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THE SYNTHESIS OF $M[Al_2(CH_3)_6NO_3]$ ($M^+ = K^+, Rb^+, Cs^+, NR_4^+$) AND THE CRYSTAL STRUCTURES OF $K[Al_2(CH_3)_6NO_3]$ AND $K[Al(CH_3)_3NO_3] \cdot C_6H_6$

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Summary

The synthesis of $M[Al_2(CH_3)_6NO_3]$ ($M^+ = K^+, Rb^+, Cs^+, N(CH_3)_4^+, N(C_2H_5)_4^+$) has been accomplished by the addition of stoichiometric ratios of trimethylaluminum to the corresponding nitrate salt in benzene. For M = alkali metal ion, the compound is an air-sensitive solid, while for M = tetraalkylammonium ion, it is an extremely air-sensitive liquid. The crystal structure of $K[Al_2(CH_3)_6NO_3]$ has been determined from single-crystal X-ray diffraction data collected by counter methods. The substance crystallizes in the monoclinic space group $P2_1/n$ with lattice dimensions a 7.975(8), b 24.512(12), c 14.601(10) Å, β 100.55(8)° and ρ_{calc} 1.17 g cm^{-3} for $Z = 8$. Least-squares refinement gave a final conventional R value of 0.103 for 411 independent observed reflections. The nitrate ion bridges the two trimethylaluminum units together via two separate oxygen atoms. There are two formula units in the asymmetric unit, and the two independent potassium ions differ markedly in their environments.

$K[Al(CH_3)_3NO_3] \cdot C_6H_6$ was obtained by the addition of dibenzo-18-crown-6 to the liquid $K[Al_2(CH_3)_6NO_3] \cdot 7.0\ C_6H_6$. The compound crystallizes in the orthorhombic space group $P2_12_12_1$ with unit cell parameters a 7.716(4), b 9.855(5), c 18.375(5) Å, and ρ_{calc} 1.20 g cm^{-3} for $Z = 4$. Least-squares refinement gave a final R value of 0.044 for 809 independent observed reflections. The nitrate ion is coordinated in a unidentate fashion to the aluminum atom at an Al—O separation of 1.930(7) Å. The potassium ion is symmetrically disposed over the benzene ring at an average K—C distance of 3.38(6) Å.

Introduction

The results of structural studies of anionic organoaluminum compounds have been recently reviewed [1]. From the synthetic standpoint the emphasis has been on the incorporation of new X ligands into the 1/1, $M[AlR_3X]$, and 2/1, $M[Al_2R_6X]$, complexes. In particular, the interesting thermal stability of organometallic compounds which incorporate certain high-oxygen content ligands has been reported [1,2]. These studies include the synthesis and crystal structure of tetramethylammonium acetatotrimethylaluminate, $[N(CH_3)_4][Al(CH_3)_3CH_3COO]$ [1], and a short report of the solution behavior of the 2/1 nitrate complexes [2]. We now wish to present a full account of the preparation of the 1/1 and 2/1 complexes based on the nitrate ligand, and to reveal the crystal structures of $K[Al_2(CH_3)_6NO_3]$ and $K[Al(CH_3)_3NO_3] \cdot C_6H_6$.

Experimental

$M[Al_2(CH_3)_6NO_3]$ ($M^+ = K^+, Rb^+, Cs^+, N(CH_3)_4^+, N(C_2H_5)_4^+$)

For $M^+ = K^+$, Rb^+, or Cs^+, a typical preparation involved the reaction of 0.01 mol of alkali metal nitrate with 0.02 mol of trimethylaluminum in 0.20 mol of benzene. Although the formation of the liquid layering characteristic of the presence of the 2/1 complex was noted immediately, complete reaction was not accomplished in less than 24 h. However, the heating of the reaction mixture at 60° C for 1 h produced in all cases the maximum composition liquid clathrate: $K[Al_2(CH_3)_6NO_3] \cdot 7.0\ C_6H_6$, $Rb[Al_2(CH_3)_6NO_3] \cdot 9.4\ C_6H_6$, $Cs[Al_2(CH_3)_6NO_3 \cdot 12.0\ C_6H_6$. All three of these substances are unstable with respect to I, but decomposition as in II has not been observed.

$$\begin{tikzcd}
& M[Al_2(CH_3)_6NO_3] \cdot n\ C_6H_6 \arrow[dl, shift left] \arrow[dr, shift left] & \\
M[Al_2(CH_3)_6NO_3] + n\ C_6H_6 \arrow[ur, shift left] & & M[Al(CH_3)_3NO_3] + Al(CH_3)_3 + n\ C_6H_6 \arrow[ul, shift left] \\
\text{(I)} & & \text{(II)}
\end{tikzcd}$$

The compositions of the liquid clathrates were deduced from NMR integrations, and that of the crystalline, colorless, air-sensitive 2/1 parent complexes, from X-ray diffraction studies and elemental analyses. (Found: C, 21.6; H, 5.5; Al, 15.6; N, 4.2. $C_6H_{18}Al_2CsNO_3$ calcd. C, 21.2; H, 5.3; Al, 15.9; N, 4.1%.)

The preparation of the complexes for $M = N(CH_3)_4^+$ or $N(C_2H_5)_4^+$ differs in two respects. First, the reaction of NR_4NO_3 with 2 $Al(CH_3)_3$ proceeds vigorously to the formation of the maximum composition liquid clathrate at room temperature in the presence of aromatic solvents: $[N(CH_3)_4][Al_2(CH_3)_6NO_3] \cdot 7.8\ C_6H_6$ and $[N(C_2H_5)_4][Al_2(CH_3)_6NO_3] \cdot 9.8\ C_6H_6$. Second, the 2/1 complexes themselves are liquids.

