being developed here for the first time for an early 3d metal. Differences between the behaviors of V and the heavier metals Mo and W are already apparent, but further work is necessary before any trends can be established. Variation of reaction stoichiometries is in progress and other products are being characterized. Further results in this rich new area will be reported in due course.

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Supplementary Material Available: Tables of atomic coordinates and isotropic and anisotropic thermal parameters (4 pages). Ordering information is given on any current masthead page.

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Articles

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Synthetic, Spectroscopic, and Solution NMR Studies of Dimethyltin(IV) Fluorosulfate Derivatives

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The ability of $(CH_3)_2Sn(SO_3F)_2$ to act as a SO_3F^- ion acceptor is illustrated by the synthesis and subsequent characterization of the new complexes $Cs[(CH_3)_2Sn(SO_3F)_3]$, $Li_2[(CH_3)_2Sn(SO_3F)_4]$, $Ba[(CH_3)_2Sn(SO_3F)_4]$, and $Sn[(CH_3)_2Sn(SO_3F)_4]$. In addition a new structural form of $(CH_3)_2Sn(SO_3F)_2$ is produced with distinctly different thermal and spectroscopic properties. The ^{119}Sn Mössbauer spectra with the isomer shift $\delta = 1.8\text{–}1.9$ mm s^{-1} and the quadrupole splitting $\Delta E_Q = 5.4\text{–}5.5$ mm s^{-1} suggest octahedral coordination in all instances, with the electronic structure of the dimethyltin group invariant in all complexes. A similar common electronic structure is found for these species in HSO_3F solution as probed by ^1H, ^{13}C, and ^{119}Sn NMR.

Introduction

Strong protonic acids like fluorosulfuric acid, HSO_3F, and related monosubstituted sulfuric acids have been used in the past to synthesize a variety of alkyltin(IV) chlorosulfonates by the solvolysis of alkyltin(IV) chlorides.[1–6] In these studies ^{119}Sn Mössbauer spectroscopy has played a pivotal role in the structural characterization of the produced materials with support from the reported crystal structure of $(CH_3)_2Sn(SO_3F)_2$,[7] revealing a sheetlike polymer, similar to the one found for $(CH_3)_2SnF_2$,[8] with a linear C–Sn–C grouping in a trans-octahedral coordination environment for tin due to bidentate-bridging fluorosulfate groups.

The observed bond parameters as well as the unusually large quadrupole splitting, ΔE_Q, of 5.54 mm s^{-1}[1,4–6] for $(CH_3)_2Sn(SO_3F)_2$ has suggested the presence of a cationic $(CH_3)_2Sn$ moiety in this compound.

A very recent study by us[9] has focused attention more narrowly on the possible existence of the $(CH_3)_2Sn^{2+}$ cation. If HSO_3F and the related superacid systems $HSO_3F/Sn(SO_3F)_4$[10] and $HSO_3F/Pt(SO_3F)_4$[11] are employed, materials containing not only this cation but also $[(CH_3)_2Sn(SO_3F)]^+$, both stabilized by $[M(SO_3F)_6]^{2-}$ with M = Sn or Pt, are obtained and stepwise, acidity dependent dissociation of $(CH_3)_2Sn(SO_3F)_2$ is postulated,[9] according to

$$(CH_3)_2Sn(SO_3F)_2(solv) \xrightleftharpoons{-SO_3F^-} [(CH_3)_2Sn(SO_3F)]^+(solv) \xrightleftharpoons{-SO_3F^-} [(CH_3)_2Sn]^{2+}(solv) \quad (1)$$

to explain the synthetic results.

In the basic region of HSO_3F, generated by dissolution of $CsSO_3F$, dimethyltin(IV) bis(fluorosulfate) acts as an acid, or SO_3F^- acceptor, and in the presence of 2 mol of $CsSO_3F$, the compound $Cs_2[(CH_3)_2Sn(SO_3F)_4]$ forms, while with $Sn(SO_3F)_2$ as donor a material tentatively identified as $Sn[(CH_3)_2Sn(SO_3F)_4]$ forms.[9]

The present study is intended to complement our earlier work[9] in several ways. Synthetic efforts are aimed primarily at the anionic dimethyltin(IV) fluorosulfate derivatives. The product of the reaction of equimolar amounts of $Sn(SO_3F)_2$ and $(CH_3)_2Sn(SO_3F)_2$ produces a complex ^{119}Sn Mössbauer spectrum with partly overlapping lines due to two different tin environments. Support for the suggested formulation as $Sn^{II}[(CH_3)_2Sn(SO_3F)_4]$ should come from the synthesis and characterization of the corresponding barium salt $Ba[(CH_3)_2Sn(SO_3F)_4]$.

The thermal stability of the anion $[(CH_3)_2Sn(SO_3F)_4]^{2-}$ is probed by the synthesis of $Li_2[(CH_3)_2Sn(SO_3F)_4]$ and a spectroscopic comparison to the previously reported $Cs_2[(CH_3)_2Sn(SO_3F)_4]$. The attempted metathesis of this cesium salt with $(CH_3)_2Sn(SO_3F)_2$ follows a recent precedent[9] involving $Cs_2[Sn(SO_3F)_6]$

$$2(CH_3)_2Sn(SO_3F)_2 + Cs_2[Sn(SO_3F)_6] \xrightarrow{HSO_3F} 2CsSO_3F + [(CH_3)_2Sn(SO_3F)]_2[Sn(SO_3F)_6] \quad (2)$$

A corresponding dimethyltetrakis(fluorosulfato)tin(IV) derivative with either $[(CH_3)_2Sn(SO_3F)]^+$ or $(CH_3)_2Sn^{2+}$ as counterion would constitute a structural or ionization isomer of the polymeric $(CH_3)_2Sn(SO_3F)_2$.[1,7] Its identification is expected to present a challenge.

Finally, the addition of SO_3F^- to $(CH_3)_2Sn(SO_3F)_2$, just like its dissociation in acidic medium, reaction sequence 1, is expected

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(1) Yeats, P. A.; Ford, B. F. E.; Sams, J. R.; Aubke, F. *J. Chem. Soc., Chem. Commun.* **1969**, 151.
(2) Yeats, P. A.; Sams, J. R.; Aubke, F. *Inorg. Chem.* **1971**, *10*, 1877.
(3) Schmeisser, M.; Sartori, P.; Lippsmeier, B. *Chem. Ber.* **1970**, *103*, 868.
(4) Tan, T. H.; Dalziel, J. R.; Yeats, P. A.; Sams, J. R.; Thompson, R. C.; Aubke, F. *Can. J. Chem.* **1972**, *50*, 1843.
(5) Yeats, P. A.; Sams, J. R.; Aubke, F. *Inorg. Chem.* **1972**, *11*, 2634.
(6) Birchall, T.; Chan, P. K. H.; Pereira, A. R. *J. Chem. Soc., Dalton Trans.* **1974**, 2157.
(7) Allen, F. H.; Lerbscher, J. A.; Trotter, J. *J. Chem. Soc. A* **1971**, 2507.
(8) Schlemper, E. O.; Hamilton, W. C. *Inorg. Chem.* **1966**, *5*, 995.
(9) Mallela, S. P.; Tomic, S. T.; Lee, K.; Sams, J. R.; Aubke, F. *Inorg. Chem.* **1986**, *25*, 2939.
(10) Mallela, S. P.; Lee, K. C.; Aubke, F. *Inorg. Chem.* **1984**, *23*, 653.
(11) Lee, K. C.; Aubke, F. *Inorg. Chem.* **1984**, *23*, 124.

0020-1669/86/1325-4074$01.50/0

to proceed stepwise according to

$$(CH_3)_2Sn(SO_3F)_2(\mathrm{solv}) \xrightleftharpoons{+SO_3F^-} [(CH_3)_2Sn(SO_3F)_3]^-(\mathrm{solv}) \xrightleftharpoons{+SO_3F^-} [(CH_3)_2Sn(SO_3F)_4]^{2-}(\mathrm{solv}) \quad (3)$$

and the attempted synthesis and subsequent characterization of $Cs[(CH_3)_2Sn(SO_3F)_3]$ is intended to close the gap.

