

Observation of inter- and intramolecular C–H···F hydrogen bonding in Gingras' salt: $[n\text{-Bu}_4\text{N}]^+[\text{Ph}_3\text{SnF}_2]^-$

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Abstract

The crystal and molecular structure of Gingras' salt $[n\text{-Bu}_4\text{N}]^+[\text{Ph}_3\text{SnF}_2]^-$ is reported, which reveals a variety of inter- and intramolecular C–H···F hydrogen bonding interactions. A ^{119}Sn MAS-NMR spectrum was recorded and a tensor analysis has been performed according to the method of Herzfeld and Berger. The results are discussed in terms of the molecular structure and are compared with the parent compound Ph_3SnF as well as with Mes_3SnF (Mes = mesityl). © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

Recently, organohalostannate(IV) anions have received renewed interest as simple hypercoordinated compounds to investigate the correlation of structural parameters obtained from X-ray analyses with those from spectroscopic methods, such as IR, Raman, ^{119}Sn MAS-NMR and ^{119}Sn Mössbauer spectroscopy [1,2]. Amongst these compounds, only very few examples containing fluoride are known, namely $[\text{Et}_4\text{N}]^+[(\text{Me}_2\text{SnF}_2)_2\text{F}]^-$ [3] and $[\text{NH}_4]_2^+[\text{Me}_2\text{SnF}_4]^{2-}$ [4] and particularly, there is no example of an archetypal triorganodifluorostannate, $[\text{R}_3\text{SnF}_2]^-$. The only report describing an X-ray structure analysis of $[\text{R}_3\text{SnF}_2]^-$, namely trimethyldifluorostannate, $[\text{Me}_3\text{SnF}_2]^-$ [5], was later shown to be incorrect [3]. Triorganodifluorostannates, $[\text{R}_3\text{SnF}_2]^-$, find applications as mild fluorinating reagents in organic [6–9] and organometallic [10] synthesis, and for Stille-type cross coupling reactions [11–13].

In the present work, we report the X-ray structure analysis of $[n\text{-Bu}_4\text{N}]^+[\text{Ph}_3\text{SnF}_2]^-$, known as Gingras'

salt [7], and compare the structure with that of the polymeric parent compound triphenyltin fluoride, Ph_3SnF [14], as well as the monomeric Mes_3SnF (Mes = mesityl) [15]. The molecular structure of $[n\text{-Bu}_4\text{N}]^+[\text{Ph}_3\text{SnF}_2]^-$ reveals a variety of intra- and intermolecular C–H···F contacts as well as C–H··· π interactions. ^{119}Sn MAS-NMR parameters of $[n\text{-Bu}_4\text{N}]^+[\text{Ph}_3\text{SnF}_2]^-$ including the results of a tensor analysis are discussed with respect to the molecular structure and are compared with the corresponding parameters of Ph_3SnF and Mes_3SnF [16,17].

2. Results and discussion

The title compound $[n\text{-Bu}_4\text{N}]^+[\text{Ph}_3\text{SnF}_2]^-$ was prepared essentially in accord with the original work of Gingras [7]. Crystals were obtained from hexane–dichloromethane and the crystal and molecular structure determined.

The molecular structure of the anion in $[n\text{-Bu}_4\text{N}]^+[\text{Ph}_3\text{SnF}_2]^-$ is shown in Fig. 1 and selected geometric parameters are collected in Table 1. The tin atom exists in a distorted trigonal bipyramidal geometry defined by a C_3F_2 donor set. The tin atom is effectively co-planar with the C_3 -trigonal plane lying 0.0006(3) Å out of this plane in the direction of F(1). The axial F–Sn–F angle