Caution must be exercised when dealing with $M[Al_2(CH_3)_6NO_3]$. The maximum aromatic composition liquid clathrates (i.e., $K[Al_2(CH_3)_6NO_3] \cdot 7.0\ C_6H_6$) decompose in the presence of oxygen or water, but in a mild fashion. However, for $M^+ = K^+$, Rb^+, or Cs^+, the parent 2/1 complex will burst into flame upon exposure to air. For $M^+ = N(CH_3)_4^+$ or $N(C_2H_5)_4^+$, the problem is more severe since the parent complexes are liquids: these compounds burst violently into flame upon exposure to air, and are comparable to trimethylaluminum in this respect. In the absence of O_2 or H_2O, the compounds are stable indefinitely at room temperature, and may be heated to approximately 100° C before any sign of decomposition is noticed.

$K[Al(CH_3)_3NO_3] \cdot C_6H_6$

The formation of this compound was accomplished by the addition of 0.01 mol of dibenzo-18-crown-6 to 0.01 mol of $K[Al_2(CH_3)_6NO_3] \cdot 7.0\ C_6H_6$.

TABLE 1

CRYSTAL DATA

	$K[Al_2(CH_3)_6NO_3]$	$K[Al(CH_3)_3NO_3] \cdot C_6H_6$
Crystal system	monoclinic	orthorhombic
Space group	$P2_1/n$	$P2_12_12_1$
Mol. wt.	245.3	251.3
a	7.975(8) Å	7.716(4) Å
b	24.512(12) Å	9.855(5) Å
c	14.601(10) Å	18.375(5) Å
β	100.55(8) Å	
Cell volume	2806.2 Å^3	1397.15 Å^3
Molecules/unit cell	8	4
Calc. density	1.17 g cm^{-3}	1.20 g cm^{-3}
Linear abs. coeff., μ,	4.06 cm^{-1}	3.46 cm^{-1}
Max. crystal dimensions	0.25 X 0.25 X 0.50 mm	0.20 X 0.25 X 0.28 mm

X-Ray data collection and structure solution for $K[Al_2(CH_3)_6NO_3]$

Single crystals of $M[Al_2(CH_3)_6NO_3]$ proved exceedingly difficult to obtain. Approximately twenty crystals of the cesium salt were placed on the diffractometer, but all were twinned or multiple. Ten of the rubidium and twenty of the potassium analogues were tried in a similar fashion. The best one was from the potassium group; it was apparently single, but the ω scan widths were near 4°, and it was a poor scatterer. Final lattice parameters as determined from a

TABLE 2

FINAL FRACTIONAL COORDINATES AND ISOTROPIC TEMPERATURE FACTORS FOR $K[Al_2(CH_3)_6NO_3]$

Atom	*x/a*	*y/b*	*z/c*	*B*
K(1)	0.250(3)	0.437(1)	0.550(1)	6.1(0.6)
K(2)	0.267(2)	0.654(1)	0.066(1)	5.3(0.5)
Al(1)	0.210(4)	0.472(1)	0.854(2)	6.3(0.8)
Al(2)	−0.277(3)	0.572(1)	0.712(2)	5.6(0.8)
Al(3)	0.741(4)	0.785(1)	0.230(2)	6.3(0.8)
Al(4)	1.221(4)	0.687(1)	0.378(2)	5.7(0.7)
O(1)	0.161(7)	0.487(2)	0.716(3)	4.5(1.3)
O(2)	−0.058(6)	0.534(2)	0.738(3)	4.3(1.3)
O(3)	−0.021(7)	0.517(2)	0.600(4)	6.9(1.7)
O(4)	0.949(9)	0.738(7)	0.258(4)	9.0(1.9)
O(5)	1.158(7)	0.690(2)	0.241(3)	5.7(1.5)
O(6)	1.048(7)	0.732(2)	0.120(4)	5.1(1.4)
N(1)	0.014(9)	0.502(3)	0.683(5)	5.1(2.3)
N(2)	1.058(10)	0.726(3)	0.204(5)	5.6(2.2)
C(1)	0.036(9)	0.424(3)	0.876(4)	4.2(2.0)
C(2)	0.430(10)	0.425(3)	0.853(4)	3.6(1.8)
C(3)	0.218(8)	0.545(2)	0.915(4)	1.6(1.6)
C(4)	−0.220(8)	0.637(2)	0.652(4)	1.7(1.7)
C(5)	−0.293(10)	0.577(3)	0.846(5)	4.8(2.1)
C(6)	−0.435(10)	0.520(3)	0.632(4)	4.5(2.0)
C(7)	0.731(9)	0.802(3)	0.363(4)	4.0(1.9)
C(8)	0.822(11)	0.849(3)	0.158(5)	7.1(2.7)
C(9)	0.570(11)	0.736(3)	0.152(5)	5.9(2.2)
C(10)	1.033(9)	0.646(3)	0.407(4)	3.9(2.0)
C(11)	1.264(9)	0.763(3)	0.416(4)	4.3(1.9)
C(12)	1.427(10)	0.650(3)	0.385(5)	5.0(2.3)