In addition to ^{119}Sn Mössbauer spectroscopy, and to a lesser extent infrared spectroscopy, high-resolution NMR (^1H, ^{19}F, ^{13}C, and ^{119}Sn) in HSO_3F now becomes a valuable tool since most of the anionic derivatives as well as $(CH_3)_2Sn(SO_3F)_2$ are found or expected to be sufficiently soluble.

Surprisingly the ^{119}Sn Mössbauer parameters for the dimethyltin(IV) fluorosulfate derivatives studied so far show a rather narrow range of quadrupole splittings (5.50–5.70 mm s^{-1}) and isomer shifts, δ (1.82 to close to 2.00 mm s^{-1}, relative to SnO_2), which suggests a rather invariant electronic structure for the dimethyltin(IV) group in cationic, neutral, and anionic compounds. It becomes interesting to probe the electronic structure by NMR in HSO_3F solution.

Two recent NMR studies in HSO_3F are relevant in this respect. The study of $(CH_3)_2Sn(SO_3F)_2$ in HSO_3F, by Birchall and Manivannan[12] using mainly ^{119}Sn NMR down to −90 °C, had suggested at low temperatures the presence of at least three different species with variations in chemical shift δ between +30 and −230 ppm relative to $(CH_3)_4Sn$. The same authors have also studied the solvolysis of methyltin(IV) hydrides of the type $(CH_3)_{4-n}SnH_n$, with $n = 1$–4, in HSO_3F down to −90 °C, by ^1H, ^{13}C, and ^{119}Sn NMR[13] and claim to have identified Sn^{2+} as well as $(CH_3)_2Sn^{2+}$ as products of these solvolysis reactions.

An additional recent NMR study on a wide range of dialkyltin(IV) derivatives, all unrelated to our study, may serve as a more general example for the application of heteronuclear NMR to structural problems in organotin(IV) chemistry.[14]

Experimental Section

Chemicals. Commercially available chemicals of analytical reagent or of reagent grade were used without further purification. Technical grade fluorosulfuric acid was purified by double distillation at atmospheric pressure.[14] Trimethyltin(IV) chloride, $(CH_3)_3SnCl$ (Aldrich Chemical Co.), was used as starting material for the synthesis of $(CH_3)_2Sn(SO_3F)_2$,[1,5] $Cs_2[(CH_3)_2Sn(SO_3F)_4]$,[9] $Sn[(CH_3)_2Sn(SO_3F)_4]$,[9] and the methyltin(IV) compounds reported here for the first time. $Sn(SO_3F)_2$ was obtained from anhydrous $SnCl_2$ and HSO_3F. All samples for NMR studies were isolated, analyzed for C and H, and/or characterized by melting points and IR spectra prior to dissolution, except where noted otherwise. SbF_5 (Ozark Mahoning) was purified by repeated distillation at atmospheric pressure.

Instrumentation. A Perkin-Elmer 598 grating infrared spectrophotometer was used with samples pressed between AgBr windows (Harshaw Chemicals) as thin films or with Nujol or hexachlorobutadiene used as mulling agents. Our Raman spectrometer has been described previously.[10]

The ^{119}Sn Mössbauer spectra were recorded in transmission mode with a constant-acceleration spectrometer of conventional design. Pulses were accumulated in a Tracor-Northern TN-1706 multichannel analyzer, from which the data were transmitted via an IBM PC to the mainframe computer for curve fitting. The latter was accomplished by using a standard nonlinear regression program with no constraints imposed on the fitting parameters. The Doppler velocity scale was calibrated by using an iron foil absorber and ^{57}Co source. Isomer shifts are reported relative to $BaSnO_3$ at 77 K.

Differential scanning calorimetry studies (DSC) were made with a Mettler DSC 20 cell and a Mettler TC 10 TA processor.

Tin-119 FT NMR spectra (decoupled) were recorded on a Varian XL 300 instrument operating at 111.86 MHz (field strength 7.10 T) and on a Bruker Spectrospin WP 80 instrument operating at 29.88 MHz (field strength 1.89 T). For spectra recorded on the Bruker WP 80, samples were contained in a 10-mm o.d. NMR tube with a concentrically placed 5-mm o.d. tube that contained acetone-d_6. The spectrometer was locked to external acetone-d_6. Samples were contained in a 5-mm o.d. NMR tube for spectra recorded on the Varian XL-300, and the tubes were sealed under vacuum. Chemical shifts were measured relative to an external reference of $(CH_3)_4Sn$ (TMT). Proton decoupled ^{13}C FT NMR spectra were obtained on a Bruker WH 400 (100.6 MHz) as well as on a Varian XL 300 instrument. Chemical shifts were recorded relative to external Me_4Si.

All reactions were performed in Pyrex reaction vials of about 40-mL capacity fitted with Kontes Teflon stem valves. Volatile materials were handled by using vacuum line techniques. Solids were manipulated in a Vacuum Atmosphere Corp. Dri Lab, Model No. HE-43-2, filled with purified dry nitrogen and equipped with a Dri-Train circulating unit, Model No. HE-93-B.

All reactions were followed by weight. Chemical analysis was carried out by Analytische Laboratorien, Gummersbach, West Germany, and by P. Borda of this department (carbon and hydrogen).

Individual Preparations. (i) Cesium Dimethyltris(fluorosulfato)stannate(IV), $Cs[(CH_3)_2Sn(SO_3F)_3]$. About 5 mL of HSO_3F was distilled onto an equimolar mixture of CsCl (500 mg, 2.969 mmol) and $(CH_3)_3SnCl$ (591.7 mg, 2.969 mmol). Initially a clear solution was obtained at room temperature, and after 30 min of vigorous stirring a white crystalline product started to precipitate out. The contents were stirred for 90 h at room temperature and later at 55 °C for 8 h. The precipitate dissolved at this temperature. All the volatiles were subsequently removed in vacuo.

The white, hygroscopic product (1702.9 mg, 2.942 mmol) does not decompose or melt below 330 °C. Anal. Calcd for $CsSnC_2H_6S_3O_9F_3$: Cs, 22.96; Sn, 20.50; C, 4.15; H, 1.04; F, 9.85. Found: Cs, 22.75; Sn, 20.75; C, 4.20; H, 1.14; F, 9.55.

(ii) Barium Dimethyltetrakis(fluorosulfato)stannate(IV), $Ba[(CH_3)_2Sn(SO_3F)_4]$. About 10 mL of HSO_3F was distilled onto a mixture of $BaCl_2$ (471 mg, 2.26 mmol) and $(CH_3)_3SnCl$ (464 mg, 2.30 mmol). The reaction vial was slowly warmed to room temperature. At ambient temperature vigorous reaction occurred, and a clear solution appeared. The HCl evolved was removed in vacuo. The contents were magnetically stirred at room temperature for 24 h. Excess solvent was removed in vacuo at ~50 °C.

The white hygroscopic, crystalline solid (1670 mg, 2.4 mmol) decomposes at 238 °C. Anal. Calcd for $BaSnC_2H_6S_4O_{12}F_4$: Ba, 20.40; Sn, 17.35; C, 3.51; H, 0.88; F, 10.85. Found: Ba, 20.10; Sn, 17.37; C, 3.46; H, 1.00; F, 11.12.

(iii) Lithium Dimethyltetrakis(fluorosulfato)stannate(IV), $Li_2[(CH_3)_2Sn(SO_3F)_4]$. The material was prepared in a similar manner. A mixture of 380 mg (8.96 mmol) of LiCl and 904 mg (4.5 mmol) of $(CH_3)_3SnCl$ was allowed to react in excess HSO_3F (~10 mL) for 24 h at room temperature. A clear solution was obtained at room temperature. The product was isolated by removing excess acid in vacuo.

