Journal of Organometallic Chemistry, 127 (1977) 403–414
© Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

THE SYNTHESIS AND CRYSTAL STRUCTURE OF TETRAMETHYLAMMONIUM ACETATOTRIMETHYLALUMINATE

Jerry L. Atwood,* William E. Hunter,
and Karen D. Crissinger

Department of Chemistry
University of Alabama
University, Alabama 35486, U.S.A.

(Received July 22nd, 1976)

Summary

The crystal structure of $[N(CH_3)_4][Al(CH_3)_3CH_3COO]$ has been determined from single-crystal X-ray diffraction data collected by counter methods. Tetramethylammonium acetatotrimethylaluminate crystallizes in the monoclinic space group $P2_1/c$ with lattice dimensions $\underline{a}$ = 6.949(5), $\underline{b}$ = 22.022(9), $\underline{c}$ = 9.576(6) Å, $\underline{\beta}$ = 94.40(5)°, and ρ_{calc} = 0.93 g cm^{-3} for Z = 4. Least-squares refinement gave a final conventional R value of 0.092 for 729 independent observed reflections. The aluminum atom is coordinated in a tetrahedral fashion with an Al–O bond length of 1.83(1) Å, and an average Al–C distance of 2.02(2) Å. The C–O–Al bond angle is 137(1)°. The compound was prepared from $[N(CH_3)_4][Al_2(CH_3)_6CH_3COO]\cdot n\text{-}C_6H_5CH_3$.

Introduction

Alkali metal halides were initially reported[1] to react with aluminum alkyls to form 1/1, $M[AlR_3X]$, and 2/1, $M[Al_2R_6X]$, compounds. Later, the area was greatly expanded with the formation of analogous 1/1 and 2/1 pseudohalide complexes.[2,3] Evidence has been presented for the existence of the 4/1 complex $[N(CH_3)_4]$-$[Al_4(CH_3)_{12}SCN]$,[4] and, more recently, the presence of the 3/1 moiety $K[Al_3(CH_3)_9SeCH_3]$ has been verified by a crystal structure analysis.[5] The scope of the original work has thus been considerably broadened by the addition of new stoichiometries and new ligands.

The unusual thermolytic, photolytic, and solution behavior of the 2/1 complexes[6] has stimulated the production of four X-ray structural analyses:

$K[Al_2(C_2H_5)_6F]$,[7] $K[Al_2(CH_3)_6F]\cdot C_6H_6$,[8]
$K[Al_2(CH_3)_6N_3]$,[9] and $K[Al_2(CH_3)_6SCN]$.[10]

Crystallographic studies have been completed on several 1/1 halide compounds,[11,12] and on three[13-15] 1/1 pseudohalide complexes in which the emphasis has been on the mode of attachment of the ligand.

As part of a continuing search for novel ligand systems, our group has previously synthesized 1/1 and 2/1 nitrate complexes.[6,16] The surprising thermal stability of these substances has led to the investigation of other high oxygen content anionic organoaluminum complexes. We report here our preparative results with the acetate ion, together with the structural parameters of the 1/1 complex of tetramethylammonium acetate with trimethylaluminum.

Experimental

Tetramethylammonium acetatotrimethylaluminate was prepared by the reaction of 0.01 mole of tetramethylammonium acetate with 0.02 mole of trimethylaluminum in toluene. The formation of the liquid layering[6] characteristic of the presence of the 2/1 compound $[N(CH_3)_4][Al_2(CH_3)_6CH_3COO]$ was noted immediately. The 2/1 complex is, however, unstable with respect to the 1/1 complex (**1**), and crystals of the latter were formed within 30 min.

$$[N(CH_3)_4][Al_2(CH_3)_6CH_3COO]\cdot \text{aromatic} \rightleftarrows [N(CH_3)_4]\text{-}[Al(CH_3)_3CH_3COO] + Al(CH_3)_3 + \text{aromatic} \qquad (\mathbf{1})$$

Only with benzene does the equilibrium (1) lie far enough to the left to permit an nmr assessment of the aromatic/anion ratio in the more dense liquid layer: $[N(CH_3)_4][Al_2(CH_3)_6CH_3COO]\cdot 6.3\ C_6H_6$.[‡] For aromatic solvents (1) lies progressively farther to the right in the order: benzene < toluene < ethylbenzene < o-xylene < p-xylene < m-xylene.

