

REACTIONS OF ORGANOTIN COMPOUNDS VII. DIMETHYLTIN DERIVATIVES

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INTRODUCTION

Investigations of numerous triorganotin derivatives¹ have indicated the occurrence of non-ionic solid-state structures. Recent spectroscopic studies of dimethyltin dinitrate² and dimethyltin chromate¹ also suggest a non-ionic constitution for these compounds. In continuation of our studies on organotin derivatives, and in order to provide a comparison between analogous tri- and diorganotin compounds, we have attempted to synthesize and examine the structural characteristics of a number of dimethyltin derivatives, such as the carbonate, the bis(tetrafluoroborate), the hexafluorosilicate, the related hexafluorophosphate, -arsenate, and -antimonate, as well as the dimethyltin derivative of $B_{12}Cl_{12}^{2-}$. We have also investigated some addition compounds of dimethyltin sulfate and dimethyltin dichloride.

EXPERIMENTAL

Except where preparations were performed in aqueous solution, all manipulations were carried out under anhydrous conditions in a nitrogen-filled dry box. Conventional vacuum techniques were used for the manipulation of volatile compounds, and a modified form of an apparatus described by Parry *et al.*³, was used for performing reactions in liquid sulfur dioxide.

Infrared spectra in the range 650–4000 cm^{-1} were recorded on a Perkin-Elmer model 21 spectrophotometer, and spectra in the 250–2000 cm^{-1} region on a Perkin-Elmer model 421 grating spectrophotometer. Samples were generally prepared in the dry box as mulls in nujol, hexachlorobutadiene, or halocarbon oil, and then placed between plates of cesium iodide, potassium bromide, or 1.0 mm sheets of silver chloride or polyethylene. The samples were protected from moisture by wrapping polyvinyl tape around the plates. Several spectra of each substance were recorded at different concentrations.

X-ray powder photographs were taken with a 14.32-cm diameter camera, using copper $K\alpha$ radiation with a nickel filter, on a G.E. X-ray unit. Quartz capillary sample tubes (0.5 or 0.3 mm diam.) were filled and sealed in the dry box. Microanalyses for C, H, N, F, and S were performed in the microanalytical laboratory

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of this department, by Dr. A. Bernhardt, Germany, or by the Schwarzkopf Micro-analytical Laboratory, New York. Boron and chlorine analyses were obtained through the courtesy of Dr. E. L. Muetterties, who also generously provided the sample of $\text{Ag}_2\text{B}_{12}\text{Cl}_{12}$.

Preparation of compounds

The compounds listed in Table 1 were prepared by the reaction of dimethyltin dichloride with the appropriate silver salt in the solvent indicated.

TABLE I
ANALYTICAL DATA

Compound	Solvent	Calcd. (%)		Found (%)	
		C	H	C	H
$(\text{CH}_3)_2\text{SnF}_2$	H_2O	12.90	3.23	12.98	3.60
$(\text{CH}_3)_2\text{SnSO}_4$	H_2O	9.80	2.47	9.67	2.46
$(\text{CH}_3)_2\text{SnSO}_4(\text{C}_5\text{H}_5\text{N})$	$\text{C}_5\text{H}_5\text{N}$	27.64	3.91	N 4.61	26.14 3.74
$(\text{CH}_3)_2\text{SnSO}_4[(\text{CH}_3)_2\text{SO}]$	$(\text{CH}_3)_2\text{SO}$	15.34	3.86	S 20.50	15.59 3.84 S 20.56
$(\text{CH}_3)_2\text{SnCl}_2[(\text{CH}_3)_2\text{SO}]_2$	$(\text{CH}_3)_2\text{SO}/\text{CHCl}_3$	19.16	4.82	S 17.07	19.14 4.64 S 16.97

The adducts of dimethyltin sulfate and dimethyltin chloride were obtained by shaking the tin compound with excess organic ligand for approximately 24 h. The reaction of dimethyltin dichloride with silver sulfate in methanol gave a mixture of silver chloride and a methanol adduct of dimethyltin sulfate. These could not be separated readily, although the methanol could be removed when the mixture was heated to 100° under vacuum for about 4 h.