The white, hygroscopic, crystalline compound melts at 240 °C. Anal. Calcd for $Li_2SnC_2H_6S_4O_{12}F_4$: C, 4.30; H, 1.08; Li, 2.48; Sn, 21.24; F, 13.60. Found: C, 4.23; H, 1.10; Li, 2.37; Sn, 21.40; F, 13.40.

(iv) Tin(II) Dimethyltetrakis(fluorosulfato)stannate(IV), $Sn[(CH_3)_2Sn(SO_3F)_4]$. Equimolar amounts of $SnCl_2$ (381.0 mg, 2.01 mmol) and $(CH_3)_3SnCl$ (400.0 mg, 2.01 mmol) were solvolyzed in an excess of fluorosulfuric acid at room temperature. After removal of all volatile byproducts (CH_4, HCl) in vacuo, stirring was continued at room temperature for 3 days before the temperature was raised to approximately 50 °C and maintained there for 3 h. The solution remained clear throughout, and after all volatiles were removed in vacuo, 1211.6 mg of a white, hygroscopic solid was obtained. It decomposes at 245–248 °C. Anal. Calcd for $SnCH_3S_2O_6F_2$: C, 3.62; H, 0.91; Sn, 35.76; F, 11.44; S, 19.33. Found: C, 3.48; H, 1.02; Sn, 36.10; F, 11.20; S, 19.43.

(v) β-Dimethyltin(IV) Dimethyltetrakis(fluorosulfato)stannate(IV), $[(CH_3)_2Sn][(CH_3)_2Sn(SO_3F)_4]$. The reaction vessel was charged with 0.972 g (3.0 mmol) of $(CH_3)_2Sn(SO_3F)_2$ and 1.192 g (1.5 mmol) of $Cs_2[(CH_3)_2Sn(SO_3F)_4]$. HSO_3F (~9 mL) was added via distillation, and the reaction mixture was allowed to warm to room temperature. The solution was warmed slowly to 65 °C and was kept stirring for 5 days. The clear solution obtained was concentrated to half the original volume. The white crystalline product obtained was vacuum filtered and washed twice with a very small amount of HSO_3F. The compound was found to be somewhat soluble in HSO_3F.

The white hygroscopic compound (~30% yield) did not melt below 300 °C. Anal. Calcd: C, 6.93; H, 1.74. Found: C, 7.00; H, 1.64.

Results and Discussion

Synthesis. With the behavior of methyltin(IV) chlorides in HSO_3F well understood from previous studies[1-6,9] and the di-

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(12) Birchall, T.; Manivannan, V. *Can. J. Chem.* **1985**, *63*, 2211.

(13) Birchall, T.; Manivannan, V. *J. Chem. Soc., Dalton Trans.* **1985**, 2671.

(14) Howard, W. F.; Crecely, R. W.; Nelson, W. H. *Inorg. Chem.* **1985**, *24*, 2204.

(15) Barr, J.; Gillespie, R. J.; Thompson, R. C. *Inorg. Chem.* **1964**, *3*, 1149.

Table I. Infrared Frequencies for $Sn[(CH_3)_2Sn(SO_3F)_4]$, $Ba[(CH_3)_2Sn(SO_3F)_4]$, and $Li_2[(CH_3)_2Sn(SO_3F)_4]$[a]

ν, cm^{-1} (int)			approx description
$Sn[(CH_3)_2Sn(SO_3F)_4]$	$Ba[(CH_3)_2Sn(SO_3F)_4]$	$Li_2[(CH_3)_2Sn(SO_3F)_4]$	
1420 (m, sh)	1410 (m, sh)		δ_{CH_3}(asym)
1355 (s)	1325 (s)	1330 (s, b)	ν_{SO_3}
1222 (w, sh)			δ_{CH_3}(sym)
1190 (vs, b)	1228 (vs, b)	1230 (vs, b)	ν_{SO_3}
1085 (ms, sh)			
1075 (s)	1075 (s)	1085 (s, b)	ν_{SO_3}
1025 (m, sh)			
975 (vw, sh), 915 (vw)	970 (w), 915 (w)	970 (w), 915 (vw, sh)	
825 (s, b)	815 (s, b)	820 (s, b)	ρ_{SnCH_3}
800 (s)	795 (s)	785 (s, sh)	ν_{SF}
614 (ms, sh)	605 (m, sh)	610 (m, sh)	ρ_{SO_3}(asym) + ν_{SnC}(asym)
596 (s)	590 (s)	600 (s)	
565 (s)	568 (s)	570 (s)	ρ_{SO_3}(sym)
472 (vw)	485 (vw, b)	480 (vw)	
422 (s)	415 (m)	425 (ms)	δ_{SO_3}
415 (s, sh)	400 (m)	410 (m, sh)	

[a] ν_{CH_3} at ~2900 cm^{-1} is not included in this listing. Key: s = strong, m = medium, w = weak, v = very, b = broad, sh = shoulder, int = estimated intensity and band description, ν = stretch, δ = bend, ρ = rock, sym = symmetric, asym = asymmetric.

methyltin(IV) group resistant to further solvolytic attack under the prevailing conditions, the cosolvolysis of trimethyltin(IV) chloride with stoichiometric amounts of either CsCl, $BaCl_2$ (1 molar ratio), or LiCl results in the straightforward preparation of compounds of the composition $Cs[(CH_3)_2Sn(SO_3F)_3]$, $Ba[(CH_3)_2Sn(SO_3F)_4]$, or $Li_2[(CH_3)_2Sn(SO_3F)_4]$ as analytically pure, moderately hygroscopic, high-melting solids. There is little doubt that the general route used here will lead to a wider range of similar derivatives with either mono- or divalent cations, as long as the metal chloride precursor dissolves and dissociates in HSO_3F. The possible extension to the corresponding trifluoromethanesulfonates should also be possible. Practical synthetic routes to these compounds have recently been explored and have resulted in the preparation of $Cs_2[(CH_3)_2Sn(SO_3CF_3)_4]$,[9] $Cs_2[Sn(SO_3CF_3)_6]$,[16] and $Cs[Sn(SO_3CF_3)_5]$,[16] with the latter two obtained by the solvolysis of SO_3F precursors in an excess of HSO_3CF_3.

The preparation and characterization of $Cs[(CH_3)_2Sn(SO_3F)_3]$ provides some tentative evidence for the presence of a genuine compound rather than a mixture of $Cs_2[(CH_3)_2Sn(SO_3F)_4]$ and $(CH_3)_2Sn(SO_3F)_2$. The material isolated from the reaction of equimolar amounts of $CsSO_3F$ and $(CH_3)_2Sn(SO_3F)_2$ in fluorosulfuric acid shows, in contrast to $Cs_2[(CH_3)_2Sn(SO_3F)_4]$, only limited solubility in HSO_3F and may be conveniently isolated by filtration. The thermal stability beyond 330 °C is in marked contrast to that of $(CH_3)_2Sn(SO_3F)_2$, where a decomposition point of 253 °C is reported. Futher clarification is expected from the spectroscopic characterization of this compound, discussed below.

The analogy between $Sn(SO_3F)_4$ and $(CH_3)_2Sn(SO_3F)_2$ as fluorosulfate ion acceptors is probed by a metathetical reaction between $(CH_3)_2Sn(SO_3F)_2$ and $Cs_2[(CH_3)_2Sn(SO_3F)_4]$ at a 2:1 molar ratio in HSO_3F. The precedent reaction

$$2(CH_3)_2Sn(SO_3F)_2 + Cs_2[Sn(SO_3F)_6] \xrightarrow[HSO_3F]{+25\ °C} [(CH_3)_2Sn(SO_3F)]_2[Sn(SO_3F)_6] + 2CsSO_3F \quad (4)$$

has been reported recently,[9] with the precipitate isolated by filtration.

