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Synthesis and Mössbauer and Vibrational Spectra of Some New Tin(IV)–Fluorine Compounds

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The solvolysis of methyltin(IV)–chlorine compounds of the general type $(CH_3)_nSnCl_{4-n}$, with *n* ranging from 0 to 4, is studied in aqueous and anhydrous hydrogen fluoride under a variety of conditions. The studies in anhydrous HF have resulted in the synthesis of the new compounds methyltin(IV) trifluoride, dimethyltin(IV) chloride fluoride, and methyltin(IV) dichloride fluoride. A convenient route to $SnCl_2F_2$ is found in addition. Interaction of this compound with either $S_2O_6F_2$ or $ClOSO_2F$ results in the formation of $SnF_2(SO_3F)_2$. Structural proposals for these compounds are based on infrared, Raman, and ^{119}Sn Mössbauer spectra. All new compounds are found to be polymeric *via* fluorine or fluorosulfate bridges, resulting in penta- or hexacoordination around tin. Signs of the electric field gradients in these and some related compounds are deduced. Dialkyltin(IV) fluorides are easily obtained when the corresponding chlorides are solvolyzed in aqueous hydrogen fluoride.

Introduction

Tin(IV)–fluorine compounds have presented interesting structural problems in the past. Coordination expansion *via* fluorine bridging appears to be a common feature as evidenced best by X-ray diffraction studies on SnF_4,[1] $(CH_3)_2SnF_2$,[2] and $(CH_3)_3SnF$,[3] where sheet-like polymers with hexacoordination around tin are found for the first two compounds and a chain type polymer with pentacoordination is indicated for $(CH_3)_3SnF$,[3] even though the complete and detailed structure is still not known with certainty.[4,5]

However, $SnCl_2F_2$, the only reported mixed tin(IV) halide, seems to be quite different. The vibrational spectrum has been interpreted in terms of a tetrahedrally coordinated species with C_{2v} symmetry by Dehnicke,[6] who also claimed the first synthesis of this compound by the interaction of $SnCl_4$ with ClF in a flow reaction. A species of identical composition had been prepared far earlier by Ruff and Plato,[7] who reported the isolation of "$SnCl_4 \cdot SnF_4$" as an intermediate in the synthesis of SnF_4 from $SnCl_4$ and anhydrous hydrogen fluoride. That this intermediate might be $SnCl_2F_2$ had already been suggested by Sidgwick,[8] but this had yet to be confirmed by experiment.

The study by Ruff and Plato[7] had indicated that anhydrous HF is a mild fluorinating agent, capable of cleaving the tin–chlorine bond under mild conditions. This suggested that HF might be also employed in the fluorination of methyltin(IV) chlorides. Neither organotin(IV) trifluorides nor mixed organotin(IV) fluoride chlorides have been synthesized and characterized to date. That this deficiency in an otherwise well-represented group of organotin(IV) compounds was due to the lack of a suitable synthetic method rather than to an inherent instability of the compounds in question seemed likely. Only the method of Krause,[9] that is the conversion of methyltin(IV) chlorides into fluorides by interaction with KF in alcoholic or aqueous solution, had found some application in the synthesis of fluorides. This method had been used recently[10] in the attempted synthesis of $(tert\text{-}C_4H_9)_2SnClF$, however the obtained product was heavily contaminated by $(tert\text{-}C_4H_9)_2SnF_2$. Since at least the lower alkyltin(IV) fluorides are relatively high melting, involatile solids only soluble in coordinating solvents, the chances for separating reaction mixtures like the one discussed above are extremely slim.

It seemed that no solvolysis of organotin(IV) halides in anhydrous or aqueous HF had been studied. Only a single report[11] could be found where a tin–carbon bond is cleaved in aqueous HF solution. However, the solvolysis of methyltin(IV) chlorides in some sulfonic acids of the type HSO_3X with X = F, Cl, CF_3, CH_3, and C_2H_5 had been studied recently[12–14] and was found to be a clean-cut synthetic route. Similar results were expected from the HF solvolysis.

The SO_3X group in the obtained methyltin(IV) sulfonates has been identified as a bidentate bridging group with bridging through two oxygen atoms. The resulting polymeric structures were reminiscent of those found for the methyltin(IV) fluorides.[2,3] The similarity was in particular apparent from a recent X-ray diffraction study of $(CH_3)_2Sn(SO_3F)_2$.[15] A compound having both F and SO_3F bound to tin would offer the possibility of a direct comparison of both as potential bridging groups. Such a compound could be synthesized in $SnF_2(SO_3F)_2$ by interaction of either $S_2O_6F_2$[16] or $ClOSO_2F$[17] with $SnCl_2F_2$

As found previously,[12–14] vibrational spectroscopy and ^{119m}Sn Mössbauer spectroscopy were useful tools in elucidating structural features.

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[1] R. Hoppe and W. Dähne, *Naturwissenschaften*, **49**, 254 (1962).

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[16] F. B. Dudley and G. H. Cady, *J. Amer. Chem. Soc.*, **79**, 513 (1957).

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Table I

Reactions of Various Methyl Methyltin(IV)–Chlorine Compounds with Anhydrous HF

Reaction no.	Substrate	mmol	HF, mmol	Reaction[a] temp	Reaction time, hr	Reaction products
1	$Sn(CH_3)_4$	5.6	~1000	25°	0.7	$(CH_3)_3SnF + CH_4$
2	$Sn(CH_3)_4$	7.0	~1000	130° max	4.0	5.5 mmol of $(CH_3)_3SnF$ + 1.5 mmol of $(CH_3)_2SnF_2 + CH_4$
3	$(CH_3)_3SnCl$	12.0	~1000	130° max	15.0	$(CH_3)_2SnF_2 + HCl + CH_4$
4	$(CH_3)_3SnCl$[b]	74.0	26.0	25°	2.0	$(CH_3)_3SnF + HCl + (CH_3)_3SnCl$ unreacted
5	$(CH_3)_2SnCl_2$	5.9	~1000	130° max	7.0	$(CH_3)_2SnF_2 + HCl$
6	$(CH_3)_2SnCl_2$[b]	41.0	25.0	25°	7.0	$(CH_3)_2SnFCl + HCl + (CH_3)_2SnCl_2$ unreacted
7	CH_3SnCl_3	18.0	~1000	130°	18.0	$CH_3SnF_3 + HCl$
8	CH_3SnCl_3[b]	15.0	15.0	25°	4.0	$CH_3SnCl_2F + HCl + CH_3SnCl_3$ unreacted
9	$SnCl_4$	200	250	65°	7.0	$SnCl_2F_2 + HCl + SnCl_4$ unreacted
10	$SnCl_4$	92	50	25°	4.5	$SnCl_2F_2 + HCl + SnCl_4$ unreacted

[a] Oil bath temperature. [b] ~50 ml of $CFCl_3$ was added as solvent.

