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# Solid-state $^{119}$Sn NMR studies of coordination in triorganyltin fluorides

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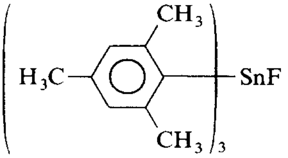
## Abstract

High-resolution $^{119}$Sn spectra of solid trimethyltin fluoride (I), tri-isobutyltin fluoride (II), and triphenyltin fluoride (III) show that all the compounds are five-coordinate in the solid state, with the $^{119}$Sn nucleus apparently equally coupled to two fluorines. In contrast, the spectrum of trimesityltin fluoride (IV) indicates, in conformity with X-ray results, that the tin is four-coordinate and couples to only one fluorine, but that there are two molecules in the asymmetric unit.

## Introduction

High-resolution $^{119}$Sn NMR spectra of solids, using cross-polarisation (CP) and magic-angle spinning (MAS), are becoming of increasing value in understanding chemical structure and bonding in organotin chemistry [1–4]. Since the technique normally uses microcrystalline powders, and may be applied equally well to amorphous materials, it is complementary to standard X-ray diffraction studies. Chemical shifts give immediate information on coordination, and the number of signals indicates the size of the crystallographic asymmetric unit.

The nature of bonding in solid triorganyltin halides has been the subject of considerable interest recently. Some years ago Clark et al. gave X-ray evidence [5] for a chain-like structure of solid trimethyltin fluoride involving fluorine bridges and pentacoordination at tin. As we have shown in a preliminary publication [6], the $^{119}$Sn CP-MAS spectrum of $Me_3SnF$ is consistent with this interpretation and indicates equivalent coupling to two fluorines. Such a situation is also found [2] for tri-n-butyltin fluoride. The X-ray structure [5] of $Me_3SnF$, however, contained some ambiguities. Recently, Reuter has demonstrated [7] that tribenzyltin fluoride has a crystal structure containing a linear chain of F–Sn–F–Sn–F–Sn atoms in which, within experimental error, the fluorine atoms are midway between the tins. On the other hand, Reuter and Puff have shown [8] that trimesityltin fluoride (IV) has a crystal structure containing molecules with tetracoordinate tin grouped in pairs. The bonded Sn–F distance is ca. 196 pm, whereas the nearest non-bonded fluorine is 446 pm from tin.



(IV)

We decided to test how efficiently solid-state NMR can detect such structural differences by obtaining $^{119}$Sn CP-MAS spectra of IV and of two other triorganyl fluorides (the isobutyl and phenyl cases) where X-ray results are not to hand. We have also repeated the earlier work on trimethyl fluoride.

## Results and discussion

Figure 1 shows the proton-decoupled $^{119}$Sn CP-MAS spectra of $^{i}$Bu$_3$SnF and Mes$_3$SnF (Mes ≡ mesityl) on the same scale. It is apparent that whereas II gives a very rich spectrum, that of Mes$_3$SnF is relatively simple. Two features lead to the complexity for II: (a) there is a triplet splitting for the centreband (indicated by arrows), resulting from coupling to two equivalent fluorines, and (b) each line in the triplet has an extensive manifold of spinning sidebands, arising from a substantial shielding anisotropy. Integration over the spinning sideband manifolds shows that the relative intensity of the three subspectra is 1 : 2 : 1 as expected. The spectrum

