596. *An X-Ray Diffraction Determination of the Crystal and Molecular Structure of Tetramethylstibonium Tetrakistrimethylsiloxyaluminate.*

By P. J. WHEATLEY.

A two-dimensional *X*-ray diffraction analysis of tetramethylstibonium tetrakistrimethylsiloxyaluminate $[Me_4Sb][Al(O{\cdot}SiMe_3)_4)]$ has been carried out. There are two formula units in the cell (space group *Pmmn*). The substance is ionic, as are the isomorphous gallium and iron salts. Thus both the cation and the anion must have *mm* symmetry. Values of 1·56 Å for Si–O and 147° for AlOSi have been obtained, on the basis of standard lengths and angles for the remaining molecular parameters.

ALKALI salts $M[X(O{\cdot}SiMe_3)_4]$ (M = Na or K; X = Al, Ga, or Fe) have been prepared by Schmidbaur and Schmidt and shown to be ionic.[1] However, the properties[2] of some pseudo-alkali analogues $[Me_4Sb]$ $[X(O{\cdot}SiMe_3)_4]$ (X = Al, Ga, or Fe) suggest that the bonding might be more covalent and that a four-membered ring consisting of one antimony, one X, and two oxygen atoms might be present. The present analysis showed that there is no essential difference between the bonding in the alkali and the pseudo-alkali salts.

Experimental.—Crystals of the three salts $[Me_4Sb][X(O{\cdot}SiMe_3)_4]$, where X = Al, Ga, or Fe, are fine needles with similar habit. When pure they are colourless, but all suffer slight hydrolysis until a skin of impermeable oxide is formed; this gives a red tinge to the iron compound. Preliminary *X*-ray examination showed that they are isomorphous, with the crystallographic constants shown in Table 1.

TABLE 1.

Crystallographic constants for $[Me_4Sb][X(O{\cdot}SiMe_3)_4]$.

X	Al	Ga	Fe	X	Al	Ga	Fe
M	565·7	608·4	594·5	D_m	1·17	1·26	1·25
Class	All orthorhombic			D_x	1·191	1·275	1·246
a (Å)	$13{\cdot}41_2$	$13{\cdot}45_0$	$13{\cdot}50_8$	Z	2	2	2
b (Å)	$11{\cdot}88_4$	$11{\cdot}93_6$	$11{\cdot}95_3$	Space group	*Pmmn*	*Pmmn*	*Pmmn*
c (Å)	$9{\cdot}89_9$	$9{\cdot}86_9$	$9{\cdot}81_6$	M. p.	180·5°	190·5°	193°
U (Å^3)	1577·8	1584·4	1584·9				

The aluminium compound was examined by means of multiple-film Weissenberg photographs taken with Cu-K_α radiation (λ 1·542 Å). Sufficiently small crystals were selected so that no correction was necessary for absorption (μ 93·8 cm.$^{-1}$). Owing to poor resolution in each projec-

---

[1] Schmidbaur and Schmidt, *Angew. Chem.*, 1962, **74**, 589; *J. Amer. Chem. Soc.*, 1962, **84**, 3600.

[2] Schmidbaur, *Angew. Chem.*, 1963, **75**, 137.

tion, all three projections were solved. 93 *hk*0, 90 *h*0*l*, and 87 0*kl* reflexions were observed to be non-zero. The only systematic absences were the *hk*0 reflexions with $h + k$ odd. The space group was assumed to be the *Pmmn* (D_{2h}^{13}, No. 59), rather than the non-centrosymmetric $P2_1mn$ or $Pm2_1n$, on the basis of the intensity distribution, and this choice was confirmed by the success of the subsequent analysis. In *Pmmn*, the molecule, if it is entirely covalent, must have *mm* symmetry; if the compound is ionic, each ion must have *mm* symmetry. The asymmetric unit, therefore, is one quarter of the formula $C_{16}H_{48}AlO_4SbSi_4$.

TABLE 2.

