

437. *The Structure of Trimethyltin Fluoride.*

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Trimethyltin fluoride differs considerably in its properties from other trimethyltin halides. The crystals are orthorhombic, with four molecules in a unit cell of dimensions $a = 4.32$, $b = 10.85$, and $c = 12.84$ Å, space group *Pmcn*. The structure, which has been determined by Patterson methods, and refined by three-dimensional Fourier synthesis, consists of Me_3Sn groups and F atoms arranged alternately in a chain-like manner along the a -axis. Two interpretations are given of the observed electron-density distribution; both contain essentially five-co-ordinate tin atoms, and non-linear unsymmetrical Sn-F...Sn bridges, consistent with a non-ionic type of compound.

ON the basis of infrared spectroscopic studies, different structures have been proposed¹ for trimethyltin fluoride, and the remaining trimethyltin halides. The former is considered to be ionic, $\text{Me}_3\text{Sn}^+\text{F}^-$, and the latter are thought to consist of covalent tetrahedral molecules. However, no structure determinations for the solid compounds have been reported. Recently, it was suggested^{2,3} that trimethyltin compounds may be associated, so that, for example, trimethyltin acetate may be composed of planar Me_3Sn groups bridged by an aceto-group. The planarity of the Me_3Sn portion of the molecule then no longer necessarily requires an ionic formulation. Such an associated structure would make the tin atom five-co-ordinate, and support for this less common co-ordination number is given by the recent reports^{4,5} of the structure of chloro(trimethyl)pyridinetin(IV), $(\text{C}_5\text{H}_5\text{N})\text{Me}_3\text{SnCl}$, in which the tin atom is at the centre of a trigonal bipyramid, the methyl groups being in the equatorial sites, and the chlorine atom and pyridine occupying the axial positions. It therefore seemed desirable to determine the crystal structure of trimethyltin fluoride.

EXPERIMENTAL

Crystals of trimethyltin fluoride consist of bundles of very fine colourless needles, elongated along the a -axis. Almost all the crystals were multiple twins, but it was possible to obtain one or two suitable single crystals by breaking up the bundles and searching for a very small fragment. The crystal used for recording the X -ray data had cross-section 0.02×0.02 mm. The unit-cell dimensions and space group were determined from various rotation, oscillation, Weissenberg (all Cu K_α), and precession films (Mo K_α).

Crystal Data [$\lambda(\text{Cu } K_\alpha) = 1.5418$ Å; $\lambda(\text{Mo } K_\alpha) = 0.7107$ Å].—Trimethyltin fluoride, Me_3SnF , $M = 182.8$, m. p. $> 360^\circ$ (decomp.), orthorhombic, $a = 4.32 \pm 0.01$, $b = 10.85 \pm 0.02$, $c = 12.84 \pm 0.02$ Å, $U = 601.8$ Å³, D_c ($Z = 4$) = 2.017, $D_m = 2.01$ g. cm.⁻³ (by flotation in silver nitrate), $F(000) = 344$. Absorption coefficient for Cu K_α X -rays, $\mu = 352$ cm.⁻¹. Absent reflexions: $h0l$ when l is odd, $hk0$ when $(h + k)$ is odd. Space group is $P2_1cn$ (C_{2v}^9) or *Pmcn* (D_{2h}^{16}). Our final structure is in agreement with *Pmcn*.

The intensities of the hkl reflexions were measured visually on Weissenberg films of the $hk0$, $hk1$, $hk2$, and $hk3$ zones, and the structure amplitudes were derived from the usual formulae. Absorption was negligible and no corrections were considered necessary. The absolute scale was established separately for each level by comparison with the calculated structure factors at each stage of the analysis.

Structure Analysis.—The y - and z -parameters of the tin atom were determined from the a -axis Patterson projection, and a Fourier series was summed, using signs based on the tin contributions only. On the resulting electron-density map three light atoms (probably carbon) were well resolved and were situated at the corners of an equilateral triangle with the tin atom

¹ Okawara, Webster, and Rochow, *J. Amer. Chem. Soc.*, 1960, **82**, 3287.

² Beattie and Gilson, *J.*, 1961, 2585.

³ Van der Kerk, Luijten, and Janseen, *Chimia (Switz.)*, 1962, **16**, 10.

⁴ Beattie, McQuillan, and Hulme, *Chem. and Ind.*, 1962, 1429.

⁵ Hulme, *J.*, 1963, 1524.

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at the centre. Structure factors were recalculated with inclusion of these three extra atoms, and a second Fourier synthesis was calculated. This map showed improved resolution of the atoms; the triangular arrangement of the light atoms suggested a structure with planar trimethyltin groups situated in the mirror plane at $x = 1/4$ of space group $Pm\bar{c}n$, with the fluorine atoms situated midway between successive tin atoms along the a -axis.

Parameters based on this structure are shown in Table 1; structure factors were calculated from these parameters for all the hkl reflexions, using the scattering factors listed by Sagel⁶

TABLE 1.
Positional and thermal parameters.