TABLE 3

FINAL FRACTIONAL COORDINATES AND THERMAL PARAMETERS [a] FOR $K[Al(CH_3)_3NO_3] \cdot C_6H_6$

Atom	x/a	y/b	z/c	β_{11}	β_{22}
K	0.9158(2)	0.7403(2)	0.2923(1)	0.0218(4)	0.0063(2)
Al	0.6312(3)	0.2824(2)	0.3730(1)	0.0186(5)	0.0077(3)
O(1)	0.8082(7)	0.1918(5)	0.3169(3)	0.0227(13)	0.0037(5)
O(2)	0.7106(11)	−0.0115(6)	0.3403(4)	0.0289(20)	0.0075(6)
O(3)	0.9339(9)	0.0159(5)	0.2706(4)	0.0266(16)	0.0072(6)
N	0.8161(11)	0.0568(7)	0.3091(5)	0.0217(17)	0.0082(7)
C(1)	0.7286(15)	0.4664(7)	0.3567(5)	0.0230(24)	0.0078(9)
C(2)	0.6390(15)	0.2110(11)	0.4720(5)	0.0380(29)	0.0193(16)
C(3)	0.4151(11)	0.2531(8)	0.3185(5)	0.0218(17)	0.0100(9)
C(4)	0.8016(18)	0.6589(17)	0.6320(8)	0.0239(32)	0.0283(25)
C(5)	0.6917(25)	0.5946(12)	0.5890(10)	0.0407(44)	0.0168(16)
C(6)	0.5836(23)	0.6598(21)	0.5434(8)	0.0314(42)	0.0376(34)
C(7)	0.5890(28)	0.8015(20)	0.5414(9)	0.0439(53)	0.0290(29)
C(8)	0.6978(26)	0.8673(13)	0.5863(10)	0.0439(48)	0.0165(16)
C(9)	0.8017(18)	0.7990(18)	0.6325(8)	0.0259(31)	0.0263(23)
H(1)(C1)	0.856	0.478	0.360 [b]		
H(2)(C1)	0.644	0.540	0.385		
H(3)(C1)	0.727	0.494	0.304		
H(4)(C2)	0.580	0.130	0.465		
H(5)(C2)	0.615	0.240	0.521		
H(6)(C2)	0.756	0.245	0.486		
H(7)(C3)	0.415	0.195	0.285		
H(8)(C3)	0.290	0.240	0.340		
H(9)(C3)	0.430	0.353	0.313		
H(10)(C4)	0.884	0.611	0.668 [c]		
H(11)(C5)	0.697	0.492	0.588		
H(12)(C6)	0.502	0.605	0.505		
H(13)(C7)	0.508	0.856	0.509		
H(14)(C8)	0.700	0.968	0.584		
H(15)(C9)	0.871	0.849	0.668		

[a] Anisotropic temperature factors of the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. [b] Hydrogen atoms bonded to the methyl carbon atoms were located on a difference Fourier map, and were given $B = 5.0$ Å^2. [c] Hydrogen atoms bonded to the benzene carbon atoms in calculated positions with $B = 5.0$ Å^2.

least-squares refinement of the angular settings of 12 reflections ($\theta > 10°$) accurately centered on an Enraf-Nonius CAD-4 diffractometer are given in Table 1. The complete set, collected in the usual manner [1], consisted of 411 observed reflections ($I > 2\sigma(I)$) out of the 1560 measured. The data shortage was particularly severe since there are two cation—anion pairs in the asymmetric unit of the monoclinic space group.

Calculations were carried out with the set of computer programs previously described [1]. The function $w(|F_0| - |F_c|)^2$ was minimized. No corrections were made for extinction or anomalous dispersion. Neutral atom scattering factors were taken from the compilations of Cromer and Waber [3] for K, Al, O, N, and C.

The structure was eventually solved with some difficulty by the application of the direct methods program, MULTAN [4]. Final least-squares refinement with isotropic temperature factors for all atoms resulted in $R_1 = \Sigma(|F_0| - |F_c|)/\Sigma|F_0| = 0.103$ and $R_2 = [\Sigma w(|F_0| - |F_c|)^2/\Sigma|F_0|^2]^{1/2} = 0.123$. Because of the limited data no attempt was made to carry out refinement with anisotropic thermal parameters, or to locate the hydrogen atoms. (There were 4 reflections per parameter

β_{33}	β_{12}	β_{13}	β_{23}
0.0060(1)	0.0011(3)	−0.0014(2)	−0.0002(1)
0.0041(1)	−0.0003(3)	0.0002(2)	−0.0001(1)
0.0048(3)	−0.0003(7)	0.0011(3)	−0.0003(3)
0.0085(4)	−0.0033(9)	0.0053(7)	0.0003(4)
0.0067(3)	0.0021(9)	0.0041(6)	0.0007(4)
0.0059(4)	0.0009(11)	0.0010(7)	0.0001(5)
0.0057(5)	−0.0018(12)	0.0014(10)	−0.0010(5)
0.0041(4)	−0.0062(21)	−0.0007(9)	−0.0005(7)
0.0054(4)	−0.0005(15)	0.0002(8)	−0.0002(6)
0.0048(6)	0.0110(22)	0.0015(13)	0.0041(11)
0.0060(7)	0.0040(24)	0.0016(17)	−0.0019(10)
0.0042(7)	−0.0050(33)	−0.0019(15)	−0.0051(12)
0.0052(8)	0.0154(36)	−0.0031(17)	0.0015(11)
0.0057(7)	0.0033(26)	0.0054(17)	0.0018(10)
0.0049(6)	−0.0077(24)	−0.0013(12)	−0.0003(10)

varied.) The weighting scheme was based on unit weights, and unobserved reflections were not included. The largest parameter shifts in the final cycle of refinement were less than 0.02 of their estimated standard deviations. The final value of the standard deviation of an observation of unit weight was 1.16. The final values of the positional and thermal parameters are given in Table 2 *.

X-Ray data collection and structure solution for $K[Al(CH_3)_3NO_3] \cdot C_6H_6$

Single crystals of the colorless, air-sensitive compound were sealed in thin-walled capillaries. Final lattice parameters as determined from a least-squares refinement of the angular settings of 15 reflections ($\theta > 20°$) accurately centered on the diffractometer are given in Table 1.