Fractional atomic co-ordinates.

Atom	*x*/*a*	*y*/*b*	*z*/*c*	Atom	*x*/*a*	*y*/*b*	*z*/*c*	Atom	*x*/*a*	*y*/*b*	*z*/*c*
Sb	0·250	0·250	0·193	O_1	0·250	0·373	0·827	C_3	0·361	0·560	0·927
Al	0·250	0·250	0·723	O_2	0·359	0·250	0·619	C_4	0·530	0·376	0·698
Si_1	0·250	0·504	0·834	C_1	0·250	0·569	0·662	C_5	0·384	0·250	0·065
Si_2	0·475	0·250	0·613	C_2	0·524	0·250	0·436	C_6	0·250	0·401	0·321

TABLE 3.

Observed and calculated structure factors for one molecule.

*hk*0	F_o	F_c	*hk*0	F_o	F_c	*h*0*l*	F_o	F_c	*h*0*l*	F_o	F_c	0*kl*	F_o	F_c
2.0.0	66·5	−70·0	10.6.0	7·9	8·9	5.0.1	10·8	−11·9	3.0.6	23·6	22·0	0.6.3	18·6	−8·3
4	90·1	91·9	12	4·3	−2·4	6	27·1	−24·4	4	26·9	25·2	7	10·2	−10·4
6	42·4	−42·7	14	2·9	2·9	7	4·6	3·4	5	11·6	−10·1	8	13·5	−13·0
8	61·2	58·5				8	12·8	10·8	6	18·4	−20·3	9	7·4	5·6
10	32·5	−33·0	1.7.0	41·2	−40·0	10	8·1	−6·3	7	16·9	16·3	12	4·6	−3·6
12	11·1	12·0	3	19·3	22·9	12	6·2	4·4	8	6·7	8·8			
14	10·7	−10·7	5	20·8	−19·0				11	6·5	6·5	0.1.4	21·0	22·0
16	3·2	3·5	7	16·8	18·0	0.0.2	55·4	−57·8				2	2·8	1·4
			9	17·2	−16·5	1	6·2	−8·1	0.0.7	5·5	−6·4	3	38·1	−37·5
1.1.0	86·0	84·2	11	6·3	6·7	2	55·7	60·7	1	8·4	−8·3	4	11·9	−14·3
3	49·4	−52·1	13	5·2	−4·5	3	7·0	−6·4	4	5·8	4·8	5	14·8	12·4
5	39·7	39·4				4	59·9	−67·0	5	6·4	−6·0	7	10·3	−13·5
7	31·4	−34·6	0.8.0	44·0	44·9	5	8·8	−11·6	9	7·5	−6·5	8	6·3	−5·5
9	25·2	26·8	2	18·7	−14·4	6	36·2	40·8				9	9·0	10·5
11	11·5	−10·9	4	29·6	32·2	7	3·6	−2·6	0.0.8	11·6	−16·4	11	3·8	−2·6
13	10·1	8·8	6	15·6	−14·6	8	24·4	−21·9	1	12·0	10·0	13	4·5	−3·3
15	3·8	−4·0	8	16·6	16·0	9	10·2	−8·5	2	13·1	15·0			
			10	10·2	−9·1	10	20·3	17·1	3	8·6	−9·0	0.1.5	9·5	−8·7
0.2.0	58·4	−66·5	12	5·4	4·5	12	9·8	−11·0	4	9·7	−10·8	2	32·0	−33·6
2	10·6	−8·1	14	4·0	−4·8				5	11·0	9·1	4	37·0	36·2
4	31·7	−32·1				0.0.3	9·9	−11·4	6	9·5	10·9	5	2·7	−1·7
6	6·8	6·2	1.9.0	17·7	19·6	1	30·3	29·3	8	7·0	−8·0	6	10·8	−13·1
8	20·1	−17·5	3	10·7	−10·8	2	51·7	56·3				8	13·6	16·2
