single crystals become available for principal susceptibilities study at very low temperatures, we speculate that they are likly to demonstrate that $[Co(NH_3)_6][FeCl_6]$ is an excellent example of a near perfect easy-axis antiferromagnet as opposed to a metamagnet. The likely small anisotropy field (H_A) and implied ($T_{Néel}$ only ~0.9 K) low value of exchange field (H_E) lead to the prediction of rather easily induced transformations in its H vs. T phase diagram. For instance one can study the antiferromagnetic to spin–flop transition ($H_{SF}\ \alpha\ (2H_AH_E)^{1/2}$) or at higher values of applied field spin–flop to "paramagnetic" transformation. We find that these can often[1] be observed in applied-field Mössbauer spectra even for powder samples (e.g., $H_{SF}[Co(pn)_3][FeCl_6]$ is ~10 kG).

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Synthesis and ^{119}Sn Mössbauer Spectra of Novel Cationic Tin(II) and Dimethyltin(IV) Compounds

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A systematic synthetic study is undertaken to obtain cationic derivatives of the tin(II) and dimethyltin(IV) cations, stabilized by weakly basic acid and superacid anions. Besides the mixed-valency compound $Sn^{II}[Sn^{IV}(SO_3F)_6]$, three types of dimethyltin compounds are reported: $(CH_3)_2Sn[M(SO_3F)_6]$ and $[(CH_3)_2Sn(SO_3F)]_2[M(SO_3F)_6]$ (M = Sn, Pt) and salts containing the $[(CH_3)_2Sn(SO_3F)_4]^{2-}$ anion. In addition some of the corresponding SO_3CF_3 derivatives are obtained as well. The solution behavior of the principal reactants in the reaction medium HSO_3F provides a rationale for the course of the various synthetic reactions. ^{119}Sn Mössbauer spectra provide evidence for an undistorted environment for Sn^{2+} and linear C–Sn–C groupings for all $(CH_3)_2Sn$-derivatives. Quadrupole splittings are found in the region 5.5–5.7 mm s^{-1} and represent the largest values reported for tin so far.

Introduction

Two dipositive cations of tin, the tin(II) ion, Sn^{2+}, and, representative for all diorganotin(IV) cations, the dimethyltin(IV) cation, $(CH_3)_2Sn^{2+}$, form the focal point of this study. Both have many common but also many diverging characteristics. The oxidation state of tin differs in the two cations, but the common ionic charge of +2 suggests formation of ionic solids with identical or similar anions. The electronic structures of the cations differ again. For the atomic ion Sn^{2+}, a valence electron configuration of $5s^2$ is expected. The molecular $(CH_3)_2Sn^{2+}$ ion is expected to have a perfectly linear C–Sn–C group, suggesting a 5sp hybridization on tin. As a direct reflection of the electronic structure of tin in the two cations, the ^{119}Sn Mössbauer spectra should differ markedly. A perfectly spherical $5s^2$ pair on Sn^{2+} should not cause any quadrupole splitting, while the high 5s-electron density suggests a high isomer shift, and a value of $\delta = +4.84$ mm s^{-1} relative to SnO_2 has been calculated.[1,2] For $(CH_3)_2Sn^{2+}$ an intermediate isomer shift of $\delta \sim 2.0$ mm s^{-1} relative to SnO_2 and a very large quadrupole splitting are expected.

Common to both cations is the frequently reported[3,4] observation that neither Sn^{2+} nor $(CH_3)_2Sn^{2+}$ exist in solid compounds in their idealized forms. In most tin(II) compounds, a distorted environment for tin is found,[3,5] and their ^{119}Sn Mössbauer spectra show, with very few exceptions, measurable quadrupole splittings and/or isomer shifts well below 4.84 mm s^{-1}.[2,6] In dimethyltin(IV) salts a linear C–Sn–C group is not always found.[5] Where this group is linear, as in $(CH_3)_2SnF_2$,[7] the structure is 2-dimensional polymeric rather than ionic. The ^{119}Sn Mössbauer spectrum with $\delta = 1.23$ mm s^{-1} relative to SnO_2 and a quadrupole splitting ΔE_Q of 4.52 mm s^{-1} [8] provides additional indications for a polymeric structure. A pronounced room-temperature effect and a noticeable asymmetry of the two quadrupole split lines, termed the Goldanskii–Karyagin effect,[9,10] are observed.[8] The relatively small energy separation in the valence shells between 5s and 5p levels, found for post transition elements and ions may be seen as the underlying reason for both the distortion about Sn^{2+} and the strong covalent "cation" and "anion" interaction in dimethyltin(IV) salts. For $Sn^{2+}(g)$ the separation of the ground state, ^1S ($5s^2$), and the lowest excited state, $^3P_0$ ($5s^15p^1$), is only 6.64 eV.[11]

In the solid state, the strong polarizable Sn^{2+} ion will gain additional stabilization energy by 5s–5p mixing, which in turn requires distortion and a departure from a centrosymmetrical coordination environment.[12] In particular, small, strongly polarizing anions like F^- induce strong distortions as evidenced by the various polymorphic forms of SnF_2[3,5] and their ^{119}Sn Mössbauer spectra,[2,3,13] all of which show nonzero quadrupole splittings. On the other hand, weakly basic and weakly polarizing anions composed of highly electronegative constituent atoms should be more capable of producing electronic environments expected for the Sn^{2+} and $(CH_3)_2Sn^{2+}$ cations.

Support for this line of reasoning is found in the structural chemistry of divalent tin as probed by ^{119}Sn Mössbauer spectroscopy. The strongly basic F^- ion is converted into the less basic anions SbF_6^- and SO_3F^- by reaction with the strong acceptors SbF_5 and SO_3, respectively. As the data collected in Table I show, the

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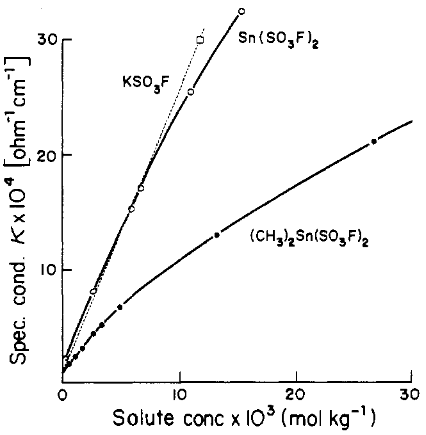

Figure 1. Electrical conductivity of $Sn(SO_3F)_2$ and $(CH_3)_2Sn(SO_3F)_2$ in HSO_3F at 25 °C.

isomer shifts for $Sn(SO_3F)_2$[14] and the related $Sn(SO_3CF_3)_2$[15] are indeed higher than that for α-SnF_2, but small quadrupole splittings remain observable. A broad single line is found for $Sn(SbF_6)_2$. A single line and the highest reported isomer shift ($\delta = 4.69$ mm s^{-1}) are found for the tin(II) cation in the mixed-valency compound $Sn^{II}[Sn(SO_3CF_3)_6]$.[15] This compound was obtained fortuitously during the rather vigorous reaction of tetravinyltin in an excess of HSO_3CF_3, a route which could not be adopted to the corresponding fluorosulfate system.

Again a single line and a high δ value of 4.66 mm s^{-1} relative to SnO_2 are found for a compound of the composition $Sn(SbF_6)_2 \cdot 2AsF_3$,[16] where X-ray diffraction reveals a somewhat distorted nine-coordinated tin(II) environment. Finally the use of crown ether ligands has provided an alternate route to "bare" Sn^{2+}.[17]