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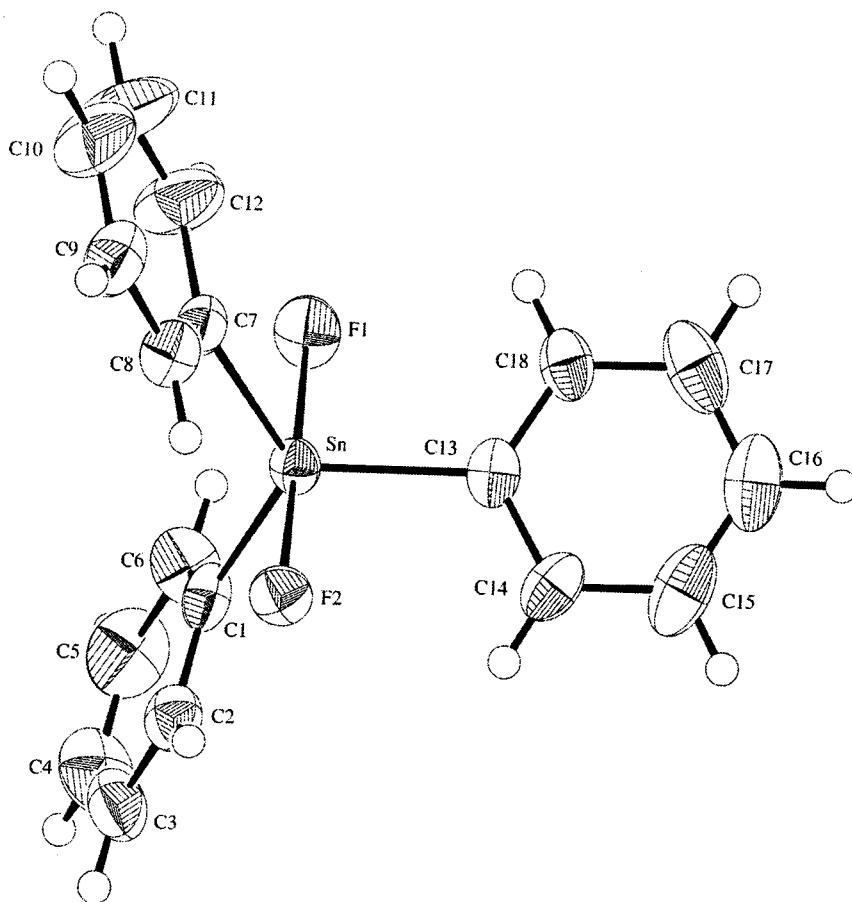


Fig. 1. Molecular structure and crystallographic numbering scheme employed for the anion in $[n\text{-Bu}_4\text{N}]^+[\text{Ph}_3\text{SnF}_2]^-$.

is $178.93(16)^\circ$. The C(1)–C(6) and C(7)–C(12) phenyl rings occupy positions consistent with a putative threefold axis of symmetry in the molecule but the C(13)–C(18) ring does not. The sequence of F(1)/Sn–C(1,7,13)/C(2,8,14) torsion angles of $178.6(5)$, $-175.9(6)$ and $-145.2(5)^\circ$, respectively, illustrates the twist about the Sn–C(13) bond. As a result of the alignment of the C(1)–C(6) and C(7)–C(12) phenyl rings with the pseudo threefold axis coincident with F–Sn–F, is the presence of close intramolecular F \cdots H interactions (Fig. 2). Thus, the four F \cdots H separations involving these groups lie in the range 2.36–2.40 Å. By contrast, these distances elongate to 2.65 and 2.75 Å for the remaining C(13)–C(18) ring.

The fluoride atoms also form intermolecular F \cdots H interactions with the cation. Thus, the separation between the C(23)–H(23b) and F(1)ⁱ atoms is 2.12 Å with C(23) \cdots F(1)ⁱ of 3.096(7) Å and the angle subtended at H(23b) of 169° ; symmetry operation *i*: $1 - x, -y, \frac{1}{2} + z$. The F(2) atom also forms a similar contact, albeit weaker: C(21)–H(21a) \cdots F(2)ⁱⁱ is 2.46 Å, C(21) \cdots F(2)ⁱⁱ is 3.417(8) Å and the angle at H(21a) is 163° ; symmetry operation *ii*: $1 + x, y, z$. There is no evidence for $\pi\cdots\pi$ interactions in the crystal structure but there are several interactions of the type C–H $\cdots\pi$.