In order to obtain a clear solution, the 2:1 molar mixture of $(CH_3)_2Sn(SO_3F)_2$ and $Cs_2[(CH_3)_2Sn(SO_3F)_4]$ in ~10 mL of HSO_3F is slowly waremed to 65 °C and maintained at this temperature for 5 days. Crystallization of a white material occurs after removal of ~5 mL HSO_3F in vacuo at room temperature, and filtration and subsequent washing with cold HSO_3F affords a material of the composition $(CH_3)_2Sn(SO_3F)_2$ in approximately 30% of the expected yield judging from the weight.

Microanalysis of C and H contents confirms the postulated composition, but is clearly of little value in this case, since the polymeric dimethyltin(IV) fluorosulfate, described by us earlier,[1,2] has the same elemental composition as the possible reaction products $[(CH_3)_2Sn(SO_3F)]_2[(CH_3)_2Sn(SO_3F)_4]$ or $(CH_3)_2Sn[(CH_3)_2Sn(SO_3F)_4]$, which may be viewed as its ionization isomers.

There are, however, some indications for the presence of a material, different from the one originally reported.[1,2] There is first the considerably lower solubility in HSO_3F at 25 °C, which has allowed isolation by filtration. The thermal behavior provides an additional clue. The solid isolated here does not appear to melt or decompose up to 330 °C, the limit of our melting point apparatus, and only a slight darkening is noted at the high-temperature end. For polymeric $(CH_3)_2Sn(SO_3F)_2$, referred to as the α-form, a decomposition point of 253 °C[2] has already been mentioned. The DSC measurement on this compound shows two sharp endothermic peaks at 226 °C (ΔH = 19.7 J g^{-1}) and 237.5 °C (ΔH = 11.5 J g^{-1}) followed by a rather broad endotherm at ~250 °C, which is difficult to integrate. The position of this peak is close to the reported decomposition point. The two sharp peaks at lower temperature may indicate phase transitions.

The material isolated here, termed β-$(CH_3)_2Sn(SO_3F)_2$ shows only a single endotherm at 239 °C (ΔH = 11.8 J g^{-1}) up to 330 °C. The ΔH value and peak position are within error limits of the second endotherm found for the α-form and may imply a similar thermal event. As in the case of $Cs[(CH_3)_2Sn(SO_3F)_3]$, more definitive differentiating features are expected from the spectroscopic measurements.

Vibrational Spectra. Vibrational information comes primarily from infrared spectra because only poor Raman spectra are obtainable due to interference from fluorescence.

The metal salts $Sn[(CH_3)_2Sn(SO_3F)_4]$, $Ba[(CH_3)_2Sn(SO_3F)_4]$, and $Li_2[(CH_3)_2Sn(SO_3F)_4]$ are all expected to have the same anion and therefore similar spectra. This is indeed the case and the band positions for the three compounds are listed in Table I, together with an approximate assignment. The spectra are in all cases dominated by the bands attributed to the SO_3F group. The CH_3 stretching and bending modes are, in compounds of this type, notoriously weak and only seen in rather concentrated mulls. The Sn–C asymmetric stretch at ~590 cm^{-1} is obscured by SO_3 bending modes and is not clearly assignable. The Sn–CH_3 rocking mode at around 800 cm^{-1} is rather intense, however, and clearly separated in all cases from the S–F stretch expected in this region. Assignment of the higher frequency band at ~820 cm^{-1} as Sn–CH_3 rock is based on the spectrum of the recently reported $Cs_2[(CH_3)_2Sn(SO_3CF_3)_4]$[9] where a strong band at 825 cm^{-1} is found and no ambiguity exists. The ν_{SF} is hence assigned to a band at 800 cm^{-1} or slightly below.

The stretching fundamentals for the fluorosulfate group result in an interesting pattern. The SO_3 stretching modes at approximately 1350, 1230, and 1080 cm^{-1} are very reminiscent of ionic fluorosulfate groups where two bands at ~1280 and 1080 cm^{-1}

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(16) Mallela, S. P.; Sams, J. R.; Aubka, F. *Can. J. Chem.* **1985**, *63*, 3305.

are usually found.[17] Coordination to tin(IV) reduces the symmetry below C_{3v} and the E mode at 1280 cm^{-1} for SO_3F^- is split and seemingly slightly lowered. This splitting is ~100 cm^{-1} for the Ba^{2+} and Li^+ salts and is slightly larger at ~165 cm^{-1} for the Sn^{2+} salt, indicative of a stronger polarizing effect exerted by this cation. In this compound the third SO_3 stretch at ~1075 is split into three components for the same reason. Weak splittings affect also the deformation mode at ~590 cm^{-1} and the rocking mode at ~410 cm^{-1}. Finally the band positions for ν_{SF} at 800 cm^{-1} or slightly below are consistent with weakly coordinated SO_3F^- ions in these compounds. Very weak, unassigned bands occur in all three spectra at 970, 915, and 480 cm^{-1}.

For salts of the type M^{2+} or $M_2{}^+[Sn(SO_3F)_6]$,[10,18] an entirely different band pattern emerges for the fluorosulfate group with ν_{SO_3} at ~1420, ~1210, and ~1000 cm^{-1} and ν_{SF} at ~850 cm^{-1}, more indicative of monodentate OSO_2F groups strongly coordinated to tin. In addition, strong and medium broad bands between 630 and 640 and at 440 cm^{-1}, attributed in part to the Sn–O skeletal vibrations, are not observed for the dimethyltin(IV) compounds discussed here.

A more complicated problem is encountered when the spectra of $Cs_2[(CH_3)_2Sn(SO_3F)_4]$ and $Cs[(CH_3)_2Sn(SO_3F)_3]$ are compared. Band positions for the former in the SO_3F stretching region do not differ markedly from the spectra in Table I. For $Cs[(CH_3)_2Sn(SO_3F)_3]$ some interesting departures are noted, resulting in greater complexity. Bands in the SO_3 stretching range at 1320 and 1150 cm^{-1} are tentatively assigned to a bidentate configuration, assumed to be bridging between two anions, with the third band expected at ~1080 cm^{-1}, possibly obscured by the third band due to the coordinated SO_3F^-. Also interesting are two SF stretching modes at 805 and 788 cm^{-1}, observed in addition to the $Sn–CH_3$ rocking mode at 830 cm^{-1}. The presence of both bridging bidentate and singly coordinated SO_3F^- is suggested, resulting in a distorted octahedral environment around tin.

Compared to the rather straightforward bidentate symmetrically bridging configuration of the fluorosulfate in α-$(CH_3)_2Sn(SO_3F)_2$, supported also by the crystal structure,[7] the spectrum of the β form is much more complex in the SO_3 stretching region. Bands due to a bidentate configuration (at 1345, 1185, and 1090 cm^{-1}) are found in addition to partly overlapping bands due to coordinated SO_3F and monodentate OSO_2F groups (at 1280 and 970 cm^{-1}). While it is difficult to provide a complete assignment, it appears a different structural form is present with a far less regular deployment of the SO_3F groups about tin.

^{119}Sn Mössbauer Spectra. In fluorosulfate complexes containing a dimethyltin moiety, the Mössbauer isomer shifts, δ, and quadrupole splittings, ΔE_Q, are both dominated by the strongly covalent and linear C–Sn–C arrangement, which may be taken to define the z axis of the electric field gradient (EFG), and show only a modest dependence on interactions with the SO_3F groups in the xy plane.[1,2,4-6,9] Thus, δ values in the vicinity of 1.8 mm s^{-1} (relative to SnO_2), and ΔE_Q values near 5.5 mm s^{-1} are expected for the present compounds, and such values are indeed found (Table III). A few comments on specific complexes are in order here.

As noted above, the high thermal stability and more complex vibrational spectrum of $Cs[(CH_3)_2Sn(SO_3F)_3]$ argue in favor of this being a genuine compound and not an equimolar mixture of $Cs_2[(CH_3)_2Sn(SO_3F)_4]$ and $(CH_3)_2Sn(SO_3F)_2$. The Mössbauer data support this conclusion, since for such a mixture ΔE_Q should not be less than 5.5 mm s^{-1}. Also, because the parameters for the latter two complexes do not exactly coincide, one would expect to see rather broad lines for a mixture of the two, but this is not observed.