Analogous dimethyltin(IV) compounds are less abundant. The compound $(CH_3)_2Sn(SbF_6)_2$ has never been obtained pure.[18] $(CH_3)_2Sn(SO_3F)_2$ and $(CH_3)_2Sn(SO_3CF_3)_2$ exhibit the largest quadrupole splittings reported so far[19] and may represent the closest approach to a bare $(CH_3)_2Sn^{2+}$. Neither substitution of CH_3 by C_2H_5, n-C_3H_7, or n-C_4H_7 nor substitution of the SO_3X group (X = F, CF_3) by $PO_2X_2^-$ (X = F, H) results in larger ΔE_Q values.[19c] The structure of $(CH_3)_2Sn(SO_3F)_2$[20] reveals a sheetlike polymer with a linear C–Sn–C grouping and symmetrically bridging O-bidentate SO_3F groups. Interestingly, the S–O bond distances within these SO_3F groups are intriguingly similar to those reported for ionic SO_3F^- in KSO_3F.[21] Additional evidence that SO_3F^- is still too basic comes from electrical conductance vs. concentration plots on solutions of $Sn(SO_3F)_2$ and $(CH_3)_2Sn(SO_3F)_2$ and the reference base KSO_3F in HSO_3F at 25 °C, as shown in Figure 1. Ionic dissociation, expected to produce 2 mol of SO_3F^-/mol of tin fluorosulfate, according to

$$R(SO_3F)_2 \xrightarrow{HSO_3F} R^{2+}(solv) + 2SO_3F^-(solv) \qquad (1)$$
$$R = Sn,\ (CH_3)_2Sn$$

appears to be incomplete, ~50% for $Sn(SO_3F)_2$ and ~30% for $(CH_3)_2Sn(SO_3F)_2$, with some noticeable curvature of the plot for the latter compound. Some complexity of the dissolution process of $(CH_3)_2Sn(SO_3F)_2$ in HSO_3F has also been suggested in a very recent NMR study in HSO_3F.[22]

The inference that superacid media are needed to stabilize the solvated cations Sn^{2+} and $(CH_3)_2Sn^{2+}$ may also be applied to solid systems. The SO_3X abstraction (X = F, CF_3) by strong acceptors, termed "ansolvo superacids" is a route to be considered. Two such acceptors, $Pt(SO_3F)_4$[23] and $Sn(SO_3F)_4$[24] (as well as $Sn(SO_3CF_3)_4$,[25] have become available, giving rise to formation of $[M(SO_3F)_6]^{2-}$ (M = Pt, Sn). The reported stabilization of cations like Ag^{2+}[26] and Pd^{2+}[27] provide precedents for the most direct synthetic approach according to

$$R(SO_3X)_2 + M(SO_3X)_4 \xrightarrow{HSO_3X} R[M(SO_3X)_6] \qquad (2)$$
$$R = Sn,\ (CH_3)_2Sn;\ X = F,\ CF_3$$

The synthetic scope of this route is widened by the recently reported[25] solvolytic conversion of the more readily obtainable fluorosulfates into trifluoromethanesulfonates.

With salts like $Cs_2[M(SO_3X)_6]$, M = Sn or Pt, X = F or CF_3, easily available,[23,24,25] metathesis according to

$$R(SO_3X)_2 + Cs_2[M(SO_3X)_6] \xrightarrow{HSO_3X} R[M(SO_3X)_6] + 2CsSO_3X \qquad (3)$$
$$X = F,\ CF_3$$

becomes a possible alternative route, with solubility differences in HSO_3X between the two reaction products hopefully permitting their separation.

A related, but different approach, leading to anionic complexes of the desired cations may be seen in the general reaction

$$R(SO_3X)_2 + nCsSO_3X \xrightarrow{HSO_3X} Cs_n[R(SO_3X)_{2+n}] \qquad (4)$$
$$R = Sn,\ (CH_3)_2Sn;\ X = F,\ CF_3$$

While anionic sulfonato complexes of this type have not been reported, there are many precedents for tin or organotin halogen complexes of this type,[3,5] and trends in bond parameters[5,28] for the dimethyltin(IV)–chloro series, $[(CH_3)_2SnCl_{2+n}]^{n-}$ (n = 0–2), appear to confirm an earlier interpretation[28] of anions of the type $[(CH_3)_2SnX_4]^{2-}$ (X = F, Cl) in terms of constituent X^- anions and a $(CH_3)_2Sn^{2+}$ cation with a linear C–Sn–C group. Such polarization should be even more pronounced where X = SO_3F or SO_3CF_3, and the ^{119}Sn Mössbauer spectra should be interesting.

With the $(CH_3)_2Sn$ moiety rather resistant to both further acidolysis, or oxidative degradation by strong protonic acids, dimethyltin(IV) compounds become the organotin reagents of choice. Initial synthetic efforts are directed toward the more readily obtainable fluorosulfates.

Experimental Section

Chemicals. Commercially available chemicals of analytical reagent or of reagent grade were generally used without further purification. HSO_3F of technical grade (Baker and Adamson) was purified by double distillation at atmospheric pressure as described previously.[23] HSO_3CF_3 (3M) was distilled shortly before use from concentrated H_2SO_4. $Sn(SO_3F)_2$ was obtained from anhydrous $SnCl_2$ and HSO_3F,[29] and both $(CH_3)_2Sn(SO_3F)_2$ and $(CH_3)_2Sn(SO_3CF_3)_2$ were obtained by solvolysis of either $(CH_3)_3SnCl$ or $(CH_3)_2SnCl_2$ in the appropriate purified acid.[19] Descriptions in recent reports were used to prepare $Cs_2[Sn(SO_3F)_6]$,[24] $Cs_2[Pt(SO_3F)_6]$,[23] $Pt(SO_3F)_4$,[23] $Sn(SO_3F)_4$,[24] $Hg(SO_3F)_2$,[30] and $Sn(SO_3CF_3)_4$.[25]

Instrumentation. Raman spectra were obtained on a Spex Ramalog 5 spectrometer equipped with an argon ion laser (Spectra Physics Model 164) operating at 514.5 nm. Infrared spectra were obtained on a Perkin-Elmer 598 grating spectrophotometer. Silver chloride and silver

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bromide were used as window materials. Samples were either mulled with Nujol or hexachlorobutadiene or were used as thin films without mulling agent. The Mössbauer spectrometer has been described before,[19] and details on electrical conductivity measurements in HSO_3F have also been reported very recently.[23,24]

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 Atmospheres 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. Vacuum filtration of moisture-sensitive material was performed in an apparatus described by Shriver.[31] Chemical analysis was carried out by Analytische Laboratorien, Gummersbach, West Germany, and by P. Borda of this department (carbon and hydrogen).

Individual Preparations. (i) Mercury(II) Hexakis(fluorosulfato)stannate(IV) ($Hg[Sn(SO_3F)_6]$). Onto an equimolar mixture of $Hg(SO_3F)_2$ (254.6 mg, 0.640 mmol) and $Sn(SO_3F)_4$ (328.6 mg, 0.639 mmol) is distilled ~8 mL of HSO_3F. The resulting suspension is warmed to 90 °C and stirred vigorously for 1 week. There is no outward sign of a reaction, and after removal of all volatiles in vacuo, a white solid is left behind; mp 290–295 °C.

Anal. Calcd for $HgSnS_6O_{18}F_6$: Hg, 21.96; Sn, 12.99; F, 12.48. Found: Hg, 22.10; Sn, 13.25; F, 12.29.

Barium hexakis(fluorosulfato)stannate(IV) ($Ba[Sn(SO_3F)_6]$) is made in an identical manner from stoichiometric amounts of $Ba(SO_3F)_2$, generated from $BaCl_2$ and HSO_3F in situ,[29] and $Sn(SO_3F)_4$. The reaction is followed by weight. The white solid does not melt or decompose below 300 °C.

(ii) Tin(II) Hexakis(fluorosulfato)stannate(IV) ($Sn[Sn(SO_3F)_6]$). About 10 mL of HSO_3F are distilled onto a nearly equimolar mixture of $Sn(SO_3F)_2$ (582.9 mg, 1.84 mmol) and $Sn(SO_3F)_4$ (934.9 mg, 1.82 mmol). When the mixture is warmed to 60 °C, an almost clear solution forms within 15 min, but slowly thereafter a white, crystalline solid starts to precipitate. The reaction is continued for 90 h, and after removal of all volatiles, a white hygroscopic solid forms; mp 210–215 °C. Anal. Calcd for $SnS_3O_9F_3$: Sn, 28.55; S, 23.14; F, 13.71. Found: Sn, 28.70; S, 23.23; F, 13.67.

