The Crystal Structure of an Aluminosiloxane containing Five-co-ordinated Aluminium

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ERCOLANI and his co-workers have studied the reaction of dichlorotrimethylsiloxyaluminium (I) with octamethylcyclotetrasiloxane. The products of the reaction were a crystalline compound of empirical formula $C_8H_{24}Al_3Cl_5O_6Si_4$ (II) and a polymeric substance of general formula $[Me_2SiOAlClO]_n$ (III). Compound (II) was identified as the same as that obtained by Zhdanov *et al.*[2] by other means.

Parallel with the chemical investigations on polymers (III), carried out by Ercolani *et al.*,[3,4] the *X*-ray crystal structures of the bromo-analogues of the chloro-compounds (I) and (II) have been determined. The structure of the bromo-analogue of the compound (I) has been described in a previous note.[5]

Crystals of $C_8H_{24}Al_3Br_5O_6Si_4$ are monoclinic and colourless. *X*-Ray data give cell dimensions $a = 11{\cdot}22 \pm 0{\cdot}03$, $b = 13{\cdot}48 \pm 0{\cdot}01$, $c = 18{\cdot}76 \pm 0{\cdot}03$ Å; $\beta = 93° 52' \pm 10'$; $U = 2832$ Å^3. Assuming $Z = 4$, then $D_c = 1{\cdot}91$ g. cm.$^{-3}$; F (000) = 1512. The space group is $P2_1/n$ from systematic absences.

The *X*-ray intensities of about 1500 independent reflections were estimated visually from sets of multiple-film equi-inclination Weissenberg photographs taken about the *b*-axis (3 layers) and [101] direction (8 layers).

All data were obtained using Cu–$K\alpha$ radiation ($\lambda = 1{\cdot}5418$ Å).

The positions of the five bromine atoms were determined from a three-dimensional Patterson synthesis, and those of the other atoms from a series of F_o and $F_o - F_c$ syntheses. After preliminary Fourier refinement, co-ordinates and anisotropic temperature factors were refined by least squares. Values at the present stage ($R = 11{\cdot}6\%$) define the bond lengths and angles given below.

TABLE

Bond lengths and angles (average) with e.s.d.s, not shown in Figures 1 and 2

Br–Al (tetrahedral)	2·222 Å	(0·011)
Si–O (with oxygen in the four-membered rings)	1·74	(0·026)
Si–O [with O(2) or O(5)] ..	1·62	(0·026)
Si–C	1·90	(0·036)
Br–Al–Br and Br–Al–O ..	114° 30′	(50′)
C–Si–C and C–Si–O	109°	(1° 30′)

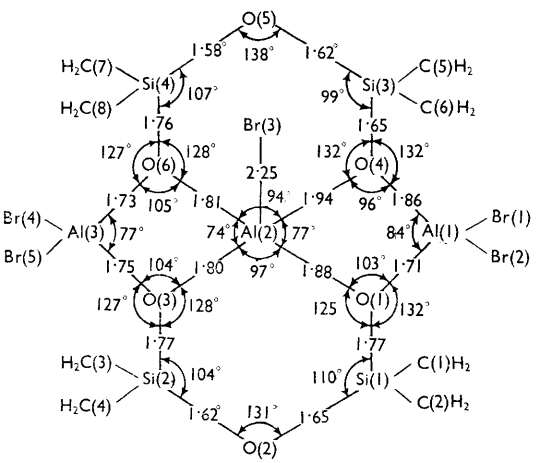

FIGURE 1

Structural formula with some bond lengths (in Å) and angles

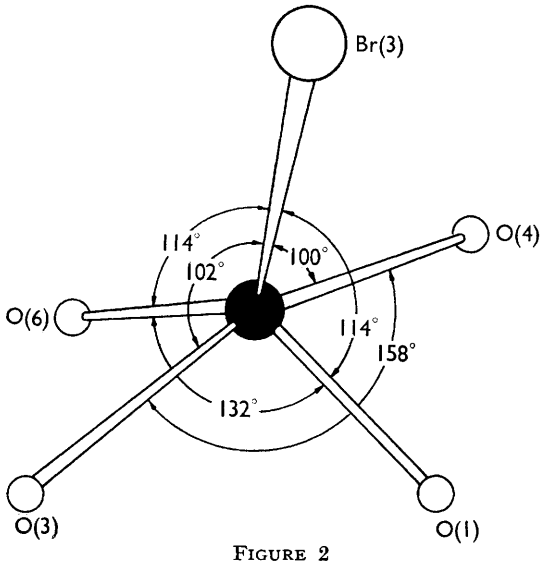

FIGURE 2

Five-co-ordination of Al(2)

The structural formula with some bond lengths and angles is shown in the Figure 1. The co-ordination of the Al(2) (central) is five and could be interpreted as a distorted trigonal bipyramid or as a distorted square pyramid (see Figure 2). The Table completes the information about bond lengths and angles (with e.s.d.s.). The two four-membered rings consisting of Al(2), O(4), Al(1), and O(1); and Al(3), O(6), Al(2), and O(3) are planar and similar to that in compound (I).[5] Intermolecular contacts are between bromine atoms and methyl groups; none of these is less than 3·3 Å.

Five-co-ordination for aluminium is rare, and in the solid crystalline state, as far as the author is aware, only one other example is known, namely $AlH_3,2Me_3N$.[6] However this substance is unstable at room temperature, whereas compound (II) is stable, and can be sublimed at 155° c under vacuum.

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