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Structural chemistry of triorganotin fluorides. The crystal structure of tricyclohexyltin fluoride revisited

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The crystal structure of tricyclohexyltin fluoride has been redetermined to be polymeric. The compound crystallizes in the trigonal $P3c1$ space group with $a = 11.103(2)$, $c = 8.708(1)$ Å and $Z = 2$. The Sn–F–Sn bridges are linear and asymmetric with Sn–F distances of 2.051(10) and 2.303(10) Å. These distances are rationalised in terms of the structure-correlation method which assumes bond-order conservation and Pauling's relationship between bond length and bond order. The polymeric structure is consistent with the physical properties of $Sn(C_6H_{11})_3F$ and variable-temperature Mössbauer spectroscopic data. It is proposed that, for rod-polymeric triorganotin fluorides, the repeat distance can give information about the Sn–F distances.

Triorganotin fluorides, unless bulky organic groups preclude association, have polymeric structures and, consequently, high melting points.[1–3] The first triorganotin fluoride studied by single-crystal X-ray diffraction was trimethyltin fluoride,[4] and the study showed a polymeric chain with non-linear asymmetric Sn–F ··· Sn bridges, planar trimethyltin groups, and trigonal-bipyramidal co-ordination at tin. Nevertheless, disorder precluded a completely satisfactory solution of the structure. A similar polymeric structure and disorder problems were found for tributyltin fluoride.[5] Later the structure of tricyclohexyltin fluoride was reported to be monomeric with discrete tetrahedral $Sn(C_6H_{11})_3F$ units.[6] Nevertheless, the temperature coefficient of the Mössbauer recoil-free fraction for this material [$a = -d(\ln A)/dT = 0.91 \times 10^{-2}$ K^{-1}] is clearly in the range for polymeric compounds,[7] and the linearity of the Sn–F ··· Sn framework has been interpreted as indicative of the onset of formation of a rod-like polymeric structure.[7] Unquestionable monomeric structures have been reported for $Sn[C(SiMe_2Ph)_3]Me_2F$,[8] $Sn[C(SiMe_3)_3]Ph_2F$[8] and $Sn(C_6H_2Me_3\text{-}2,4,6)_3F$.[9] From these compounds it is established that the Sn–F single-bond distance in a four-co-ordinate tin(IV) species is about 1.96 Å.[10] On the other hand, polymeric structures have been reported for $Sn(CH_2SiMe_3)_3F$,[11] $Sn(CH_2Ph)_3F$[12] and $SnPh_3F$.[13] In contrast to $SnMe_3F$, these compounds have linear Sn–F ··· Sn bridges. In order to rationalise the Sn–F distances, it is expected that on going from mono- to poly-meric triorganotin fluorides the Sn–F distance should increase as the Sn ··· F distance becomes shorter.[14] In this way the strongest intermolecular association reported so far for a triorganotin fluoride has been found for $SnPh_3F$ which displays linear symmetric Sn–F–Sn bridges with Sn–F distances as short as 2.1458(3) Å.[13]