Dimethyltin dichloride (1.085 g) and silver carbonate (1.362 g) were shaken in 50 ml of methanol for 3 days. Removal of the solvent under vacuum gave a white solid whose X-ray powder photograph showed no lines due to either of the reactants. Because of its insolubility, the dimethyltin carbonate could not be obtained free from silver chloride. Treatment of the mixture with hot water caused decomposition to dimethyltin oxide. The infrared spectrum was unaffected by exposure of the mixture to moist air.

Attempted preparations of dimethyltin salts of fluoro acids

(a) Dimethyltin dichloride (0.640 g) and silver hexafluorosilicate (1.043 g) were mixed in methanol (25 ml). The precipitated silver chloride was filtered off, and the methanol removed under vacuum to leave dimethyltin difluoride. (Found: C, 12.85; H, 3.21. $\text{C}_2\text{H}_6\text{F}_2\text{Sn}$ calcd.: C, 12.90; H, 3.23%.) The X-ray powder photograph and infrared spectrum were also identical with those of an authentic sample. The methanol recovered from the above reaction was highly acidic and contained silicon and fluorine.

(b) Dimethyltin dichloride (0.647 g) and silver tetrafluoroborate (1.470 g) were allowed to react in anhydrous methanol (25 ml). Precipitated silver chloride (0.837 g, calcd. 0.844 g) was removed by filtration, and the methanol was removed under vacuum to give a white solid (I). (Found: C, 10.47; H, 2.82; F, 32.47.) $\text{C}_2\text{H}_6\text{B}_2\text{F}_8\text{Sn}$ calcd.: C, 7.44; H, 1.87; F, 47.14%.) That partial decomposition to dimethyltin di-

fluoride and boron trifluoride had occurred was confirmed by the following observations. (i) A portion of the recovered methanol was condensed on to about 10 ml of pyridine. Upon evaporation under vacuum, a white solid was left whose infrared spectrum was identical with that reported⁴ for the $\text{BF}_3 \cdot \text{C}_5\text{H}_5\text{N}$ adduct. (ii) Another portion of the recovered methanol gave a positive test for fluorine and boron, and was markedly acidic. (iii) Approximately half of the solid (I) was insoluble in methanol and this insoluble portion was characterized (from its infrared spectrum, X-ray powder photograph and analytical data) as dimethyltin difluoride.

When the solid mixture (I) was heated under vacuum at 60–70° for about 6 h, the solid did not sublime nor did it show any change in its infrared spectrum or composition. Other attempts to prepare pure $(\text{CH}_3)_2\text{Sn}(\text{BF}_4)_2$ by reactions in ether or liquid sulfur dioxide were unsuccessful, and in all cases mixtures of $(\text{CH}_3)_2\text{SnF}_2$ with the desired $(\text{CH}_3)_2\text{Sn}(\text{BF}_4)_2$ were obtained.

(c) The reaction of dimethyltin dichloride with silver hexafluorophosphate in liquid sulfur dioxide led to the precipitation of silver chloride containing dimethyltin difluoride. Fractionation of the solvent and other volatile material gave a fraction rich in phosphorus oxytrifluoride, POF_3 , as shown by its infrared spectrum. The remaining involatile solid also contained dimethyltin difluoride, identified by its X-ray powder photograph. A similar attempt to prepare dimethyltin bis(hexafluoroarsenate) in anhydrous methanol likewise led to an impure product containing dimethyltin difluoride.

(d) Dimethyltin dichloride and silver hexafluoroantimonate were allowed to react in liquid sulfur dioxide (25 ml) and the precipitated silver chloride was filtered off. Removal of sulfur dioxide under vacuum gave a very hygroscopic solid, whose X-ray powder photograph did not show lines due to dimethyltin difluoride. The infrared spectrum was recorded, but analytical data were not obtained.