(iii) Dimethyltin(IV) Hexakis(fluorosulfato)platinate(IV) ($(CH_3)_2Sn[Pt(SO_3F)_6]$). To a nearly equimolar mixture of $Pt(SO_3F)_4$, (349.5 mg, 0.59 mmol) and $(CH_3)_2Sn(SO_3F)_2$ (215.9 mg, 0.62 mmol) is added ~5 mL of HSO_3F by distillation in vacuo. The mixture is warmed to room temperature and stirred for 96 h. The initial brownish yellow color gradually changes to light yellow, and a yellow precipitate forms, which is separated by vacuum filtration, washed with small amounts of HSO_3F, and dried in vacuo. The yellow, hygroscopic solid is slightly soluble in HSO_3F and analyses as $(CH_3)_2Sn[Pt(SO_3F)_6]$; mp 175 °C. Anal. Calcd for $C_2H_6SnPtS_6O_{18}F_6$: C, 2.56; H, 0.64; Sn, 12.65; Pt, 20.79; F, 12.15. Found: C, 2.59; H, 0.60; Sn, 12.52; Pt, 20.69; F, 12.03. IR: 3040 w, 2940 w, 1420 vs, 1385 vs, 1335 sh, 1225 sh, 1170 s, vbr, 1140 ms, 1060 w, 970 m, 920 m, 835 m, 790 m, 650 s, 630 s, sh, 610 sh, 585 vs, 550 vs, 455 vs, 410 sh cm^{-1}. Raman: 1242 vs, 1209 w, 1060 m, 985 m, 805 vw, 639 s, sh, 629 vs, 520 s, 450 sh, 445 s, 285 s, 270 s, 227 s cm^{-1}.

(iv) Dimethyltin(IV) Hexakis(fluorosulfato)stannate(IV) ($(CH_3)_2Sn[Sn(SO_3F)_6]$). In a manner similar to that described in part iii, $Sn(SO_3F)_4$ (435.0 mg, 0.85 mmol) is allowed to react with $(CH_3)_2Sn(SO_3F)_2$ (293.5 mg, 0.85 mmol) in ~5 mL of HSO_3F at 60 °C for 96 h. A clear solution forms initially, followed by slow precipitation of a white crystalline solid. Removal of all volatiles in vacuo yields 729.2 mg (0.85 mol) of a white hygroscopic solid, which is moderately soluble in HSO_3F; mp 240 °C dec. The composition is confirmed by analysis. Anal. Calcd for $CH_3SnS_3O_9F_3$: C, 2.79; H, 0.70; Sn, 27.54; F, 13.22. Found: C, 2.95; H, 0.75; Sn, 27.45; F, 13.10.

(v) Bis(dimethyl(fluorosulfato)tin(IV)) Hexakis(fluorosulfato)platinate(IV) ($[(CH_3)_2Sn(SO_3F)]_2[Pt(SO_3F)_6]$) and Bis(dimethyl(fluorosulfato)tin(IV)) Hexakis(fluorosulfato)stannate(IV) ($[(CH_3)_2Sn(SO_3F)]_2[Sn(SO_3F)_6]$). In about 5 mL of HSO_3F, 919.0 mg (0.87 mmol) of $Cs_2[Pt(SO_3F)_6]$ and 604.0 mg (1.74 mmol) of $(CH_3)_2Sn(SO_3F)_2$ are dissolved and stirred at 25 °C. Immediately a yellow precipitate forms, which is separated after 46 h from the liquid solution by filtration. Subsequent washing with small quantities of HSO_3F and drying in vacuo yields a light yellow, crystalline hygroscopic solid, which melts at 165 °C and dissolves sparingly in HSO_3F. Anal. Calcd for $C_4H_{12}Sn_2PtS_8O_{24}F_8$: C, 3.74; H, 0.94; Sn, 18.47; Pt, 15.18; S, 19.96; F, 11.83. Found: C, 3.82; H, 0.82; Sn, 18.60; Pt, 15.25; S, 19.79; F, 11.73. IR: 3080 w, sh, 3040 m, 2945 m, 1415 m, sh, 1385 vs, 1350 s, 1230 w, 1215 s, sh, 1180 vs, br, 1080 sh, 1065 ms, 1005 ms, 955 s, 925 s, 820 vs, 800 s, sh, 745 w, sh, 650 m, 630 m, 610 w, 590 sh, 585 ms, 555 m, 546 ms, 455 m, br, 440 sh cm^{-1}. Raman: 1230 s, 1042 m, 1005 w, 635 s, 530 s, 448 m, 286 vs, 220 vs cm^{-1}. $[(CH_3)_2Sn(SO_3F)]_2[Sn(SO_3F)_6]$ is prepared in an identical manner from 1673.3 mg (1.71 mmol) of $Cs_2[Sn(SO_3F)_6]$ and 1185.9 mg (3.42 mmol) of $(CH_3)_2Sn(SO_3F)_2$. The white crystalline, hygroscopic solid begins to melt at 200 °C and is slightly soluble in HSO_3F. Anal. Calcd for $C_4H_{12}Sn_3S_8O_{24}F_8$: C, 3.97; H, 1.00; Sn, 29.47; S, 21.23; F, 12.58. Found: C, 4.09; H, 1.00; Sn, 29.55; S, 21.04; F, 12.34.

(vi) Cesium Dimethyltetrakis(fluorosulfato)stannate(IV) ($Cs_2[(CH_3)_2Sn(SO_3F)_4]$). To a mixture of $(CH_3)_2SnCl_2$ (500.0 mg, 2.27 mmol) and CsCl (766.0 mg, 4.55 mmol) is distilled an excess of ~8 mL of HSO_3F in vacuo. When the mixture is warmed to room temperature, vigorous gas evolution is noted and a clear solution forms. The solution is stirred magnetically for about 85 h. Removal of all volatiles in vacuo affords 1840 mg (2.276 mmol) of a white, chloride-free hygroscopic solid, identified as $Cs_2[(CH_3)_2Sn(SO_3F)_4]$. The material is extremely soluble in HSO_3F and does not melt below 300 °C. Anal. Calcd for $Cs_2C_2H_6SnS_4O_{12}F_4$: C, 2.96; H, 0.75; Cs, 32.78; Sn, 14.64; F, 9.37. Found: C, 2.68; H, 0.74; Cs, 32.67; Sn, 14.74; F, 9.25.

Attempts to prepare $Cs_2[(CH_3)_2Sn(SO_3CF_3)_4]$ in an identical manner are unsuccessful. A white precipitate, identified as $(CH_3)_2Sn(SO_3CF_3)_2$,[19] forms at 25 °C and dissolves on heating, but reappears on cooling. An alternative route is described below.

(vii) Cesium Dimethyltetrakis(trifluoromethanesulfonato)stannate(IV) ($Cs_2[(CH_3)_2Sn(SO_3CF_3)_4]$). To 784.6 mg (0.97 mmol) of $Cs_2[(CH_3)_2Sn(SO_3F)_4]$ is distilled approximately 5 mL of HSO_3CF_3 in vacuo. The inhomogeneous-looking mixture is warmed to 60 °C and stirred for 48 h. Dissolution during this time is incomplete. The white hygroscopic solid, obtained after removal of all volatiles in vacuo, weighs 1010.3 mg (0.99 mmol); mp 205–210 °C. Anal. Calcd for $Cs_2C_6H_6SnS_4O_{12}F_{12}$: C, 7.13; H, 0.60. Found: C, 7.00; H, 0.56. IR: 3020 w, br, 2950 w, 1395 m, 1310 s, br, 1235 m, 1200 s, 1035 s, sh, 1015 s, 950 s, sh, 890 w, 820 s, 765 m, s, 635 vs, 615 sh, 590 m, 580 m, 575 m, 520 s, 385 sh, 375 sh, 360 m cm^{-1}.

(viii) Dimethyltin(IV) Hexakis(trifluoromethanesulfonato)stannate(IV) ($(CH_3)_2Sn[Sn(SO_3CF_3)_6]$). To an approximately equimolar mixture of $Sn(SO_3CF_3)_4$ (1009.5 mg, 1.41 mmol) and $(CH_3)_2Sn(SO_3CF_3)_2$ (647.6 mg, 1.44 mmol) is distilled about 8 mL of HSO_3CF_3. After being warmed to 70 °C, the mixture is stirred at this temperature for 42 h. A clear, colorless solution is noted at 70 °C, but when it is cooled to room temperature a white precipitate forms. After removal of all volatiles in vacuo, a white, hygroscopic material is obtained which melts between 255 and 260 °C. Anal. Calcd for $C_8H_6Sn_2S_6O_{18}F_{18}$: C, 8.27; H, 0.53; Sn, 20.43; S, 16.55; F, 29.43. Found: C, 8.40; H, 0.60; Sn, 20.45; S, 16.71, F, 29.20. IR: 3040 sh, 2960 m, vbr, 1425 s, sh, 1395 sh, 1355 s, 1315 s, sh, 1230 s, sh, 1202 vs, 1140 s, 1110 sh, 980 vs, 930 s, sh, 895 sh, 835 m, 770 m, 625 vs, 610 s, sh, 575 sh, 530 sh, 515 m, sh, 495 w, 380 m, 340 w cm^{-1}.