When trying to understand the structural relationship among different triorganotin fluorides, as well as that between structure and physical properties, we have found that the structure reported for $Sn(C_6H_{11})_3F$[6] is disturbing for the following reasons. (*i*) The intermolecular Sn ··· F distance (3.32 Å)[6] indicates that the intermolecular association is not very strong. Therefore, it is expected that the Sn–F bond length should not be much longer than the single-bond distance (*i.e.* 1.96 Å)[8–10] and the reported distance of 2.45(1) Å[6] seems too long. (*ii*) It may be argued that, because of problems in the crystal structure determination,[6] the position of the F atom was not accurately determined. Nevertheless, for rod-polymeric triorganotin fluorides, the repeat distance[15] is the sum of the Sn–F and Sn ··· F distances. As the intermolecular Sn ··· F distance becomes longer the Sn–F distance becomes shorter,[14] and for monomeric compounds the Sn–F bond length should be about 1.96 Å,[8–10] while the intermolecular Sn ··· F distance should be longer than the sum of the van der Waals radii (*i.e.* 3.63 Å).[16] Therefore, we expect that repeat distances longer than *ca.* 5.6 Å would be indicative of a monomeric structure, and the repeat distance reported for $Sn(C_6H_{11})_3F$ is 5.769 Å.[6] In disagreement with the monomeric structure, the temperature coefficient of the Mössbauer recoil-free fraction ($a = 0.91 \times 10^{-2}$ K^{-1}) would be more compatible with a polymeric structure.[7] (*iii*) The melting points reported for $Sn(C_6H_{11})_3X$ are 305 (decomp.), 129–130, 77 and 65 °C for X = F, Cl, Br and I, respectively.[17] While the structures of $Sn(C_6H_{11})_3X$ (X = Br or I) are clearly monomeric,[6] that of $Sn(C_6H_{11})_3Cl$[18] shows a weak intermolecular interaction with a Sn–Cl bond distance of 2.407 Å and an intermolecular Sn ··· Cl distance of 3.30 Å, which is shorter than the sum of the van der Waals radii.[16] Bearing in mind that the melting point should reflect the magnitude of the intermolecular forces,[19] the sharp increase in melting point on going from $Sn(C_6H_{11})_3Cl$ to $Sn(C_6H_{11})_3F$ suggests that the latter compound should have a strongly associated structure. (*iv*) Considering that $Sn(C_6H_{11})_3OH$ has a polymeric structure,[20] it seems reasonable that $Sn(C_6H_{11})_3F$ should also be polymeric. (*v*) The unit-cell and positional parameters (and, therefore, bond lengths and angles) reported for $Sn(C_6H_{11})_3F$[6] and $Sn(C_6H_{11})_3Cl$[18] are very similar to each other. From these facts, we suspected that the structure reported for $Sn(C_6H_{11})_3F$[6] was wrong, and that this material should have a polymeric structure. We report herein our revised structure, which is more compatible with both its physical properties and the structure of other triorganotin fluorides.

Experimental

Preparation of tricyclohexyltin fluoride

An aqueous solution of HF (13.84 g, 40%, 276.66 mmol) was added, with stirring, to a suspension of $Sn(C_6H_{11})_3OH$ (3.52 g, 9.14 mmol) in ethanol (185 cm^3) contained in a polyethylene beaker. A milky precipitate was formed immediately. After stirring for 2 h at room temperature the white solid was filtered on filter-paper, in a polyethylene funnel, and washed with three portions of ethanol (10 cm^3 each). The solid was dried in the air and extracted with boiling dimethylacetamide in a Soxhlet apparatus. The purification was repeated once more, and the solid washed with diethyl ether and air dried, yielding $Sn(C_6H_{11})_3F$ (2.47 g, 70%) as colourless needles, m.p. 304 °C (decomp.) [lit.,[17] 305 °C (decomp.)] (Found: C, 55.5; H, 8.4. Calc. for $C_{18}H_{33}FSn$: C, 55.8; H, 8.6%). IR: 492m [ν_{asym}(SnC)], 424w [ν_{sym}(SnC)] and 338vs cm^{-1} [ν(SnF)]. Raman: 489m [ν_{asym}(SnC)], 424w [ν_{sym}(SnC)] and 321vw cm^{-1} [ν(SnF)].

Physical measurements

The microanalyses (C and H) were carried out with a Perkin-Elmer 2400 CHN elemental analyser. The IR spectrum was recorded as a Nujol mull on a Perkin-Elmer 1650 FT-IR instrument, the Raman spectrum at room temperature on a Dilor XY spectrometer, using the Raman microscope and an argon laser (5145 Å). X-Ray powder diffraction data were obtained with a Siemens D-5000 diffractometer using Cu-Kα radiation.

Crystallography

Crystals were grown by slow cooling of a hot dimethylacetamide solution.

Crystal data. $C_{18}H_{33}FSn$, $M = 387.1$, trigonal, space group $P3c1$ (no. 158), $a = 11.103(2)$, $c = 8.708(1)$ Å, $U = 929.7(3)$ Å^3 (by least-squares refinement on diffractometer angles for 12 automatically centred reflections within the range θ 20–25°, $\lambda = 1.541\,78$ Å), $T = 293(2)$ K, $Z = 2$, $D_c = 1.383$ g cm^{-3}, $F(000) = 400$. Colourless prisms. Crystal dimensions: 0.2 × 0.2 × 0.4 mm, μ(Cu-Kα) = 10.915 mm^{-1}.