Experimental Section

I. **Chemicals.**—Anhydrous hydrogen fluoride of a purity listed as 99.9% minimum was obtained from Matheson of Canda Ltd. and was used without further purification. Transfer was accomplished in a monel vacuum line. Aqueous HF (48%) was a product of Fisher Scientific. Tetramethyltin was purchased from the Pennsinsular Chemresearch Calgon Corp. The chlorides $(CH_3)_3SnCl$, $(CH_3)_2SnCl_2$, CH_3SnCl_3, $(C_2H_5)_2SnCl_2$, $(n\text{-}C_3H_7)_2SnCl_2$, $(n\text{-}C_4H_9)_2SnCl_2$, and $(n\text{-}C_8H_{17})_2SnCl_2$ (Alfa Inorganic Chemicals) were sublimed before use when necessary. $(CH_3)_2SnO$ and $(CH_3)_2SnF_2$ were also supplied by Alfa Inorganic Chemicals. Their purity was checked from melting points and vibrational spectra. Stannic chloride (Fisher Scientific Corp.) was vacuum distilled repeatedly before being used. Trichlorofluoromethane was obtained from Matheson of Canada and dried over molecular sieves before being used. Also obtained from Matheson of Canada were Cl_2 (99.5% min. purity) and ClF_3 (98.0% min. purity). Peroxydisulfuryl difluoride, $S_2O_6F_2$, was prepared from SO_3 and F_2 (both from Allied Chemical Corp.) in a catalytic reactor according to Cady and Shreeve.[18] Chlorine(I) fluorosulfate was obtained, according to Gilbreath and Cady,[17] using Cl_2 and $S_2O_6F_2$. The purity of both compounds was checked by their ^{19}F nmr spectra.

II. **Instrumentation.**—Infrared spectra were recorded on a Perkin-Elmer 457 grating spectrophotometer. Silver chloride, cesium iodide, and KRS-5 windows (all from Harshaw Chemicals) were used either with Nujol or without any mulling agent.

Raman spectra on the solid samples were obtained with a Cary 81 spectrometer, quipped with a Model 125 He–Ne gas laser (Spectra Physics Corp.). The 6328-Å wavelength line was used as exciting light. The samples were contained in 5-mm o.d. Pyrex tubes with flat bottoms.

The Mössbauer spectrometer has been described before in detail.[19] Measurements were made with the absorber either at 80 or 298°K and the $Ba^{119m}SnO_3$ source at 298°K. All isomer shifts are reported relative to SnO_2 absorber at 80°K. The confidence limit for both isomer shifts and quadrupole splittings is judged to be ±0.03 mm/sec.

All manipulations of solid materials was carried out in a Vacuum Atmosphere Corp. "Dri-Lab" Model No. HE-43-2 filled with purified dry nitrogen and equipped with "Dri-Train" Model No. HE-93B.

III. **The Anhydrous HF Reactor.**—We were unable to adopt the original method used in the synthesis of $SnCl_4 \cdot SnF_4$ by Ruff and Plato.[7] The authors employed a platinum metal reactor which was not available to us. Preliminary attempts under a variety of conditions led to the reactor design shown in Figure 1. Monel was used as construction material and all seals were made either by silver soldering or argon welding. The reactor was found to be suitable for reaction temperatures between −80 and +110° under atmospheric pressure. The reaction mixture was stirred externally with a magnetic stirrer and the course of the reaction was followed by pressure measurements. During a reaction, the reactor was attached to a Monel manifold equipped with a Helicoid test gauge (1–1000 mm pressure), an air bleed with a P_2O_5 guard tube, and an assembly of two Kel-F storage traps of known volume. A trichloroethylene–Dry Ice mixture was used in the dewar of the reflux apparatus. Solid reactants and products were added to and removed from the reactor inside the drybox. All volatile materials were removed by vacuum distillation. It was found useful to condition the reactor before preparations by filling it with about 25 ml of anhydrous HF and heating to ~100° for 8 hr. Details of the reactions are given in Table I and discussed in a later section.

IV. **Reactions in Aqueous HF.**—A simple 400-ml nalgene beaker was used as the reactor. The substrate was finely ground in a mortar and pestle and after being transferred to the beaker, was covered with aqueous HF. Methanol was added in some cases to achieve better "wetting" of the substrate. The beaker was placed on a hot plate and the excess HF slowly evaporated at a temperature of about 50°. The product was scraped out of the beaker and was subjected to further drying in a 120° oven. The purity was checked by microanalysis.

V. **Analytical Details.**—Microanalysis of carbon and hydrogen was carried out in this department by Mr. P. Borda. Elemental

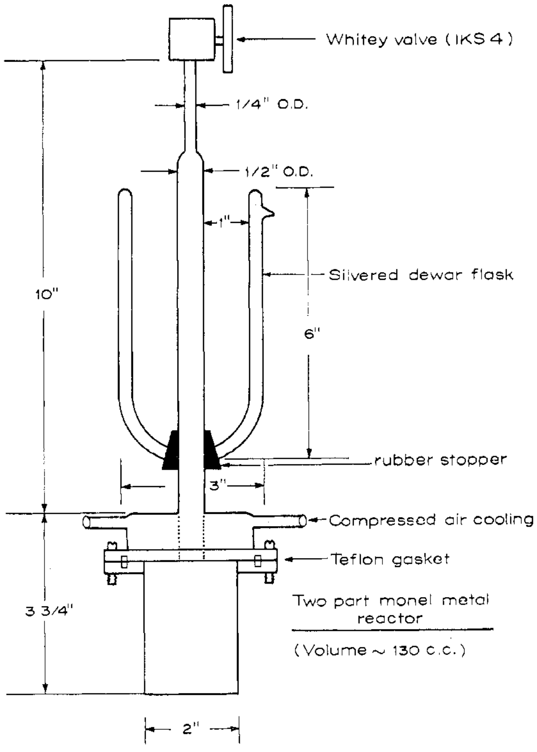

Figure 1.—HF Monel metal reflux reactor.