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* Tables of structure factors for both compounds, have been deposited as NAPS Document, No. 03262, with National Auxiliary Publications Service, c/o Microfiche Publications, 440 Park Ave. So., New York, New York 10016. A copy may be secured by citing the document and remitting $ 1.50 for microfiche or $ 5.00 for photocopies. Advance payment is required. Make checks payable to Microfiche Publications.

Following the data collection procedure mentioned previously, one independent octant of data was measured out to $2\theta = 50°$. The data set consisted of 809 observed reflections ($I > 3\sigma(I)$) out of 1620 possible unique reflections.

The structure was solved by the application of MULTAN [4], and refined to final values of $R_1 = 0.044$ and $R_2 = 0.047$. All non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms bonded to the methyl carbon atoms were located on a difference Fourier map, while those bonded to the benzene ring were placed in calculated positions. The hydrogen atom parameters were not refined. The weighting scheme was based on unit weights, and unobserved reflections were not included. The largest parameter shifts in the final cycle of refinement were less than 0.01 of their estimated standard deviations. The final value of the standard deviation of an observation of unit weight was 0.78. The final values of the positional and thermal parameters are given in Table 3.

Discussion

$K[Al_2(CH_3)_6NO_3]$

The molecular structure and atom labeling scheme for $K[Al_2(CH_3)_6NO_3]$ are presented as Figs. 1 and 2, while the potassium ion environments are given in Figs. 3 and 4. Similar illustrations for $K[Al(CH_3)_3NO_3] \cdot C_6H_6$ are given in Figs. 5 and 6.

The ways in which the nitrate group can interact with metals have been well summarized by Addison et al. [5]. For a nitrate ion to act as a bridge between two metal atoms, there exist possibilities III and IV. Although III is by far the most common, IV is not without precedent [6]. In the case of $K[Al_2(CH_3)_6NO_3]$ situation III clearly pertains. Because of the limited data, the bond lengths (given in Table 4) are not particularly meaningful, but two important observations can be made. The first concerns the rather different configurations of the methyl groups of the two independent anions.

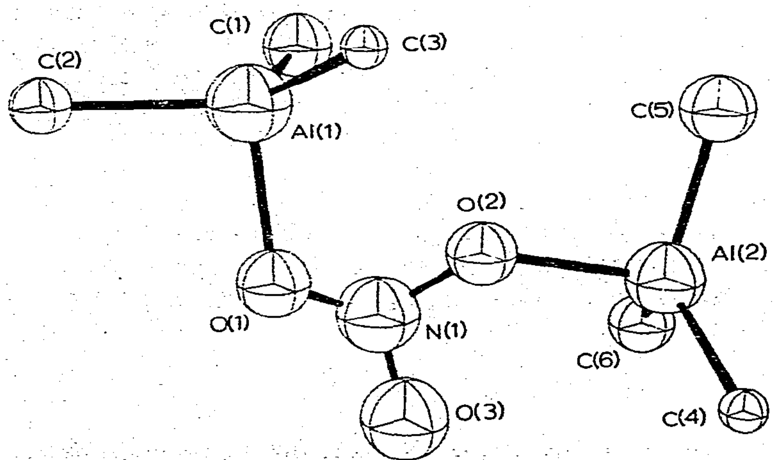


Fig. 1. Structure of the $[Al_2(CH_3)_6NO_3]^-$ anion which contains Al(1) and Al(2) with the atoms represented by their 50% probability spheres.

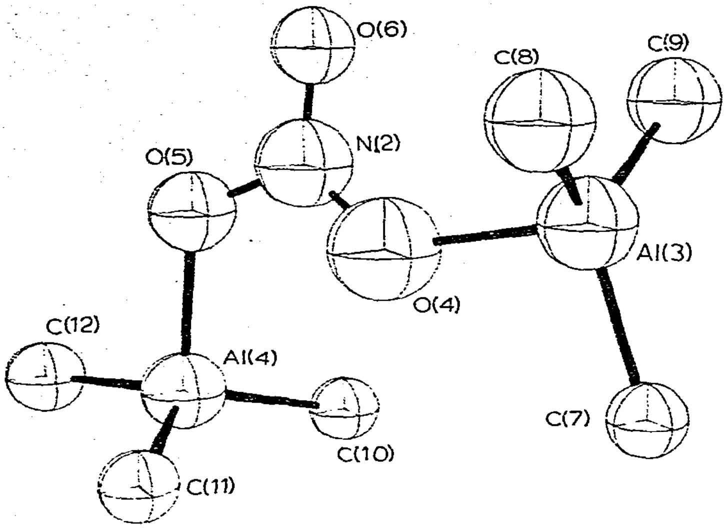


Fig. 2. Structure of the $[Al_2(CH_3)_6NO_3]^-$ anion which contains Al(3) and Al(4).

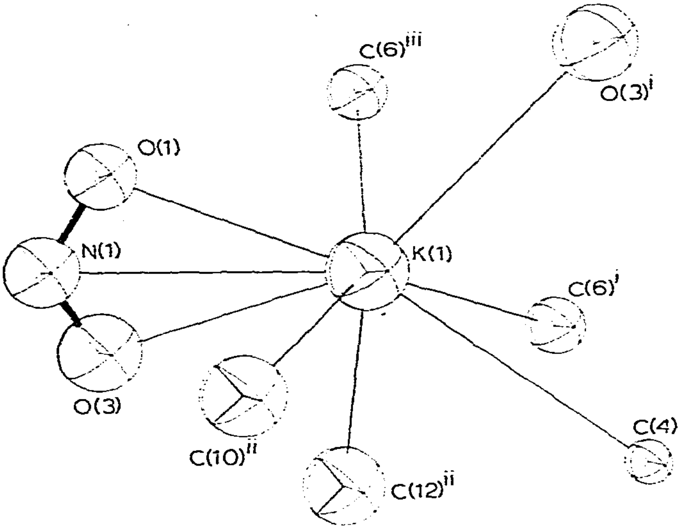


Fig. 3. Environment of K(1) to 3.5 Å. Primes atom notation corresponds to that given in Table 4.