Data collection and processing. Syntex P-1 diffractometer, θ-2θ scan mode, Ni-filtered Cu-Kα radiation; 1062 reflections collected ($4.6 \leqslant \theta \leqslant 66.1$, $-11 \leqslant h \leqslant 0$, $0 \leqslant k \leqslant 13$, $0 \leqslant l \leqslant 10$), 346 unique observed with $I \geqslant 3\sigma(I)$ (merging $R = 0.020$). Three standard reflections monitored every 100 showed no significant decay (*ca.* 0.1%). Diffractometer data were processed by the program PROFIT[21] with profile analysis of reflections. An empirical absorption correction was made (maximum, minimum transmission factors = 0.248, 0.141).[22]

Structure analysis and refinement. The structure was solved by the heavy-atom method using the SHELXTL package.[23] After that all reflections with $I < 3\sigma(I)$ were excluded from calculations. Refinement was done by full-matrix least squares based on F^2 using SHELXL 93.[24] All non-hydrogen atoms were refined anisotropically, and hydrogens were fixed in calculated positions with a common isotropic thermal parameter. The cyclohexyl rings are disordered with alternate positions [C(3A), C(3B); C(5A), C(5B)] for two carbon atoms. A population parameter of 0.5 was assigned to the disordered carbon atoms. The disorder is reflected in the bad geometry of the cyclohexyl groups and thermal parameters. The refinement converged at $R1 = 0.0154$, $wR2 = 0.0328$ for 346 observed reflections, goodness of fit on F^2, $S = 1.228$, absolute structure parameter $x = -0.03(3)$. The largest residual peak and hole were 0.145 and −0.301 e Å^{-3}. The weighting scheme used was $w = 1/[\sigma^2(F_o)^2 + (0.0326P)^2 + 0.0328P]$ where $P = [\max(F_o^2, 0) + 2F_c^2]/3$. Refinement of the inverted structure gave higher R factors, and according to Flack's test[25] the selected configuration is the correct one. Scattering factors were taken from ref. 26.

Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/27.

Results and Discussion

The solid-state infrared spectra of several polymeric triorganotin fluorides show ν(SnF) in the range 340–380 cm^{-1}.[27] On the other hand, the gas-phase spectrum of the same compounds shows ν(SnF) in the range 550–590 cm^{-1}.[27] This indicates that while ν(SnF) appears below 400 cm^{-1} for polymeric triorganotin fluorides, it should appear above 500 cm^{-1} for monomeric compounds. Indeed, a band at 535 cm^{-1} in the IR spectrum of monomeric $Sn(C_6H_2Me_3\text{-}2,4,6)_3F$, has been assigned to ν(SnF).[9] The infrared spectrum of $Sn(C_6H_{11})_3F$ shows ν(SnF) at 338 cm^{-1}. In addition, the appearance of a weak band at 424 cm^{-1}, which can be assigned to ν_{sym}(SnC),[28] indicates that the SnC_3 arrangement is not strictly planar. Therefore, the IR spectrum suggests that $Sn(C_6H_{11})_3F$ has a polymeric structure with asymmetric Sn–F ··· Sn bridges. The suggestion that the structure is different from that reported previously[6] was confirmed by the powder X-ray diffraction pattern, which was not compatible with the published unit-cell parameters.[6] Therefore, we proceeded with the single-crystal structure determination. In order to confirm that the crystal selected is representative of the structure of the bulk material[29] we compared the experimental powder X-ray diffraction pattern with that simulated from the single-crystal data.[30]

The structure of $Sn(C_6H_{11})_3F$ is shown in Fig. 1 and selected bond lengths and angles are collected in Table 1. The cyclohexyl groups are disordered and Fig. 1 shows the alternative positions for C(3) and C(5). As suggested by the infrared spectrum, $Sn(C_6H_{11})_3F$ has a polymeric structure with bridging F atoms and a distorted trigonal-bipyramidal environment about the Sn atom. In contrast to the structure of $SnPh_3F$,[13] the Sn–F distances [2.051(10) and 2.303(10) Å] are not identical, thus

