $Cs[Al_7O_6Me_{16}]\cdot 3C_6H_5Me$.[8] A view of this anion is given in Figure 2.

The above observations have two important implications: (1) the $[Al_7O_6Me_{16}]^-$ anion presents an important configuration in the decomposition pathway of high-oxygen content organoaluminum compounds and may probably be viewed as a thermodynamic sink and (2) the decomposition of the superoxide complex probably passes through the same intermediate as that of the oxide itself.

The anion, as shown in either Figure 1 or Figure 2, essentially consists of an open Al_6O_6 cage capped by a seventh Al atom which is bonded to three alternate O atoms in the cage. The six Al atoms are bonded to two terminal methyl groups each, while the unique Al atom is attached to only one methyl group. Each O atom is three-coordinate: the ones on the exterior (not bonded to the unique Al atom) bridge two Al atoms and also are bonded to one methyl group each. Both types of O atoms exhibit bond angles as expected for sp^2 hybridization: the

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(8) The interaction of the cation with the aromatic molecules in these and related complexes are described in detail elsewhere: Atwood, J. L.; Rogers, R. D. *J. Inclusion Phenomena* **1983**, *1*, 000.

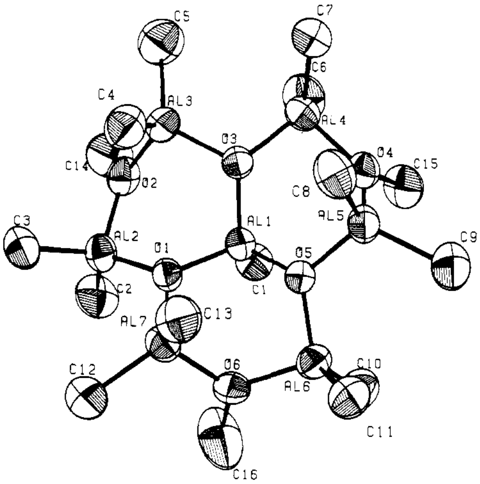

Figure 1. $[Al_7O_6Me_{16}]^-$ anion with numbering scheme for $K[Al_7O_6Me_{16}]\cdot C_6H_6$. The atoms are represented by their 50% probability ellipsoids for thermal motion.

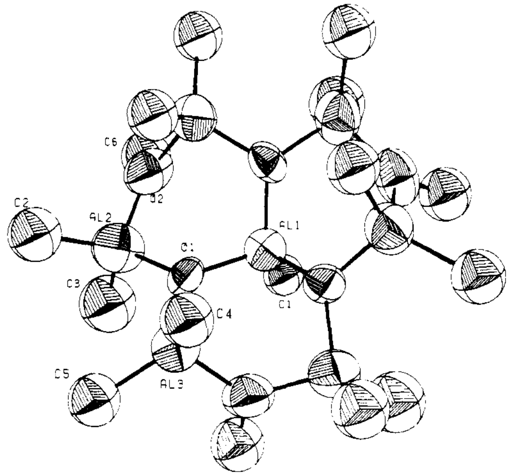

Figure 2. $[Al_7O_6Me_{16}]^-$ anion for $Cs[Al_7O_6Me_{16}]\cdot 3C_6H_5Me$. The anion contains a crystallographic threefold axis.

angles at the O atoms range from 117 to 123°. The bond angles at the Al atoms of the Al_6O_6 unit are near the tetrahedral value except for the O–Al–O interior ones which range from 97 to 99°. For the unique Al atom, even the O–Al–O values, 106–108°, are close to those predicted for sp^3 hybridization.

The anion exhibits its maximum symmetry in the configuration shown in Figure 2. A crystallographic threefold axis contains the unique Al atom and its methyl group. The anion in Figure 1 is oriented exactly as that in Figure 2. Although there is no noticeable difference, the former possesses no crystallographic symmetry. (Since the cation must also be considered, it is likely that its environment causes the difference in the solid state anionic geometry.)

The structural parameters for $K[Al_7O_6Me_{16}]\cdot C_6H_6$ are much more accurately determined than are those for $Cs[Al_7O_6Me_{16}]\cdot 3C_6H_5Me$ (see the Experimental Section). Nonetheless, excellent agreement between related bond lengths and angles in the two studies may be noted (Tables I and II). Within each the Al–O length is shorter for the unique Al, 1.81 (1) and 1.81 (2) Å, than for the other six, 1.842 (8) and 1.84 (1) Å. Both types of Al–O distances are, however, on the short end of the range (1.8–2.0 Å) found in organometallic complexes.[3] No other distances within the cage are noteworthy.