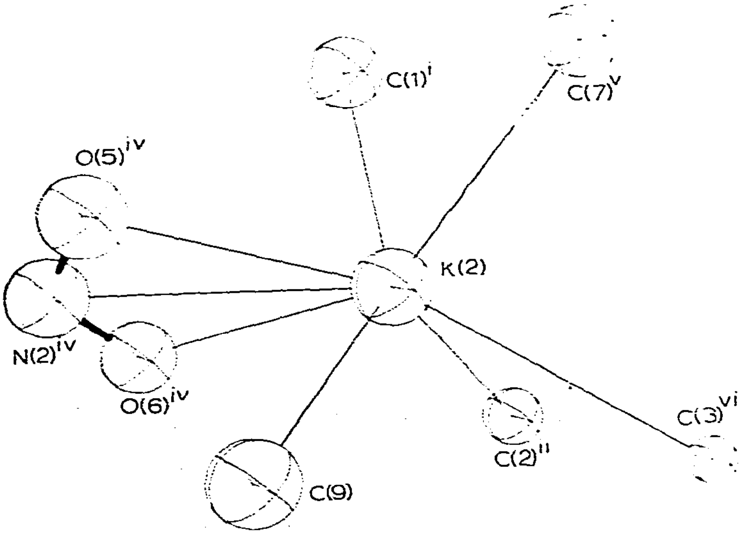
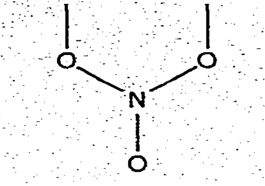
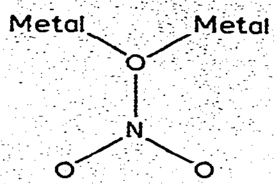


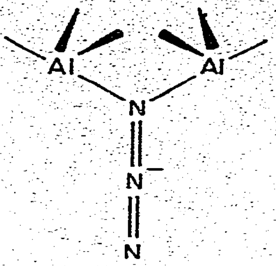
Fig. 4. Environment of K(2) to 3.5 Å



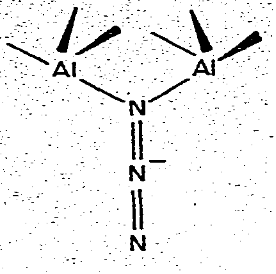
(III)



(IV)



(V)



(VI)

When there are two crystallographically independent molecules (or ions) in a unit cell, the actual physical differences are often very slight [7,8]. However, major discrepancies have been seen: the most notable example is the closely related compound $K[Al_2(CH_3)_6N_3]$ [9]. Here one could envision two possible configurations of the trimethylaluminum groups, V and VI, and indeed both are formed. With $K[Al_2(CH_3)_6NO_3]$, the anion containing Al(1) and Al(2) shows a staggered methyl group configuration (as in VI), with C(2) and C(5) out of the plane of the nitrate ion by 0.31 and 0.16 Å, respectively. The anion including Al(3) and Al(4) shows considerably more distortion of this geometry, with C(7) and C(12) out of the plane of the second nitrate ion by 0.45 and 0.60 Å, respectively.

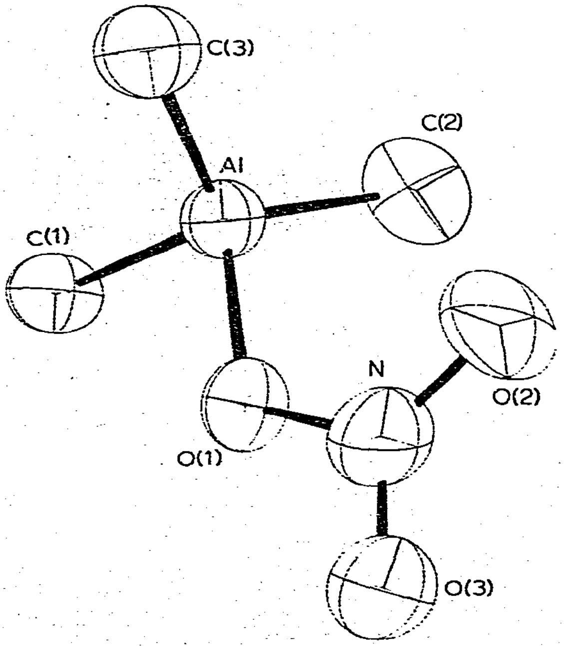


Fig. 5. Structure of the $[Al(CH_3)_3NO_3]^-$ anion with the atoms represented by their 50% probability ellipsoids for thermal motion.

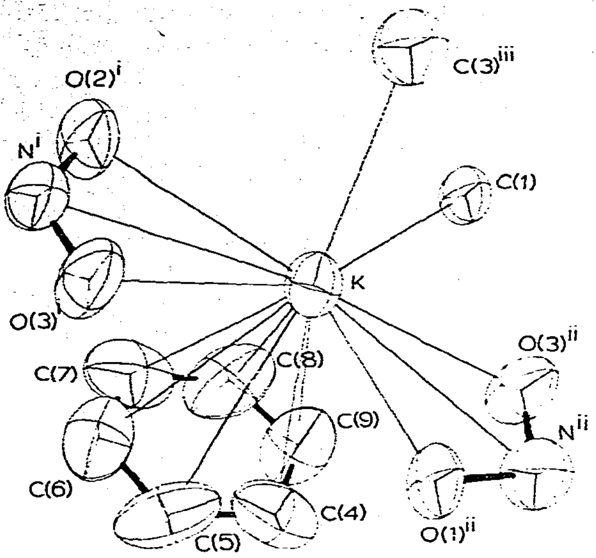


Fig. 6. Packing of the potassium atom of $K[Al(CH_3)_3NO_3] \cdot C_6H_6$.