Dimethyltin derivative of $\text{B}_{12}\text{Cl}_{12}^{2-}$

Dimethyltin dichloride and $\text{Ag}_2\text{B}_{12}\text{Cl}_{12}$ were allowed to react in anhydrous methanol (25 ml). Removal of the silver chloride by filtration, and of the methanol under vacuum left a white, hygroscopic solid. The recovered methanol was not acidic and gave negative tests for boron and chlorine. The solid retained traces of methanol tenaciously, which were not removed after heating at 100° under vacuum for 24 h. (Found: B, 16.4; Cl, 57.8. $\text{C}_2\text{H}_6\text{B}_{12}\text{Cl}_{12}\text{Sn}(\text{CH}_3\text{OH})$: B, 17.6; Cl, 57.8. Calcd. for $\text{C}_2\text{H}_6\text{B}_{12}\text{Cl}_{12}\text{Sn}(\text{CH}_3\text{OH})_2$: B, 16.9; Cl, 55.4%.) Its infrared spectrum was recorded and was observed to change markedly as the sample was caused to hydrolyze in air.

DISCUSSION

The possibility that dimethyltin difluoride may have a polymeric structure, in which an octahedrally coordinated tin atom is surrounded by two *trans*-methyl groups and four bridging fluorine atoms, was first suggested by Beattie and Gilson⁵. The observed infrared absorption bands were at 3040 (w) and 2940 (vw) (C–H stretch), 1410 (vw) (CH_3 asym. deformation), 1210 (vw) (CH_3 sym. deformation), 785 (m) (CH_3 rock), 595 (m) (Sn–C asymmetric stretch) and 373 (vs) cm^{-1} (Sn–F stretch). The assignment of the most intense band at 373 to the Sn–F stretching vibration is consistent with a similar assignment of the 355 cm^{-1} band observed¹ in the spectrum

of trimethyltin fluoride which is known⁶ to have a non-ionic structure. It is also comparable to the reported⁷ Sn-O asymmetric stretching frequency of the dimethyltin acetylacetonato complex, $(\text{CH}_3)_2\text{Sn}(\text{C}_5\text{H}_7\text{O}_2)_2$ which is considered to have a *trans* octahedral structure. Certainly the infrared spectrum of dimethyltin difluoride is consistent with a non-ionic solid state structure*.

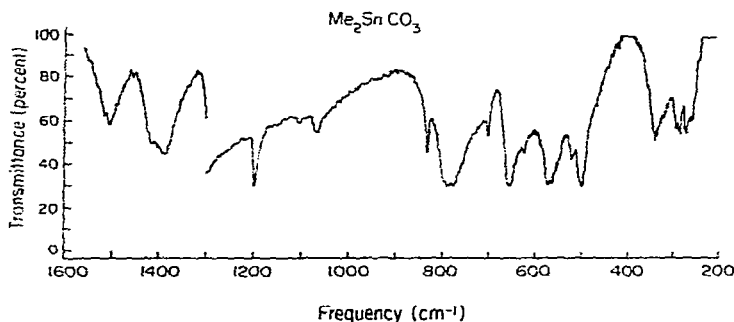


Fig. 1. Infrared spectrum of the $(\text{CH}_3)_2\text{SnCO}_3/\text{AgCl}$ mixture.

Dimethyltin carbonate could not be obtained as a pure compound because of its insolubility, but only as an intimate mixture with silver chloride. The absence from the mixture of dimethyltin dichloride, dimethyltin oxide, or silver carbonate was confirmed by X-ray powder photography. The infrared spectrum ($250\text{--}2000\text{ cm}^{-1}$) of the mixture (Fig. 1), which can only be composed of dimethyltin carbonate and silver chloride, showed absorption at the frequencies indicated in Table 2, which also

TABLE 2

INFRARED ABSORPTION SPECTRUM OF DIMETHYLTIN CARBONATE

vs = very strong; s = strong; m = medium; w = weak; sh = shoulder.