Single crystals of the colorless, air-sensitive compound were sealed in thin-walled glass capillaries. Final lattice parameters as determined from a least-squares refinement of the angular settings of 15 reflections accurately centered on an Enraf-Nonius CAD-4 diffractometer are given in Table 1.

Table 1. Crystal Data

Mol. formula: $[N(CH_3)_4][CH_3COOAl(CH_3)_3]$

Mol. wt.: 205.28

Linear abs. coeff. μ: 1.19 cm^{-1}

Calc. density: 0.93 g cm^{-3}

Max. crystal dimensions: 0.15 x 0.20 x 0.60 mm

Space group: monoclinic, $P2_1/c$

Molecular/unit cell: 4

Cell constants[a]: $\underline{a}$ = 6.949(5), $\underline{b}$ = 22.022(9), $\underline{c}$ = 9.576(6)Å, $\underline{\beta}$ = 94.40(5)°

Cell volume: 1461.1$Å^3$

[a] MoKα radiation, λ = 0.71069Å. Ambient temperature of 24 ± 1°C.

Data were collected on the diffractometer with graphite crystal monochromated molybdenum radiation. The diffracted intensities were collected by the ω-2θ scan technique with a take-

---

[‡] The composition was deduced from N.M.R. integrations. A satisfactory elemental analysis was obtained for $[N(CH_3)_4][Al(CH_3)_3CH_3COO]$: Found: C, 51.0; H, 10.5; N, 6.2; Al, 13.0. Calcd: C, 52.7; H, 11.8; N, 6.8; Al, 13.1.

off angle of 3.5°. The scan rate was variable and was determined by a fast 20° min^{-1} prescan. Calculated speeds for the slow scan (based on the net intensity gathered in the prescan) ranged from 7 to 0.4° min^{-1}. Moving-crystal moving-counter backgrounds were collected for 25% of the total scan width at each end of the scan range. For each intensity the scan width was determined by the equation, scan range = $A + B \tan \theta$, where $A = 0.9°$ and $B = 0.25°$. Aperture settings were determined in a like manner with $A = 4$ mm and $B = 4$ mm. Other diffractometer parameters and the method of estimation of standard deviations have been described previously.[17] As a check on the stability of the instrument and crystal, two reflections were measured after every 30 reflections; no significant variation was noted.

One independent quadrant of data was measured out to $2\theta = 50°$; a slow scan was performed on a total of 729 out of 1327 possible unique reflections. Since these data were scanned at a speed which would yield a net count of 4000, the calculated standard deviations were all very nearly equal. No reflection was subjected to a slow scan unless a net count of 20 was obtained in the prescan. Based on these considerations, the data set of 729 reflections (used in the subsequent structure determination and refinement) was considered observed, and consisted in the main of those for which $I > 3\sigma(I)$. The intensities were corrected for Lorentz and polarization effects, but not for absorption (the crystal was mounted with the needle axis parallel to the ϕ axis of the goniometer, and the path lengths within the crystal were very nearly equal for all reflections).