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analysis of Sn and F was carried out by Alfred Bernhardt, West Germany. Chloride was determined by titration with $AgNO_3$.

(a) *Anal.* Calcd for CH_3SnF_3 (white powder, dec pt 321–327°): Sn, 62.23; F, 29.88; C, 6.30; H, 1.59. Found: Sn, 62.34; F, 29.96; C, 6.30; H, 1.80.

(b) *Anal.* Calcd for CH_3SnCl_2F (white powder, hygroscopic, dec pt 160°): Sn, 53.07; Cl, 31.71; F, 8.50. Found: Sn, 52.94; Cl, 30.1; F, 8.59.

(c) *Anal.* Calcd for $(CH_3)_2SnClF$ (white powder, hygroscopic, dec pt 155–160°): Sn, 58.42; Cl, 17.45; C, 11.82; F, 9.35; H, 2.96. Found: Sn, 58.32; Cl, 17.2; C, 11.88; F, 9.45; H, 2.88.

(d) *Anal.* Calcd for $SnF_2(SO_3F)_2$ (white powder, very hygroscopic, dec pt 235°): Sn, 33.45; F, 21.42. Found: Sn, 33.29; F, 21.59.

(e) *Anal.* Calcd for $SnCl_2F_2$ (white powder, very hygroscopic, dec pt 160–170°): Cl, 31.1; F, 16.90. Found: Cl, 31.7; F, 16.69.

Results and Discussion

I. Synthesis.—The metal reactor described in detail in the Experimental Section was found very useful for all solvolysis reactions in anhydrous HF. The advantage over a closed metal reactor is quite obvious: The evolution of HCl or CH_4 can be monitored by a pressure gauge and allows one to adjust to the right reaction temperature. The progress and the end of a reaction can thus be estimated and potentially hazardous pressure buildups are avoided. In addition we were unable to synthesize $SnCl_2F_2$ in a closed reactor even though numerous attempts were made. This compound is easily obtained in the described reactor.

Conditions and results of all solvolysis reactions of methyltin(IV) chlorine compounds in anhydrous hydrogen fluoride are summarized in Table I. As can be seen clearly, both the Sn–Cl and the Sn–CH_3 bonds can be cleaved. The order of preference is also very recognizable: the tin–chlorine bond is more easily cleaved than is the tin–carbon bond as exemplified by reactions 4–8. This finding is in complete agreement with our observations for the solvolysis of the same substrates in sulfonic acids,[12–14] but different from the solvolysis of $(CH_3)_3SnCl$ in some haloacetic acids,[20] where only one Sn–CH_3 bond is cleaved.

Also, as found for the sulfonic acids, disubstitution occurs where the acid is present in an excess with the release of HCl and CH_4, respectively, however as exemplified by reactions 1 and 2 heating will be required when $(CH_3)_4Sn$ is used as substrate.

The only exception is the solvolysis of CH_3SnCl_3 in HF where, after prolonged reaction time at elevated temperature, complete substitution of chlorine by fluorine occurs with formation of CH_3SnF_3. This compound was not obtainable under identical reaction conditions from $Sn(CH_3)_4$ or any of the other methyltin(IV) chlorides (reactions 2, 3, and 5), where $(CH_3)_2SnF_2$ appears to be the final product. It can be argued that in this compound, the Sn–C bond is exceptionally short[2] and therefore more stable toward solvolysis.

The fact that the Sn–Cl bond is more easily cleaved than the Sn–CH_3 bond reflects differences in bond polarities as a consequence of electronegativity differences, however this rationale does not explain the observation by Wang and Shreeve,[20] when relatively weak protonic acids are used.

The fact, that all reactions seem to proceed stepwise makes reactions 6 and 8 very attractive routes for the synthesis of the hitherto unknown methyltin(IV) chloride fluorides. A separation of the new compounds from the excess of $(CH_3)_2SnCl_2$ or CH_3SnCl_3 is easily accomplished either by sublimation or by solvent extraction with CCl_4 or $CHCl_3$. The insolubility of $(CH_3)_2SnClF$ and CH_3SnCl_2F in these solvents may be taken as initial evidence for the polymeric or ionic nature of the compounds. Only CH_3SnCl_2F was found to be noticeably sublimable at temperatures of 90° and a pressure of 10^{-2} mm. The sublimation is found to be very slow but the compound can be purified this way.

All attempts to synthesize the last missing methyltin(IV) chloride fluoride, CH_3SnClF_2, pure were unsuccessful. Reactions with CH_3SnCl_3 and anhydrous HF in a mole ratio of 1:1.5–2.0 resulted in products of roughly the required composition, but both infrared and ^{119}Sn Mössbauer spectra indicated a mixture. It appears once CH_3SnCl_2F is formed further solvolysis does not proceed in two distinct steps as would be necessary.

An attempt to obtain CH_3SnClF_2 by pyrolysis of CH_3SnCl_2F yielded a similar result. It was noted that CH_3SnCl_2F at atmospheric pressure and ~160° decomposed with the release of CH_3SnCl_3, thus suggesting the reaction

$$2CH_3SnCl_2F \xrightarrow{160°} CH_3SnClF_2 + CH_3SnCl_3$$

However analysis indicated that a mixture of presumably CH_3SnF_3 and CH_3SnClF_2 was formed. Even though, as can be seen from Table I, both $(CH_3)_3SnF$ and $(CH_3)_2SnF_2$ are obtainable *via* solvolysis of the substrates $(CH_3)_4Sn$, $(CH_3)_3SnCl$, and $(CH_3)_2SnCl_2$ in anhydrous HF, the described method appears neither simple nor practical as a convenient route to the fluorides. Solvolysis of the same substrates in aqueous HF however was easily accomplished with very simple equipment. The results are summarized as follows: Trimethyltin(IV) fluoride is obtained from trimethyltin(IV) chloride and tetramethyltin(IV). The conversion of the former is quantitative, whereas the latter is obtained in about 11% yield, however the product was formed in rather long (3–7 mm) needles and not as a microcrystalline powder, obtained from $(CH_3)_3SnCl$. This indicates that the Sn–C bond can be cleaved, even under such mild conditions with temperatures of 40–50°.