The two most prominent C–H $\cdots\pi$ interactions involve the C(13)–C(18) aromatic ring so that the distance between C(31)–H(31a) and the ring centroid of the C(13)–C(18) ring is 2.79 Å with an angle of 163° subtended at the H(31a) atom; symmetry operation *iii*: $\frac{1}{2} + x, \frac{1}{2} - y, z$. The second interaction of 2.85 Å involves C(31)–H(30c) with an angle of 177° at H(30c); symmetry operation: *ii*. The C–H $\cdots\pi$ contacts thus described occur above and below the C(13)–C(18) ring as indicated by the angle calculated for H(31a) \cdots ring centroid \cdots H(30c) of 171° . There are only two other

Table 1
Selected bond lengths (Å) and bond angles ($^\circ$) for $[n\text{-Bu}_4\text{N}]^+[\text{Ph}_3\text{SnF}_2]^-$

| | | | |
|---------------------|------------|---------------|----------|
| <i>Bond lengths</i> | | | |
| Sn–F(1) | 2.072(4) | Sn–F(2) | 2.063(4) |
| Sn–C(1) | 2.148(7) | Sn–C(7) | 2.135(6) |
| Sn–C(13) | 2.127(5) | | |
| <i>Bond angles</i> | | | |
| F(1)–Sn–F(2) | 178.93(16) | F(1)–Sn–C(1) | 89.8(2) |
| F(1)–Sn–C(7) | 89.1(2) | F(1)–Sn–C(13) | 91.3(3) |
| F(2)–Sn–C(1) | 90.8(2) | F(2)–Sn–C(7) | 89.8(2) |
| F(2)–Sn–C(13) | 89.3(3) | C(1)–Sn–C(7) | 126.2(2) |
| C(1)–Sn–C(13) | 117.9(2) | C(7)–Sn–C(13) | 115.9(2) |

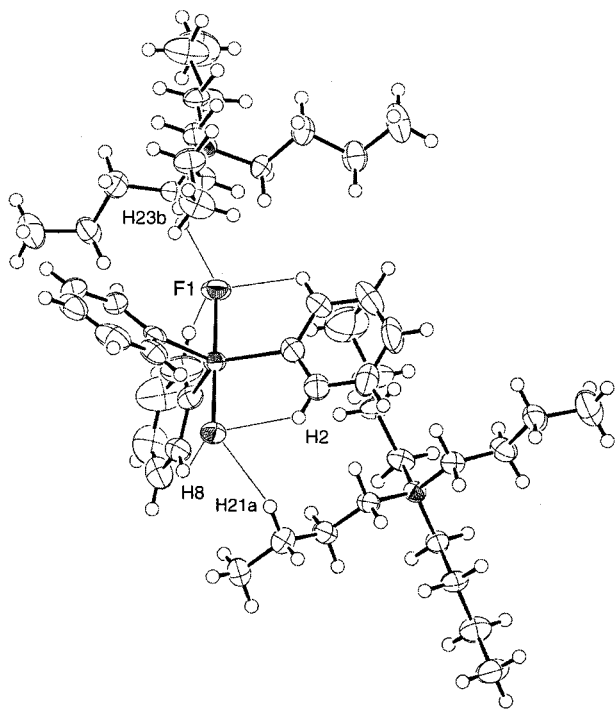


Fig. 2. Diagram showing the intra- and inter-molecular F...H interactions in the structure of $[n\text{-Bu}_4\text{N}]^+[\text{Ph}_3\text{SnF}_2]^-$.