Fourier calculations were made with the FOURIER program.[18] The full-matrix least-squares refinement was carried out using the Busing and Levy program ORFLS.[19] The function $w(|F_o| - |F_c|)^2$ was minimized. No corrections were made for extinction or anomalous dispersion. Neutral atom scattering factors were taken from the compilations of Cromer and Waber[20] for Al, O, N, and C. Final bond distances, angles, and errors were computed with the Busing, Martin, and Levy ORFFE program. Crystal structure illustrations were obtained with the program ORTEP.[22]

Solution and Refinement of Structure

The crystal structure was solved by the application of the direct methods program MULTAN.[23] Least-squares refinement with isotropic temperature factors afforded a reliability index of $R_1 = \Sigma(|F_o| - |F_c|)/\Sigma|F_o| = 0.147$. Conversion to anisotropic temperature parameters together with further refinement led to final values of $R_1 = 0.092$ and $R_2 = [\Sigma w(|F_o| - |F_c|)^2/\Sigma|F_o|^2]^{\frac{1}{2}} = 0.096$. Although there were several peaks of $\sim 0.7e^-/\text{Å}^3$ on the difference Fourier map, no attempt was made to locate the hydrogen atoms. The weighting scheme was based on unit weights, and unobserved reflections were not inlcuded. 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 0.01. The final values of the positional and thermal parameters are given in Table 2.*

Discussion

Two factors govern the preparation and stability of $M[Al_2(CH_3)_6CH_3COO]\cdot$aromatic: the lattice energy of MCH_3COO and the nature of the aromatic substance. The 2/1 tetramethyl-

---

*The table of structure factors has been deposited as NAPS Document, No. 02924, with National Auxilliary 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 is required. Make checks payable to Microfiche Publications.

Table 2. Final Fractional Coordinates and Thermal Parameters[a] for Tetramethylammonium Acetatotrimethylaluminate

Atom	x/a	y/b	z/c	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Aℓ	-0.0190(6)	0.1415(2)	0.1617(5)	0.0337(11)	0.0040(1)	0.0213(7)	-0.0018(4)	-0.0001(7)	0.0008(3)
O1	-0.2835(15)	0.1037(6)	0.5064(13)	0.0407(36)	0.0060(5)	0.0261(20)	0.0019(10)	0.0102(22)	0.0019(8)
O2	-0.1191(14)	0.1169(4)	0.3240(10)	0.0333(28)	0.0044(3)	0.0193(15)	0.0007(7)	0.0025(17)	0.0017(6)
N	0.2685(15)	0.0659(6)	0.6875(11)	0.0329(34)	0.0044(4)	0.0166(18)	0.0011(10)	0.0008(19)	-0.0000(7)
C1	-0.3520(24)	0.1964(8)	0.3723(20)	0.0467(59)	0.0039(5)	0.0400(42)	0.0073(15)	0.0083(37)	0.0024(12)
C2	-0.2493(22)	0.1365(9)	0.4072(17)	0.0298(44)	0.0058(8)	0.0174(25)	-0.0021(16)	0.0040(28)	-0.0011(12)
C3	-0.2280(19)	0.1259(8)	0.0083(15)	0.0322(42)	0.0066(7)	0.0219(25)	0.0013(13)	-0.0043(26)	-0.0000(11)
C4	0.2112(18)	0.0840(8)	0.1469(15)	0.0289(41)	0.0061(6)	0.0226(27)	0.0016(13)	0.0066(25)	0.0004(11)
C5	0.0723(25)	0.2280(7)	0.1813(19)	0.0602(68)	0.0036(5)	0.0370(39)	-0.0050(15)	0.0002(39)	0.0016(12)
C6	0.0785(21)	0.0436(9)	0.7475(18)	0.0288(43)	0.0090(8)	0.0251(29)	-0.0008(16)	0.0094(29)	0.0018(13)
C7	0.4343(20)	0.0293(7)	0.7564(16)	0.0368(44)	0.0054(7)	0.0238(27)	0.0045(14)	-0.0099(28)	0.0009(11)
C8	0.2544(20)	0.0512(8)	0.5333(15)	0.0378(45)	0.0078(8)	0.0135(21)	0.0022(15)	-0.0016(24)	-0.0007(10)
C9	0.3039(28)	0.1306(7)	0.7153(22)	0.0838(84)	0.0020(5)	0.0443(45)	0.0004(16)	0.0116(46)	-0.0014(12)