Dimethyltin(IV) dichloride and also dimethyltin(IV) oxide are easily converted into the difluoride. The latter reaction was described previously.[21] Easy conversion of other dialkyltin(IV) dichlorides R_2SnCl_2 is achieved following the same route for R = C_2H_5, *n*-C_3H_7, *n*-C_4H_9, and *n*-C_8H_{17} without any evidence for a cleavage of the tin–carbon bonds.

Methyltin(IV) trichloride does not react under the same conditions and it seems doubtful whether CH_3SnF_3 can be synthesized this way. As is apparent from their hygroscopic nature, none of the methyltin(IV) chloride fluorides can be obtained this way.

It seems safe to say that again the tin–chlorine bond is preferentially cleaved and that aqueous HF is a very good reagent for the facile synthesis of trialkyltin(IV) fluorides and dialkyltin(IV) difluorides.

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(20) C. S. Wang and J. M. Shreeve, *Chem. Commun.*, 151 (1970).

(21) C. W. Hobbs and R. S. Tobias, *Inorg. Chem.*, **9**, 1037 (1970).

TABLE II

VIBRATIONAL FREQUENCIES OF SOME METHYLTIN(IV)–FLUORINE COMPOUNDS,[a] CM^{-1}

1 $(CH_3)_3SnF$		2 $(CH_3)_2SnF_2$		3 CH_3SnF_3		4 $(CH_3)_2SnClF$		5 CH_3SnCl_2F		
Ir	Raman	Ir	Raman	Ir	Raman	Ir	Raman	Ir	Raman	Assignment
780 vs, b	n.o.	788 vs, b	n.o.	822 vs, b	n.o.	796 vs, b	n.o.	795 vs	n.o.	Sn–CH$_3$ rock
				646 vs 629 s	644 s					Sn–F$_t$ str
555 s	n.o. 559 w	598 vs	n.o.			582 s	588 mw			Sn–C str asym
				548 vs 535 s	544 vs			555 s	558 ms	Sn–C str
	521 s		536			528 ms	536 vs			Sn–C str sym
335 vs, b	n.o.	360 vs, b	n.o.	425 vs, b	n.o.	365 vs, b	n.o.	398 vs, b	n.o.	Sn–F$_b$ str
								385 s, sh	390 m	Sn–Cl str asym
						335 s	334 s			Sn–Cl str
								370 s	365 vs	Sn–Cl str sym
				328 mw 322 mw						Sn–F$_t$ bend?
				287 ms 278 m						Sn–C bend?

[a] vs, very strong; s, strong; m, medium; w, weak; b, broad; sh, shoulder; n.o., not observed; asym, asymmetric; sym, symmetric; F$_t$, terminal fluorine; F$_b$, bridging fluorine. In addition to the listed bands we observed the following modes: CH_3SnF_3: 2944, 2905, 2886, 1415, and 1212 cm^{-1}; $(CH_3)_2SnClF$: 2943, 2929, 2905, 2868, 1410, and 1212 cm^{-1}; CH_3SnCl_2F: 2944, 2906, 2872, and 1205 cm^{-1}.

Finally it was found that "$SnCl_4 \cdot SnF_4$"[7] is indeed easily formed in anhydrous HF with $SnCl_4$ as substrate, independent of the mole ratios. Attempts to obtain a $SnCl_3F$ by reacting an excess of $SnCl_4$ with HF resulted in the sole formation of "$SnCl_4 \cdot SnF_4$." This product is indeed identical with $SnCl_2F_2$ synthesized according to Dehnicke,[5] as evidenced by the decomposition point and infrared and ^{119}Sn Mössbauer spectra. Samples obtained from HF solvolysis were very pure, whereas in our experience fluorination with ClF or, as recommended by Dehnicke a ClF_3–Cl_2 mixture, can lead very easily to higher fluorinated products as is very apparent from the ^{119}Sn Mössbauer spectra obtained on some of the samples.

Replacement of Cl by the SO_3F group in $SnCl_2F_2$ was easily accomplished by either $S_2O_6F_2$ or $ClOSO_2F$ at a maximum temperature of 50° in a very smooth reaction. The physical properties of $SnF_2(SO_3F)_2$ compare quite well with the previously synthesized $Sn(SO_3F)_4$ and $SnCl_2(SO_3F)_2$.[19] All are relatively high melting, hygroscopic white solids.

II. Vibrational Spectra. (a) **Methyltin(IV) Fluoro Compounds.**—The vibrational frequencies in the range of 1000–250 cm^{-1} are listed in Table II for all methyltin(IV) fluorine derivatives. The C–H stretching modes (found at 2870–3000 cm^{-1}) as well as the bending modes (1420 and 1215 cm^{-1}) were found not to vary in position appreciably for all compounds, therefore interest is directed toward the lower frequency range where the tin–carbon and tin–halogen stretching modes are expected.

Agreement with previous reports on the spectra of $(CH_3)_3SnF$[4,5,22] and $(CH_3)_2SnF_2$[21] is good with respect to peak position and assignment. As found previously,[4,21] no Raman absorption was noted in the region of 340–360 cm^{-1} where very strong and broad infrared bands are found, due to the stretching mode or modes involving tin and bridging fluorine. As is obvious from the Sn–F distances reported for both compounds,[2,3] the tin–fluorine bond is weak and very polar[2] so that detection by Raman spectroscopy on solid compounds becomes a difficult task.

The same observation can be made for the new compounds. All have strong and broad infrared bands in the region of 365–425 cm^{-1} with no corresponding Raman bands. We assign these bands to Sn–F bridging stretching modes.

For $(CH_3)SnF_3$ (the ir spectrum is shown in Figure 2) an infrared active doublet at 646 and 629 cm^{-1} with only one counterpart in the Raman spectrum (644 cm^{-1}) is assigned to a stretching mode involving tin and fluorine in a terminal position. The tin–carbon stretch is again split into a doublet in the ir spectrum (548 and 535 cm^{-1}) but only one Raman band (544 cm^{-1}) is observed. The peak separation (~15 cm^{-1}) in both doublets is identical within the limits of error. Vibrational coupling in the obviously polymeric substance seems the most likely cause for the observed splitting. The assignment of the lower frequency doublets as Sn–C and Sn–F$_t$ bending modes is not supported by the Raman spectrum where no reliable spectrum could be obtained in this low range.