Frequency (cm^{-1})	Assignment
1510 (vs)	C=symm. stretch (ν_1)
1415 (sh)	CH_3 asymm. deformation
1385 (vs)	CO_2 asymm. stretch (ν_4)
1200 (m)	CH_3 symm. deformation
1105 (w)	CO_2 symm. stretch (ν_2)
1068 (m)	
832 (m)	CO_3 out-of-plane deformation (ν_6)
785 (s)	CH_3 rock
700 (m)	CO_2 symm. deformation (ν_3)
655 (s)	CO_2 asymm. deformation (ν_5)
576 (s)	Sn-C asymm. stretch
523 (m)	Sn-C symm. stretch
500 (s)	Sn-O asymm. stretch (and lattice modes?)
340 (m)	
275 (m)	

* After the submission of this paper, the crystal structure of dimethyltin fluoride was described in detail [E. O. Schlemper and W. C. Hamilton, *Inorg. Chem.*, 5 (1966) 995]. The structure consists of an infinite two-dimensional network of tin atoms and bridging fluorine atoms with the methyl groups above and below the plane completing the octahedral co-ordination of the tin.

gives the suggested assignments. The bands due to the $(\text{CH}_3)_2\text{Sn}$ group are readily distinguished, and assigned as shown. Of particular interest are the two bands assigned to the Sn-C stretching vibrations at 576 and 523 cm^{-1} . These may be compared with those of dimethyltin dichloride⁸ at 567 and 515 cm^{-1} . In both compounds, the observation of both the symmetric and asymmetric Sn-C stretching vibrations indicates the non-linear nature of the $(\text{CH}_3)_2\text{Sn}$ group. For the carbonate group, the bands at 1510 and 1385 cm^{-1} clearly arise from the splitting of the doubly degenerate ν_3 mode of the free ion⁹. The situation is therefore very similar to that of the CO_3 group in transition metal carbonate complexes, and differs from that of some ionic carbonates where crystal field effects are observed¹⁰ in the infrared spectra. The other carbonate bands of $(\text{CH}_3)_2\text{SnCO}_3$ can be assigned equally satisfactorily as shown. Absorption bands in the 250 – 500 cm^{-1} region are probably associated with Sn-O stretching vibrations as well as with absorptions due to lattice modes. Similar bands at 450 , 375 , and 250 cm^{-1} have been observed¹¹ in the spectrum of trimethylantimony carbonate, while a band at 388 cm^{-1} in the spectrum of bis(triethyltin) carbonate has been assigned¹² to an Sn-O vibration. It is clear, therefore, that the carbonate infrared absorption bands can be interpreted in terms of a distorted CO_3 group of C_{2v} or lower symmetry, and that a polymeric structure based on non-linear $(\text{CH}_3)_2\text{Sn}$ groups bridged by co-ordinated carbonate groups can be suggested. It is interesting that the splitting of the ν_3 mode of the free CO_3^{2-} ion into the two bands at 1510 and 1385 cm^{-1} in dimethyltin carbonate is much less than the separation of the 1715 and 1280 cm^{-1} bands in $(\text{CH}_3)_3\text{SbCO}_3$ ¹¹. The spectroscopic features of the latter compound are much closer to those of dimethyl carbonate, and presumably any covalent interaction between $(\text{CH}_3)_3\text{Sb}$ and CO_3 groups is greater than between $(\text{CH}_3)_2\text{Sn}$ and CO_3 .

