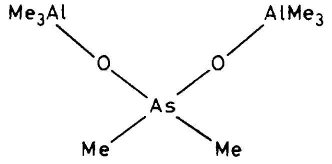
The Formation and Structure of the Novel Aluminoxane Anion $[Me_2AlO{\cdot}AlMe_3]_2^{2-}$

Jerry L. Atwood* and Michael J. Zaworotko

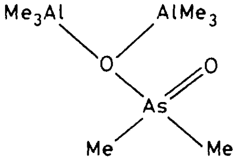
Department of Chemistry, University of Alabama, University, AL 35486, U.S.A.

Trimethylaluminium methylates the cacodylate anion ($[AsMe_2O_2]^-$) with the formation of $[AsMe_4]_2[Me_2AlO{\cdot}AlMe_3]_2$, and an *X*-ray crystal structure has shown the aluminoxane anion to consist of a planar Al_2O_2 ring with $AlMe_3$ molecules co-ordinated to the oxygen atoms.

The biomethylation of compounds of toxic elements, particularly those of arsenic, has been the subject of considerable discussion.[1,2] Although the use of common organometallic methylating reagents plays no direct role in the biological processes, such techniques have proved useful in the synthesis of natural products.[3] In an effort to learn more about the basic organometallic chemistry of these reactions, we have investigated the interaction of sodium cacodylate ($Na[AsMe_2O_2]$) with trimethylaluminium, and now report the surprising result. The reaction was instantaneous in benzene at room temperature. A two-phase liquid (liquid clathrate)[4] resulted, and by analogy with other high-oxygen content anions[5–7] structures (**1**) or (**2**) are probable. Over several weeks colourless, air-sensitive crystals of $[AsMe_4]_2$ $[Me_2AlO{\cdot}AlMe_3]_2$ were obtained in good yield. [Although mechanistic data are not available, (**2**) would seem to lend itself to the formation of the observed aluminoxane anion.] This result is significant in two regards. Firstly, it demonstrates the complete methylation of the cacodylate anion to $[AsMe_4]^+$, and secondly, it affords structural parameters for the novel anion. The wide variation in aluminoxane structures has been recently noted.[8,9]



(**1**)



(**2**)

The anion, Figure 1, resides on a crystallographic centre of inversion, and may be viewed as two trimethylaluminium molecules co-ordinated to $[Me_2Al(\mu\text{-}O)_2AlMe_2]^{2-}$. Interestingly, it has a direct analogy in $[Cl_2AlO{\cdot}AlCl_3]_2^{2-}$ (isolated during the reaction of $NbCl_5$, C_6Me_6, $AlCl_3$, and Al in CH_2Cl_2),[10] and must therefore represent a favourable geometrical framework. The geometry within the four-membered Al_2O_2 ring is similar to that found in the electron-diffraction study of $[Me_2AlOBu^t]_2$.[11] The angle at the oxygen atom is 96° in the former compared to 98° in the latter, and in both cases the rings are required by symmetry to be planar. The independent Al–O bond lengths are nearly equal, 1.78(2) and 1.80(2) Å, and are at the short end of the normal range, 1.8—2.0 Å.[7] Indeed, the Me_3Al–O distance is the shortest yet observed (for the co-ordination of an Me_3Al molecule).

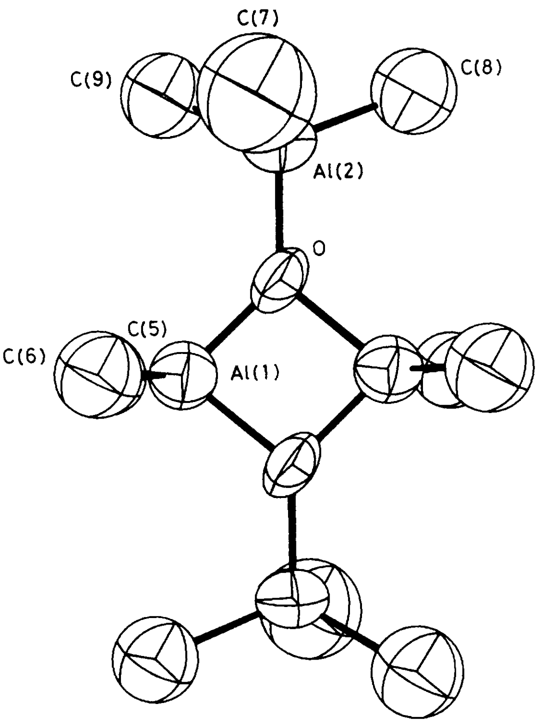


Figure 1. Structure of the $[Me_2AlO{\cdot}AlMe_3]_2^{2-}$ anion.

Crystal data: $[AsMe_4]_2[Me_2AlO{\cdot}AlMe_3]_2{\cdot}C_6H_6$, $C_{24}H_{60}Al_4As_2O_2$, monoclinic, space group $P2_1/n$, $M = 638.5$, $a = 9.829(3)$, $b = 15.247(5)$, $c = 13.641(4)$ Å, $\beta = 97.37(2)$°, $U = 2027$ Å^3, $Z = 2$, $D_c = 1.05$ g cm^{-3}, μ(Mo-K_α) = 18.5 cm^{-1}. The structure was refined to $R = 0.083$, $R_w = 0.087$, based on 442 observed reflections.†

We thank the U.S. National Science Foundation for support of this research.

Received, 22nd December 1982; Com. 1471

References

1 W. P. Ridley, L. Dizikes, A. Cheh, and J. M. Wood, *Environ. Health Perspect.*, 1977, **19**, 43.
2 M. Vahter, *Environ. Res.*, 1981, 286.
3 J. S. Edmonds, K. A. Francesconi, J. R. Cannon, C. L. Raston, B. W. Skelton, and A. H. White, *Tetrahedron Lett.*, 1977, 1543.
4 J. L. Atwood, *Rec. Dev. Sep. Sci.*, 1977, **3**, 195; J. L. Atwood in 'Inclusion Compounds,' Vol. I, eds. J. L. Atwood, J. E. Davies, and D. D. MacNicol, Academic Press, London, 1983.
5 J. L. Atwood, K. D. Crissinger, and R. D. Rogers, *J. Organomet. Chem.*, 1978, **155**, 1.
6 D. C. Hrncir, R. D. Rogers, and J. L. Atwood, *J. Am. Chem. Soc.*, 1981, **103**, 4277.
7 M. J. Zaworotko, R. D. Rogers, and J. L. Atwood, *Organometallics*, 1982, **1**, 1179.
8 J. L. Atwood, D. C. Hrncir, R. D. Priester, and R. D. Rogers, *Organometallics*, submitted for publication.
9 For related oligomers of the $(AlN)_n$ framework, see P. B. Hitchcock, J. D. Smith, and K. M. Thomas, *J. Chem. Soc., Dalton Trans.*, 1976, 1433, and references therein.
10 U. Thewalt and F. Stollmaier, *Angew. Chem. Suppl.*, 1982, 209.
11 A. Haaland and O. Stokkeland, *J. Organomet. Chem.*, 1975, **94**, 345.

---

† Atomic co-ordinates for the structure are available on request from the Director of the Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.