TABLE 4

INTERATOMIC DISTANCES (Å) FOR $K[Al_2(CH_3)_6NO_3]$

Bond distances			
Al(1)—O(1)	2.01(5)	Al(2)—O(2)	1.95(5)
Al(1)—C(1)	1.91(8)	Al(2)—C(4)	1.91(5)
Al(1)—C(2)	2.12(8)	Al(2)—C(5)	1.99(7)
Al(1)—C(3)	1.99(6)	Al(2)—C(6)	2.00(8)
N(1)—O(1)	1.23(7)	N(1)—O(2)	1.33(7)
N(1)—O(3)	1.24(6)	Al(1)—Al(2)	4.71(2)
Al(3)—O(4)	2.01(7)	Al(4)—O(5)	1.98(5)
Al(3)—C(7)	2.01(6)	Al(4)—C(10)	1.91(7)
Al(3)—C(8)	2.06(9)	Al(4)—C(11)	1.96(7)
Al(3)—C(9)	2.02(8)	Al(4)—C(12)	1.86(8)
N(2)—O(4)	1.30(7)	N(2)—O(5)	1.23(7)
N(2)—O(6)	1.23(7)	Al(3)—Al(4)	4.71(2)
K(1)—O(3) [a]	2.82(6)	K(2)—O(6) [d]	2.80(5)
K(1)—O(1)	2.92(5)	K(2)—O(5) [d]	2.98(5)
K(1)—O(3)	3.11(6)	K(2)—C(7) [e]	3.11(7)
K(1)—C(10) [b]	3.18(8)	K(2)—C(2) [b]	3.15(8)
K(1)—C(6) [c]	3.29(8)	K(2)—C(9)	3.21(8)
K(1)—N(1)	3.34(8)	K(2)—C(1) [a]	3.30(8)
K(1)—C(12) [b]	3.35(9)	K(2)—N(2) [d]	3.34(8)
K(1)—C(6) [a]	3.43(7)	K(2)—C(3) [f]	3.44(5)
K(1)—C(4) [a]	3.44(6)		

[a] Related to the atom in Table 2 by ($\overline{x}$, $1-y$, $1-z$). [b] ($1-x$, $1-y$, $1-z$). [c] ($1+x$, y, z). [d] ($x-1$, y, z). y, z). [e] ($-\frac{1}{2}+x$, $1\frac{1}{2}-y$, $-\frac{1}{2}+z$). [f] (x, y, $z-1$).

A second noteworthy point concerns the packing of the potassium ions. This is the third structure in the series which demonstrates two different potassium ion environments, and all of these are of compounds that exhibit the liquid-layering or liquid clathrate effect [2]. In K[$Al_2(CH_3)_6N_3$], one K^+ ion was packed close to four methyl groups and the terminal nitrogen atoms of two azide ions. The other was near six methyl groups [9]. In K[$Al_3(CH_3)_9SeCH_3$] · 2 C_6H_6 [10], one crystallographically independent K^+ was packed amid the anions, while the other was sandwiched between benzene molecules. For K[$Al_2(CH_3)_6NO_3$] essentially the same effect is seen: K(1) has its closest contacts with three oxygen atoms (at 2.82, 2.92, and 3.11 Å), while K(2) has only two oxygen atoms (2.80 and 2.98 Å) within a sphere of 4 Å radius. The difference in cation packing has been used as the basis of an explanation of the solution behavior of these compounds [2].

As was previously mentioned the individual bond lengths have such large standard deviations that no significance can be attached to small discrepancies. However, the average of the twelve Al—C bond distances, 1.98 Å, agrees well with those found in related compounds [10]. In a like manner, the average of the four Al—O distances, 1.99 Å, probably represents a realistic estimate for a bridging nitrate ion.

TABLE 5

INTERATOMIC DISTANCES (Å) AND ANGLES (Deg) FOR K[$Al(CH_3)_3NO_3$] · C_6H_6

Bond distances			
Al—O(1)	1.930(6)	Al—C(1)	1.966(9)
Al—C(2)	1.952(10)	Al—C(3)	1.986(8)
N—O(1)	1.340(7)	N—O(2)	1.201(9)
N—O(3)	1.221(9)	Al—O(2)	3.021(6)
C(4)—C(5)	1.32(2)	C(5)—C(6)	1.35(2)
C(6)—C(7)	1.40(2)	C(7)—C(8)	1.34(2)
C(8)—C(9)	1.35(2)	C(9)—C(4)	1.38(2)
K—O(3) [a]	2.749(5)	K—O(3) [b]	2.751(6)
K—O(1) [b]	2.965(6)	K—O(2) [a]	3.043(7)
K—N [a]	3.227(7)	K—N [b]	3.320(9)
K—C(3) [c]	3.269(9)	K—C(1)	3.282(8)
K—C(8) [d]	3.29(1)	K—C(9) [d]	3.31(1)
K—C(7) [d]	3.36(2)	K—C(6) [d]	3.43(1)
K—C(4) [d]	3.43(1)	K—C(5) [d]	3.46(1)
Bond angles			
O(1)—Al—C(1)	94.3(4)	O(1)—Al—C(2)	108.0(4)
O(1)—Al—C(3)	105.1(3)	C(1)—Al—C(2)	117.2(4)
C(1)—Al—C(3)	112.3(4)	C(2)—Al—C(3)	116.6(4)
Al—O(1)—N	123.3(6)	O(2)—N—O(3)	126.6(7)
O(1)—N—O(2)	118.4(8)	O(1)—N—O(3)	115.0(8)
C(4)—C(5)—C(6)	123(1)	C(5)—C(6)—C(7)	118(2)
C(6)—C(7)—C(8)	119(2)	C(7)—C(8)—C(9)	121(1)
C(8)—C(9)—C(4)	120(1)	C(9)—C(4)—C(5)	119(1)