Pure dimethyltin sulfate was readily obtained from aqueous solution; it is insoluble in most organic solvents. Its infrared spectrum showed absorption bands (250 – 2000 cm^{-1} region) of the $(\text{CH}_3)_2\text{Sn}$ group at 1238 (w) (CH_3 symm. deformation), 805 (s) (CH_3 rock), and 600 (s) (Sn-C asymm. stretch) cm^{-1} , consistent with a linear geometry. For the SO_4 group, bands were observed at 1095 (vs, broad) and 670 (m) cm^{-1} , these being assigned¹ to the ν_3 and ν_4 modes of the tetrahedral SO_4 group. The spectrum can therefore be interpreted in terms of $(\text{CH}_3)_2\text{Sn}^{2+}$ and SO_4^{2-} ions, but equally well in terms of a polymeric structure in which every oxygen atom of each SO_4 group is co-ordinated to a tin atom. Such an arrangement would make the tin atom six co-ordinate, and would preserve both the T_d symmetry of the SO_4 group as well as the linearity of the $(\text{CH}_3)_2\text{Sn}$ group.

When dimethyltin dichloride and silver sulfate were allowed to react in anhydrous methanol, a mixture of silver chloride with presumably a methanol adduct of dimethyltin sulfate was obtained. Although the adduct could not be obtained pure, the sulfate infrared bands of this mixture were quite different from those of pure dimethyltin sulfate, and were observed at 1210 (m) (SO_2 asymm. stretch ν_6), 1175 (s) (SO_2 symm. stretch ν_1), 1065 (s) (SO_2^* asymm. stretch ν_8), 995 (s) (SO_2^* symm. stretch ν_2), 655 (s) (SO_4 rock ν_7), 606 (s) (SO_2 bend ν_3), 585 (sh) (SO_4 rock ν_9), and 475 (m) (SO_2^* bend ν_4) cm^{-1} . These assignments have been made on the basis of C_{2v} symmetry of the SO_4 group, and certainly the observed frequencies lie in the same range as those observed for the bidentate sulfato group¹³. Moreover, the O-H stretching vibration of methanol is lowered considerably to 3110 cm^{-1} from 3400

cm^{-1} for free methanol, suggesting that the methanol is co-ordinated. The infrared spectrum of the mixture changed markedly on exposure to moist air, presumably due to hydrolysis of the methanol adduct. Also, when the mixture was heated under vacuum at 100° for 4 hours, all methanol was removed, and the infrared spectrum was then identical to that of pure dimethyltin sulfate. Although the constitution of the methanol adduct is uncertain, the fact that the presence or absence of small amounts of co-ordinated methanol cause such significant changes in the sulfate infrared bands can only be interpreted in terms of a co-ordinated structure which is changed considerably by solvation.

The formation of addition compounds of organotin halides is well-known¹⁴, and invariably diorganotin (IV) derivatives give 1 : 2 adducts with monodentate bases, e.g. $(\text{CH}_3)_2\text{SnCl}_2 \cdot (\text{C}_5\text{H}_5\text{N})_2$. We have repeated the preparation of this latter compound and have confirmed the infrared spectral data of Beattie and McQuillan¹⁴. We have also found independently that dimethyltin dichloride forms a 1 : 2 adduct with dimethyl sulfoxide, in agreement with the very recent report of Langer and Blut¹⁵. In view of the structural characteristics suggested above for dimethyltin sulfate, which is then structurally different from dimethyltin dichloride, it is not too surprising that the sulfate forms 1 : 1 complexes (not 1 : 2 adducts) with pyridine and dimethyl sulfoxide, $(\text{CH}_3)_2\text{SnSO}_4 \cdot \text{C}_5\text{H}_5\text{N}$ and $(\text{CH}_3)_2\text{SnSO}_4 \cdot \text{DMSO}$.