The title compounds are related in a fashion to three areas of endeavor. Mention will be made, but further investigations will be needed to clarify the role of the novel anion $[Al_7O_6Me_{16}]^-$ in the broad spectrum of aluminum chemistry. Aluminoxanes have fallen under scrutiny in recent years in part because of implications for Ziegler–Natta catalysis.[9] These are generally written as neutral species and have not yet been structurally well-characterized to our knowledge. Rather large oligomeric compounds such as $[MeAlNMe]_7$ have been crystallographically studied and are reported in an excellent series of papers by Smith and co-workers.[10] However, these bear

Table II. Bond Lengths (Å) and Angles (deg) for $Cs[Al_7O_6Me_{16}]\cdot 3C_6H_5Me$

Bond Distances

Al(1)–O(1)	1.83 (2)	Al(1)–C(1)	2.03 (6)
Al(2)–O(1)	1.80 (2)	Al(2)–O(2)	1.83 (3)
Al(2)–C(2)	2.06 (4)	Al(2)–C(3)	2.04 (5)
Al(3)–O(1)	1.81 (2)	Al(3)–O(2)	1.85 (3)
Al(3)–C(4)	2.01 (4)	Al(3)–C(5)	1.97 (4)
O(2)–C(6)	1.51 (5)		
Cs–C(4)	3.72 (3)	Cs–C(7)	3.72 (4)
Cs–C(8)	3.86 (4)	Cs–C(9)	3.93 (3)
Cs–C(10)	3.86 (3)	Cs–C(11)	3.72 (3)
Cs–C(12)	3.65 (4)		

Bond Angles

O(1)–Al(1)–C(1)	111.7 (8)	O(1)–Al(2)–O(2)	98 (1)
O(1)–Al(2)–C(2)	112 (1)	O(2)–Al(2)–C(2)	108 (1)
O(1)–Al(2)–C(3)	108 (2)	O(2)–Al(2)–C(3)	114 (2)
C(2)–Al(2)–C(3)	115 (2)	O(1)–Al(3)–C(4)	110 (1)
O(1)–Al(3)–C(5)	114 (1)	C(4)–Al(3)–C(5)	115 (2)
O(1)–Al(3)–O(2)	99 (1)	O(2)–Al(3)–C(4)	109 (1)
O(2)–Al(3)–C(5)	109 (1)	Al(1)–O(1)–Al(2)	122 (1)
Al(1)–O(1)–Al(3)	119 (1)	Al(2)–O(1)–Al(3)	118 (1)
O(1)–Al(1)–O(1)	107.2 (9)	O(1)–Al(1)–O(1)	107.2 (9)
Al(2)–O(2)–C(6)	118 (2)	Al(2)–O(2)–Al(3)	122 (1)
Al(3)–O(2)–C(6)	119 (1)		

Table III. Crystal Data and Summary of Intensity Data Collection and Structure Refinement

compd	$K[Al_7O_6C_{16}H_{48}]\cdot C_6H_6$	$Cs[Al_7O_6C_{16}H_{48}]\cdot 3C_6H_4Me$
mol wt	642.6	934.8
space group	*P*1	$P2_13$
cell const		
a, Å	12.095 (5)	17.512 (8)
b, Å	12.222 (5)	
c, Å	13.893 (5)	
α, deg	105.56 (3)	
β, deg	94.52 (2)	
γ, deg	83.98 (2)	
cell vol, $Å^3$	1964.9	5370.4
molecules/unit cell	2	4
ρ(calcd), g cm^{-3}	1.09	1.16
μ(calcd), cm^{-1}	3.23	8.56
radiation	Mo Kα	Mo Kα
max cryst dimens, mm	1.3 × 1.0 × 1.2	0.28 × 0.28 × 0.28
scan width	0.80 + 0.20 tan θ	0.80 + 0.20 tan θ
std reflctns	600, 080, 0,0,10	200, 020, 002
variation of stnds	±2%	±2%
reflctns measd	2879	1961
2θ range, deg	4–36	4–50
reflctns considered obsd $I \geqslant 3\sigma(I)$	2509	460
no. of parameters varied	325	81
GOF	1.91	5.05
R	0.042	0.075
R_w	0.042	0.078

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(9) Sinn, H.; Kaminsky, W. *Adv. Organomet. Chem.* **1980**, *18*, 140.