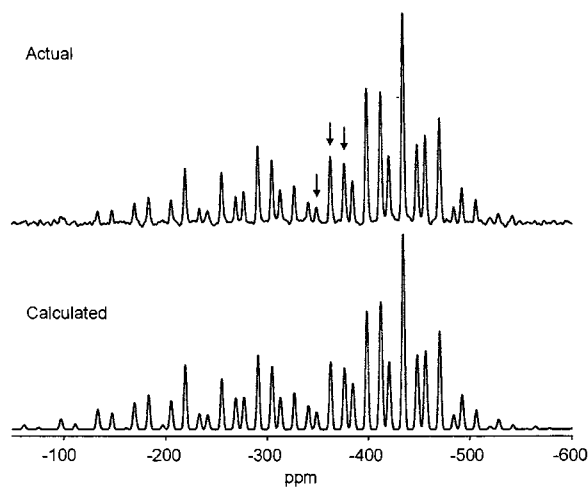


Fig. 3. ^{119}Sn MAS-NMR spectrum of $[n\text{-Bu}_4\text{N}]^+[\text{Ph}_3\text{SnF}_2]^-$ (spinning speed 6.5 KHz). The center triplet is indicated by arrows.

C–H... π interactions less than 3.4 Å in the structure and each of these involves the C(1)–C(6) phenyl ring. The longer distances (3.09 and 3.25 Å, respectively) coupled with the observed angles subtended at the respective hydrogen atoms of 123 and 110°, suggest that these interactions are not as significant as those involving the C(13)–C(18) ring. It is suggested that in the anion, the deviation from threefold symmetry may be related to the requirements of efficient crystal packing.

There are relatively few ionic organotin fluorides that have been characterized by X-ray crystallography. The

most relevant structure for comparison is that of Ph_3SnF [14]. This structure also features a trigonal bipyramidal geometry owing to the presence of symmetric Sn–F bridges; the molecule has crystallographically imposed symmetry, i.e. mutually perpendicular three and twofold axes. As expected, the Sn–F bond distance of 2.1458(3) Å is longer than the Sn–F bond distances of 2.072(4) and 2.063(4) Å found in the present structure. By contrast, a monomeric structure is found for Mes_3SnF for which significant shorter Sn–F bond distances of 1.957(4) and 1.965(4) Å are found for the two independent molecules comprising the crystallographic asymmetric unit [15].

The ^{119}Sn MAS-NMR spectrum (spinning speed: 6.5 kHz) of $[n\text{-Bu}_4\text{N}]^+[\text{Ph}_3\text{SnF}_2]^-$ is fully consistent with the structure described above and shows a triplet centred at -362.7 ppm with the $^1J(^{119}\text{Sn}\text{--}^{19}\text{F})$ coupling being 2050 Hz and the accompanying sets of spinning sidebands (Fig. 3). The ^{119}Sn spectrum of $[n\text{-Bu}_4\text{N}]^+[\text{Ph}_3\text{SnF}_2]^-$ in CD_2Cl_2 shows a triplet at -342.4 ppm with a $^1J(^{119}\text{Sn}\text{--}^{19}\text{F})$ coupling of 1971 Hz [7], which almost resembles the aforementioned solid-state parameters, and consequently, the solid-state and solution structures can be considered to be essentially the same. The ^{119}Sn MAS-NMR parameters of $[n\text{-Bu}_4\text{N}]^+[\text{Ph}_3\text{SnF}_2]^-$ can be best compared with those of Ph_3SnF and Mes_3SnF , for which ^{119}Sn MAS-NMR chemical shifts have been reported of -211.9 and $-70.6/-82.2$ ppm (two crystallographic sites) with $^1J(^{119}\text{Sn}\text{--}^{19}\text{F})$ couplings of 1530 and 2300/2256 Hz, respectively [16,17]. Thus, the $^1J(^{119}\text{Sn}\text{--}^{19}\text{F})$ coupling increases in the order: $\text{Ph}_3\text{SnF} < [\text{Ph}_3\text{SnF}_2]^- < \text{Mes}_3\text{SnF}$, which is in agreement with the observed magnitude of the Sn–F bond lengths within these compounds. Given the electronic influence of the organic substituents on the ^{119}Sn MAS chemical shift is ca. the same for all three compounds, this parameter correlates best with the ‘relative’ co-ordination number of the tin atoms, which increases in the order: $\text{Mes}_3\text{SnF} < \text{Ph}_3\text{SnF} < [\text{Ph}_3\text{SnF}_2]^-$. The integration over all respective spinning sideband manifolds confirms the required ratio of 1:2:1 for a triplet. The three large sideband manifolds in the spectrum (Fig. 3) were used to perform a tensor analysis according to the method of Herzfeld and Berger [18,19]. The isotropic chemical shift (δ_{iso}), anisotropy (ζ), asymmetry (η) and chemical shift tensor components (σ_{11} , σ_{22} , σ_{33}), represented in the Haeberlen convention [20], are listed alongside the same parameters for Ph_3SnF and Mes_3SnF in Table 2 [16,17]. It is worth mentioning that the parameters derived from the outer lines of the triplet are affected by both $^1J(^{119}\text{Sn}\text{--}^{19}\text{F})$ couplings and shielding, whereas those of the centre line are due to shielding only.