The pyridine adduct, $(\text{CH}_3)_2\text{SnSO}_4 \cdot \text{C}_5\text{H}_5\text{N}$, gave the following infrared bands: 3100 (w), 3050 (w), 2940 (w), 2450 (vw), 1605 (s), 1492 (m), 1450 (s), 1410 (w), 1360 (vw), 1245 (sh), 1232 and 1217 (m), 1208 (sh), 1200 (s), 1160 (vw), 1090 (s), 1066 (s), 1025 (s), 992 (m), 887 (vw), 800 (s), 765 (s), 692 (s), 655 (s), 637 (s), 598 (s), 590 (s), 576 (m), 510 (vw), 465 (m), 425 (m), and 417 (sh) cm^{-1} . Many of these bands can be assigned to co-ordinated pyridine¹⁶ and many similarities to the spectrum of $(\text{CH}_3)_2\text{SnCl}_2 \cdot 2 \text{C}_5\text{H}_5\text{N}$ are apparent. It is thus possible to conclude that the strong bands at 1200, 1090, 1025 and 992 cm^{-1} in the spectrum of the sulfate adduct can be attributed to the sulfate group. Similarly, in the lower frequency region, the bands at 655, 590, 576, and 465 cm^{-1} are associated with the sulfate group. The bands at 598 and 800 cm^{-1} can be assigned to the Sn-C asymmetric stretch and CH_3 -Sn rocking modes respectively of the $(\text{CH}_3)_2\text{Sn}$ group of the sulfate adduct, compared with 560 and 780 cm^{-1} in $(\text{CH}_3)_2\text{SnCl}_2 \cdot 2 \text{C}_5\text{H}_5\text{N}$. In both compounds, the $(\text{CH}_3)_2\text{Sn}$ group must therefore be linear, and apparently the sulfate adduct contains a co-ordinated sulfato group.

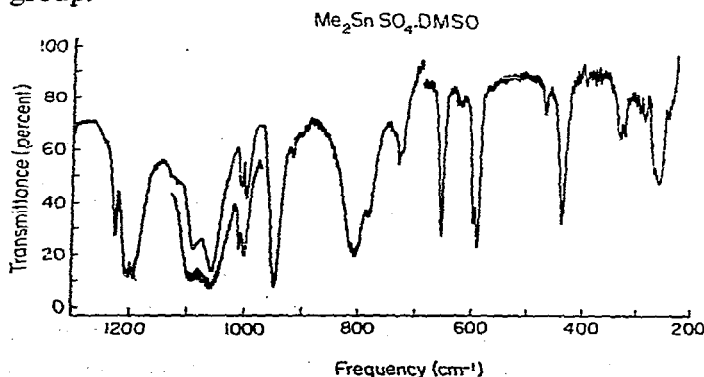


Fig. 2. Portion of the infrared spectrum of $(\text{CH}_3)_2\text{SnSO}_4 \cdot \text{DMSO}$.

TABLE 3

INFRARED ABSORPTION SPECTRA OF DMSO ADDUCTS OF $(\text{CH}_3)_2\text{SnCl}_2$ AND $(\text{CH}_3)_2\text{SnSO}_4$ Frequencies in cm^{-1} ; s = strong; m = medium; w = weak; vw = very weak; sh = shoulder. * denotes the oxygen atoms of the SO_4 group involved in bonding, based on C_{2v} symmetry.

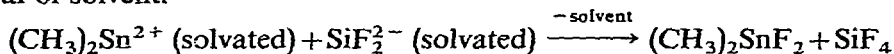
$(\text{CH}_3)_2\text{SnSO}_4 \cdot \text{DMSO}$	$(\text{CH}_3)_2\text{SnCl}_2 \cdot 2 \text{DMSO}$	Assignment
3040 w	3030 w }	C-H stretch
2960 w	2930 w }	
1455 sh	1457 sh	
1443 s	1430 s	
1420 w	1410 m	
	1365 vw	
1323 m	1320 m	
1300 w	1300 m }	
	1295 m }	
1225 m		
1202 s }		SO_2 asymm. stretch ν_6
1193 }		
1080 s		
1045 s		SO_2 symm. stretch ν_1
		SO_2^* asymm. stretch ν_8
	1034 s	
1000 m	995 s	
989 m		SO_2^* symm. stretch ν_2
945 s	943 s	$\nu(\text{S-O})$ DMSO
915 w	910 m	
805 s	788 s	CH_3 rock
783 sh		
727 m	720 m	
655 s		SO_4 rock ν_7
597s	573s	Sn-C asymm. stretch
590 s		SO_2 bend ν_3
	508 vw	
468 m		SO_2^* bend ν_4
437 s	415 s	Sn-O stretch
330 m	340 s	
	312 s	Sn-Cl stretch
255 m	255 m	