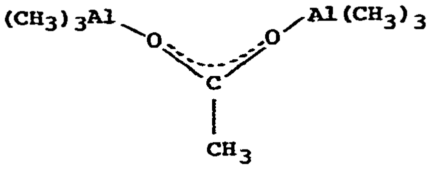
[a] Anisotropic thermal parameters defined by $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}\ell^2 + \beta_{12}hk + \beta_{13}h\ell + \beta_{23}k\ell)]$.

ammonium compound is thermally stable indefinitely at room temperature, but slowly decomposes at 60°C. (The decomposition products have not been identified; the color changes, from clear to yellow to deep red, are characteristic of other processes involving oxygen-containing anions.) It has not been possible to prepare alkali metal derivatives from the reaction of MCH_3COO with $Al(CH_3)_3$ because the lattice energy of the Group I acetates cannot be overcome below 60°. At 90° reaction occurs, but leads directly to decomposition products.

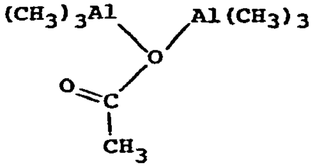
It is significant to note the effect of the aromatic on the stability of the 2/1 complexes. As was mentioned in the Experimental section, equilibrium (1) governs the conversion of the 2/1 into the 1/1 compound. Thus, the 2/1 liquid complex of benzene is completely stable at room temperature, while that of m-xylene does not exist.

Nuclear magnetic resonance studies of the 2/1 complexes also illustrate the stability of the substances. For the room temperature preparation of $[N(CH_3)_4][Al_2(CH_3)_6CH_3COO]\cdot 6.3\ C_6H_6$, the $Al-CH_3$ resonance occurs at -0.46δ (relative to the internal C_6H_6 assumed to be at 7.37δ). There is also a small peak at -0.29δ. An identical preparation except for a 12h period of heating at 50° shows, however, three major $Al-CH_3$ resonances at -0.19, -0.30, and -0.38δ. The solution shows no visible sign of decomposition under the mild conditions. The presence of the new peaks may therefore be indicative of either the formation of new linkage isomers of (A), such as (B), or stable intermediates in the decomposition process. Studies aimed at the isolation and identification of these compounds are in progress.

The structures of both the tetramethylammonium cation and the acetatotrimethylaluminate anion are shown in Figure 1. The coordination about the aluminum atom is tetrahedral, and the Al-C distances of 2.01(1), 2.01(1), and 2.05(1)Å (Table 3) are



(A)



(B)

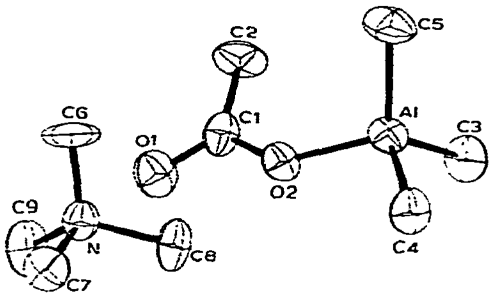


Figure 1. Structure of tetramethylammonium acetatotrimethylaluminate with the atoms displayed as their 40% probability ellipsoids for thermal motion.

Table 3. Interatomic Distances (Å) and Angles (Deg) for $[N(CH_3)_4][CH_3COOAl(CH_3)_3]$.

Bond Distance

Al-O2	1.83(1)	Al-C4	2.05(1)
Al-C3	2.01(1)	Al-C5	2.01(1)
C1-O2	1.32(2)	C1-O1	1.23(2)
C1-C2	1.52(2)	N -C6	1.56(2)
N -C7	1.52(2)	N -C8	1.51(2)
N -C9	1.46(2)		