It is interesting to note that the quadrupole splitting of 5.39 mm s^{-1} for $Cs[(CH_3)_2Sn(SO_3F)_3]$ is slightly lower than the 5.50 mm s^{-1} value found for $Cs_2[(CH_3)_2Sn(SO_3F)_4]$, while the isomer shifts are identical within error limits. The lower value is attributed to a slightly distorted octahedral coordination environment of tin due to the presence of both bridging bidentate and terminal fluorosulfate groups.

Table II. Infrared Spectra of α-$(CH_3)_2Sn(SO_3F)_2$, β-$(CH_3)_2Sn(SO_3F)_2$, $Cs[(CH_3)_2Sn(SO_3F)_3]$, and $Cs_2[(CH_3)_2Sn(SO_3F)_4]$ between 1500 and 400 cm^{-1}

ν, cm^{-1} (int)			
α-$(CH_3)_2$-$Sn(SO_3F)$[a]	β-$(CH_3)_2$-$Sn(SO_3F)_2$	$Cs[(CH_3)_2$-$Sn(SO_3F)_3]$	$Cs_2[(CH_3)_2$-$Sn(SO_3F)_4]$[b]
[1455 (m)][c]	[1430 (w)]	1420 (m)	1360 (s, sh)
		1368 (s, sh)	1360 (s, sh)
1350 (vs)	1345 (vs, b)	1340 (vs, b)	1335 (vs, b)
	1280 (mw)	1320 (m, sh)	
		1245 (m, sh)	
[1222 (m, sh)]	[1222 (m)]	[1225 (s, sh)]	
	1185 (s, b)	1205 (s, sh)	[1210 (s, sh)]
		1185	
1180 (vs, b)	1150 (m, sh)	1150 (m, sh)	1185 (vs, b)
	1120 (s)		
1088 (m, sh)	1090 (s, sh)	1082 (s)	
1072 (s, b)	1050 (m, sh)	1055 (vs)	1065 (s, sh)
	970 (s)	1030 (mw)	1050 (vs)
	900 (w)	890 (w)	924 (m), 882 (w)
[827 (s, sh)]	[818 (vs, b)]	[830 (s, sh)]	[830 (s, sh)]
798 (vs, b)	790 (s)	805 (s, sh)	
650 (vw)		788 (vs)	765 (vs)
620 (m, sh)	615 (w, sh)	610 (w)	600 (m, sh)
590 (m, s)	600 (ms)	600 (m)	590 (s, sh)
576 (s)	580 (m, sh)	585 (m)	578 (s)
554 (ms)	560 (m)	565 (m)	558 (s)
417 (s)	420 (m)	420 (m)	415 (ms)
		402 (m)	410 (w)
360 (w)			

[a] Reference 2. [b] Reference 9. [c] Brackets indicate $SnCH_3$ fundamentals.

Table III. ^{119}Sn Mössbauer Data at 77 K

compd	isomer shift[a,b] δ, mm s^{-1}	quadrupole splitting[a] ΔE_Q, mm s^{-1}	line widths[a,c] Γ, mm s^{-1}		ref
$Cs_2[(CH_3)_2Sn(SO_3F)_4]$	1.83	5.50	0.97	0.94	9
$Li_2[(CH_3)_2Sn(SO_3F)_4]$	1.77	5.42	0.98	1.04	this work
$Ba[(CH_3)_2Sn(SO_3F)_4]$	1.76	5.37	1.19		this work
$Sn[(CH_3)_2Sn(SO_3F)_4]$[d]	1.87	5.38	*g*		this work
$Sn[(CH_3)_2Sn(SO_3F)_4]$[e]	3.84		*g*		this work
$Cs[(CH_3)_2Sn(SO_3F)_3]$	1.80	5.39	0.95	0.99	this work
α-$(CH_3)_2Sn(SO_3F)_2$[f]	1.82	5.58	1.13	1.18	this work
β-$(CH_3)_2Sn(SO_3F)_2$	1.80	5.48	0.94	1.07	this work

[a] Error limit ±0.03 mm s^{-1}. [b] Relative to $BaSnO_3$ at 77 K. [c] Full width at half height; no constraints imposed. [d] Tin(IV) environment. [e] Tin(II) environment. [f] Remeasured; see also ref 1 and 2. [g] See text.

By a similar argument, the complex we have here called the β-isomer of $(CH_3)_2Sn(SO_3F)_2$ is unlikely to be either of the ionization isomers $[(CH_3)_2Sn(SO_3F)]_2[(CH_3)_2Sn(SO_3F)_4]$ or $(CH_3)_2Sn[(CH_3)_2Sn(SO_3F)_4]$, since on the basis of previous work[9] the cationic species in either of the latter derivatives should have $\delta \geq 1.90$ mm s^{-1}. Thus, overlapping spectra from cationic and anionic species in such complexes would result in very substantial line broadening. The line widths, however, are quite normal, and there is no reason to suppose on the basis of the Mössbauer spectra that there is more than one tin environment present in this complex. Within experimental error the isomer shift and quadrupole splitting for β-$(CH_3)_2Sn(SO_3F)_2$ at 77 K are essentially the same as those of the previously reported α-isomer. An important difference between the two forms, however, is that whereas the α-isomer gives a strong Mössbauer absorption at 298 K, no room-temperature resonance could be detected for the newly prepared complex.

The four complexes that contain the $[(CH_3)_2Sn(SO_3F)_4]^{2-}$ anion have isomer shifts and quadrupole splittings in the narrow ranges $\delta = 1.82 \pm 0.06$ mm s^{-1}, and $\Delta E_Q = 5.44 \pm 0.07$ mm s^{-1}. There is no evident systematic dependence of isomer shift on the nature of the cation, which is perhaps not surprising. For the quadrupole

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[17] Qureshi, A. M.; Carter, H. C.; Aubke, F. *Can. J. Chem.* **1971**, *49*, 35.

[18] Yeats, P. A.; Sams, J. R.; Aubke, F. *Inorg. Chem.* **1973**, *59*, 189.

splitting, however, the Ba^{2+}, Sn^{2+}, and Li^+ derivatives all have identical values within experimental error (5.39 ± 0.03 mm s^{-1}), whereas that for the Cs^+ salt is higher at 5.50 mm s^{-1}. The reason for this may be that Cs^+ is the largest and least polarizing of these four cations.

The only complex studied here that contains both divalent and tetravalent tin, $Sn[(CH_3)_2Sn(SO_3F)_4]$, has a Mössbauer spectrum at 77 K consisting of a line at −0.82 mm s^{-1} and a broader absorption envelope of approximately twice the area centered at about +4.2 mm s^{-1}. The latter is readily resolved into two lines at 3.84 and 4.56 mm s^{-1}. From this spectrum and the nature of the compound it is clear that one of these high-velocity lines must be paired with the line at negative velocity to form a quadrupole doublet arising from the Sn(IV) site, while the remaining line is attributable to the Sn(II) site. There are then two ways of assigning the lines and two correspondingly different possible sets of Mössbauer parameters. As all three lines have very similar widths and intensities, area considerations are not helpful in choosing the correct assignment. If we assume a "nested" configuration such that lines 1 and 3 (numbering from low to high velocity) belong to Sn(IV) and line 2 to Sn(II), we obtain δ = 1.87 mm s^{-1} and ΔE_Q = 5.38 mm s^{-1} for the Sn(IV) site and δ = 3.84 mm s^{-1} for the Sn(II) species. The alternative "crossed" configuration gives δ = 1.51 mm s^{-1} and ΔE_Q = 4.66 mm s^{-1} for Sn(IV) and δ = 4.56 mm s^{-1} for Sn(II).