It is interesting to note that the anisotropies (ζ) of Ph_3SnF and $[\text{Ph}_3\text{SnF}_2]^-$ are very similar for the three components of the spinning-sideband manifold, but

substantially different to those of Mes_3SnF . If the measured MAS NMR nucleus lies across a threefold (or higher) symmetry axis, group theory requires that $\sigma_{11} = \sigma_{22}$, and thus, $\eta = 0$ [21]. The geometry of Ph_3SnF fully meets this criterion, and consequently the asymmetry (η) reveals the required value for all components of the triplet. In contrast, the geometry of the anion $[\text{Ph}_3\text{SnF}_2]^-$ shows a slight deviation from a threefold symmetry axis. This deviation is also reflected in the asymmetry: $\eta = 0$ only for the middle component of the triplet, but $\eta = 0.2$ for both the right and the left components of the triplet. In the Mes_3SnF the mesityl groups are crystallographically independent, and thus the structure lacks a threefold symmetry axis. Therefore, the asymmetry differs substantially from zero for both tin sites.

3. Experimental

The ^{119}Sn CP-MAS-NMR spectra were obtained using a JEOL Eclipse + 400 MHz NMR spectrometer (149.05 MHz for ^{119}Sn). An 8 μs (90°) pulse, 5 ms contact time and recycle delay of 10 s were used. Spectra were recorded on 250–350 mg of sample packed into 6 mm diameter rotors. Chemical shifts are quoted relative to Me_4Sn , using solid *c*-Hex $_4\text{Sn}$ ($\delta_{\text{iso}} = -97.35$ ppm) as a secondary external reference. Typically 15 000 transients were recorded in order to achieve a reasonable signal-to-noise ratio. At least two experiments with sufficiently different spinning rates, ranging from 4 to 7 kHz, were recorded in order to determine the isotropic chemical shift. Analysis of the principal components of the ^{119}Sn shielding tensors was performed with WINFIT software [22] using the method of Herzfeld and Berger [18]. They are reported using Haebleren's notation [20] as the isotropic chemical shift ($\delta_{\text{iso}} = -\sigma_{\text{iso}}$), the anisotropy ($\zeta = \sigma_{33} - \sigma_{\text{iso}}$) and the asymmetry ($\eta = |\sigma_{22} - \sigma_{11}|/|\sigma_{33} - \sigma_{\text{iso}}|$), σ_{11} , σ_{22} and σ_{33} being the three components of the shielding tensor

expressed in its principal axis system with the following convention: $|\sigma_{33} - \sigma_{\text{iso}}| \geq |\sigma_{11} - \sigma_{\text{iso}}| \geq |\sigma_{22} - \sigma_{\text{iso}}|$. With this convention, ζ is a signed value expressed in ppm and η is a dimensionless parameter, the value of which varies between 0 and 1.