Bond Angle

O2-Al-C3	105.6(6)	O2-Al-C4	103.0(5)
O2-Al-C5	110.4(7)	C3-Al-C4	111.5(6)
C3-Al-C5	115.7(8)	C4-Al-C5	110.4(7)
Al-O2-C1	137.4(1.1)	O1-C1-O2	117.1(1.8)
O1-C1-C2	124.2(1.6)	C2-C1-O2	118.7(1.6)
C6-N -C7	107.9(1.2)	C6-N -C8	107.5(1.1)
C7-N -C9	109.1(1.4)	C8-N -C9	112.7(1.3)

normal for the situation in which the methyl hydrogen atoms have not been located.[9] The Al-O length of 1.83(1)Å is compared with others from organometallic structures in Table 4. In most cases the value is near that found in the present study. Exceptions are noted for complexes with neutral donor ligands such as dioxane[24] and coordinated CO,[25] and for five-coordinate aluminum.[26] Here, the Al-O lengths are close to 2.0Å.

Table 4. Comparison of Aluminum-Oxygen Bond Distances in Organometallic Compounds.

Compound	Coordination Number		Distance (Å)	Ref.
	Al	O		
$[(CH_3)_2AlOC(C_6H_5)N(C_6H_5)]_2$	4	2	1.805(6)	a
$[(CH_3)_2AlOC(C_6H_5)N(C_6H_5)]\cdot ON(CH_3)_3$	4	2	1.771(7) 1.815(8)	b
$Cl_3Al\cdot OC(C_6H_5)Cl$	4	2	1.819(5)	c
$[N(CH_3)_4][Al(CH_3)_3CH_3COO]$	4	2	1.83(1)	this study
$Fe_2(\eta^5-C_5H_5)_2(CO)_2[CO\cdot Al(C_2H_5)_3]_2$	4	2	2.00(2)	25
$[(CH_3)_3SiOAlBr_2]_2$	4	3	1.79(1) 1.80(1)	d
$Mg[Al(OCH_3)_2(CH_3)_2]_2\cdot C_4H_8O_2$	4	3	1.80(2) 1.86(1)	e
$[(CH_3)_2AlOCH_3]_3$	4	3	1.851(3)	f
$[Al(CH_3)_3]_2\cdot C_4H_8O_2$	4	3	2.02(2)	24
$[(CH_3)_2AlOC(C_6H_5)N(C_6H_5)\cdot CH_3CHO]_2$	5	3	1.868(6) 1.966(6)	26
		2	2.047(7)	

[a] Y. Kai, N. Yasuoka, N. Kasai, and M. Kakudo, J. Organometal. Chem., 32 (1971) 165.

[b] Y. Kai, N. Yasuoka, N. Kasai, M. Kakudo, H. Yasuda, and H. Tani, Chem. Commun. (1971) 940.

[c] S. E. Rasmussen and N. C. Broch, Acta Chem. Scand., 20 (1966) 1351.

[d] M. Bonamico and G. Dessy, J. Chem. Soc. (A), (1967) 1786.

[e] J. L. Atwood and G. D. Stucky, J. Organometal. Chem., 13 (1968) 53.

[f] D. A. Drew, A. Haaland, and J. Weidlein, Z. Anorg. Allg. Chem., 398 (1973) 241.

The structural parameters of the acetate portion of the anion are similar to those found in organic acetates, $R\text{-}O\text{-}\overset{O}{\overset{\|}{C}}\text{—}CH_3$. The C-O single bond length (Table 3) of 1.32(2)Å may be compared with 1.364(6)Å in juncusol diacetate,[27] and the C=O length of 1.23(2)Å with 1.200(8)Å.

The unit cell packing, shown in Figure 2, is typical of a compound of this type. The closest approach of the anion to the nitrogen atom of the cation is the N-O1 separation of 3.77(2)Å.