The nested configuration provides δ and ΔE_Q values for the $[(CH_3)_2Sn(SO_3F)_4]^{2-}$ ion that are very similar to those in the corresponding Ba^{2+}, Li^+, and Cs^+ salts, although the δ value for Sn(II) is substantially below the value for this ion in $Sn[Sn(SO_3F)_6]$.[9] On the other hand, the crossed configuration gives unreasonably low values of both δ and ΔE_Q for the Sn(IV) site in $Sn[(CH_3)_2Sn(SO_3F)_4]$. In view of the fact that all other complexes we have studied that contain the species $[(CH_3)_2Sn]^{2+}$, $[(CH_3)_2Sn(SO_3F)]^+$, $(CH_3)_2Sn(SO_3X)_2$, and $[(CH_3)_2Sn(SO_3X)_4]^{2-}$ (X = F, CF_3) show δ = 1.88 ± 0.14 mm s^{-1} and ΔE_Q = 5.54 ± 0.16 mm s^{-1} at 77 K, it would seem impossible to explain the Sn(IV) parameters obtained for the crossed configuration. We therefore take the nested configuration to be correct, and the parameters shown in Table III were derived accordingly.

The low isomer shift value for the Sn(II) ion in $Sn[(CH_3)_2Sn(SO_3F)_4]$, compared to those found in $Sn[Sn(SO_3X)_6]$ (X = F, CF_3), is indicative of a significantly lower 5s electron density in this case. This could arise from a somewhat stronger cation–anion interaction, probably via bridging SO_3F groups. Such an interaction would cause a much more significant perturbation of the Sn(II) ion that of the Sn(IV) site, so it is not too surprising that the Mössbauer parameters of the anion are similar to those in the other three salts containing this species. In view of the small Sn(II) isomer shift we might expect to see a quadrupolar interaction at this ion arising from an imbalance in 5p orbital charge densities, as observed[14,15] in $Sn(SO_3X)_2$ (X = F, CF_3). However, the Sn(II) line in $Sn[(CH_3)_2Sn(SO_3F)_4]$ is not unduly broad, and it may be that any 5p electron density on the Sn(II) ion is fairly evenly distributed amongst the three p orbitals. In any case, the overlap of the Sn(II) absorption with the high-velocity component of the Sn(IV) doublet would make it difficult to resolve the former into two lines, and no attempt to do so has been made.

Consistent with the suggestion of significant cation–anion interaction in $Sn[(CH_3)_2Sn(SO_3F)_4]$ is the observation of a weak ^{119}Sn Mössbauer spectrum at room temperature, in contrast to the case of $Cs_2[(CH_3)_2Sn(SO_3F)_4]$ (and the corresponding SO_3CF_3 salt),[9] where no room temperature spectra were seen. However, the effect was so small (~0.3% absorption for the envelope of maximum intensity) that a satisfactory fit of the spectrum to three lines could not be achieved. A two-line fit gave an area ratio of about 2:1 for the two absorption envelopes, similar to the value at 77 K, suggesting that at both temperatures the Sn(II) site is responsible for ~$^1/_3$ of the total spectral area. Weak room-temperature spectra were also seen for the lithium and barium salts reported here.

Finally, it is appropriate to comment on a recent paper in which Birchall and Manivannan[12] reported, inter alia, Mössbauer data for a frozen solution of $(CH_3)_2Sn(SO_3F)_2$ in HSO_3F. As noted above, their ^{119}Sn NMR spectra suggested the presence of more than one tin species in solution at low temperature. In frozen solution an asymmetric two-line Mössbauer spectrum was observed, which the authors were able to deconvolute into two quadrupole doublets, with δ_1 = 1.94 mm s^{-1}, ΔE_{Q1} = 5.51 mm s^{-1}; δ_2 = 1.73 mm s^{-1}, and ΔE_{Q2} = 5.08 mm s^{-1}. From these values it can be deduced that the low-velocity lines of these two doublets coincide at −0.81 mm s^{-1}; this set of parameters is therefore unique if the spectrum is assumed to consist of two quadrupole pairs. Birchall and Manivannan[12] attribute both these doublets to polymeric solution species consisting of linear $(CH_3)_2Sn$ moieties with four fluorosulfate groups completing the tin octahedron, the latter either hydrogen bonded to solvent molecules or cross-linked to adjacent $(CH_3)_2Sn$ units. The second structure is identical with that of $(CH_3)_2Sn(SO_3F)_2$ in the solid state.[7] Although the latter solution species could conceivably give rise to the quadrupole doublet with the larger splitting, we doubt very strongly that the doublet with ΔE_Q = 5.08 mm s^{-1} could possibly result from a linear $(CH_3)_2Sn$ group in the presence only of fluorosulfate ions, whether in solution or in the solid state. As noted above, all known complexes of this type have quadrupole splittings that cover a very narrow range and the smallest value yet found is 5.37 mm s^{-1}, and we cannot conceive of any mechanisms that would lead to a splitting of only 5.08 mm s^{-1} for a linear $(CH_3)_2Sn$ species in fluorosulfuric acid.

NMR Studies in HSO_3F. α-$(CH_3)_2Sn(SO_3F)_2$ and all anionic dimethyltetrakis(fluorosulfato)tin(IV) derivatives are sufficiently soluble in HSO_3F for a complete range of multinuclear NMR studies to be undertaken, at temperatures of +25 to −90 °C. Only in the case of $Ba[(CH_3)_2Sn(SO_3F)_4]$ does the ^{13}C NMR spectrum, taken at −90 °C, show a marked deterioration caused by solute crystallization. In general, concentrations between 0.43 and 1.16 M were found suitable and were readily attainable. On the other hand, $(CH_3)_2Sn(SO_3CF_3)_2$ was found to be insufficiently soluble in its parent acid and no ^{119}Sn resonance could be observed even at room temperature.

The presence of four suitable nuclei in all solutes, ^1H, ^{13}C, ^{19}F, and ^{119}Sn is expected to provide interesting structural information, but these expectations are only realized for ^{13}C and ^{119}Sn NMR studies.

The ^1H NMR spectra are, in agreement with previous work in HSO_3F,[6,13] straightforward. A single resonance due to the methyl protons is observed over the whole temperature range between δ = 1.55 to ~1.80 relative to Me_4Si, and depending on solute, the solvent proton resonance is found between δ = 8.00 and ~9.0.

The ^{19}F NMR spectra obtained on ~1 M solutions of three of the solutes show single resonances only with the following peak positions (low temperature values at −90 °C in parentheses): for α-$(CH_3)_2Sn(SO_3F)_2$, 40.7 ppm (41.6 ppm); for $Cs[(CH_3)_2Sn(SO_3F)_3]$, 40.3 ppm (41.6 ppm); for $Cs_2[(CH_3)_2Sn(SO_3F)_4]$ 40.5 ppm (41.7 ppm). The values are all relative to $CFCl_3$ and are very similar indeed and hardly shifted from the solvent resonance at 40.56 ppm.

While rapid SO_3F^- exchange is expected for the first two solutes, a separation into solvent and solute resonance is anticipated for the $[(CH_3)_2Sn(SO_3F)_4]^{2-}$ anion, in analogy to solutions of $[Sn(SO_3F)_6]^{2-}$ in HSO_3F studied previously at room temperature.[10]

The failure to observe an independent resonance for the anion $[(CH_3)_2Sn(SO_3F)_4]^{2-}$ appears to be caused by rapid SO_3F–HSO_3F exchange and is consistent with the structural difference between the two anions, apparent from the vibrational spectra, which had suggested a greater degree of covalency for $[Sn(SO_3F)_6]^{2-}$ and weakly coordinated SO_3F^- ion for $[(CH_3)_2Sn(SO_3F)_4]^{2-}$.