Atom	From a -axis projection			Final disordered structure				B (Å ²)	
	Position	x	y	z	Position	x	y		z
Sn	4(c)	1/4	0.0654	0.2114	4(c)	1/4	0.0654	0.2114	6.0
C ₁	4(c)	1/4	0.065	0.368	4(c)	1/4	0.065	0.368	6.0
C ₂	4(c)	1/4	0.232	0.131	8(\bar{d})	± 0.20	0.232	0.131	6.0
C ₃	4(c)	1/4	-0.105	0.131	8(\bar{d})	± 0.20	-0.105	0.131	6.0
F	4(c)	3/4	0.065	0.211	[4(c)	3/4	0.065	0.211]	6.0

for uncharged tin, fluorine, and carbon atoms. The very good agreement between measured and calculated structure factors (Table 2) and the normal interatomic distances suggested that this structure was a very plausible one.

TABLE 2.
Structure factor agreement.

	No. of reflexions included in refinement		R for obs. reflexions (ordered structure)	R for obs. reflexions (approximation to final disordered structure)
	Observed	Unobserved		
0 kl	116	18	0.125	0.125
1 kl	69	36	0.132	0.132
2 kl	34	37	0.130	0.130
3 kl	10	26	0.103	0.090
hkl	229	117	0.127	0.126

However, there were one or two anomalies in the a -axis electron-density projection. (i) The peak electron-density at one of the carbon atoms (C₁) was considerably higher than that at the other two. (ii) The projection contained some diffuse density around the lines between Sn and the two lower-density carbon atoms. (iii) The integrated electron-density of the Sn peak was 50.08 electrons, so that, even allowing for possible errors in the electron count,⁷ it seemed that the fluorine atom was not situated on top of the tin in projection.

To resolve these anomalies, the three-dimensional electron-density distribution was calculated. The Sn and C₁ atoms were represented by well resolved spherical peaks, but both of the other carbon atoms were split into two half-atoms, one on each side of the mirror plane. The electron-density distribution at the fluorine atom was even more remarkable, being spread out over parts of the surface of a sphere with the tin atom as centre. The density was greatest in position above the C₁-Sn-C₂ and C₁-Sn-C₃ angles, but was low above the C₂-Sn-C₃ angle. Typical sections of the three-dimensional Fourier synthesis illustrating these features are shown in Fig. 1.

Since the compound has a very high melting point ($>360^\circ$), these effects cannot be the result of thermal vibrations, and our interpretation of the electron-density distribution is that Sn and C₁ are in ordered positions, while the fluorine is obviously disordered and occupies two sections of the surface of a sphere. The atoms C₂ and C₃ each statistically occupy one of two positions in space group $Pm\bar{c}n$. The disorder of these two atoms could be removed by reducing the symmetry to $P2_1cn$, but this is probably incorrect. The structure consists of chains of trimethyltin groups and fluorine atoms along a , with only weak van der Waals forces between these chains. This explains the crystal habit of bundles of very fine needles, and also suggests

⁶ Sagel, "Tabellen zur Röntgenstrukturanalyse," Springer-Verlag, Berlin, 1958.

⁷ Ibers, *Acta Cryst.*, 1961, **14**, 538.

occupy one of two positions displaced from the mirror plane. It was more difficult to include the unusual distribution of the fluorine atom, so it was situated midway between the Sn atoms for the structure-factor calculation. These co-ordinates are included in Table 1, and the corresponding structure-factor agreement in Table 2. Final measured and calculated structure factors are listed in Table 3.

The standard deviations of the atomic positions, calculated from Cruickshank's formulae,⁸