[a] Related to the atom given in Table 3 by (x, 1 + y, z). [b] (2 − x, $\frac{1}{2}$ + y, $\frac{1}{2}$ − z). [c] (1 − x, $\frac{1}{2}$ + y, $\frac{1}{2}$ − z). [d] ($\frac{1}{2}$ + x, $1\frac{1}{2}$ − y, 1 − z).

TABLE 6

COMPARISON OF STRUCTURAL PARAMETERS FOR COMPOUNDS WHICH CONTAIN THE UNIDENTATE NITRATE LIGAND

Compound	Δ[(metal—O(1)—(metal—O(2)] [a]	N—O(1)	N—O(2)	N—O(3)	Ref.
$Cu(IM)_4(NO_3)_2$ [b]	1.64	1.226(9)	1.199(11)	1.273(9)	11
	1.64	1.222(8)	1.222(9)	1.280(8)	
$VO(NO_3)_2(NCCH_3)$	1.20	1.45(3)	1.19(3)	1.24(3)	12
$Mn(BIPY)(NO_3)_3$ [c]	1.15	1.24(1)	1.23(2)	1.12(1)	13
$Ni(LL)(NO_3)_2$ [d]	1.15	1.279(7)	1.225(6)	1.205(8)	14
$Ni(TRI)(H_2O)_2(NO_3)_2$ [e]	1.14	1.28(2)	1.23(2)	1.22(2)	15
$Ni(C_5H_5N)_2(NO_3)_2(H_2O)_2$	1.14	1.267(3)	1.231(4)	1.258(3)	16
$K[Al(CH_3)_3NO_3] \cdot C_6H_6$	1.09	1.340(7)	1.201(9)	1.221(9)	This study
$Cu(NO_3)[P(CH_3)(C_6H_5)_2]_3$	1.04	1.166(8)	1.247(8)	1.209(8)	17
$Sn(CH_3)_3(NO_3)(H_2O)$	1.01	1.33(2)	1.18(2)	1.26(2)	18
$[Cu(CAF)(NO_3)(H_2O)_3NO_3$ [f]	0.92	1.278(4)	1.215(6)	1.218(4)	19
$K[Au(NO_3)_4]$	0.88	1.39(3)	1.22(3)	1.20(2)	20
	0.83	1.34(2)	1.24(3)	1.14(3)	
$Sn(C_6H_5)_3(NO_3)[(C_6H_5)_3PO]$	0.85	1.30(3)	1.22(3)	1.22(3)	21
$[Cu(C_5H_5NO)_2(NO_3)_2]_2$	0.83	1.316(9)	1.227(10)	1.222(10)	22
	0.78	1.304(8)	1.221(8)	1.234(9)	
$[Cu(DACH)_2(NO_3)]NO_3 \cdot [Cu(DACH)_2(H_2O)]NO_3$ [g]	0.77	1.26(1)	1.22(1)	1.21(1)	23
Average		1.293	1.217	1.217	

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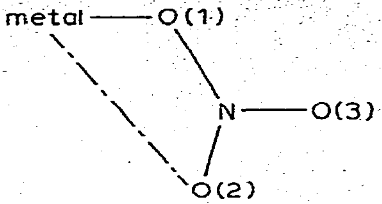
[a] Δ in Å: nitrate coordination is assumed to be monodentate if Δ > 0.75. [b] IM = imidazole. [c] BIPY = 2,2′-bipyridyl. [d] LL = 2,6-diacetylpyridinebisanil. [e] TRI = tribenzo[*b*,*f*,*j*][1.5.9]triazacycloduodecine. [f] CAF = caffeine. [g] DACH = 1,4-diazacycloheptane.

K[Al(CH₃)₃NO₃] · C₆H₆

The structure of $K[Al(CH_3)_3NO_3] \cdot C_6H_6$ shows that the nitrate ion is clearly bonded to the aluminum atom in a unidentate fashion (Table 5). In order to make comparisons with other studies it is necessary to differentiate this case from that of the unsymmetrical bidentate nitrate coordination. Addison et al. have used the criterion that the metal—O(1) bond be 0.8 Å shorter than the metal—O(2) bond in VII.



(VII)

On this basis the data in Table 6 have been compiled. Although the structures are from a wide range of compounds [11—23] in all except one [17] the N—O (coordinated) bond length is elongated with respect to those involving uncoordinated oxygen atoms. The averages of N—O (coordinated), 1.293 Å, and N—O (uncoordinated), 1.217 Å, compare favorably with those found in $K[Al(CH_3)_3NO_3] \cdot C_6H_6$, 1.340(7) and 1.211(14) Å, respectively. For $NaNO_3$ all the N—O bond lengths are equal at 1.241(2) Å [24].