Discussion

(a) Synthesis. The availability of two SO_3F^- acceptors, $Pt(SO_3F)_4$ and $Sn(SO_3F)_4$, both readily obtainable by metal oxidation with bis(fluorosulfuryl) peroxide ($S_2O_6F_2$) in HSO_3F as reaction medium,[23,24] offers some advantages in this study. The anion $[Pt(SO_3F)_6]^{2-}$ should allow the study of the cations by ^{119}Sn Mössbauer spectroscopy without interference from overlapping lines caused by two tin environments. Tin tetrakis(fluorosulfate) ($Sn(SO_3F)_4$) is found in previous studies on Ag(II) and Pd(II) complexes[26,27] to be the stronger acceptor of the two. For this reagent, ^{119}Sn Mössbauer spectroscopy can be used conveniently to follow the complex formation reaction by focusing attention on the anion. With isomer shifts generally at −0.25 mm s^{-1} relative to SnO_2, the quadrupole splitting ΔE_Q should provide a useful criterion for the reaction

$$Sn(SO_3F)_4 + 2SO_3F^- \rightarrow [Sn(SO_3F)_6]^{2-} \quad (5)$$

The doublet with $\Delta E_Q = 1.34$ mm s^{-1} reported for $Sn(SO_3F)_4$[33] should collapse to a single line, indicative of a regular octahedral environment for tin(IV). This is indeed the case for $[Sn(SO_3F)_6]^{2-}$ salts with univalent cations like K^+, Cs^+, NO^+ or ClO_2^+.[24,32] Whether this criterion holds for dipositive cations is unclear. For

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(31) Shriver, D. F. *The Manipulation of Air-Sensitive Compounds*; McGraw-Hill: New York, 1969.

(32) Yeats, P. A.; Poh, B. L.; Ford, B. F. E.; Sams, J. R.; Aubke, F. *J. Chem. Soc. A* **1970**, 2188.

(33) Yeats, P. A.; Sams, J. R.; Aubke, F. *Inorg. Chem.* **1973**, *12*, 328.

$Ag[Sn(SO_3F)_6]$, the only example in this group for which a Mössbauer spectrum is reported,[26] a small quadrupole splitting of 0.53 mm s^{-1} is found. Decreased ionic character owing to the strongly polarizing Ag^{2+} ion or Jahn–Teller distortion expected for this ion, transmitted to tin through bridging SO_3F groups, are both plausible causes for a distorted tin environment.

The synthesis of $Hg[Sn(SO_3F)_6]$ according to

$$Hg(SO_3F)_2 + Sn(SO_3F)_4 \xrightarrow{HSO_3F} Hg[Sn(SO_3F)_6] \quad (6)$$

followed by ^{119}Sn Mössbauer spectroscopy should allow clarification.

Two additional aspects recommend "test" reaction 6. (i) The polymeric $Hg(SO_3F)_2$[29,30] lacks solubility in HSO_3F, as does $Sn(SO_3F)_4$. The attempted reaction should allow the establishment of reaction conditions and of criteria for a successful completion. (ii) Vibrational spectra for $Hg[Sn(SO_3F)_6]$ are expected to be useful for an intended comparison to the spectra of $Sn[Sn(SO_3F)_6]$ as well as those of $(CH_3)_2Sn[Sn(SO_3F)_6]$. For the very same purpose $Ba[Sn(SO_3F)_6]$ is prepared in an identical manner.

The fluorosulfate ion abstraction according to reaction 6 indeed proceeds at 90 °C, with a reaction time of 1 week. However there is no visible sign of a reaction. A large amount of solid is present throughout, and no color change occurs.

The initial use of stoichiometric amounts of solid reactants and the subsequent isolation of the solid reaction product by removal of all HSO_3F reduce the value of chemical analysis in product identification. While analysis permits one to rule out unexpected side reactions, evidence for a successful reaction rests with spectroscopic and physical measurements, and the following three criteria are particularly useful. (i) A single-line ^{119}Sn Mössbauer spectrum with $\delta = -0.27$ mm s^{-1} and a line width of 1.15 mm s^{-1} is found at 77 K. (ii) The infrared spectrum to be discussed later is sufficiently different from those of $Hg(SO_3F)_2$ or $Sn(SO_3F)_4$. (iii) The product melts at 290–295 °C to a clear liquid. For $Sn(SO_3F)_4$ and $Hg(SO_3F)_2$ decomposition at 196 and 297 °C, respectively, is found.

A clearer situation is encountered with $Sn(SO_3F)_2$ and $(CH_3)_2Sn(SO_3F)_2$ as reactants, since both are soluble and behave as bases in HSO_3F (Figure 1). The SO_3F^- ion generated allows dissolution of $Sn(SO_3F)_4$, presumably with formation of the known anions,[24] $[Sn(SO_3F)_5]^-$ and, eventually, $[Sn(SO_3F)_6]^{2-}$. The reaction mixtures appear to be almost clear before precipitation occurs. In each case the reaction appears to go to completion. The materials isolated quantitatively are high-melting solids, and chemical analyses confirm the compositions $Sn(SO_3F)_3$ and $CH_3Sn(SO_3F)_3$, respectively.

It is interesting to note that an earlier unsuccessful attempt by us to obtain a compound of the composition $CH_3Sn(SO_3F)_3$ in a more direct manner was reported.[19b] The attempted solvolysis of CH_3SnCl_3 in an excess of HSO_3F at elevated temperature according to

$$CH_3SnCl_3 + 3HSO_3F \xrightarrow[HSO_3F]{\sim 100\ °C} CH_3Sn(SO_3F)_3 + 3HCl \quad (7)$$

produced, surprisingly, $SnCl_2(SO_3F)_2$[32] instead. An analogous reaction in anhydrous HF had allowed preparation of CH_3SnF_3.[8]

To obtain the corresponding trifluoromethanesulfonate of the composition $CH_3Sn(SO_3CF_3)_3$, the reaction of $(CH_3)_2Sn(SO_3CF_3)_2$ with $Sn(SO_3CF_3)_4$ in HSO_3CF_3 is chosen. The reaction proceeds at 70 °C within 42 h. A precipitate forms only after allowing the reaction mixture to cool to room temperature.

Fluorosulfate abstraction with $Pt(SO_3F)_4$ is successful only with $(CH_3)_2Sn(SO_3F)_2$ as reactant. With both reagents soluble in HSO_3F, the reaction proceeds smoothly at room temperature. The initially brownish yellow solution undergoes a rather subtle color change to light yellow before a yellow precipitate forms.

When $Pt(SO_3F)_4$ is allowed to react with an equimolar amount of $Sn(SO_3F)_2$ in fluorosulfuric acid, the color quickly changes to dark brown and a brown, almost black precipitate forms. The ^{119}Sn Mössbauer spectrum indicates the presence of tin(IV) and only a small amount of divalent tin. It appears that partial oxidation of tin(II) and presumably reduction of Pt(IV) has occurred. Attempts to isolate and identify a single Pt(II)–Sn(IV) fluorosulfate have so far failed, and only mixed products are obtained.

Equally unsuccessful is the attempted analogous reaction between $Sn(SO_3F)_2$ and $Cs_2[Sn(SO_3F)_6]$ in HSO_3F. The reaction mixture remains clear throughout, and the solid obtained after removal of HSO_3F in vacuo is a mixture of the starting materials according to the ^{119}Sn Mössbauer spectrum.