10	7·8	6·7	5	12·1	10·1	3	5·7	6·7	0.0.9	11·8	−11·9	10	5·3	−6·7
12	4·5	−2·7	7	7·0	−9·0	4	36·1	−32·2	1	9·0	7·9	12	5·0	5·5
14	5·4	4·5	9	9·5	8·7	5	11·1	11·0	3	6·2	−6·5			
			11	3·8	−3·2	6	38·5	36·5	4	4·8	−4·3	0.1.6	8·8	−10·0
1.3.0	71·5	−73·1	13	2·7	2·4	7	7·0	7·7	5	6·8	−7·8	2	9·4	8·4
3	9·8	11·0				8	17·7	−15·2				6	6·5	5·4
5	26·3	−24·5	0.10.0	18·0	−17·3	9	18·1	18·1				8	7·1	6·7
7	13·8	16·5	4	5·8	−5·4	10	12·0	10·8	0*kl*					
9	34·1	−30·1	8	6·1	−6·0	11	2·1	1·3	0.1.1	5·5	−4·3	0.1.7	20·8	−17·6
11	5·8	5·2	10	3·8	2·9	12	9·8	−9·8	2	27·7	33·0	2	9·5	8·4
13	8·1	−6·3							3	8·1	10·1	3	21·6	20·8
			1.11.0	7·9	−8·4	0.0.4	33·4	−28·7	4	3·3	2·3	4	5·7	−6·9
0.4.0	72·9	72·0	3	5·2	4·5	1	10·2	13·0	5	28·6	−31·4	5	18·7	−20·0
2	34·0	−33·0	5	7·3	−7·7	2	4·2	−3·5	6	12·0	10·6	6	8·1	9·5
4	33·7	31·6	7	3·3	2·7	3	21·2	−20·3				7	9·0	10·1
6	22·1	−21·0	9	5·5	−4·7	4	5·1	−3·7	0.1.2	71·4	−64·6	9	6·8	−6·0
8	30·6	28·1				5	4·6	−3·1	2	19·8	16·9			
10	16·3	−14·5	0.12.0	12·5	11·5	6	7·0	−5·4	3	51·4	54·4	0.1.8	11·7	11·9
12	8·3	7·7	2	6·2	−6·3	7	12·7	−15·0	4	12·3	−9·4	3	3·9	−3·7
14	6·5	−4·2	4	6·9	7·3	8	5·6	−6·5	5	39·4	−45·4	5	4·7	6·2
			6	3·9	−4·6	9	2·9	1·8	6	10·8	10·2			
1.5.0	26·9	29·2	8	4·8	5·2	11	8·8	−8·6	7	19·6	21·5	0.1.9	10·5	8·5
3	10·3	−12·4	10	2·4	−2·8				8	20·6	−20·3	2	4·4	3·4
5	24·4	26·4				0.0.5	31·8	28·5	9	14·0	−18·0	3	9·3	−8·3
7	6·4	−7·8	1.13.0	5·0	5·8	1	9·5	−7·9	10	3·6	2·4	4	8·5	−7·9
9	18·5	15·8				2	18·1	−19·8	11	9·3	7·3	5	9·4	8·8
11	2·7	−2·1	0.14.0	4·5	−3·8	4	27·3	26·0	12	4·3	−3·4	7	4·2	−3·9
13	6·8	6·0				6	11·3	−12·8	13	6·5	−4·4	8	4·9	−4·8
			*h*0*l*			8	11·0	12·6						
0.6.0	59·0	−55·9	0.0.1	6·1	6·3	10	9·2	−7·5	0.1.3	7·5	9·0	0.2.10	6·3	−7·3
2	7·3	10·4	1	17·5	13·9				2	5·1	3·3	4	3·8	2·8
4	16·6	−19·5	2	51·1	−54·4	0.0.6	12·1	14·7	3	33·9	−32·4			
6	6·9	6·6	3	4·8	4·0	1	11·1	−11·3	4	24·5	−27·6			
8	14·1	−17·5	4	15·5	−12·8	2	27·6	−28·5	5	9·8	10·4			