The ^{13}C NMR data are summarized in Table IV. The proton-decoupled spectra show single-line resonances with ^{119}Sn satellite peaks in most of the room-temperature spectra resolved. Chemical shifts vary little from one solute to the other, and no marked temperature dependence is noted. Agreement with recently reported room-temperature data on $(CH_3)_2Sn^{2+}$(solv) is very good.[13] As for the proton spectra, there is no splitting of the

Table IV. ^{13}C Nuclear Magnetic Resonance Data for Dimethyltin(IV) Fluorosulfate Derivatives in HSO_3F

solute	temp, °C	concn, mol L^{-1}	chem shift,^{c} δ	$J(^{119}Sn-^{13}C)$, Hz	$(^{117}Sn-^{13}C)$, Hz
$(CH_3)_2Sn(SO_3F)_2$	*d*	1.16	15.1	596	569
$(CH_3)_2Sn(SO_3F)_2$	−90	1.16	15.3	604^a	
$Cs[(CH_3)_2Sn(SO_3F)_3]$	*d*	0.9	14.2	616	594
$Cs[(CH_3)_2Sn(SO_3F)_3]$	−90	0.9	14.8	604^a	
$Cs_2[(CH_3)_2Sn(SO_3F)_4]$	*d*	0.8	14.2	633	603
$Cs_2[(CH_3)_2Sn(SO_3F)_4]$	−90	0.8	14.5	604^a	
$Ba[(CH_3)_2Sn(SO_3F)_4]$	*d*	1.0	14.6	633^a	
$Ba[(CH_3)_2Sn(SO_3F)_4]$	−90	1.0	14.3	*b*	
$Sn[(CH_3)_2Sn(SO_3F)_4]$	*d*	0.64	14.5	590	578
$Li_2[(CH_3)_2Sn(SO_3F)_4]$	*d*	1.0	14.6	631^a	

^{a}Denoted $J(^{117/119}Sn-^{13}C)$. ^{b}Weak resonance due to solute crystallization. ^{c}Relative to tetramethylsilane. ^{d}Room temperature.

peaks noted at −90 °C. The coupling constants $^1J(^{119}Sn-^{13}C)$, $^1J(^{119/117}Sn-^{13}C)$, and $^1J(^{117}Sn-^{13}C)$ range from ~570 to ~630 Hz and again agree well with previous work in HSO_3F[13] on the solvolysis of methylstannanes.

A recently reported relationship between $^1J(^{119}Sn-^{13}C)$ and the C–Sn–C bond angle[14] on the other hand would suggest a bond angle of ~120° in all instances. It should be pointed out however that the octahedral dialkyltin species studied[14] are coordination complexes formed with bidentate chelating ligands such as acetylacetonate, with $CDCl_3$ as the solvent, and that the $^1J(^{119}Sn-^{13}C)$ vs. C–Sn–C relationship is based on five closely related examples only and may not be generally applicable. The difference in the nature of both the compounds studied and solvents used also limits comparison to earlier[19,20] correlations between $^1J(^{119}Sn-^{13}C)$ and coordination number on solution studies, and even very recent bond angle–coupling constant relations based on cross-polarization magic-angle spinning (CPMAS) ^{13}C solid-state NMR[21] are not applicable. Disappointingly, CPMAS studies on $(CH_3)_2SnF_2$, the only compound studied with some features similar to those displayed by the dimethyltin(IV) fluorosulfate derivatives discussed here, does not yield a $^1J(^{119}Sn-^{13}C)$ value.[22]

It appears then that structural and bonding dissimilarities between cationic dimethyltin(IV) derivatives studied here and dimethyltin(IV) coordination complexes measured generally[14,19,21] severely restrict comparisons and the generalization of possibly quite reasonable correlations. Due to the stated lack of comparisons a greater emphasis needs to be placed on internal consistency of data and comparison with immediately relevant studies as those of Birchall and his co-workers.[6,12,13]

Such comparisons have generally produced excellent agreement, as stated; however, some discrepancies emerge when the ^{119}Sn NMR data are compared. Our results are summarized in Table V and reflect for all solutes concentration, temperature, and field dependence of the chemical shifts, in agreement with the earlier study of $(CH_3)_2Sn(SO_3F)_2$ in HSO_3F.[12] However, there is disagreement regarding the chemical shift observed at room temperature and the low-temperature spectra. All solutes studied by us show a 25 °C sharp single-line ^{119}Sn resonance between ~−200 and −227 ppm relative to tetramethyltin for the spectra obtained at 7.10 T with some dependence on the solute; e.g., for 0.64 M solutions, the resonance moves upfield from −204 ppm for $Cs_2[(CH_3)_2Sn(SO_3F)_4]$. On the other hand, the resonance for $Cs[(CH_3)_2Sn(SO_3F)_3]$ is observed at −201 ppm. A slight upfield shift is also noted on addition of 2 mol of $CsCO_3F$ to a 0.64 M solution of $(CH_3)_2Sn(SO_3F)_2$. No pronounced cation dependency of the resonance for several dimethyltetrakis(fluorosulfate)tin(IV) derivatives is noted with the highest chemical shift found for the Ba^{2+} salt at 25 °C.

The lack of solubility found for $(CH_3)_2Sn^{2+}$ and $(CH_3)_2Sn(SO_3F)^+$ derivatives with $M(SO_3F)_6^{2-}$ (M = Pt or Sn[9]) prompted us to generate an acidic medium by the addition of ~1 M SbF_5 to an equimolar solution of $(CH_3)_2Sn(SO_3F)_2$. The resulting upfield shift to −230 ppm must be viewed with caution, because the presence of $[SbF_n(SO_3F)_{6-n}]^-$ and similar magic acid anions may change the immediate coordination environment of the $(CH_3)_2Sn$ moiety from oxygen only to oxygen–fluorine.

Table V. ^{119}Sn Nuclear Magnetic Resonance Chemical Shifts for Dimethyltin(IV) Fluorosulfate Derivatives in HSO_3F at 111.86 MHz (7.10 T)

solute	concn, mol L^{-1}	temp, °C	δ rel to TMT	$\Delta W_{1/2}$, Hz
$(CH_3)_2Sn(SO_3F)^a$	1.16	*d*	−200	74
$(CH_3)_2Sn(SO_3F)_2$	1.16	−90	−230	1261
$(CH_3)_2Sn(SO_3F)_2$	1.16	*d*	−205	55
$(CH_3)_2Sn(SO_3F)_2$	1.16	−75	−234	2237
$(CH_3)_2Sn(SO_3F)_2$	0.64	*d*	−204	89
$(CH_3)_2Sn(SO_3F)_2$ at 1.89 T	0.64	*d*	−196	20
$(CH_3)_2Sn(SO_3F)_2$ + 1 M SbF_5	~1.0	*d*	−230	120
$(CH_3)_2Sn(SO_3F)_2$ + 2 mol of $CsSO_3F$	0.64	*d*	−207	sharp
$Cs_2[(CH_3)_2Sn(SO_3F)_4]$	0.80	*d*	−215	75
$Cs_2[(CH_3)_2Sn(SO_3F)_4]$	0.80	−75	−242	1455
$Cs_2[(CH_3)_2Sn(SO_3F)_4]$	0.64	*d*	−214	1.78
$Cs_2[(CH_3)_2Sn(SO_3F)_4]$	0.43	*d*	−199	91
$Cs_2[(CH_3)_2Sn(SO_3F)_4]$ at 1.89 T	0.64	*d*	−209	sharp
$Cs[(CH_3)_2Sn(SO_3F)_3]$	0.9	*d*	−210	72
$Cs[(CH_3)_2Sn(SO_3F)_3]$	0.9	−70	−233	1450
$Cs[(CH_3)_2Sn(SO_3F)_3]$	0.64	*d*	−201	71
$Li_2[(CH_3)_2Sn(SO_3F)_4]$	0.9	*d*	−221	80
$Ba[(CH_3)_2Sn(SO_3F)_4]$	1.0	*d*	−227	137
$Sn[(CH_3)_2Sn(SO_3F)_4]^b$	0.9	*d*	−211	67
$Sn[(CH_3)_2Sn(SO_3F)_4]$	0.9	−90	−241	3540
$Sn[(CH_3)_2Sn(SO_3F)_4]$	0.64	*d*	−203	112
$Sn[(CH_3)_2Sn(SO_3F)_4]^c$	0.9	*d*	+238	88
$Sn(SO_3F)_2$	~0.5	*d*	+274	67
$Cs_2[Sn(SO_3F)_6]$	0.57	*d*	−891	18

^{a}Solute prepared in situ by solvolysis of $(CH_3)_3SnCl$. ^{b}Denotes Sn(IV) resonance. ^{c}Denotes Sn(II) resonance. ^{d}Room temperature.