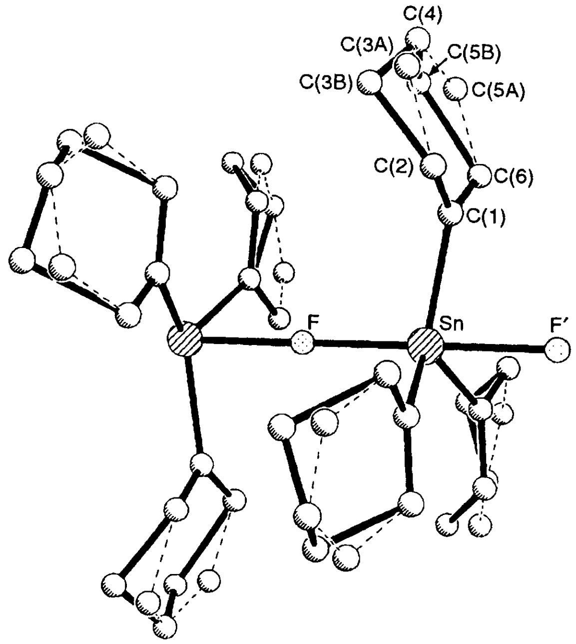

Fig. 1 The polymeric chain in $Sn(C_6H_{11})_3F$ showing the disordered, alternative orientations of the cyclohexyl groups

Table 1 Relevant bond distances (Å) and angles (°) in $Sn(C_6H_{11})_3F$

Sn–F	2.051(10)	Sn–F′	2.303(10)
Sn–C(1)	2.176(6)		
F–Sn–F′	180	Sn–F–Sn″	180
F–Sn–C(1)	100.39(14)	C(1)–Sn–C(1‴)	116.85(9)

Symmetry codes: (′) $1 - y, 1 - x, z + \frac{1}{2}$; (″) $1 - y, 1 - x, z - \frac{1}{2}$; (‴) $1 - y, x - y, z$.

causing the C–Sn–F and C–Sn–C bond angles to deviate from those expected for a regular trigonal bipyramid (see Table 1). The deviation of the SnC_3 group from planarity accounts for the appearance of $\nu_{sym}(SnC)$ in the IR spectrum. Another interesting aspect of the structure is that the polymeric Sn–F ··· Sn–F chain is strictly linear as predicted from variable-temperature Mössbauer spectroscopy (VTMS).[7] Bearing in mind that VTMS is currently used to distinguish between mono- and poly-meric structures of organotin compounds,[31,32] the fact that $Sn(C_6H_{11})_3F$ is a rod polymer rather than a monomer[6] supports the use of VTMS as a structural technique. Nevertheless, although the temperature coefficient of the Mössbauer recoil-free fraction for $Sn(C_6H_{11})_3F$ ($a = 0.91 \times 10^{-2}$ K^{-1})[7] is clearly in the range for polymeric compounds, we have shown that the use of VTMS data as a guide to the strength of the intermolecular interactions or the tertiary structure of the polymeric chain requires considerable caution.[13] Indeed, although $SnPh_3F$ has a higher a value than that of $Sn(C_6H_{11})_3F$ (1.49×10^{-2} *vs.* 0.91×10^{-2} K^{-1}),[7] it also has a significantly shorter internuclear Sn ··· F distance [2.1458(3) *vs.* 2.303(10) Å],[13] against the general trend of lower a values as the extent of intermolecular association increases.* It is also interesting to confirm that the high melting point and the insolubility at room temperature of $Sn(C_6H_{11})_3F$ are strong indicators of its polymeric structure.

The crystal structures of $Sn(C_6H_{11})_3F$ and $SnPh_3F$[13] can give information about the path from poly- to mono-meric triorganotin fluorides, by applying the structure-correlation method of Britton and Dunitz.[14] In this model bond-order conservation is assumed, as well as Pauling's relationship between bond length and bond order [equation (1)], where d(n)

$$d(\mathrm{n}) - d(1) = -c \log n \qquad (1)$$

is the bond length, d(1) is the single-bond length and the value of c depends on the type of bond. By assuming that the sum of the bond orders for the Sn–F and Sn ··· F bonds is one, on going from mono- to poly-meric triorganotin fluorides, the Sn–F distance becomes longer as the Sn ··· F distance becomes shorter, until both distances are identical [2.1458(3) Å] for $SnPh_3F$.[13] Bearing in mind that the single-bond distance is 1.96 Å,[8,10] and that $n = 0.5$ for $SnPh_3F$, c turns out to be 0.62 Å and equation (1) transforms into (2). The Sn–F ··· Sn bridges in

$$d(\mathrm{n})/\text{Å} = 1.96 - 0.62 \log n \qquad (2)$$

$Sn(C_6H_{11})_3F$ are significantly more asymmetric than in $SnPh_3F$,[13] and the bond distances are perfectly rationalised in terms of equation (2). Indeed, a bond order of 0.72 for the Sn–F bond (0.18 for Sn ··· F) leads to Sn–F and Sn ··· F distances of 2.048 and 2.303 Å, respectively, in excellent agreement with the experimental results (see Table 1).