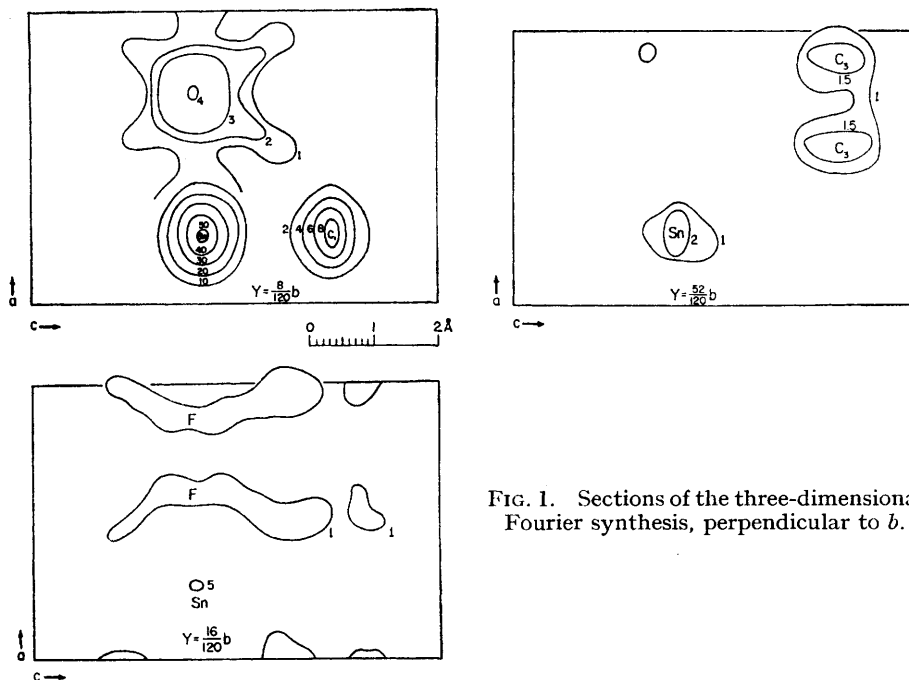


FIG. 1. Sections of the three-dimensional Fourier synthesis, perpendicular to b .

are $\sigma(x) = 0$ for Sn and C_1 , $\sigma(y) = \sigma(z) = 0.003 \text{ \AA}$ for Sn, 0.014 \AA for C_1 ; the values for C_2 , C_3 , and F are not meaningful. The bond distances are Sn-C $\sim 2.1 \text{ \AA}$, Sn-F $\sim 2.1 \text{ \AA}$, Sn \cdots F $\sim 2.2\text{--}2.6 \text{ \AA}$.

DISCUSSION

As a result of the peculiarities in the three-dimensional electron-density distribution, two interpretations can be offered. One is that within any one chain the atoms C_2 and C_3 are ordered and both displaced from the plane $x = 1/4$ in the opposite direction to the Sn-F bond (Fig. 2), while the fluorine atoms are disordered, occupying any position on parts of a spherical surface about 2.15 \AA from one tin atom, so that Sn-F \cdots Sn is not linear. The disorder of C_2 and C_3 , and the further disordering represented by reflexion of the fluorine density in the mirror plane at $x = 3/4$, are a consequence of the ability of the chains to align themselves in either direction along a . A lack of planarity for the trimethyltin group is consistent with the observation of a previously unreported symmetric Sn-C stretching vibration at 515 cm^{-1} in the infrared spectrum of very concentrated Nujol mulls of trimethyltin fluoride. Alternatively, however, this may just be a forbidden transition of low intensity, arising from a planar Me_3Sn group.

In the second structure (Fig. 3) the Me_3Sn groups are planar and tilted alternately with respect to the a -axis. The fluorine atoms must again be considered disordered to the extent that they occupy any position on parts of a spherical surface as in the first model. However, as a consequence of the alternate tilting of the Me_3Sn groups, the fluorine atoms

⁸ Cruickshank, *Acta Cryst.*, 1949, **2**, 65.

must be ordered with respect to their alternate placing on either side of the Sn-Sn axis. Again, since the chains can be aligned in either direction along a , the disorder represented by reflexion of the fluorine density in the mirror plane at $x = 3/4$ is again observed. However, in any one chain the repeat distance is twice the cell length.

Of the two possibilities, the latter may be preferred if only on account of its greater symmetry, but both are consistent with the observed electron-density distribution. Independently of the form preferred, it is clear that trimethyltin fluoride is not a purely ionic solid. If ionic species were present it would be expected that (a) the fluorine atom would lie on the axis of, and equidistant from, two tin atoms, and (b) the trimethyltin group would be a planar cation lying perpendicular to the tin-tin axis. None of these requirements is met. In fact, the non-linear unsymmetrical Sn-F...Sn arrangement is a definite indication of some covalent interaction. The chemical and physical properties of trimethyltin fluoride are consistent with a polymeric chain structure. Its high melting point, low solubility in organic solvents, and only moderate solubility in hydrolytic solvents are consistent with a very high lattice energy, which cannot be anticipated for a purely ionic structure containing the large, highly polarizable singly charged Me_3Sn^+ cation.

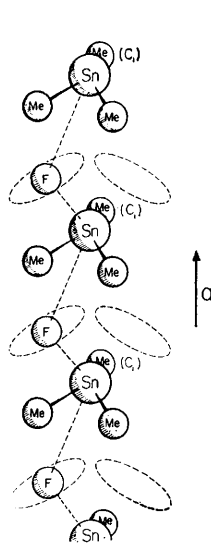


FIG. 2.

Possible structures for trimethyltin fluoride.

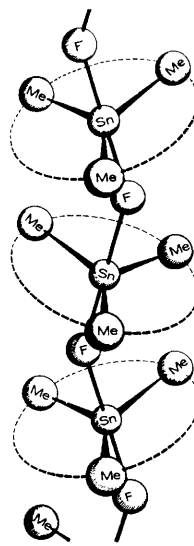


FIG. 3.

That trimethyltin fluoride can exist in a discrete form is suggested by the fact that, if anhydrous potassium fluoride and trimethyltin bromide are heated together at 170° , a white sublimate is evolved which has the correct analysis for $\text{C}_3\text{H}_9\text{SnF}$. This possibly results from the decomposition of a complex fluoride, perhaps KMe_3SnF_2 .

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