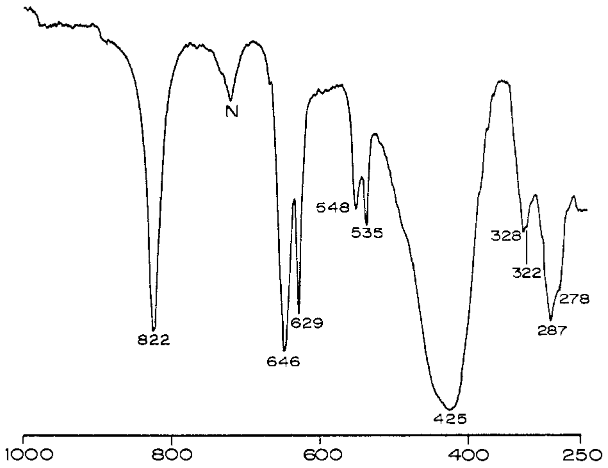

Figure 2.—Infrared spectrum of methyltin(IV)trifluoride from 1000 to 250 cm^{-1}.

It seems safe to conclude that CH_3SnF_3 contains fluorine in both bridging and terminal position. Since no further absorption is found in the Sn–F$_t$ range, it appears that one fluorine is in terminal position which

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(22) R. Okawara, D. E. Webster, and E. G. Rochow, *J. Amer. Chem. Soc.*, **82**, 3287 (1970).

TABLE III

VIBRATIONAL SPECTRUM OF $SnF_2(SO_3F)_2$ AND RELATED COMPOUNDS, CM^{-1}

1 $SnF_2(SO_3F)_2$			2 $SnCl_2(SO_3F)_2$[a]	3 $(CH_3)_2$-$Sn(SO_3F)_2$[b]	KSO_3F[c]	
Ir	Raman	Assignment	Ir	Ir	Raman	Assignment
1420 m, sh	1431 ms	SO_3 str (A″)	1385	1350		
1405 vs, b	1410 m				1285	SO_3 str asym (E)
1115 vs, b	1108 s	SO_3 str (A′)	1130	1180		
1103 s, sh	1093 s					
1070 s, b	1068 s	SO_3 str (A′)	1087	1072	1079	SO_3 str sym (A_1)
	884 vw	?				
855 vs	862 s	SF str	864	827	745	SF str (A_1)
691 s	n.o.	Sn F str asym			594	SO_3 bend asym (E)
n.o.	612 vs	SnF str sym			586	
628 sm	630 m	SO_3 bend (A′)	628	620		
590 s	590 mw	SO_3 bend (A″)	586	590	570	SO_3 bend sym (A_1)
548 vs	551 m	SO_3 bend (A′)	555	554		
430 sm	437 mw	SO_3 rock (A″)	446	417	407	SO_3F rock (E)
~350 m		Sn–O str				
260 w		Sn–F bend				
280 m, sh	277 ms	SO_3F torsion (A′)	312	304		

[a] See ref 19; the Sn–Cl modes are omitted. [b] See ref 14; the Sn–C and the CH_3 modes are omitted. [c] See ref 26.

leaves two per formula unit in bridging positions, resulting in hexacoordination around tin.

Only bridging fluorine seems to be present in CH_3SnCl_2F and $(CH_3)_2SnClF$. An assignment of the observed bands is presented in Table II and indicates that two Sn–Cl stretches are observed for the former, and two Sn–C stretches for the latter compound. All are Raman and infrared active. It must be concluded that the Cl–Sn–Cl and the C–Sn–C groups in the respective compounds are not linear. The observed tin–chlorine stretch for $(CH_3)_2SnClF$ is found in the same region as in $(CH_3)_3SnCl$.[23] Some weak chlorine bridging, as found recently for $(CH_3)_2SnCl_2$[24] in an X-ray diffraction study, cannot be ruled out.

A rather interesting trend is observed for $\nu(Sn-F_b)$. The rather broad infrared band shifts gradually upwards from the lowest position at 340 cm^{-1} ($(CH_3)_3SnF$) as CH_3 is replaced by Cl or F. For CH_3SnF_3 this band centers around 425 cm^{-1}. It seems reasonable to assume that the bond polarity of the $Sn-F_b$ bond will decrease and the covalent bond character increase when Sn is coordinated to highly electronegative ligands.

Vibrational coupling as observed for CH_3SnF_3 seems to be absent for these compounds.

(b) Tin(IV) Difluorobis(fluorosulfate) and Tin(IV) Dichloride Difluoride.—It has been pointed out previously[12–14,19,25] that the C_{3v} symmetry of the free SO_3F^- ion is reduced to C_s when the group acts as a monodentate or bidentate covalent group. A distinction between both conformations can be made on the basis of the S–O stretching frequencies which are found in different regions of the spectrum.[19,25] Extensive information of the vibrational frequencies for bridging SO_3F groups has been obtained on a number of methyltin(IV) fluorosulfates[12–14] and recently confirmation from an X-ray diffraction study of $(CH_3)_2Sn(SO_3F)_2$[15] could be obtained. Since the infrared spectrum of $SnF_2(SO_3F)_2$ gave no indication of the characteristic absorption band for Sn–F bridge stretching, commonly found at 350–450 cm^{-1}, the presence of bridging SO_3F groups was considered to be more likely.

That bridging SO_3F groups are indeed present can be seen from Table III where the observed infrared and Raman bands for $SnF_2(SO_3F)_2$ are listed together with those for $SnCl_2(SO_3F)_2$,[19] $(CH_3)_2Sn(SO_3F)_2$,[14] and KSO_3F.[26] As expected, the number of internal SO_3F vibrational modes is increased from 6 for SO_3F^- (3 A_1 modes and 3 E modes) to 9 (3 A″ modes and 6 A′ modes). These can be described as 3 SO_3 stretching modes, 1 SF stretch, 3 SO_3 bending modes, and 2 SO_3 rocking and torsional modes. The two SO_3 stretching modes at ~1400 and at ~1100 cm^{-1} can be thought to originate from the splitting of the E mode at ~1285 cm^{-1} for the SO_3F^- ion. This splitting apparently increases from ~170 cm^{-1} to 225 cm^{-1} to about 300 cm^{-1} in the series $X_2Sn(SO_3F)_2$ with X being CH_3, Cl, and F, respectively. The tin–SO_3F bond apparently becomes more covalent; the observed trend is obviously the same as that noted for the methyltin(IV) fluorides where the $Sn-F_b$ stretch was found to increase in the same direction as the number of fluorine atoms increases.