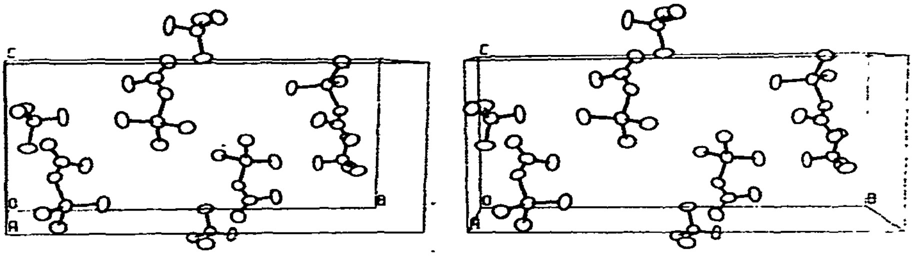


Figure 2. Stereoscopic view of the unit cell packing for $[N(CH_3)_4][Al(CH_3)_3CH_3COO]$.

Acknowledgements

We wish to thank M. Beth Humphrey for experimental assistance, and the National Science Foundation for support of this work under Grant CHE-75-04927.

References

1. K. Ziegler, R. Köster, H. Lehmkuhl, and K. Reinert, Justus Liebigs Ann. Chem., 629 (1960) 33.
2. J. L. Atwood, P. A. Milton, and S. K. Seale, J. Organometal. Chem., 28 (1971) C29.
3. F. Weller, I. L. Wilson, and K. Dehnicke, J. Organometal. Chem., 30 (1971) C1.
4. F. Weller and K. Dehnicke, J. Organometal. Chem., 36 (1972) 23.
5. J. L. Atwood and S. K. Seale, J. Organometal. Chem., 114 (1976) 107.

6. J. L. Atwood and J. D. Atwood, Adv. Chem. Ser., **150** (1976) 112.

7. G. Allegra and G. Perego, Acta Crystallogr., **16** (1963) 185.

8. J. L. Atwood and W. R. Newberry, J. Organometal. Chem., **66** (1974) 15.

9. J. L. Atwood and W. R. Newberry, J. Organometal. Chem., **65** (1974) 145.

10. J. L. Atwood and W. E. Hunter, unpublished results.

11. G. Hencken and E. Weiss, J. Organometal. Chem., **73** (1974) 35.

12. J. L. Atwood, W. R. Newberry, and D. C. Hrncir, Cryst. Struct. Commun., **3** (1974) 615.

13. J. L. Atwood and R. E. Cannon, J. Organometal. Chem., **47** (1973) 321.

14. S. K. Seale and J. L. Atwood, J. Organometal. Chem., **64** (1974) 57.

15. J. L. Atwood and W. R. Newberry, J. Organometal. Chem., **87** (1975) 1.

16. J. L. Atwood, K. D. Crissinger, and M. B. Humphrey, unpublished results.

17. J. L. Atwood and K. D. Smith, J. Amer. Chem. Soc., **95** (1973) 1488.

18. D. J. Hodgson's version of Dellaca and Robinson's FOURIER Program, as locally implemented for the UNIVAC 1110, University of Alabama.

19. W. R. Busing, K. O. Martin and H. A. Levy, "ORFLS, A Fortran Crystallographic Least-Squares Program," Report ORNL-TM-305, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1962.

20. D. T. Cromer and J. T. Waber, Acta Crystallogr., **18** (1965) 104.

21. W. K. Busing, K. O. Martin, and H. A. Levy, "ORFFE, A Fortran Crystallographic Function and Error Program," Report ORNL-TM-306, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1964.

22. C. K. Johnson, "ORTEP, A Fortran Thermal-Ellipsoid Plot Program for Crystal Structure Illustrations," Report ORNL-3794, Revised, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1965.

23. G. Germain, P. Main, and M. M. Woolfson, Acta Crystallogr., **A27** (1971) 368.

24. J. L. Atwood and G. D. Stucky, J. Amer. Chem. Soc., **89** (1967) 5362.

25. N. J. Nelson, N. E. Kime, and D. F. Shriver, J. Amer. Chem. Soc., 91 (1969) 5173.

26. Y. Kai, N. Yasuoka, N. Kasai, M. Kakudo, H. Yasuda, and H. Tani, Chem. Commun. (1969) 575.

27. D. H. Miles, J. L. Atwood, and S. Black, J. Amer. Chem. Soc., submitted.