For rod-polymeric triorganotin fluorides (*i.e.* polymers with linear Sn–F ··· Sn bridges)[7] the Sn ··· Sn distance along the propagation axis of the polymer is the repeat distance (d_r),[15,34] which equals the sum of the Sn–F and Sn ··· F bond distances. Therefore, for these compounds, the repeat distance is related to the Sn–F bond order by means of equation (3). The use of

$$d_r/\text{Å} = 3.92 - 0.62 \log (n - n^2) \qquad (3)$$

equations (3) and (2) may allow the calculation of the Sn–F and Sn ··· F distances from the unit-cell data, as indicated in the following examples.

From the space group ($P\bar{3}c1$) and number of molecules in the unit cell ($Z = 2$) of $Sn(C_6H_{11})_3F$ it can be concluded that, unless the Sn or F atoms are disordered, they must lie on a three-fold axis, and the structure is rod polymeric with a repeat distance of 4.354 Å (half the c axis). The use of equation (3) gives a bond order $n = 0.72$ for the Sn–F bond, and equation (2) gives 2.048 and 2.306 Å for the Sn–F and Sn ··· F distances, respectively, in excellent agreement with the experimental results (see Table 1).

Tribenzyltin fluoride has been reported to crystallise in the hexagonal $P6_3cm$ space group with $a = 10.870(3)$, $c = 8.654(4)$ Å and $Z = 2$.[12] From this information we can conclude that again the Sn and F atoms lie on a three-fold axis and $Sn(CH_2Ph)_3F$ is a rod polymer with a repeat distance of 4.327 Å. The use of equation (3) gives a bond order $n = 0.67$, which according to equation (2) gives 2.068 and 2.259 Å for the Sn–F and Sn ··· F distances, respectively. Although the experimental distances, 2.12(12) and 2.21(12) Å,[12] agree with our expectations, the standard deviations are too high.

Equation (2) and the concept of bond-order conservation quantify the idea that as the intermolecular Sn ··· F distance becomes longer the Sn–F distance becomes shorter.[14] On the other hand, equation (3) indicates that, for rod-polymeric triorganotin fluorides, the repeat distance increases as the intermolecular association becomes weaker. Finally, for monomeric compounds, the Sn–F bond length should be about 1.96 Å,[8,10] while the intermolecular Sn ··· F distance should be longer than the sum of the van der Waals radii (*i.e.* 3.63 Å).[16] Therefore, in the pathway from poly- to mono-meric structures, we expect that equations (2) and (3) will no longer be valid when the structure is essentially monomeric. In addition, the assumption that the sum of the Sn–F and Sn ··· F bond orders is one is not valid for all the triorganotin fluorides. Indeed, the structure of $Sn(CH_2SiMe_3)_3F$ contains planar SnC_3 units and long symmetrical Sn–F–Sn bridges with a Sn–F distance of 2.565 Å.[11] According to equation (2), each of the Sn–F bonds has a bond order $n = 0.106$, which indicates that the Sn–F bonds are essentially ionic. It has recently been argued that the cation $[(SnEt_3)_2OH]^+$ represents the closest approach to the stannylium ion based on solid-state structural parameters, because the lengthening of the Sn–O bond, with respect to the single-bond distance, corresponds to a bond order of 0.54.[35] It is clear that $Sn(CH_2SiMe_3)_3F$ represents a much closer approach to the $[SnR_3]^+$ ion.

Polymorphism is a common phenomenon in chemistry,[28,36] and the present results cannot exclude that the previously reported structure[6] corresponds to a polymorphic form of $Sn(C_6H_{11})_3F$. Nevertheless, the close similarity to the structure of $Sn(C_6H_{11})_3Cl$[18] leads to the suspicion that the latter compound was indeed studied. This kind of error is not unprecedented. For example, a structure reported to contain the $[SnMe_3F_2]^-$ anion[37] was later shown to contain instead $[SnMe_3Cl_2]^-$.[38] It is expected that this work will stimulate research on the structural chemistry of triorganotin fluorides. Results in this area would be relevant for the interpretation of solid-state NMR data.[39,40] In addition, there has been recent interest in Sn–F distances, in relation to the concept of hypervalency in stannatranes.[41]

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* Throughout this paper it is assumed that shortening of a bond reflects strengthening. Nevertheless, a caveat for this widely accepted idea has been published recently.[33]

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