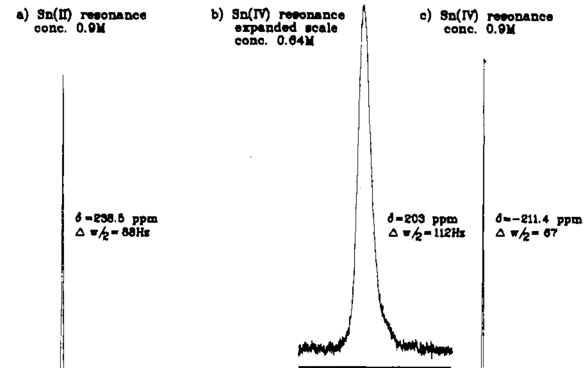

Figure 1. ^{119}Sn NMR spectrum of $Sn[(CH_3)_2Sn(SO_3F)_4]$ in HSO_3F at 25 °C. Reference: tetramethyltin at 111.86 MHz (7.10 T).

Dissolution of $Sn[(CH_3)_2Sn(SO_3F)_4]$ in HSO_3F generates the $[(CH_3)_2Sn(SO_3F)_4]^{2-}$(solv) ion in solution, resulting in a sharp

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(19) Mitchell, T. N. *J. Organomet. Chem.* **1973**, *59*, 189.

(20) Davies, A. G.; Smith, P. J. In *Comprehensive Organometallic Chemistry*; Wilkinson, G.; Stone, F. G. A.; Abel, E. W., Eds.; Pergamon: Oxford, England, 1982; Vol. 2, p 529.

(21) Lockhart, T. P.; Manders, W. F.; Zuckerman, J. J. *J. Am. Chem. Soc.* **1985**, *107*, 4546.

(22) Lockhart, T. P.; Manders, W. F. *J. Am. Chem. Soc.* **1985**, *107*, 5863.

resonance at −211 ppm relative to $(CH_3)_4Sn$. As shown in the figure, an equally sharp resonance line of comparable intensity is observed at $\delta = +238$. This resonance is attributed to a solvated Sn^{2+} cation, with support derived from a sharp resonance at $\delta = +274$ measured on a ~0.5 M solution of $Sn(SO_3F)_2$ in HSO_3F.

This assignment is at variance with previous reports. Solvolysis of methylstannanes of the formula $(CH_3)_{4-n}SnH_n$ in HSO_3F had generated a resonance at −1780 ppm,[23] or as reported more recently[13] at −1601 ppm assigned to Sn^{2+}(solv), with solutions of $Sn(SO_3F)_2$ in HSO_3F reportedly giving a resonance in the same region.[13] In spite of extensive efforts on our part, we are unable to detect any resonance in solutions of $Sn(SO_3F)_2$ in HSO_3F other than the one at 274 ppm listed in Table V.

Finally, the spectrum of $[Sn(SO_3F)_6]^{2-}$ discussed previously by us[10] is included in Table V. The sharp resonance at −891 ppm is clearly separated from the spectra produced by the dimethyltin(IV) fluorosulfate species in HSO_3F. The location of the resonance compares well with a δ value of −810.8 reported for SnF_6^{2-}.[24] The absence of a resonance in this region rules out for all the $(CH_3)_2Sn^{2+}$ derivatives studied here that either further acidolysis by HSO_3F or ligand rearrangement reactions leading to $[Sn(SO_3F)_6]^{2-}$ occur at room temperature.

The chemical shifts with δ between ~−200 to −227 for all dimethyltin(IV) fluorosulfate species studied here agree reasonably well, considering differences in concentration and field strength, with room temperature values of −185 and −183 ppm, respectively, observed during the solvolysis of $(CH_3)_2SnH_2$ in HSO_3F[13] and attributed to $(CH_3)_2Sn^{2+}$. They differ from a value of −106 ppm reported for a 1.16 M solution of $(CH_3)_2Sn(SO_3F)_2$ in HSO_3F at 93.2 MHz.[12] Our measurements at 111.86 MHz on solutions of identical concentration with $(CH_3)_2(SO_3F)_2$ either redissolved after isolation and analysis or generated from $(CH_3)_3SnCl$ in situ give chemical shifts of −200 and −205 ppm, respectively, with $\Delta W_{1/2}$ of 74 and 55 Hz, respectively, also quite different from the reported value of 460 Hz.[12]

Likewise the temperature dependence of the ^{119}Sn resonances differs. In all instances the resonance shifts upfield, usually by approximately 30 ppm on lowering the temperature to −75 °C or in one instance to −90 °C, and broadens considerably. No splitting of the line is observed in any instance, and we are unable to confirm reported lines at −14 and 7.3 ppm at a temperature of −75 °C.

It remains to point out that our measurements, with one exception as noted in Table V are obtained on solutions formed by redissolving previously isolated, analytically pure fluorosulfate solutes. The results obtained for ^{13}C, ^{1}H, and ^{119}Sn NMR are internally consistent and point to a similar electronic structure for the dimethyltin(IV) moiety in all instances. These results are also consistent with the ^{119}Sn Mössbauer spectra of the various solutes with a rather narrow range of isomer shift and quadrupole splittings, and the temperature dependence of the ^{119}Sn chemical shift is rather similar to the behavior of $(C_2H_5)_2Sn(SO_3F)_2$ reported by Birchall and Manivannan,[12] except for a general upfield shift to −253 ppm at room temperature. This reported discrepancy[12] between dimethyl- and diethyltin bis(fluorosulfate) solutions again is not reflected in their respective Mössbauer spectra.[4]

Our results suggest that all dimethyltin(IV) fluorosulfate species studied in solution of HSO_3F have a common species, a linear dimethyltin(IV) moiety with the coordination environment completed to coordination number 6 for tin by either fluorosulfate anion or HSO_3F depending on the type of solute used with SO_3F–HSO_3F as well as proton exchange between solvent and solute providing plausible pathways. Such a monomeric species can be described by the general formula $[(CH_3)_2Sn(SO_3F)_n(HSO_3F)_{4-n}]^{(2-n)+}$. In addition, at higher concentration or lower temperature, solute association via fluorosulfate bridges is possible with retention of the coordination environment for tin resulting in rather similar ^{1}H, ^{13}C and, ^{119}Sn spectra, reflecting an invariant electronic structure of the dimethyltin(IV) group.

Conclusions. The ability of dimethyltin(IV) fluorosulfate to act as a SO_3F^- acceptor found recently[9] is substantiated by the isolation and characterization of $Cs[(CH_3)_2Sn(SO_3F)_3]$ and additional salts containing the $[(CH_3)_2Sn(SO_3F)_4]^{2-}$ ion with the countercations Li^+, Ba^{2+}, and Sn^{2+}. The ^{119}Sn Mössbauer spectra show a rather narrow range in both the isomer shift ($\delta = 1.8$ to ~1.9 mm s^{-1}) and the quadrupole splitting ($\Delta E_Q = \sim 5.4$–5.6 mm s^{-1}) and differ little from the data recently reported[9] for cationic dimethyltin(IV) fluorosulfate derivatives.

Our conclusion that the Mössbauer spectra are dominated by the $(CH_3)_2Sn$ moiety and are rather insensitive to the variations in bidentate, anisobidentate, or ionic SO_3F groups completing the coordination sphere of tin extends also to solutions in HSO_3F, as the ^{1}H (CH_3), ^{13}C, and ^{119}Sn NMR spectra between +25 and −90 °C indicate.

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(23) Webster, J. R.; Jolly, W. L. *Inorg. Chem.* **1971**, *10*, 877.

(24) Dillon, K. B.; Marshall, A. *J. Chem. Soc., Dalton Trans.* **1984**, 1245.