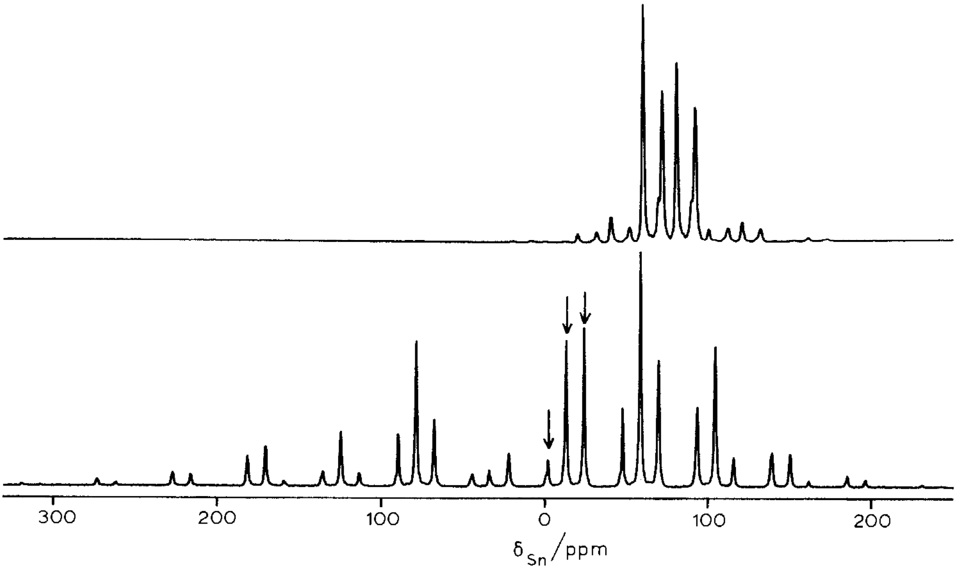


Fig. 1. Tin-119 CP-MAS NMR spectra at 111.9 MHz of (below) $^{i}$Bu$_3$SnF (II) and (above) Mes$_3$SnF (IV), on the same scale. The centrebands for II are indicated by vertical arrows. Spectrometer operating conditions: Contact time 5 ms (II) and 2 ms (IV); Recycle delay 1 ms; Number of transients 2000 (II) and 5800 (IV); Spinning speed 5130 Hz (II) and 4420 Hz (IV).

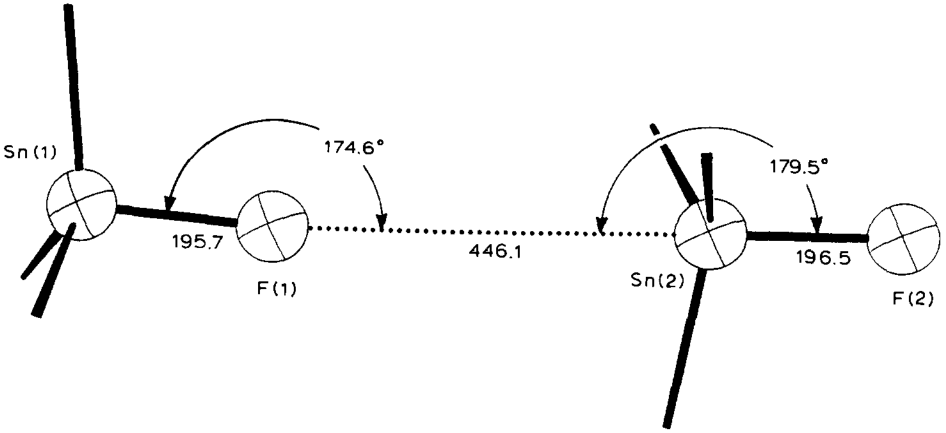


Fig. 2. Geometry of the crystallographic asymmetric unit for $Mes_3SnF$ (IV) [8].

indicates that the crystallographic asymmetric unit is a single $^iBu_3SnF$ moiety but that the structure is that of a chain polymer. This is fully in accord with the known [7] crystal structure of tribenzyl tin fluoride and with the somewhat ambiguous earlier X-ray work [5] on I. The spectrum of II is very similar to those of $Me_3SnF$ and $^nBu_3SnF$ published earlier [2,6] in all respects save the value of the isotropic shift.

By contrast, the spectrum of IV shows four major resonances, with weak spinning sidebands. Spectra obtained at two different magnetic fields prove that two of the spacings are caused by spin–spin coupling (invariant, when expressed in Hz, to a change in $B_0$), but that there are two different chemical shifts. The number of centrebands, along with their doublet splitting caused by the coupling to a single fluorine, indicates that the asymmetric unit consists of two $Mes_3SnF$ molecules with tetracoordinated tin atoms. Thus the NMR data are in full agreement with the results of the X-ray structure analysis [8]. The full crystal structure consists of two independent molecules with tetrahedrally coordinated tin atoms. These molecules are grouped in pairs with a very long (446.1 pm) non-bonding intermolecular tin–fluorine interaction and a nearly linear Sn–F $\cdots$ Sn–F arrangement. However, the minor differences in geometry (Fig. 2) revealed by the X-ray study lead to a substantial chemical shift variation, though doubtless the intermolecular environments of the two types of molecule also have an effect. The weakness of the spinning sidebands implies that the shielding anisotropy is very small. The spectrum of IV contains two additional weak shoulders centred at $\delta = -79.8$ ppm (separated by a typical $|J(\mathrm{SnF})|$ for tetracoordination) whose origin is uncertain. They may arise from a polymorphic form of the molecule.