Precipitation is indeed noted, when $(CH_3)_2Sn(SO_3F)_2$ is reacted with equimolar amounts of either $Cs_2[Pt(SO_3F)_6]$ or $Cs_2[Sn(SO_3F)_6]$ in HSO_3F, and product isolation by filtration is possible. The yield, estimated from the weight of the isolated material, is low (~30%), and melting points as well as vibrational and to a lesser extent Mössbauer spectra differ slightly from those obtained for $(CH_3)_2Sn[M(SO_3F)_6]$ with M = Sn or Pt, obtained by SO_3F^- abstraction. More tellingly the compositions suggested by chemical analysis are $C_4H_{12}Sn_2PtS_8O_{24}F_8$ and $C_4H_{12}Sn_3S_8O_{24}F_8$, respectively, and better yields of these materials are obtained when 2 mol of $(CH_3)_2Sn(SO_3F)_2$/mol of $Cs_2[M(SO_3F)_6]$ are employed. For reasons discussed later on, the new materials are formulated as $[(CH_3)_2Sn(SO_3F)]_2[M(SO_3F)_6]$ (M = Sn, or Pt) and the formation reaction may be suggested as

$$2(CH_3)_2Sn(SO_3F)_2 + Cs_2[M(SO_3F)_6] \xrightarrow{HSO_3F} [(CH_3)_2Sn(SO_3F)]_2[M(SO_3F)_6] + 2CsSO_3F \quad (8)$$

The yield is estimated to be about 60%, based on the weight of the isolated product. This may be due to the filtration method of product isolation, with the product being somewhat soluble in HSO_3F. There is also the possibility of a side reaction involving the $CsSO_3F$ formed during metathesis and $(CH_3)_2Sn(SO_3F)_2$ according to

$$nCsSO_3F + (CH_3)_2Sn(SO_3F)_2 \xrightarrow{HSO_3F} Cs_n[(CH_3)_2Sn(SO_3F)_{2+n}] \quad n = 1, 2 \quad (9)$$

This possibility is subsequently explored by using 2 mol of $CsSO_3F$ and 1 mol of $(CH_3)_2Sn(SO_3F)_2$, with both conveniently prepared in situ from the corresponding chlorides. The mixture is allowed to react at room temperature by using an excess of HSO_3F, sufficient to keep $(CH_3)_2Sn(SO_3F)_2$ from precipitating. There is no outward sign of a reaction. Almost all of the HSO_3F has to be removed in vacuo before a precipitate begins to form.

The following observations allow the conclusion that a reaction has, indeed, occurred: (i) The material obtained after complete solvent removal is extremely soluble in HSO_3F and does not melt below 300 °C. $(CH_3)_2Sn(SO_3F)_2$ is moderately soluble in HSO_3F and melts at 253 °C. (ii) The ^{119}Sn Mössbauer parameters are intriguingly similar to those of $(CH_3)_2Sn(SO_3F)_2$, but no room temperature effect is observed. (iii) There are shifts in vibrational bands, in particular in the SO_3-stretching region, and new bands are observed in the IR spectrum. The formation reaction follows closely a published report on the synthesis of salts containing the $[(CH_3)_2SnF_4]^{2-}$ ion.[34]

Solvolysis of $Cs_2[(CH_3)_2Sn(SO_3F)_4]$ in a large excess of HSO_3CF_3 at 60 °C affords quantitatively $Cs_2[(CH_3)_2Sn(SO_3CF_3)_4]$. Details of this general reaction type, allowing the complete conversion of fluorosulfates into trifluoromethane sulfonates have been summarized recently.[25] Again, no measurable Mössbauer effect is observed at room temperature, but at 77 K a well-resolved spectrum is found with both the isomer shift and the quadrupole splitting slightly different from values reported for $(CH_3)Sn(SO_3CF_3)_2$.[19]

The anion $[(CH_3)_2Sn(SO_3F)_4]^{2-}$ appears to be present also in the product of the reaction of $(CH_3)_2Sn(SO_3F)_2$ and $Sn(SO_3F)_2$ at a 1:1 mole ratio in HSO_3F according to

$$Sn(SO_3F)_2 + (CH_3)_2Sn(SO_3F)_2 \xrightarrow{HSO_3F} Sn[(CH_3)_2Sn(SO_3F)_4] \quad (10)$$

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(34) Krause, E. *Ber. Dtsch. Chem. Ges.* **1918**, *51*, 1447.

It is reasonable that $Sn(SO_3F)_2$, the stronger base of the two (see Figure 1), should act as a SO_3F^- donor. Detailed characterization of this compound will be presented in an upcoming publication.[35]

Attempts to have tin(II) fluorosulfate act as a fluorosulfate acceptor in the presence of $CsSO_3F$ at either a 1:1 or 1:2 molar ratio, according to

$$n\mathrm{CsSO_3F} + \mathrm{Sn(SO_3F)_2} \xrightarrow{\mathrm{HSO_3F}} \mathrm{Cs}_n[\mathrm{Sn(SO_3F)}_{2+n}] \quad n = 1, 2 \qquad (11)$$

do not lead to isolable new products.

In order to rationalize the course of the reactions discussed above and the formation of the various products obtained, it is useful to focus attention on (a) the principal reaction medium, fluorosulfuric acid, and (b) the established solution behavior at room temperature in HSO_3F, displayed by the solutes employed in above synthetic reactions.

The solvent HSO_3F undergoes self-ionization via proton transfer:[36]

$$\begin{gathered} 2\mathrm{HSO_3F} \rightarrow \mathrm{H_2SO_3F^+} + \mathrm{SO_3F^-} \\ K_{\mathrm{id}} = 3.8 \times 10^{-8}\ \mathrm{mol^2\ kg^{-2}} \end{gathered} \qquad (12)$$

Its acidity in terms of the Hammett acidity parameter, H_0, of -15.07[37] may range from -13.2 in basic medium to -19.35 for the superacid HSO_3F–$3SO_3$–SbF_5.[37] This implies considerable acidity variation owing to changing acid ($H_2SO_3F^+$) or base (SO_3F^-) ion concentrations.

The reagents used here may be classified as solutes in HSO_3F in the following manner: (i) *bases*, with SO_3F^- generated either by solute dissociation or by proton transfer from HSO_3F and to a lesser extent $H_2SO_3F^+$, with strictly qualitative ranking in order of decreasing base strength suggesting the sequence $CsSO_3F > Sn(SO_3F)_2 > (CH_3)_2Sn(SO_3F)_2 > Cs_2[Sn(SO_3F)_6] \sim Cs_2[Pt(SO_3F)_6]$; (ii) *acids*, consisting of $Sn(SO_3F)_4$[24] and $Pt(SO_3F)_4$,[23] which both have the ability to form salts with the anion $[M(SO_3F)_6]^{2-}$ with M = Sn or Pt.

Except for the previously discussed interference from a redox reaction involving the reactant couple Sn(II)/Pt(IV), the reactions of both $M(SO_3F)_4$ toward either $(CH_3)_2Sn(SO_3F)_2$ or $Sn(SO_3F)_2$ result in salt formations with $(CH_3)_2Sn^{2+}$ or Sn^{2+} as cations, similar in type to the formation of $Cs_2[M(SO_3F)_6]$[23,24,33] from $M(SO_3F)_4$ and $CsSO_3F$ in HSO_3F. Even formation of the acid salts $Cs[M(SO_3F)_5]$ (M = Sn or Pt)[23,24] follows this rationale, at least in a formal sense

$$\begin{gathered} \mathrm{Cs_2[M(SO_3F)_6]} + \mathrm{M(SO_3F)_4} \xrightarrow{\mathrm{HSO_3F}} 2\mathrm{Cs[M(SO_3F)_5]} \\ \mathrm{M = Pt, Sn} \end{gathered} \qquad (13)$$

even though the published syntheses involve the reactions of $M(SO_3F)_4$ and $CsSO_3F$ at a strictly 1:1 molar ratio.[23,24]

The proposed relative order of base strength allows one to also rationalize reactions within this group. Substitution of the acids $M(SO_3F)_4$ by the weak bases $Cs_2[M(SO_3F)_6]$ with M = Sn or Pt, appears to suppress the stepwise basic dissociation of $(CH_3)_2Sn(SO_3F)_2$:

$$\mathrm{(CH_3)_2Sn(SO_3F)_2} \xrightarrow{\mathrm{HSO_3F}} [\mathrm{(CH_3)_2Sn(SO_3F)}]^+ + \mathrm{SO_3F^-} \qquad (14)$$

$$[\mathrm{(CH_3)_2Sn(SO_3F)}]^+ \xrightarrow{\mathrm{HSO_3F}} [\mathrm{(CH_3)_2Sn}]^{2+} + \mathrm{SO_3F^-} \qquad (15)$$

with $[(CH_3)_2Sn(SO_3F)]^+$ now the principal ionic species involved in salt formation with the anion $[M(SO_3F)_6]^{2-}$. Toward the stronger bases $CsSO_3F$ and $Sn(SO_3F)_2$, dimethyltin(IV) bis(fluorosulfate) acts now as an acid or SO_3F^- ion acceptor under formation of the anion $[(CH_3)_2Sn(SO_3F)_4]^{2-}$. Differences in base strength between $CsSO_3F$ and $Sn(SO_3F)_2$ appear to be too small to induce $Sn(SO_3F)_2$ to exhibit similar ampholytic behavior as shown by $(CH_3)_2Sn(SO_3F)_2$.