Some small splittings of vibrational modes are found in the stretching region. This can be explained either by a strong vibrational coupling in the polymeric framework or by the presence of slightly nonequivalent SO_3F groups. The splitting does not seem to be resolvable in the range of deformation modes.

Assignment of the ir band at 691 cm^{-1} as the asymmetric Sn–F stretch and the Raman band at 612 cm^{-1} as the corresponding symmetric stretch is in good agreement with the proposed assignment of $\nu(Sn-F_t)$ in CH_3SnF_3 at ~640 cm^{-1}. Since mutual exclusion for both stretching modes is found, one can conclude that the F–Sn–F group is linear or near linear in this compound. The same conclusions had been reached previously for the chlorine[19] and the methyl[12] derivatives, thus indicating that all three compounds have closely related structures.

The vibrational frequencies for $SnCl_2F_2$ are listed in Table IV together with the values and assignments

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TABLE IV

VIBRATIONAL FREQUENCIES OF $SnCl_2F_2$

Cm⁻¹				
Ir[a]	Raman[a]	Ir[b]	Raman[b]	Assignment
555 vs, b		555 vs	568 w	SnF_2 asym str
495 s, b		491 s	500 m	SnF_2 sym str
402 ms	415 s	405 m	403 s	$SnCl_2$ sym str
392 s	370 ms	392 s	370 m	$SnCl_2$ asym str
		292 w		SnF_2 deformation
278 ms		283 w		
			170 m	$SnCl_2$ deformation
			148 s	

[a] This work. [b] Reference 6.

TABLE V

^{119}Sn MÖSSBAUER DATA OF SOME METHYLTIN(IV) FLUORIDES AND DIALKYLTIN(IV) DIFLUORIDES

		mm/sec			
Compound	Temp, °K	Isomer shift, δ	Quadrupole splitting, Δ	Line width,[a] Γ	RT effect, $\epsilon_{298}/\epsilon_{80}$
$(CH_3)_3SnF$	80	1.27	3.90	1.21 1.23	
	298	1.26	4.01	1.08 1.19	
$(CH_3)_2SnF_2$	80	1.23	4.52	1.08 1.20	
	298	1.20	4.47	0.87 0.83	
CH_2SnF_3	80	0.76	3.24	1.70 1.81	0.74
	298	0.74	3.24	1.20 1.24	
CH_3SnCl_2F	80	1.08	2.69	1.30 1.25	0.50
	298	1.03	2.65	1.03 1.00	
$(CH_3)_2SnClF$	80	1.32	3.80	1.05 1.10	0.53
	298	1.27	3.79	1.01 1.00	
$(C_2H_5)_2SnF_2$	80	1.40	4.43	1.21 1.19	0.37
$(n\text{-}C_3H_7)SnF_2$	80	1.38	4.40	1.07 1.09	0.21
$(n\text{-}C_4H_9)_2SnF_2$	80	1.42	4.48	1.05 1.12	0.16
$(n\text{-}C_8H_{17})_2SnF_2$	80	1.42	4.50	1.17 1.19	0.32

[a] Line width is the line width at half peak height. [b] RT effect is the room temperature effect. ϵ_T is the magnitude of the Mössbauer effect at temperature *T*.

reported by Dehnicke.[6] We were only able to find two bands in the Raman spectrum, at 370 and 415 cm^{-1}. This fact precludes any reasonable assignment; however some of our observations seem to contradict the previous assignment. (1) The bands at 555 cm^{-1} and 495 cm^{-1} are decidedly too low for Sn–F$_t$ stretches. An average value of 525 cm^{-1} is found, considerably lower than that for either ν(Sn–F$_t$) in CH_3SnF_3 or the average of the Sn–F stretching frequencies for $SnF_2(SO_3F)_2$, 652 cm^{-1}. It seems unlikely that the discrepancy can be accounted for by invoking inductive effects alone. In addition the band contours are extremely broad, quite in contrast to that for the infrared bands due to ν(Sn–F$_t$) in our compounds. The absence of pronounced Raman bands and the broadness of the ir peaks is in fact reminiscent of the stretching modes due to bridging fluorine even though the band position is rather high. Some association *via* fluorine bridges can nevertheless exist. The solid-state structure of $(CH_3)_2SnCl_2$[24] may serve as an example where the halogen is preferentially bonded to one tin atom and weakly bonded to another tin atom. (2) The peak separation for the symmetric and asymmetric $SnCl_2$ stretches increases from about 10 cm^{-1} in the infrared to 45 cm^{-1} in the Raman spectrum, assuming the proposed assignment.[6] This is rather unprecedented.[14] (3) The physical properties are indicative of a polymeric substance notwithstanding the reported molecular weight determination in $POCl_3$. The solvent is an excellent donor ligand; the 2:1 complex with $SnCl_4$ has been well investigated.[27] Since SnF_4 is also known[28,29] to form coordination complexes with oxygen donor ligands, it seems possible that $SnCl_2F_2$ might do the same thus rendering the molecular weight determination meaningless with respect to its structure in the solid state. On all these grounds the postulated monomeric nature in the solid state and C_{2v} symmetry seem to be rather questionable. The structure is certainly more complex and a definite assignment based solely on the vibrational spectrum is in our view impossible.

III. ^{119}Sn Mössbauer Effect Studies.—The ^{119}Sn Mössbauer data for the methyltin(IV) fluorides and some related compounds of the type R_2SnF_2 with R = C_2H_5, n-C_3H_7, n-C_4H_9, and n-C_8H_{17} are listed in Table V. Agreement with previous work on $(CH_3)_3SnF$[3,30–33] and the R_2SnF_2[24] series is generally quite good. For the quadrupole splitting of $(CH_3)_2SnF_2$, Davies and coworkers[24,34] and Parish and Platt[35] report values of 4.11 and 4.12 mm/sec, respectively, at liquid nitrogen temperature, whereas Herber and Chandra[36] quote splittings of 4.65 mm/sec (78°K) and 4.54 mm/sec (294°K). Our data were obtained on four samples of different origin obtained commercially or synthesized *via* solvolysis in anhydrous or aqueous hydrogen fluoride. The composition was determined each time by analysis and the Δ values obtained were internally consistent, lying in the range 4.50–4.58 mm/sec (80°K). To exclude a possible systematic instrumental error, Mössbauer spectra of one of the samples were recorded by Liengme[37] on a different spectrometer, yielding the values 4.50 mm/sec (80°K) and 4.48 mm/sec (295°K).