Figure 3 summarises the interpretation of the spectra of compounds II and IV. It also shows, by comparison with Fig. 1, which doublet lines for IV are connected. It is clear that CP-MAS NMR can give, by inspection, immediate information about the coordination and bonding type of triorganyltin fluorides in the solid state. A CP-MAS spectrum of triphenyltin fluoride was also obtained, though with some difficulty because the cross-polarisation characteristics are not so favourable as for the other compounds. It shows the characteristic pattern of pentacoordination, and a fluorine-bridged chain structure for this compound is evident.

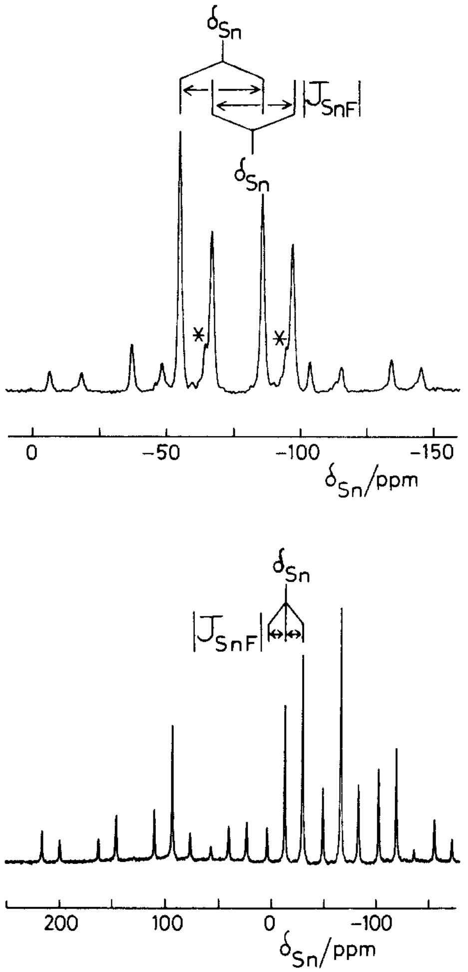


Fig. 3. Tin-119 CP-MAS spectra at 74.6 MHz of (below) $^{i}\mathrm{Bu}_3\mathrm{SnF}$ (II) and (above) $\mathrm{MeS}_3\mathrm{SnF}$ (IV) to show the interpretation of the centrebands discussed in the text. The asterisks indicate the weak unassigned shoulders (see text). Spectrometer operating conditions: Contact time 5 ms; Recycle delay 2 s (II) and 5 s (IV); Number of transients 4134 (II) and 8626 (IV); Spinning speed 3090 Hz.

The NMR results for the four compounds are given in Table 1. The isotropic chemical shifts cover a wide range and the difference in coordination of IV is not immediately apparent. However, if IV were pentacoordinate, a similar shift to that of $\mathrm{Ph}_3\mathrm{SnF}$ would be expected. The observed shift is therefore indicative of tetracoordination. However, the differences in coupling are perhaps even more convincing. For tribenzyltin fluoride Sn–F distances are 212 and 221 pm [7]—equal within experimental error—whereas the two non-equivalent molecules of IV have distances of 195.7 and 196.5 pm. As might be anticipated, the longer Sn–F distances (and the "sharing" of fluorines between two tin atoms) for the bridged systems leads to a substantial lowering of $|J(\mathrm{SnF})|$. It is tempting to link the resonance for IV at $\delta = -70.6$ ppm (which has the larger $|J(\mathrm{SnF})|$) with the molecule which has the shorter Sn–F distance, but we have no proof of this assertion.