The infrared absorption frequencies of $(\text{CH}_3)_2\text{SnSO}_4 \cdot \text{DMSO}$ (Fig. 2) and $(\text{CH}_3)_2\text{SnCl}_2 \cdot 2 \text{DMSO}$ and some assignments are given in Table 3. Only the S-O stretching frequency is assigned for DMSO and the values agree well with those of Langer and Blut¹⁵, indicating co-ordination through the oxygen atom. The other frequencies due to DMSO are readily apparent from the similar absorptions of the two compounds. Thus the bands of $(\text{CH}_3)_2\text{SnSO}_4 \cdot \text{DMSO}$ at 1202–1193, 1080, 1045, 989, 655, 590 and 468 cm^{-1} are readily assigned, as shown, to vibrations of an SO_4 group of C_{2v} (or lower) symmetry, and are remarkably similar to analogous bands in $(\text{CH}_3)_2\text{SnSO}_4 \cdot \text{C}_5\text{H}_5\text{N}$. The assignment of bands at 805 and 597 cm^{-1} indicates the presence of linear $(\text{CH}_3)_2\text{Sn}$ groups, and for both DMSO adducts a band in the 410–440 cm^{-1} region can be assigned to a Sn-O vibration. For $(\text{CH}_3)_2\text{SnCl}_2 \cdot 2 \text{DMSO}$, in the low frequency region, the bands at 340 and 255 cm^{-1} have been attributed to vibrations of DMSO itself¹⁷, so that only the 312 cm^{-1} band can be

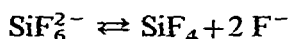
due to an Sn-Cl vibration. This suggests a *trans* octahedral structure for $(\text{CH}_3)_2\text{-SnCl}_2 \cdot 2 \text{DMSO}$.

It is certainly of interest that the presence of the bidentate SO_4 group should lead to the formation of the 1 : 1 complexes with pyridine and DMSO, whereas diorganotin dihalides with the monodentate halide ligands give 1 : 2 complexes. For $(\text{CH}_3)_2\text{SnSO}_4 \cdot \text{C}_5\text{H}_5\text{N}$ and $(\text{CH}_3)_2\text{SnSO}_4 \cdot \text{DMSO}$, the infrared evidence seems to suggest structures, either monomeric or polymeric, in which the tin atom is penta-coordinate (two CH_3 + ligand + bridging or bidentate SO_4) and a detailed structural investigation would be of interest.

Attempts to prepare dimethyltin derivatives of fluoro anions were not successful in producing the pure, desired compounds. Nevertheless, the reactions are interesting and demonstrate the instability of the free $(\text{CH}_3)_2\text{Sn}^{2+}$ ion in the solid state. This is best illustrated by the attempt to prepare dimethyltin hexafluorosilicate, $(\text{CH}_3)_2\text{-SnSiF}_6$ by the metathetical reaction between dimethyltin dichloride and silver hexafluorosilicate in anhydrous methanol. Other than silver chloride, the products were dimethyltin difluoride and apparently silicon tetrafluoride. Since the methanol solution appeared stable, the following decomposition apparently accompanied the removal of solvent.



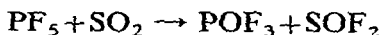
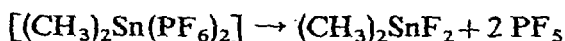
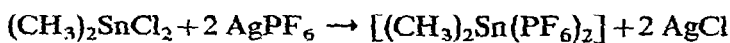
The equilibrium constant for the decomposition of SiF_6^{2-} in aqueous solution,



is 1×10^{-6} at 20° (ref. 18), and the heat of formation, ΔH_f° of the SiF_6^{2-} ion in aqueous solution¹⁹ is $-558.5 \text{ kcal} \cdot \text{mole}^{-1}$. Although different values would hold for methanol solutions, these values at least indicate that complete decomposition to dimethyltin difluoride and silicon tetrafluoride must involve very strong interaction between $(\text{CH}_3)_2\text{Sn}$ and SiF_6 groups.