Table IV. Final Fractional Coordinates for $K[Al_7O_6Me_{16}]\cdot C_6H_6$

atom	*x/a*	*y/b*	*z/c*	atom	*x/a*	*y/b*	*z/c*
K	0.2365 (1)	0.6287 (1)	0.90610 (9)	H(7)[C(3)]	0.5586	0.5184	0.1362
Al(1)	0.2476 (1)	0.7729 (1)	0.3134 (1)	H(8)[C(3)]	0.6204	0.5014	0.2223
Al(2)	0.4927 (1)	0.6594 (1)	0.3084 (1)	H(9)[C(3)]	0.6368	0.6265	0.2025
Al(3)	0.4176 (1)	0.8627 (1)	0.2036 (1)	H(10)[C(4)]	0.5010	0.7281	0.0508
Al(4)	0.1952 (1)	1.0091 (1)	0.2589 (1)	H(11)[C(4)]	0.3781	0.7871	0.0268
Al(5)	0.0193 (1)	0.8182 (1)	0.2037 (1)	H(12)[C(4)]	0.3893	0.6790	0.0762
Al(6)	0.0525 (1)	0.6145 (1)	0.2975 (1)	H(13)[C(5)]	0.4672	1.0612	0.2568
Al(7)	0.2966 (1)	0.5098 (1)	0.2246 (1)	H(14)[C(5)]	0.4501	1.0187	0.1448
O(1)	0.3458 (2)	0.6495 (3)	0.2735 (2)	H(15)[C(5)]	0.5559	1.0000	0.2098
O(2)	0.4986 (3)	0.8057 (3)	0.3002 (3)	H(16)[C(6)]	0.3206	1.1424	0.3817
O(3)	0.2800 (2)	0.8748 (3)	0.2504 (2)	H(17)[C(6)]	0.1965	1.1869	0.3988
O(4)	0.0611 (3)	0.9581 (3)	0.2764 (2)	H(18)[C(6)]	0.2520	1.1002	0.4334
O(5)	0.1119 (2)	0.7277 (3)	0.2653 (2)	H(19)[C(7)]	0.1113	1.0481	0.0924
O(6)	0.1813 (3)	0.5231 (3)	0.3079 (2)	H(20)[C(7)]	0.1965	1.1180	0.1363
C(1)	0.2533 (5)	0.8335 (5)	0.4573 (4)	H(21)[C(7)]	0.2417	1.0113	0.0800
C(2)	0.5305 (5)	0.6465 (6)	0.4438 (5)	H(22)[C(8)]	0.0163	0.8459	0.0336
C(3)	0.5901 (5)	0.5636 (5)	0.2066 (5)	H(23)[C(8)]	0.0399	0.7105	0.0287
C(4)	0.4237 (5)	0.7492 (5)	0.0739 (4)	H(24)[C(8)]	0.1413	0.7937	0.0602
C(5)	0.4716 (5)	1.0065 (6)	0.2038 (6)	H(25)[C(9)]	−0.1684	0.7456	0.1713
C(6)	0.2353 (6)	1.1261 (5)	0.3765 (5)	H(26)[C(9)]	−0.1781	0.8846	0.2102
C(7)	0.1838 (5)	1.0494 (5)	0.1328 (5)	H(27)[C(9)]	−0.1515	0.8079	0.2905
C(8)	0.0599 (5)	0.7889 (5)	0.0649 (4)	H(28)[C(10)]	−0.0805	0.7182	0.4201
C(9)	−0.1388 (5)	0.8123 (5)	0.2216 (5)	H(29)[C(10)]	0.0403	0.7007	0.4778
C(10)	−0.0158 (5)	0.6619 (6)	0.4266 (5)	H(30)[C(10)]	−0.0419	0.5976	0.4476
C(11)	−0.0405 (5)	0.5279 (5)	0.1878 (4)	H(31)[C(11)]	−0.0249	0.4483	0.1736
C(12)	0.4015 (5)	0.3842 (5)	0.2447 (5)	H(32)[C(11)]	−0.0334	0.5522	0.1248
C(13)	0.2371 (5)	0.4917 (5)	0.0869 (4)	H(33)[C(11)]	−0.1219	0.5468	0.2028
C(14)	0.5708 (6)	0.8770 (6)	0.3697 (5)	H(34)[C(12)]	0.4562	0.3741	0.2007
C(15)	−0.0014 (5)	1.0146 (5)	0.3632 (4)	H(35)[C(12)]	0.4486	0.4042	0.2994
C(16)	0.1942 (7)	0.4680 (8)	0.3848 (7)	H(36)[C(12)]	0.3690	0.3212	0.2387
C(17)	−0.139 (1)	1.1489 (8)	0.1752 (7)	H(37)[C(13)]	0.2925	0.4827	0.0460
C(18)	−0.0885 (9)	1.236 (1)	0.240 (1)	H(38)[C(13)]	0.1919	0.4239	0.0650
C(19)	−0.151 (1)	1.3167 (8)	0.3095 (7)	H(39)[C(13)]	0.1877	0.5649	0.0845
C(20)	−0.264 (1)	1.3055 (9)	0.3104 (7)	H(40)[C(14)]	0.5698	0.9585	0.3665
C(21)	−0.3109 (6)	1.218 (1)	0.245 (1)	H(41)[C(14)]	0.6448	0.8363	0.3487
C(22)	−0.248 (1)	1.1400 (7)	0.1769 (7)	H(42)[C(14)]	0.5616	0.8772	0.4412
H(1)[C(1)]	0.2465	0.7791	0.4959	H(43)[C(15)]	0.0265	1.0854	0.4078
H(2)[C(1)]	0.1910	0.8961	0.4760	H(44)[C(15)]	−0.0823	1.0473	0.3664
H(3)[C(1)]	0.3236	0.8706	0.4799	H(45)[C(15)]	0.0058	0.9377	0.3817
H(4)[C(2)]	0.4899	0.7037	0.5027	H(46)[C(16)]	0.1434	0.4690	0.4305
H(5)[C(2)]	0.6133	0.6507	0.4578	H(47)[C(16)]	0.1792	0.4019	0.3205
H(6)[C(2)]	0.5175	0.5664	0.4461	H(48)[C(16)]	0.2398	0.4249	0.4042