All the alkyltin(IV) fluorides studied give well-resolved Mössbauer spectra at room temperature, as illustrated by Figure 3, which shows a spectrum obtained for CH_3SnF_3 at 298°K. This can be taken as good evidence for polymeric structures in these compounds, as suggested above from the vibrational spectra. The Mössbauer spectra of the two new methyltin(IV) chloride fluorides show that both are true compounds with tin in only one chemical environment. No dissociation into the corresponding chlorides and fluorides seems to occur at ambient temperature. The strong room-temperature resonance absorptions observed are again indicative of polymeric structures for these compounds. The Mössbauer data for $SnF_2(SO_3F)_2$ and SnF_2Cl_2 are listed in Table VI, together with parameters found for some structurally related compounds. Again intermolecular association is in-

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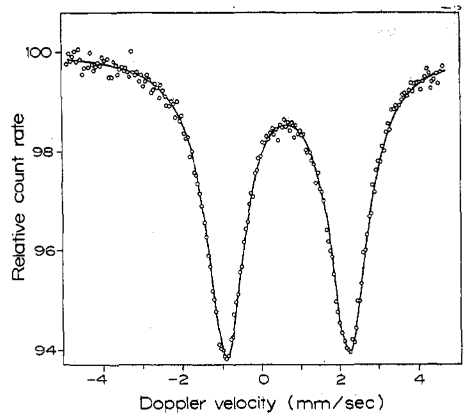

Figure 3.—^{119}Sn Mössbauer spectrum of CH_3SnF_3 at 298°K.

dicated for both compounds even though only a weak room-temperature coefficient is found for $SnCl_2F_2$.

The Mössbauer quadrupole splittings given in Tables V and VI, together with those for $(CH_3)_2Sn(SO_3F)_2$[12] and $(CH_3)ClSn(SO_3F)_2$,[14] enable us to arrive at some interesting conclusions concerning the sign of the electric field gradient (efg) in the compounds reported here. For ^{119}Sn, the quadrupole splitting can be written as

$$\Delta = {}^1/_2 eQV_{zz}(1 + \eta^2/3)^{1/2}$$

where eQ is the nuclear quadrupole moment of the $I = {}^3/_2$ excited state, V_{zz} the (negative) efg, and η the asymmetry parameter. Since eQ is negative for ^{119}Sn, Δ and V_{zz} carry opposite signs. We adopt the usual convention that $\Delta > 0$ (hence $V_{zz} < 0$) implies that the ${}^1/_2 \rightarrow {}^3/_2$ transition lies to higher energy than the ${}^1/_2 \rightarrow {}^1/_2$ transition, and that the charge distribution about tin is prolate.[38,39]

TABLE VI

^{119}Sn MÖSSBAUER DATA OF SOME TIN(IV)–FLUORINE –CHLORINE AND –FLUOROSULFATE COMPOUNDS

Compound	Temp, °K	mm/sec Isomer shift, δ	mm/sec Quadrupole splitting, Δ	mm/sec Line width, Γ	RT effect, $\epsilon_{298}/\epsilon_{80}$
$SnF_2(SO_3F)_2$	80	−0.23	1.96	1.07 1.22	0.36
	298	−0.26	1.99	1.02 0.98	
$SnCl_2F_2$	80	+0.19	1.50	1.16 1.20	*a*
$SnCl_4$[b]	80	+0.78	...		
SnF_4[c]	80	−0.26	1.80		0.73
$SnCl_2(SO_3F)_2$[d]	80	+0.34	2.29		0.46
$Sn(SO_3F)_4$[d]	80	−0.27	1.34		0.42
$(CH_3)_2Sn(SO_3F)_2$[e]	80	1.82	5.54		0.09

[a] A small but noticeable effect was obtained at 298°K. [b] Reference 31. [c] References 30 and 33. [d] Reference 19. [e] Reference 12.

Several trans-octahedral tin compounds of the general formula R_2SnX_4 have been examined using the magnetic perturbation technique,[38–40] and in every case V_{zz} is found to be negative. Herber and Chandra[36] have recently shown $V_{zz} < 0$ for $(CH_3)_2SnF_2$ from the Gol'danskii–Karyagin asymmetry in this compound. (In ref 36, Herber and Chandra state that V_{zz} is positive for $(CH_3)_2SnF_2$. This is due to assuming a positive sign for eQ. In a later publication (*J. Chem. Phys.*, **53**, 3330 (1970) these signs are both reversed.) It is therefore entirely safe to assume $V_{zz} < 0$ for $(CH_3)_2Sn(SO_3F)_2$. However, the sign of V_{zz} is not immediately obvious for species such as $Y_2Sn(SO_3F)_2$ ($Y = Cl, F, SO_3F$) and Y_2SnF_2 ($Y = Cl, F$), especially in the cases where all four ligands are the same but two are bridging and two terminal.

Consider the first four fluorosulfate derivatives (Table VI; ref 12, 14), all of which we assume to have trans-octahedral configurations. Several groups of workers have found that it is often possible to obtain a linear correlation between Δ and Taft σ constants in isostructural series of compounds. Thus, Bryuchova, *et al.*,[41] found such a relation for R_3SnBr ($R = CH_3, C_2H_5, C_6H_5$); Poder and Sams[42] for $(CH_3)_3SnO_2CCH_nX_{3-n}$ ($X = F, Cl, Br, I$), Ford and Sams[43] for the corresponding triphenyltin haloacetates, and Parish and Platt[35] for R_3SnX ($R = CH_3, C_2H_5$; $X = F, Cl, Br, I$). In the present case it is found that a plot of Δ as a function of the sum of the σ values for the axial ligands is quite accurately linear if V_{zz} is taken to be negative throughout the series. A nonweighted least-squares analysis gives $\Delta = -0.565\sigma + 5.51$ mm/sec, with a standard deviation of only 7×10^{-2}.