A corresponding systematic synthetic and solution study in the $SO_3CF_3^-/HSO_3CF_3$ system should be possible but is not undertaken here for three reasons:

(i) Trifluoromethyl sulfates are more difficult to prepare and often require the corresponding fluorosulfates as precursors.

(ii) Where ^{119}Sn Mössbauer data (to be discussed below) are available for both fluorosulfates and trifluoromethanesulfonates, the ones for the latter show generally a less pronounced cationic character.

(iii) Vibrational spectra for trifluoromethanesulfonates are notoriously complex and less easily interpreted than spectra of their fluorosulfate counterparts.

(b) Vibrational Spectra. With ^{119}Sn Mössbauer spectra of principal importance when the cationic nature of the tin-containing moiety is probed in the new compounds, vibrational spectroscopy assumes a supporting role only. Vibrational spectra are useful in ascertaining the bond type of the sulfonate group in the compounds. To avoid undue complexity and to allow for a good comparison the infrared spectra of four tin fluorosulfate derivatives $Sn[Sn(SO_3F)_6]$, $Cs_2[(CH_3)_2Sn(SO_3F)_4]$, $(CH_3)_2Sn[Sn(SO_3F)_6]$, and $[(CH_3)_2Sn(SO_3F)]_2[Sn(SO_3F)_6]$ are selected and listed together with the corresponding spectra for $Hg[Sn(SO_3F)_6]$ and $Ba[Sn(SO_3F)_6]$ in Table II. IR bands found for the remaining new compounds are included in the Experimental Section. Suffice it to say that bands found for $[Pt(SO_3F)_6]^{2-}$ salts are in positions almost identical with those of their tin(IV) analogues and that the trifluoromethanesulfonates give IR spectra consistent with monodentate OSO_2CF_3 groups in most cases.

Since all sulfonate bands are both IR and Raman active, the most effective use of Raman spectra is made when probing the configuration of the C–Sn–C group in dimethyltin(IV) compounds is probed, in particular since some of the Raman spectra obtained are of low quality and show only a limited number of the expected bands. In this study only the $[Pt(SO_3F)_6]^{2-}$ derivatives give moderately satisfactory Raman spectra with Raman shifts listed in the experimental section. Strong fluorescence is noted for the remaining samples and often not more than one or two bonds are observable.

In the dimethyltin(IV) compounds studied here ν_{sym}(Sn–C) is found in the Raman spectrum only at $\sim$530 cm^{-1}. This region is clear in the IR spectrum and is not obscured by SO_3F deformation modes. Assignment of ν_{asym}(Sn–C) is more difficult. The region of $\sim$580 cm^{-1} suggested previously for dimethyltin(IV) sulfonates[19] is now partly obscured by a SO_2 bending mode. While all IR spectra of dimethyltin(IV) derivatives have intense doublets in this area with single-line counterparts in the Raman spectra, the small band separation of $\sim$10 cm^{-1} permits no clear assignment. Hence a linear C–Sn–C grouping is suggested, but not unambiguously established, by vibrational spectroscopy.

The data collected in Table II are for the most part consistent with the presence of monodentate-OSO_2F groups in all six compounds. A similar spacing of vibrational bands has been found previously[24,33] for $[Sn(SO_3F)_6]^{2-}$ derivatives, and the proposed assignment is adopted from there. Not unexpectedly the band centers in the SO_3F stretching region are shifted slightly to lower wavenumbers for the salt $Cs_2[(CH_3)_2Sn(SO_3F)_4]$ and the smaller band separation between the two SO_2 stretches at $\sim$1400 and 1200 cm^{-1} may be taken as evidence for the enhanced ionic nature of the Sn–OSO_2F bond in the anion.

In spite of extensive band proliferation in the SO_3F stretching region, two additional SO_3 stretching vibrations are found in the infrared spectrum of $[(CH_3)_2Sn(SO_3F)]_2[Sn(SO_3F)_6]$. Both bands at 1148 and 1067 cm^{-1} have counterparts in the corresponding spectrum of $[(CH_3)_2Sn(SO_3F)]_2[Pt(SO_3F)_6]$ and are reminiscent of a bridging bidentate configuration as found in $(CH_3)_2Sn(SO_3F)_2$ at 1180 and 1076 cm^{-1}, respectively.[19] The remaining two stretching fundamentals at $\sim$1350 and 830 cm^{-1} and the deformation mode are not clearly distinguishable from the bands due to monodentate OSO_2F groups.

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[35] Mallela, S. P.; Yap, S.; Sams, J. R.; Aubke, F., submitted for publication in *Inorg. Chem.*

[36] Thompson, R. C. In *Inorganic Sulphur Chemistry*; Nikless, G., Ed.; Elsevier: Amsterdam, 1968; p 587.

[37] Gillespie, R. J.; Peel, T. E. *J. Am. Chem. Soc.* **1973**, *95*, 5173.

Table I. Representative ^{119}Sn Mössbauer Data for Sn Compounds at 77 K

compd	isomer shift rel to SnO_2 δ, mm s^{-1}	quadrupole splitting ΔE_Q, mm s^{-1}	line widths Γ, mm s^{-1}	ref	compd	isomer shift rel to SnO_2 δ, mm s^{-1}	quadrupole splitting ΔE_Q, mm s^{-1}	line widths Γ, mm s^{-1}	ref
α-SnF_2 monoclinic	3.40	1.52		13	$Sn(SbF_6)_2 \cdot 2AsF_3$	4.66	0	0.92	16
$Sn(SO_3F)_2$	4.18	0.68	1.33	14	$Sn[Sn(SO_3CF_3)_6]$[a]	4.69	0	1.14	15
$Sn(SO_3CF_3)_2$	4.15	0.84	0.98	15	$Sn(ClO_4)_2$(15-crown-5)$_2$	4.53	0		17
$Sn(SbF_6)_2$	4.44	0	1.21	14					

[a] Sn^{2+} environment only.

Table II. Infrared Spectra and Approximate Assignments for $(CH_3)_2Sn[Sn(SO_3F)_6]$, $[(CH_3)_2Sn(SO_3F)]_2[Sn(SO_3F)_6]$, $Cs_2[(CH_3)_2Sn(SO_3F)_4]$, $Sn[Sn(SO_3F)_6]$, $Ba[Sn(SO_3F)_6]$, and $Hg[Sn(SO_3F)_6]$[a]

$(CH_3)_2Sn$-$[Sn(SO_3F)_6]$[a]		$[(CH_3)_2Sn$-$(SO_3F)]_2$-$[Sn(SO_3F)_6]$[c]		$Cs_2[(CH_3)_2Sn$-$(SO_3F)_4]$[d]		$Sn[Sn(SO_3F)_6]$		$Ba[Sn(SO_3F)_6]$		$Hg[Sn(SO_3F)_6]$		
ν, cm^{-1}	intens	ν, cm^{-1}	intens	ν, cm^{-1}	intens	ν, cm^{-1}	intens	ν, cm^{-1}	intens	ν, cm^{-1}	intens	approx description
1415	m, sh	1430	ms, sh			1425	m, sh	1420	m, sh	1415	ms	
1390	s, sh	1400	s	1360	s, sh	1390	s, sh	1380	vs	1390	s, sh	$\nu_{as}(SO_2)$ monodentate or bidentate + CH_3 bend
1370	vs, b	1380	ms, sh	1335	vs, b	1368	vs	1355	s, sh	1360	vs, b	
1340	s, sh	1350	vs, b			1355	s, sh					
1240	w, sh	1235	m, sh			1240	w, sh	1260	vw	1260	m, sh	CH_3 bend + $\nu_{sym}(SO_2)$ monodentate or anisobidentate
1195	vs	1195	vs	1210	s	1200	vs	1232	s, sh	1195	s	
1170	vs, sh	1185	vs	1185	vs, b			1210	vs			
						1170	vs, b			1125	vs, b	$\nu(SO)$ bidentate bridging
		1148	s, sh					1098	vw			$\nu_{sym}(SO_2)$ bidentate bridging
		1067	s							1065	m, sh	
1035	s	1015	vs	1065	sh	1028	s, sh			1015	s	ν(SO–OSn) monodentate
1010	vs			1050	vs	1011	vs	1015	vs, b			
965	s, sh	990	vs, sh			995	s, sh	950	s, sh	965	s	
				924	m							
		850	w, sh	882	m–w	855	m, sh					
830	vs, b	825	vs	830	s, sh	825	s	830	s, b	830	s, sh	$\nu(SF)$ mono- or bidentate
						812	s, sh			800	vs, b	
		631	ms, sh			631	ms					
625	ms	621	s	600	m, sh	622	w, sh	625	ms	625	m	$\nu(SnO)$ + SO_3F def mode
		610	ms, sh									
592	s, sh	596	s, sh	590	s, sh							$\delta_{as}(SO_2)$ mono- or bidentate + ν_{as}(Sn–C) str
580	s	585	s	578	s	585	ms	590	ms	585	ms	
551	s	555	s	558	s	552	s	560	s	548	s	$\delta_{sym}(SO_2)$ mono- or bidentate
		448	ms					450	m			
435	ms	440	ms			435	ms	438	w, sh			$\nu(SnO)$ + SO_3F rock
		430	m, sh	415	ms	425	s, sh	420	vw	436	m, w	
405	vw	405	vw	410	w			405	vw	418	vw	$\delta(SO_3F)$

