Crystallographic Evidence of the Three-Centre Bond in Hexamethyldialuminium

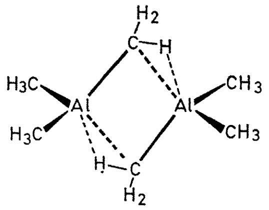
By J. C. HUFFMAN* and W. E. STREIB

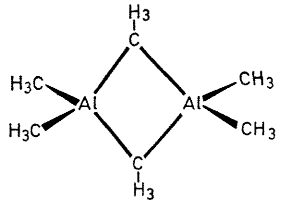
(*Department of Chemistry, Indiana University, Bloomington, Indiana* 47401)

Summary Three dimensional *X*-ray data collected at approximately −170 °C clearly located all hydrogen positions in hexamethyldialuminium and confirmed that the bridging methyl groups form three-centre bonds with the aluminium atoms, without aluminium–hydrogen bridging.

THERE has been considerable debate recently concerning the nature of the bonding in the trimethylaluminium dimer. Refinement of the data of Vranka and Amma[2] showed[1] that the bridging methyl groups bonded to produce a hydrogen-bridge bond as shown in (I), while nuclear quadrupole resonance data[3] supported (II), the structure originally proposed by Longuet-Higgins.[4] It was recently pointed out[5] that the published *X*-ray structural data was not sufficiently accurate to rule out either structure, as the errors associated with the hydrogen positional parameters are compatible with both alternatives.

Using a nitrogen vapour cold stream,[6] a crystal of hexamethyldialuminium was grown and three-dimensional data were collected to $\sin\theta/\lambda = 0{\cdot}93$ using Mo radiation on a Picker automated diffractometer equipped with a highly orientated graphite monochromator. The compound crystallized in space group $C2/c$, as previously reported;[2,7] $a = 12{\cdot}433(6)$ Å, $b = 6{\cdot}919(2)$ Å, $c = 14{\cdot}442(6)$ Å, and $\beta = 123{\cdot}21(1)°$ (at −170°). Of the 1046 unique intensities


(I)


(II)

collected, 824 had intensity greater than the standard error and were used in the refinement. The starting co-ordinates for the least-squares refinement were the positional parameters reported by Vranka and Amma.[2] The function $\Sigma w(F_0^2 - F_c^2)^2$ was minimized in the refinement in which the positional parameters of all atoms were varied, as well as isotropic thermal parameters for the hydrogens and anisotropic thermal parameters for all nonhydrogen atoms. The final residual, R, was found to be 0·029 for 824 observed reflections.

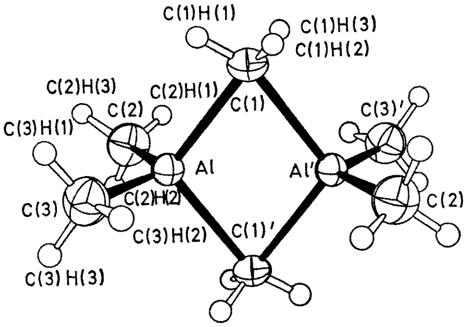


FIGURE. *Structure of hexamethyldialuminium. Primed atoms are related to the unprimed atoms by a centre of symmetry located in the centre of the ring.*

The molecule is shown in the Figure and important intermolecular distances and angles are given in the Table. The distances and angles of the non-hydrogen atoms agree well with those of Vranka and Amma.[2] The three bonds to the hydrogens of the carbon atom, C(1), are seen to be tetrahedral with respect to a vector directed towards the centre of the dimer, and the plane defined by C(1)'–C(1)–C(1)H(1) was found to be rotated 3·3 ± 2·2° from the Al–C(1)–Al plane. The Al–C(1)H(1) distance was found to be 2·17(3) Å, compared to the value of 1·78 Å reported by Byram *et al.*,[1] indicating that little, if any, bonding occurs between the bridging methyl hydrogen and aluminium atom. A final difference map revealed several peaks whose intensities were less than 0·5 electrons, the two largest lying nearly at the centre of the Al–C(3) and Al–C(2) bonds. Several other peaks appeared in the vicinity of the three centre bond, and further work is contemplated to resolve their significance.

Interatomic distances (Å) *and angles* (*deg*)

Distances

Al–C(1) = 2·125(2)[a]
Al–C(2) = 1·956(2)
Al–C(3) = 1·949(2)
Al–C(1)' = 2·123(2)
Al–Al' = 2·606(2)
C(1)–C(1)' = 3·355(4)
C(1)–C(2) = 3·271(4)
C(1)–C(3) = 3·275(3)
C(1)'–C(2) = 3·284(3)
C(1)'–C(3) = 3·282(3)
C(1)–C(1)H(1) = 0·88(3)
C(1)–C(1)H(2) = 0·94(4)
C(1)–C(1)H(3) = 0·96(4)

Angles

Al–C(1)–Al' = 75·7(1)
C(1)–Al–C(1)' = 104·3(1)
C(2)–Al–C(3) = 123·2(1)
C(1)–Al–C(2) = 106·5(1)
C(1)–Al–C(3) = 106·9(1)
C(1)'–Al–C(2) = 107·2(1)
C(1)'–Al–C(3) = 107·3(1)
C(1)'–C(1)–C(1)H(1) = 118·0(20)
C(1)'–C(1)–C(1)H(2) = 117·7(22)
C(1)'–C(1)–C(1)H(3) = 115·9(23)
C(1)H(1)–C(1)–C(1)H(2) = 102·1(27)
C(1)H(1)–C(1)–C(1)H(3) = 99·5(26)
C(1)H(2)–C(1)–C(1)H(3) = 100·4(29)

[a] Standard errors are those calculated using Busing and Levy's ORFEE program, utilizing the variance–covariance matrix generated by the least squares program.

We thank the National Science foundation for purchase of the Picker diffractometer.

(*Received, May 5th,* 1971; *Com.* 706.)

---

[1] S. K. Byram, J. K. Fawcett, S. C. Nyburg, and R. J. O'Brien, *Chem. Comm.* 1970, 16.
[2] R. G. Vranka and E. L. Amma, *J. Amer. Chem. Soc.*, 1967, **89**, 3121.
[3] M. J. S. Dewar and D. B. Patterson, *Chem. Comm.*, 1970, 544.
[4] H. C. Longuet-Higgins, *J. Chem. Soc.*, 1946, 139.
[5] F. A. Cotton, *Inorg. Chem.*, 1970, **9**, 2804.
[6] J. C. Huffman, J. M. Mueller, and W. E. Streib, unpublished data.
[7] P. H. Lewis and R. E. Rundle, *J. Chem. Phys.*, 1953, **21**, 986.