Table 1

$^{119}$Sn NMR data for solid triorganyl fluorides

| Compound | $\delta$(Sn) (ppm) [a] | $\lvert J(\mathrm{SnF})\rvert$ (Hz) [b] | Linewidth (Hz) | Structure type |
|---|---|---|---|---|
| $Me_3SnF$ (I) | 24.3 | 1300 | 110 | Polymeric |
| $^{n}Bu_3SnF$ [c] | −9.3 | 1291 | – | Polymeric |
| $^{i}Bu_3SnF$ (II) | −13.1 | 1260 | 80 | Polymeric |
| $Ph_3SnF$ (III) | −211.9 | 1530 | 110 | Polymeric |
| $Mes_3SnF$ (IV) | −70.6 | 2300 | 110 | Monomeric |
|  | −82.2 | 2256 | 140 | Monomeric |

[a] Estimated accuracy ± 0.5 ppm. [b] Estimated accuracy ± 10 Hz. [c] Ref. 2.

Analysis of the spinning sideband manifold of the central isotropic line for $Me_3SnF$, $^{i}Bu_3SnF$ and $Ph_3SnF$, using a computer program previously discussed [9], shows that the shielding tensor is axially symmetric in each case, with anisotropy values $\beth = \sigma_{\parallel} - \sigma_{iso} = -197$, $-208$ and ca. $-255$ ppm respectively. In contrast, similar analysis for $Mes_3SnF$ (which is less accurate because fewer sidebands are accessible) indicates a high asymmetry and a low anisotropy: the average values for the four lines are $\beth =$ ca. $-36$ ppm and $\eta \geqslant 0.9$. It seems that shielding tensor data are characteristically different for pentacoordination and tetracoordination of solid triorganyltin fluorides. It may be noted that the anisotropies for the pentacoordinated compounds are much more similar than the isotropic shifts and must, therefore, be more closely related to the effects of chemical structure. It is interesting to note that the high asymmetry for trimesityltin fluoride parallels that [10] for $^{207}$Pb in one of two molecules in the asymmetric crystallographic unit of hexaphenyldiplumbane, $Ph_2Pb_6$. The molecule in question has one phenyl group in a $Ph_3Pb$ moiety with its plane oriented parallel to the Pb–Pb bond.

The full theory of spinning sideband intensities for the outer isotropic lines of the pentacoordinate triorganyltin fluorides (involving dipolar as well as shielding tensors) is being actively investigated, and a full analysis will be published in a spectroscopic journal at a later date.

## Experimental

Tin-119 spectra were obtained at 111.9 and 74.6 MHz using Varian VXR 300 and Bruker CXP 200 spectrometers respectively, in each case using double-bearing MAS. Rotors were 7 mm in outside diameter. Methodological details have been given previously [11]. The chemical shifts are quoted, using the high-frequency-positive convention, with respect to the resonance of $SnMe_4$. Centrebands were identified by varying the spinning speed.

The sample of $Me_3SnF$ was supplied by P. Granger. Details of the preparation of $Mes_3SnF$ have been given previously [8]. $^{i}Bu_3SnF$ and $Ph_3SnF$ were prepared by the procedures described in refs. 12 and 13, respectively:

$^{i}Bu_3SnF$: To a solution of 6.51 g (20 mmol) tri-isobutyltin chloride [14,15] in 100 ml ethanol, 1.74 g (30 mmol, excess) potassium fluoride, dissolved in 30 ml distilled water were added. A white precipitate was formed immediately. The resulting mixture was refluxed with stirring for 4 h. After cooling, the solid was filtered off and dried in air. Yield: 5.76 g (93%); IR: $\bar{\nu}$(Sn–F) = 365 cm$^{-1}$ (br, s).

$Ph_3SnF$: 3.85 g (10 mmol) of commercially available triphenyltin chloride (Aldrich) were dissolved as far as possible in 250 ml ethanol and the solution cleared by filtration. Thereafter 0.90 g (15.5 mmol, excess) of potassium fluoride, dissolved in 15 ml distilled water, were added. A white precipitate was formed immediately. The resulting mixture was refluxed with stirring for 4 h. After cooling the product was filtered off and dried in air. Yield: 3.38 g (92%); IR: $\bar{\nu}$(Sn–F) = 375 cm$^{-1}$ (br, s).

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