The *hk*0 projection was readily solved because of the concentration of scattering material at $\frac{1}{4}$, $\frac{1}{4}$, 0. In the later refinement only one phase needed to be altered. The *h*0*l* projection was solved from a sharpened Patterson synthesis. Refinement of the *h*0*l* and 0*kl* projections

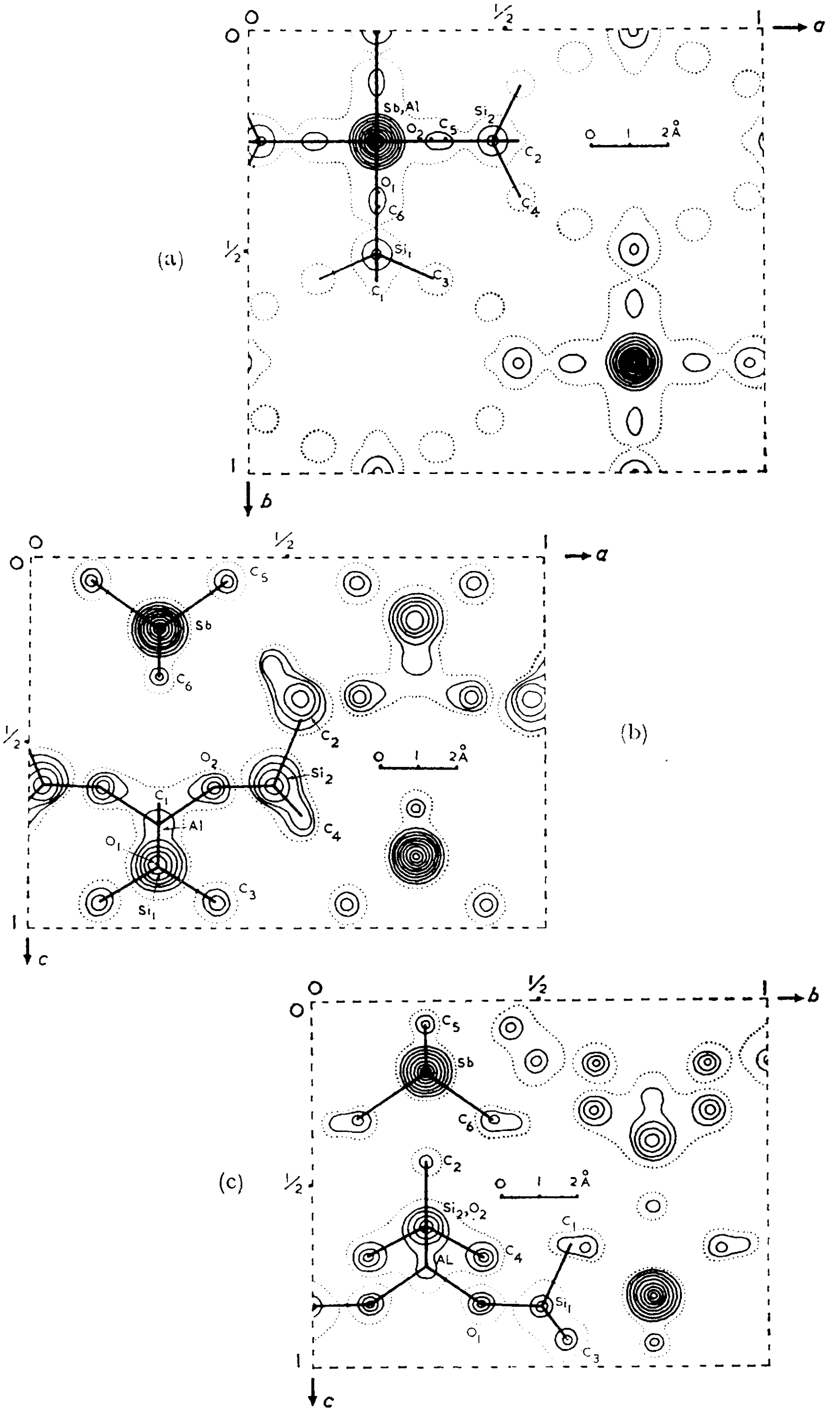

FIG. 1. (a) Projection of the contents of the unit cell down [*c*]. (b) Projection of the contents of the unit cell down [*b*]. (c) Projection of the contents of the unit cell down [*a*].