The Al—O(1) bond length of 1.930(6) Å is quite long for a compound of this type. In $[N(CH_3)_4][Al(CH_3)_3CH_3COO]$ [1], the value is 1.83(1) Å, and in fact, the only longer Al—O lengths reported for organometallic compounds involve

TABLE 7

LEAST-SQUARES PLANES FOR $K[Al_2(CH_3)_6NO_3]$

Plane
A $-0.5403X - 0.8414Y + 0.0119Z = -9.5231$
B $-0.5656X - 0.7759Y - 0.2795Z = -10.0000$

Deviation of atoms from planes (Å) [a]

Atom	Plane A	Atom	Plane B
N(1)	0.20	N(2)	−0.09
O(1)	−0.07	O(4)	0.03
O(2)	−0.05	O(5)	0.03
O(3)	−0.09	O(6)	0.04
Al(1)	0.25	Al(3)	0.12
C(1)	2.04	C(7)	−0.45
C(2)	0.31	C(8)	−1.29
C(3)	−1.21	C(9)	2.05
Al(2)	0.04	Al(4)	−0.51
C(4)	−1.65	C(10)	1.06
C(5)	0.16	C(11)	−2.25
C(6)	1.63	C(12)	0.60

[a] The atoms of the nitrate groups were used to compute the planes.

TABLE 8

LEAST-SQUARES PLANES FOR $K[Al(CH_3)_3NO_3] \cdot C_6H_6$

Plane
A $-0.6013X + 0.0550Y - 0.7972Z + 8.2870 = 0$
B $0.7045X - 0.0228Y - 0.7094Z + 4.0440 = 0$

Deviation of atoms from planes (Å)

Atom	Plane A [a]	Atom	Plane B
N	0.003	C(4)	0.019
O(1)	−0.001	C(5)	−0.003
O(2)	−0.001	C(6)	−0.012
O(3)	−0.001	C(7)	0.012
		C(8)	0.004
Al	0.047	C(9)	−0.019
C(1)	−0.067		
C(2)	−1.479	K	2.803
C(3)	1.832		

[a] The atoms of the nitrate group were used to compute Plane A, and Plane B was based on the atoms of the benzene molecule.

either uncharged donor ligands (2.00(2) Å in $Fe_2(\eta^5\text{-}C_5H_5)_2(CO)_2[CO \cdot Al(C_2H_5)_3]_2$ [25] and 2.02(2) Å in $[Al(CH_3)_3]_2 \cdot C_4H_8O_2$ [26]) or a five-coordinate aluminum atom (2.047(7) Å for one of the Al—O bonds in $[(CH_3)_2AlOC(C_6H_5)N(C_6H_5) \cdot CH_3CHO]_2$ [27]). The average Al—C distance of 1.968(14) Å is normal, and the nitrate group is planar to within 0.003 Å.

Another important feature of the structure involves the dynamic role of the benzene molecule. The potassium ion is symmetrically coordinated to the ring at K—C distances of 3.29 to 3.46 Å, with an average of 3.38(6) Å. This may be compared with the K—C separation of 3.41 Å in $K[Al_3(CH_3)_9SeCH_3] \cdot 2\ C_6H_6$ [10]. In each of these cases the benzene molecule undoubtedly participates in a

TABLE 9

BOND ANGLES (Deg) FOR $K[Al_2(CH_3)_6NO_3]$

Bond angles			
O(1)—Al(1)—C(1)	106(3)	O(2)—Al(2)—C(4)	102(3)
O(1)—Al(1)—C(2)	96(3)	O(2)—Al(2)—C(5)	93(3)
O(1)—Al(1)—C(3)	106(2)	O(2)—Al(2)—C(6)	106(3)
C(1)—Al(1)—C(2)	106(3)	C(4)—Al(2)—C(5)	117(3)
C(1)—Al(1)—C(3)	117(3)	C(4)—Al(2)—C(6)	116(3)
C(2)—Al(1)—C(3)	123(3)	C(5)—Al(2)—C(6)	118(3)
N(1)—O(1)—Al(1)	116(5)	N(1)—O(2)—Al(2)	129(5)
O(1)—N(1)—O(2)	120(7)	O(2)—N(1)—O(3)	112(7)
O(4)—Al(3)—C(7)	96(3)	O(5)—Al(4)—C(10)	101(3)
O(4)—Al(3)—C(8)	103(3)	O(5)—Al(4)—C(11)	104(3)
O(4)—Al(3)—C(9)	102(4)	O(5)—Al(4)—C(12)	98(3)
C(7)—Al(3)—C(8)	114(3)	C(10)—Al(4)—C(1)	123(3)
C(7)—Al(3)—C(9)	122(3)	C(10)—Al(4)—C(12)	117(4)
C(8)—Al(3)—C(9)	115(3)	C(11)—Al(4)—C(12)	109(3)
N(2)—O(4)—Al(3)	129(6)	N(2)—O(5)—Al(4)	120(5)
O(4)—N(2)—O(6)	130(8)	O(5)—N(2)—O(6)	116(8)
O(4)—N(2)—O(5)	110(8)		

substantial bonding interaction with the potassium ion. On the other hand, the C_6H_6 in $K[Al_2(CH_3)_6F] \cdot C_6H_6$ [28] is held into the crystal lattice by packing forces, and does not interact to any significant extent with the potassium ion. (There are six methyl-carbon atoms within 3.47 Å, and the closest aryl-carbon atom approach is 3.95 Å.) In $K[Al(CH_3)_3NO_3] \cdot C_6H_6$, the remainder of the potassium ion's coordination sphere is filled by two pairs of oxygen atoms at 2.749(5), 2.751(6), 2.965(6), and 3.043(7) Å, and two methyl groups at 3.269(9) and 3.282(8) Å (Fig. 5).

In Tables 7 and 8 the least-squares planes for $K[Al_2(CH_3)_6NO_3]$ and $K[Al(CH_3)_3NO_3] \cdot C_6H_6$ are given, in Table 9 the bond angles for $K[Al_2(CH_3)_6NO_3]$.

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