For $Cl_2Sn(SO_3F)_2$, the sign of V_{zz} can be deduced in another, independent way. Any additive model of quadrupole interactions predicts that Δ for $(CH_3)ClSn(SO_3F)_2$ should be the arithmetic mean of the Δ values for $(CH_3)_2Sn(SO_3F)_2$ and $Cl_2Sn(SO_3F)_2$. If we assume $V_{zz} < 0$ for the latter, then the predicted splitting for the methyl-chloro derivative is $\Delta_{\text{pred}} = +3.91$ mm/sec. Taking $V_{zz} > 0$ for the dichloro compound yields $\Delta'_{\text{pred}} = -1.62$ mm/sec. The measured splitting for $(CH_3)ClSn(SO_3F)_3$[14] is $|\Delta_{\text{obsd}}| = 3.77$ mm/sec, which clearly confirms a negative V_{zz} for the dichloro derivative. It would be exceedingly difficult to reconcile a sign change between $Cl_2Sn(SO_3F)_2$ and $F_2Sn(SO_3F)_2$ or $Sn(SO_3F)_4$, and we again conclude $V_{zz} < 0$ for all the trans-octahedral fluorosulfate compounds.

For the fluorides, $(CH_3)_2SnF_2$, CH_3SnF_3, and SnF_4 also show a linear dependence of Δ upon the sum of the Taft factors for the axial substituents, if the latter two compounds are assumed to have negative V_{zz}, as found previously[36] for $(CH_3)_2SnF_2$. We consider this to be good evidence both that we have chosen the sign of the efg correctly, and that CH_3SnF_3 has a trans-octahedral structure with one terminal and two bridging fluorines.

The negative sign of V_{zz} for SnF_4 and $Sn(SO_3F)_4$ has an important implication for the bonding in these compounds, since it indicates a greater electron density in the tin bonding orbitals directed towards terminal F or SO_3F groups than in those orbitals involved in bonding to the same groups acting as bridging ligands.

The Δ value for $SnCl_2F_2$ (Table VI) falls well below the straight line obtained for the other hexacoordinated tin(IV) fluorides, suggesting that this compound is not isostructural with the other three derivatives. In view of Dehnicke's[6] assignment of a tetrahedral structure for this molecule, the question arises as to the Δ value to be expected for such a structure. This is difficult

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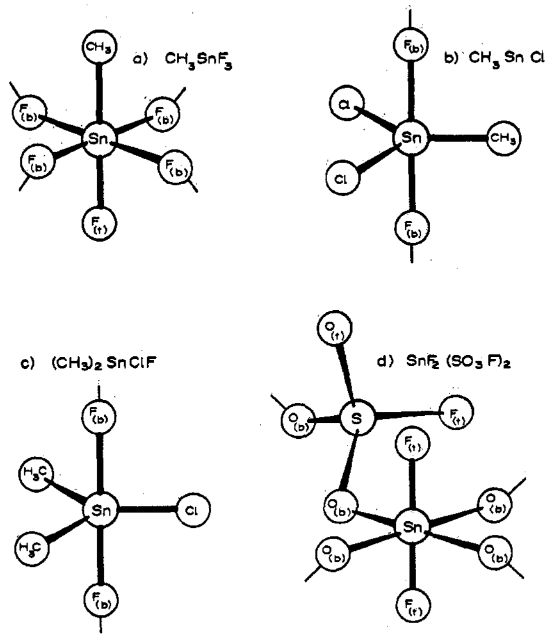

Figure 4.—Suggested configurations around tin for the fluoro derivatives. Explanation: $F_{(b)}$, F atom in bridging position; $F_{(t)}$, F atom in terminal position; $O_{(b)}$, O atom in bridging position; $O_{(t)}$, O atom in terminal position.

to answer with precision, since the presence of terminal rather than bridging fluorines could have quite a large effect on the quadrupole splitting, but a rough estimate can be obtained as follows. Data in Table VI for $SnCl_2(SO_3F)_2$ and $SnF_2(SO_3F)_2$ allow one to estimate the relative contributions of terminal Cl and F to the splittings. These values, with the point-charge expression for a tetrahedral MA_2B_2 molecule,[44] yield a predicted splitting of about ±0.20 mm/sec. (The sign is ambiguous, since $\eta = 1$ in this case.) While admittedly very crude, this estimate is hardly in error by more than a factor of 2 or 3, which certainly suggests that $SnCl_2F_2$ does not have a simple tetrahedral structure. The fact that a weak but noticeable room-temperature Mössbauer resonance is observed argues some form of intermolecular association, but no definite conclusions concerning the structure of $SnCl_2F_2$ can be drawn at this time.

Finally, the Mössbauer data for the two methyltin(IV) chloride fluorides appear to be consistent with a positive sign for V_{zz}, as found very recently for $(CH_3)_3SnF$.[5] However, the quadrupole splitting values for these three compounds are not linearly dependent upon σ, suggesting the possibility of slight structural variations within this group of compounds. In particular, the high Δ value found for $(CH_3)_2SnClF$ may be indicative of weak chlorine bridging, a possibility already raised by the position of ν(Sn–Cl) in this derivative.

IV. Structural Conclusions.—As evidenced by their physical properties and the vibrational and the ^{119}Sn Mössbauer spectra, the new compounds are all polymeric. The repeating units, showing the coordination around the central tin atoms, are shown in Figure 4. The proposed configuration for CH_3SnF_3 is derived from the known structure of $(CH_3)_2SnF_2$[2] by substituting terminal fluorine for one of the methyl groups. In the same way the structures of the methyltin(IV) chloride fluorides are derived from a rather idealized structure for $(CH_3)_3SnF$ where first one and then a second CH_3 group is replaced by chlorine. Whether all three groups in the equatorial plane are exactly coplanar and whether the bridging fluorines are equidistant from tin is impossible to decide at the moment. These points are apparently not even settled for $(CH_3)_3SnF$.[2,4,5]

The suggested structure for $SnF_2(SO_3F)_2$ has precedents in the structures of $(CH_3)_2Sn(SO_3F)_2$[26] and $SnCl_2(SO_3F)_2$[19] with bridging SO_3F groups rather than bridging fluorine.

Even though our evidence does not indicate a tetrahedrally coordinated configuration with C_{2v} symmetry, as suggested earlier[6] the true structure of $SnCl_2F_2$ is still very much in doubt. A final decision will have to be made from an X-ray determination.

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