(The contours are drawn every ten arbitrary units in the C and O atoms, and every fifty units in the Sb, Si, and Al atoms.)

was carried out by successive Fourier syntheses. In order to obtain the final atomic co-ordinates, various assumptions were made. The positions of the antimony, silicon, and aluminium atoms were taken from the Fourier maps. It was then assumed that the antimony atom was co-ordinated by four carbon atoms at a distance of 2·20 Å to form a regular tetrahedron. Similarly the aluminium atom was assumed to be tetrahedrally co-ordinated by four oxygen atoms at a distance of 1·79 Å. The Si–C distances were assumed to be 1·87 Å, and the OSiC angles 112°.[3] These assumptions were consistent with the Fourier maps.

The co-ordinates derived in this way and used in the calculation of the final structure factors are shown in Table 2. The observed and calculated structure factors are given in Table 3. The final Fourier maps are shown in Fig. 1(a—c). The scattering factors used are those given in International Tables, with the antimony curve corrected for the real part of dispersion. An isotropic temperature factor $B = 6{\cdot}4$ Å^2 proved adequate for all three projections. The values of the agreement index R are 7·5%, 9·5%, and 10·6%, for the $hk0$, $h0l$, and $0kl$ projections, respectively.

Results.—Only two parameters remain to be determined, the Si–O distance and the AlOSi angle. The two independent determinations of each are: Si–O 1·56, 1·56 Å; AlOSi 147·4°, 147·0°. It is difficult to assess the reliability of these values, as they depend on the values assumed for the Al–O length and the OAlO angle, but the agreement between the independent values is reassuringly good. The Si–O distance is rather short compared with the standard value[4] but is consistent with other experimental observations that indicate a high degree of $d_\pi p_\pi$-bonding.[1,5] The angle at the oxygen atom is an unpredictable quantity, but the value found here agrees with that in α-quartz.[6]

The compound is clearly ionic in character as Fig. 1(b,c) show. The closest approach between the two ions in the general direction of z is 3·30 Å between a methyl group of the cation and an oxygen atom of the anion. Contacts in the x- and the y-direction are between methyl groups and are all over 4 Å.

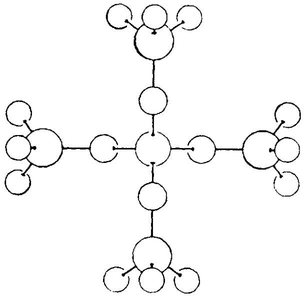

FIG. 2. Configuration of the anion.

Fig. 2 shows the configuration of the anion. A careful examination shows that, although the ion does have the required mm symmetry, it does not have $\bar{4}$ symmetry because of the different orientation of one pair of trimethylsilyl groups relative to that of the other pair.

I thank Dr. H. Schmidbaur of the University of Marburg for providing the sample.

MONSANTO RESEARCH S.A., BINZSTRASSE 39,
ZURICH 3/45, SWITZERLAND.

[*Received, November 19th,* 1962.]

---

[3] Wheatley, *J.*, 1962, 1721.

[4] Sutton *et al.*, " Tables of Interatomic Distances," *Chem. Soc. Special Publ.*, 1958, No. 11.

[5] Schmidbaur and Schmidt, *J. Amer. Chem. Soc.*, 1962, **84**, 1069.

[6] Driel and Verweel, *Z. Krist.*, 1936, **95**, 308.