little structural similarity to $[Al_7O_6Me_{16}]^-$. Interestingly, the closest materials to the title compounds may be the well-known zeolites.[11] Work aimed at an elucidation of this relationship is in progress.

Experimental Section

All reactions were carried out under a nitrogen atmosphere by using Schlenk techniques or an inert atomosphere box. Solvents were dried and degassed in the normal manner. Trimethylaluminum, cesium oxide, and potassium superoxide were purchased from Alfa Products, and the crown ether was purchased from Aldrich Chemical Co. All were used without further purification.

Preparation of [K·dibenzo-18-crown-6][$Al_2Me_6O_2$]. A mixture of 1.00 mL of $AlMe_3$ (0.01 mol) was added to a slurry of 1.80 g of dibenzo-18-crown-6 (0.005 mol) and 0.36 g of KO_2 (0.005 mol) in ca. 30 mL of toluene. The reaction mixture was heated to 80 °C for 6 h. Complete reaction was evidenced by the formation of the liquid layering effect (liquid clathrate).

Preparation of $K[Al_7O_6Me_{16}]\cdot C_6H_6$. A mixture of 1.00 mL of $AlMe_3$ (0.01 mol) was added to 0.36 g of KO_2 (0.005 mol) suspended in ca. 30 mL of benzene. The mixture was brought to reflux, but some unreacted KO_2 was evident and no liquid layering was observed. After 48 h, the mixture was cooled, and large, colorless, air-sensitive crystals were obtained. The X-ray diffraction experiment showed the composition to be $K[Al_7O_6Me_{16}]\cdot C_6H_6$.

Preparation of $Cs[Al_7O_6Me_{16}]\cdot 3C_6H_5Me$. The complex was formed by the addition of 1 mL of $AlMe_3$ (0.01 mol) to a suspension of 1.41 g of Cs_2O (0.005 mol) in ca. 30 mL of toluene. The reaction was complete after 12 h at room temperature as evidenced by the formation of two liquid layers. (The lower layer presumably contained $Cs_2[Al_2Me_6O]\cdot nC_6H_5Me$.) Upon cooling to −10 °C, colorless, air-sensitive needles of the compound resulted. The X-ray diffraction study showed the correct formulation to be $Cs[Al_7O_6Me_{16}]\cdot 3C_6H_5Me$.

X-ray Data Collection, Structure Determination, and Refinement for $K[Al_7O_6Me_{16}]\cdot C_6H_6$. Single crystals of the air-sensitive compound were sealed under N_2 in thin-walled glass capillaries. Final lattice parameters as determined from a least-squares refinement of $((\sin\theta)/\lambda)^2$ values for 15 reflections ($\theta > 16°$) accurately centered on the diffractometer are given in Table III. The space group (either $P1$ or $P\bar{1}$) was shown to be $P\bar{1}$ by the successful solution and refinement.

Data were collected on an Enraf-Nonius CAD-4 diffractometer by the θ–2 θ scan technique. The method has been previously described.[12] A summary of data collection parameters is given in Table III. The intensities were corrected for Lorentz and polarization effects but not for absorption.