[a] Abbreviations: s = strong, m = medium, w = weak, v = very, b = broad, sh = shoulder, as = asymmetric, sym = symmetric, bend = bending, rock = rocking, def = deformation. [b] CH_3 bands: 3058, 2940, 2840 (C–H str), 1210 (bend), 795 (rock). [c] CH_3 bands: 3100, 3040, 2945 (str), 800 (rock) cm^{-1}. [d] CH_3 bands: 3060, 2940 (str), 1225 (bend), 765 (rock) cm^{-1}.

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

	isomer shift[a,b] δ, mm s^{-1}	quadrupole[a] splitting ΔE_Q, mm s^{-1}	line widths[a,c] Γ, mm s^{-1}
$(CH_3)_2Sn[Pt(SO_3F)_6]$	1.95	5.67	0.97, 0.95
$(CH_3)_2Sn[Sn(SO_3F)_6]$	2.01[d]	5.64[d]	0.94, 0.98[d]
	−0.17[e]	0[e]	0.89[e]
$(CH_3)_2Sn[Sn(SO_3CF_3)_6]$	1.95[d]	5.52[d]	0.98, 1.03[d]
	−0.16[e]	0[e]	1.09[e]
$[(CH_3)_2Sn(SO_3F)]_2[Pt(SO_3F)_6]$	1.96	5.70	0.95, 0.98
$[(CH_3)_2Sn(SO_3F)]_2[Sn(SO_3F)_6]$	1.91[d]	5.56[d]	0.93, 0.97[d]
	−0.22[e]	0[e]	0.99[e]
$Cs_2[(CH_3)_2Sn(SO_3F)_4]$	1.83	5.50	0.97, 0.94
$Cs_2[(CH_3)_2Sn(SO_3CF_3)_4]$	1.74	5.39	0.91, 0.94
$Hg[Sn(SO_3F)_6]$	−0.27	0	1.15
	(−0.25)[f]	(0.41)[f]	(0.93, 0.97)[f]
$Ba[Sn(SO_3F)_6]$	−0.31	0	1.34
	(−0.28)[f]	(0.47)[f]	(0.95, 1.19)[f]
$Sn[Sn(SO_3F)_6]$	−0.27[g]	0[g]	1.24[g]
	(−0.31)[f]	(0.39)[f]	(1.12, 0.93)[f]
	4.48[h]	0[h]	1.17[h]

[a] Error limit ±0.03 mm s^{-1}. [b] Relative to SnO_2 at 77 K. [c] Full width at half-height; no constraints imposed. [d] Values for the cationic species. [e] Values for the anionic species. [f] See text for discussion. [g] Tin(IV) environment. [h] Tin(II) environment.

It is in our view reasonable to assume that sheet-like, polymeric $(CH_3)_2Sn(SO_3F)_2$[20] ionizes in the first step, to give a polymeric cation of the type $[(CH_3)_2Sn(SO_3F)]_n^{n+}$(solv) in HSO_3F with retention of bidentate bridging fluorosulfate groups, followed by precipitation in the presence of $[M(SO_3F)_6]^{2-}$ (M = Sn, Pt). Formulation of the resulting solids as $[(CH_3)_2Sn(SO_3F)]_2[M(SO_3F)_6]$ as suggested, appears, in the absence of more information regarding the precise nature of the polymeric cation, approximate but reasonable.

The observation of similar bands at 1125 and 1065 cm^{-1} for $Hg[Sn(SO_3F)_6]$ and at 1170 cm^{-1} for $Sn[Sn(SO_3F)_6]$ strongly suggests some bridging function of the fluorosulfate group, most pronounced for the mercury compound. Such a configuration with strong coordination to Sn(IV) and relatively weak coordination to M^{II} (M = Hg, Sn), termed aniso-bidentate bridging, had previously been suggested for $Ag[Sn(SO_3F)_6]$[26] and $Pd[Sn(SO_3F)_6]$.[27]

(c) Mössbauer Spectra. For the complexes $(CH_3)_2Sn(SO_3X)_2$ (X = F, CF_3, CH_3), we have previously proposed[19b] structures in which linear $(CH_3)_2Sn^{2+}$ cations interact covalently with symmetrically bridging SO_3X^- anions via weak polar 3-center 4-electron bonds to provide hexacoordination at tin. The $(CH_3)_2Sn^{2+}$ cation is viewed as utilizing $5sp_z$ hybrid orbitals on tin, with the cation–anion interaction involving the $5p_x$ and $5p_y$ tin orbitals. According to this picture, the greater the covalent interaction the greater will be the electron density at tin in its $5p_{x,y}$ orbitals. This would serve to increase screening of tin 5s electron density, thereby lowering the isomer shift, and at the same time to decrease the imbalance in p-orbital charge density, thus decreasing the quadrupole splitting. Trends in δ and ΔE_Q with changes in X were fully consistent with this view.

At 77 K, $(CH_3)_2Sn[Pt(SO_3F)_6]$ exhibits a Mössbauer spectrum with both isomer shift and quadrupole splitting somewhat larger than those reported[19] for $(CH_3)_2Sn(SO_3F)_2$, suggesting a weaker cation–anion interaction and a "purer" $(CH_3)_2Sn^{2+}$ cation in the former complex (Table III). The cationic species in $(CH_3)_2Sn[Sn(SO_3X)_6]$ (X = F, CF_3) also show very similar δ and ΔE_Q values, indicative of very weak cation–anion interactions in all three cases. The modest differences between the Mössbauer parameters of $(CH_3)_2Sn(SO_3F)_2$ and of these three complexes, however, imply there are no gross differences in cation–anion interactions, even though the vibrational spectra of the present derivatives are consistent with the presence of only monodentate OSO_2X groups. Clearly the Mössbauer parameters of the $(CH_3)_2Sn$ moieties are controlled primarily by the linear C–Sn–C arrangement (taken here to define the z axis of the electric field gradient (EFG) tensor) and are relatively insensitive to the weak interactions in the xy plane.[38]

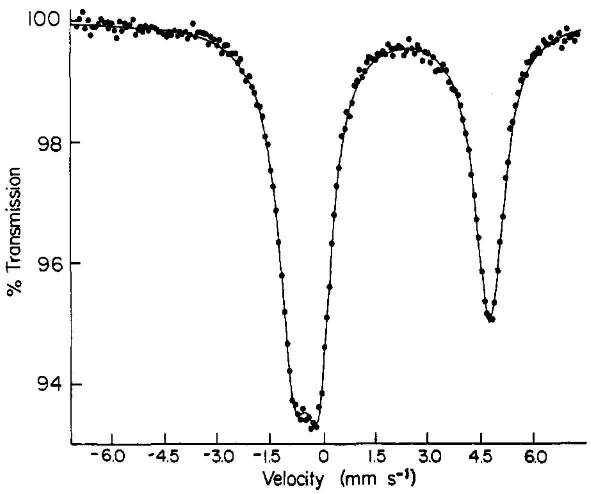

Figure 2. ^{119}Sn Mössbauer spectrum of $[(CH_3)_2Sn(SO_3F)]_2[Sn(SO_3F)_6]$ at 77 K.