3.1. Synthesis of $[n\text{-Bu}_4\text{N}]^+[\text{Ph}_3\text{SnF}_2]^-$

The title compound was prepared essentially according to the original procedure, [7] however, aq. *n*-Bu $_4\text{NF}$ was used because it is more economical.

A solution of *n*-Bu $_4\text{NF}$ (100.00 g of a 75% w/w aq. solution, 0.287 mol) and Ph_3SnF (105.85 g, 0.287 mol) in 300 ml CH_2Cl_2 was stirred at room temperature for 1 h. The solution was filtered to remove insoluble material and 90% of the solvent removed in vacuo. Addition of C_6H_{14} gave crystals of $[n\text{-Bu}_4\text{N}]^+[\text{Ph}_3\text{SnF}_2]^-$ which were collected by vacuum filtration and dried overnight at 80 °C and 5 Torr (148.4 g, 82%). Crystals suitable for X-ray analysis were obtained by slow evaporation of a $\text{C}_6\text{H}_{14}\text{-CH}_2\text{Cl}_2$ solution.

3.2. Crystal structure determination of $[n\text{-Bu}_4\text{N}]^+[\text{Ph}_3\text{SnF}_2]^-$

Crystal data: $\text{C}_{34}\text{H}_{51}\text{F}_2\text{NSn}$, $M = 630.5$, orthorhombic, $a = 18.571(7)$, $b = 11.502(5)$, $c = 15.679(9)$ Å, $T = 173$ K, space group $Pna2_1$, $Z = 4$, $\mu(\text{Mo-K}\alpha) = 7.95$ cm^{-1} , 4300 reflections measured on a Rigaku AFC7R, $\theta_{\text{max}} 27.5^\circ$, 3977 unique and 2520 with $[I \geq 2.0\sigma(I)]$. Refinement on F^2 converged with final $R = 0.030$ and $wR = 0.069$ for 'observed' data and $R = 0.084$ and $wR = 0.085$ for all data. The Flack parameter = 0.00(3). The data was processed with TEXSAN [23a], solved using DIRDIF [23b] corrected for absorption using DIFABS [23c] and refined with SHELXL-97 [23d]. The absolute structure was determined by an analysis of the Flack parameter [23e]. The figures were drawn with ORTEP [23f] (50% displacement ellipsoids) and PLATON [23g] was employed in the analysis of the structure.

Table 2
Selected ^{119}Sn MAS-NMR parameter for $[n\text{-Bu}_4\text{N}]^+[\text{Ph}_3\text{SnF}_2]^-$ and the related compounds Ph_3SnF and Mes_3SnF [16,17]

| Compound | δ_{iso} (ppm) | ζ (ppm) | η | σ_{11} (ppm) | σ_{22} (ppm) | σ_{33} (ppm) |
|--------------------------------------|-----------------------------|---------------|--------|---------------------|---------------------|---------------------|
| Ph_3SnF | -198.1 | -306 | 0.0 | 351 | 351 | -108 |
| | -211.9 | -255 | 0.0 | 340 | 340 | -43 |
| | -225.2 | -188 | 0.0 | 321 | 321 | 37 |
| $[\text{Ph}_3\text{SnF}_2]^-$ | -348.8 | -276.5 | 0.20 | 514.7 | 459.4 | 72.3 |
| | -362.7 | -222.7 | 0.00 | 474.1 | 474.1 | 140.0 |
| | -376.5 | -158.0 | 0.20 | 471.3 | 439.7 | 218.5 |
| Mes_3SnF (site 1) | -54.0 | -51 | 0.2 | 85 | 74 | 3 |
| | -84.8 | 75 | 0.1 | 42 | 53 | 160 |
| (site 2) | -65.9 | -62 | 0.3 | 107 | 87 | 3 |
| | -96.0 | 63 | 0.3 | 55 | 74 | 159 |

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 167521. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk of [www: http://www.ccdc.cam.ac.uk](http://www.ccdc.cam.ac.uk)).

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