Calculations were carried out with the SHELX system of computer programs.[13] Neutral atom scattering factors for K, Al, O, and C were taken from Cromer and Waber,[14] and the scattering

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Table V. Final Fractional Coordinates for Cs[$Al_7O_6Me_{16}$]·3C_6H_5Me

atom	*x/a*	*y/b*	*z/c*
Cs	0.9196 (2)	0.9196 (2)	0.9196 (2)
Al(1)	0.1215 (6)	0.1215 (6)	0.1215 (6)
Al(2)	0.0195 (8)	0.0517 (7)	0.2542 (8)
Al(3)	−0.0547 (7)	0.1513 (7)	0.1289 (8)
O(1)	0.029 (1)	0.103 (1)	0.166 (1)
O(2)	0.104 (2)	−0.010 (1)	0.244 (1)
C(1)	0.188 (2)	0.188 (2)	0.188 (2)
C(2)	−0.076 (2)	−0.017 (2)	0.256 (2)
C(3)	0.026 (3)	0.128 (3)	0.342 (3)
C(4)	−0.091 (2)	0.099 (2)	0.033 (2)
C(5)	−0.134 (2)	0.170 (2)	0.207 (2)
C(6)	0.159 (2)	−0.014 (2)	0.310 (3)
C(7)	0.336 (3)	0.442 (2)	0.219 (2)
C(8)	0.412 (3)	0.426 (2)	0.238 (2)
C(9)	0.455 (3)	0.480 (2)	0.278 (2)
C(10)	0.423 (3)	0.549 (2)	0.299 (2)
C(11)	0.347 (3)	0.566 (2)	0.280 (2)
C(12)	0.304 (3)	0.512 (2)	0.239 (2)
C(13)	0.297 (3)	0.385 (3)	0.180 (3)

for potassium was corrected for the real and imaginary components of anomalous dispersion using the table of Cromer and Liberman.[15] Scattering factors for H were from ref 16.

The structure was solved by the straight-foward application of the direct methods program MULTAN.[17] Least-squares refinement with isotropic thermal parameters led to $R = \sum||F_o| - |F_c||/\sum|F_o| = 0.096$. The hydrogen atoms of the benzene ring were placed at calculated positions 1.00 Å from the bonded carbon atom and were not refined. The methyl hydrogen atoms were located with the aid of a difference Fourier map. Refinement of the non-hydrogen atoms with anisotropic temperature factors led to final values of $R = 0.042$ and $R_w = 0.042 = \{\sum w(F_o - F_c)^2/\sum w(F_o)^2\}^{1/2}$. A final difference Fourier showed no feature greater than 0.3 e/Å^3. The weighting scheme was based on unit weights: no systematic variation of $w(|F_o| - |F_c|)$ vs. $|F_o|$ or $(\sin \theta)/\lambda$ was noted. The final values of the fractional coordinates are given in Table IV. The final values of the thermal parameters are given in the supplementary material.[18]

X-ray Data Collection, Structure Determination, and Refinement for Cs[$Al_7O_6Me_{16}$]·3C_6H_5Me. Data collection procedures were the same as those given above. The position of the cesium atom was located from a Patterson map, and the remaining non-hydrogen atoms were found with the aid of a difference Fourier map phased on the cesium atom. The carbon atoms of the toluene molecule exhibited high thermal motion (which was in large measure responsible for the small percentage of observed reflections), and the molecule was treated as a rigid group. The C–C bond lengths were set at 1.40 Å and the C–C–C bond angles at 120°. Because of the low number of observed data, none of the carbon atoms (including those of the anion) were refined with anisotropic thermal parameters, and no hydrogen atoms were located. The final features of the refinement are listed in Table III, and the fractional coordinates are given in Table V. The thermal parameters are available as supplementary material.[18]

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Registry No. K[$Al_7O_6Me_{16}$]·C_6H_6, 85355-14-2; Cs[$Al_7O_6Me_{16}$]·3C_6H_5Me, 85355-16-4; KO_2, 12030-88-5; $AlMe_3$, 75-24-1; K·[dibenzo-18-crown-6][$Al_2Me_6O_2$], 78762-95-5; Cs_2O, 20281-00-9; dibenzo-18-crown-6, 14187-32-7.

Supplementary Material Available: Tables of thermal parameters and structure factors for both K[$Al_7O_6Me_{16}$]·C_6H_6 and Cs[$Al_7O_6Me_{16}$]·3C_6H_5Me, and hydrogen atom coordinates for the former (22 pages). Ordering information is given on any current masthead page.

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[18] See paragraph at the end of paper regarding supplementary material.