In the Mössbauer spectra of $(CH_3)_2Sn[Sn(SO_3X)_6]$ (X = F, CF_3) the anions show single-line absorptions with line widths comparable to those of the cations, suggesting little if any unresolved quadrupole interaction. The anion isomer shifts are about 0.1 mm s^{-1} more positive than those reported[33] for $M_2[Sn(SO_3F)_6]$ (M = K^+, Cs^+, NO^+, ClO_2^+), implying a slightly less positive effective nuclear charge on tin in the present complexes. This could conceivably result from weak interactions between the $(CH_3)_2Sn^{2+}$ cations and the SO_3X groups in the anions.

It is at first glance rather surprising that the complexes formulated on the basis of vibrational spectra as $[(CH_3)_2Sn(SO_3F)]_2[M(SO_3F)_6]$ (M = Pt, Sn) should have Mössbauer isomer shifts and quadrupole splittings that are so similar to the values for the corresponding $(CH_3)_2Sn[M(SO_3F)_6]$ derivatives. However, this is undoubtedly a manifestation of the fact that the Mössbauer parameters of the cations are dominated by the linear and strongly covalent C–Sn–C bonding and only weakly dependent on interactions in the equatorial plane.[38] Thus the Mössbauer spectra are effectively mute concerning the correctness of the suggested formulation and the possible structure of the cation.

It should perhaps be mentioned here that, in those complexes above that contain Sn(IV) in both a cationic and an anionic environment, there are two ways of assigning the partly overlapping Mössbauer spectral lines, as seen in Figure 2. The alternative assignment to that used in deriving the values given in Table III leads to extremely improbable parameters. For example, the alternative assignment for $(CH_3)_2Sn[Sn(SO_3F)_6]$ gives δ = 2.33 mm s^{-1} and ΔE_Q = 5.00 mm s^{-1} for the $(CH_3)_2Sn^{2+}$ ion (clearly inconsistent with values for the corresponding Pt complex), and

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(38) Sham, T. K.; Bancroft, G. M. *Inorg. Chem.* **1795**, *14*, 2281.

$\delta = -0.81$ mm s^{-1} for the $[Sn(SO_3F)_6]^{2-}$ ion (0.5 mm s^{-1} more negative than any previously reported[32] value for this species). We should also point out that both the Mössbauer and vibrational spectra of this complex are inconsistent with the assumption that it could be an equimolar mixture of $(CH_3)_2Sn(SO_3F)_2$ and $Sn(SO_3F)_4$. The two cesium salts $Cs_2[(CH_3)_2Sn(SO_3X)_4]$, (X = F, CF_3) have δ and ΔE_Q values that are strongly reminiscent of those found[19a] for the polymeric $(CH_3)_2Sn(SO_3X)_2$ species. This is not unexpected, as the immediate coordination sphere about the tin atom is identical in the two cases. In both instances the $Sn-OSO_2X$ bonding is highly ionic, and the difference between monodentate and bidentate SO_3X groups has little effect on the Mössbauer parameters. However, an important difference between the monomeric $[(CH_3)_2Sn(SO_3X)_4]^{2-}$ ions and the polymeric $(CH_3)_2Sn(SO_3X)_2$ complexes is seen in the temperature dependence of the Mössbauer recoilless fractions. Both of the $(CH_3)_2Sn(SO_3X)_2$ derivatives exhibit well-resolved Mössbauer spectra at room temperature,[19] whereas no room-temperature absorption was detected for either of the $Cs_2[(CH_3)_2Sn(SO_3X)_4]$ salts. Indeed, these are the only two complexes studied here for which there was not at least a weak room-temperature effect.

Each of the compounds $M[Sn(SO_3F)_6]$ (M = Hg, Sn, Ba) gives what is visually a single-line Mössbauer absorption due to the $[Sn(SO_3F)_6]^{2-}$ ion. (For $Sn[Sn(SO_3F)_6]$ there is an additional absorption from the Sn^{2+} ion as discussed below.) These spectra were computer-fitted both as singlets and as convolutions of two lines, assuming the presence of small quadrupole interactions. The results of both procedures are given in Table III, with the latter in parentheses. In no case was there an improvement in the fit, either statistically or visually, when two lines were assumed rather than one, and we consider the doublet fits to be less than reliable for the following reasons. First, it is unwise in general to put much faith in apparent quadrupole splittings that are only about 0.2 of the sum of the constituent line widths. At best they give an indication of the maximum value of ΔE_Q if there really is a quadrupole interaction. Second, when unconstrained fitting parameters are used, the areas of the two apparent lines always differ by at least 40%, and in the case of the Sn(IV) resonance in $Sn[Sn(SO_3F)_6]$, they differ by more than a factor of 2. This is most unrealistic physically and suggests that the two-line fits are probably spurious.

It is our view, therefore, that in none of these three derivatives is there a clearly resolved quadrupole splitting. Although the vibrational spectra suggest that the fluorosulfate moieties in these complexes are functioning as bridging groups, the near-spherical charge distribution at tin in the $[Sn(SO_3F)_6]^{2-}$ ions indicate that any inequivalence of the SO_3F groups that might arise from cation-anion interation is not being very effectively transmitted to the central Sn(IV) site. On the other hand, the quadrupole splitting in the Mössbauer spectrum of $Ag[Sn(SO_3F)_6]$[26] is clearly discerned by visual inspection, and the unconstrained fit to a quadrupole doublet produced lines of equal area (area ratio, 1.06). It seems probable that this clearly resolved splitting is due to a Jahn-Teller distortion of the Ag^{2+} ion, relayed to tin by bridging SO_3F groups.

A comparison of the Mössbauer data for $Sn[Sn(SO_3CF_3)_6]$[15] with those for $Sn[Sn(SO_3F)_6]$ in Table III suggests a significantly greater cation-anion interaction in the latter. First, the isomer shift of 4.48 mm s^{-1} for Sn(II) is 0.2 mm s^{-1} lower than that found for this species in $Sn[Sn(SO_3CF_3)_6]$, indicating a less pure $5s^2$ Sn(II). A second important difference between the two $Sn[Sn(SO_3X)_6]$ complexes is seen in the relative intensities of the Sn(II) and Sn(IV) absorption lines and how these change with temperature. For X = CF_3, it was found[15] that $ISn^{II}/ISn^{IV} = 0.61$ at 77 K and that it had decreased almost to zero at room temperature. For X = F, on the other hand, $ISn^{II}/ISn^{IV} = 0.88$ at 77 K and 0.37 at room temperature; i.e. the Sn(II) resonance is much stronger relative to the Sn(IV) resonance in this case. Both of these features, the lower δSn(II) and the larger values of ISn^{II}/ISn^{IV}, are consistent with greater cation-anion interaction for X = F than for X = CF_3.

Conclusions. A direct synthetic route to mixed-valency Sn(II)-Sn(IV) sulfonates is presented to complement the earlier[15] accidental synthesis of $Sn[Sn(SO_3CF_3)_6]$. Sulfonate abstraction under various conditions yields surprisingly not just $(CH_3)_2Sn^{2+}$ derivatives but also salts containing the polymeric $[(CH_3)_2Sn(SO_3F)]^+$ cation. In addition, stabilization of $(CH_3)_2Sn^{2+}$ by the anion SO_3X^- (X = F, CF_3) is observed in the cesium complexes $Cs_2[(CH_3)_2Sn(SO_3X)_4]$ (X = F, CF_3).

The quadrupole splittings ranging up to 5.70 mm s^{-1} represent the closest approach to true $(CH_3)_2Sn^{2+}$ cations, and it may be argued that such cations with linear C-Sn-C groups will in the solid state interact with even the least basic counteranions, on account of the empty, low-energy 5p orbitals on tin. The strong similarity of the Mössbauer parameter for all new $(CH_3)_2Sn$ derivatives reported here is however surprising.

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Registry No. $Hg[Sn(SO_3F)_6]$, 102922-11-2; $Sn[Sn(SO_3F)_6]$, 102922-12-3; $(CH_3)_2Sn[Pt(SO_3F)_6]$, 102922-13-4; $(CH_3)_2Sn[Sn(SO_3F)_6]$, 102922-14-5; $[(CH_3)_2Sn(SO_3F)]_2[Pt(SO_3F)_6]$, 102940-27-2; $[(CH_3)_2Sn(SO_3F)]_2[Sn(SO_3F)_6]$, 102940-28-3; $Cs_2[(CH_3)_2Sn(SO_3F)_4]$, 102922-15-6; $Cs_2[(CH_3)_2Sn(SO_3CF_3)_4]$, 102922-16-7; $(CH_3)_2Sn[Sn(SO_3CF_3)_6]$, 102940-30-7; $Ba[Sn(SO_3F)_6]$, 102922-17-8.