Similarly, the metathetical reaction between dimethyltin dichloride and silver tetrafluoroborate gave a mixture of dimethyltin difluoride and dimethyltin bis(tetrafluoroborate), containing approximately 46% $(\text{CH}_3)_2\text{Sn}(\text{BF}_4)_2$ and 54% $(\text{CH}_3)_2\text{-SnF}_2$. The liberation of BF_3 was also established. These results, therefore, are identical to those obtained in the attempted preparation¹¹ of $(\text{CH}_3)_3\text{Sb}(\text{BF}_4)_2$. Moreover, the infrared spectrum of this present mixture did not show the characteristic infrared bands of the free BF_4^- ion²⁰, but bands at 1280, 1207, 1195, 1157, 1095, 1066, 1047, 1030, 940, 760, 525-510, 455, and 410 cm^{-1} must be associated with the BF_4 group. This complexity of the spectrum, even allowing for isotope effects, clearly indicates the low symmetry of the BF_4 group (C_{2v} or lower), and together with the partial decomposition to $(\text{CH}_3)_2\text{SnF}_2$ and BF_3 , emphasizes the strong interaction which occurs between $(\text{CH}_3)_2\text{Sn}$ and BF_4 groups in the solid state. Interestingly, when the mixture is exposed briefly to moist air, the infrared spectrum is changed to show the characteristic $1110\text{-}1025 \text{ cm}^{-1}$ and $535\text{-}520 \text{ cm}^{-1}$ bands of the free BF_4^- ion.

When dimethyltin chloride and silver hexafluorophosphate were allowed to react in sulfur dioxide, silver chloride was formed quantitatively, the other products being dimethyltin difluoride and phosphorus oxytrifluoride. The situation is therefore analogous to that of the attempted preparation of $(\text{CH}_3)_3\text{SnPF}_6$ ²¹ and involves the reactions



Likewise, pure $(\text{CH}_3)_2\text{Sn}(\text{AsF}_6)_2$ could not be obtained, but rather a solid product containing appreciable amounts of dimethyltin difluoride. The infrared spectrum of this mixture showed bands at 1210 (CH_3 symm. deformation), 825 , 800 (ICH_3 rock), 760 , 718 , 595 ($\text{Sn}-\text{C}$ asymm. stretch), 475 and 375 cm^{-1} . The two bands at 760 and 718 cm^{-1} are two components of the triply degenerate ν_3 mode of the AsF_6^- ion and similarly the 475 and 375 cm^{-1} bands are components of the ν_4 mode. These compare favorably with the frequencies observed for the AsF_6 group in trimethyltin hexafluoroarsenate²¹, and together with the formation of $(\text{CH}_3)_2\text{SnF}_2$, emphasize the interaction between $(\text{CH}_3)_2\text{Sn}$ and AsF_6 groups.

Likewise, an attempt to obtain dimethyltin bis(hexafluoroantimonate) gave an extremely hygroscopic solid which did not contain dimethyltin difluoride. Its infrared spectrum was similar to that of $(\text{CH}_3)_3\text{SnSbF}_6$ ²¹, showing three bands at 675 , 650 and 635 cm^{-1} , apparently arising from the ν_3 mode of the free ion, and bands at 445 , 365 , and 290 cm^{-1} probably associated with the ν_4 mode. On hydrolysis of this product, the characteristic 660 cm^{-1} band of the free SbF_6^- ion appeared.

Finally attempts were made to prepare the dimethyltin derivative of $\text{B}_{12}\text{Cl}_{12}^{2-}$. An analytically pure compound was not obtained, but there were no signs of decomposition of the $\text{B}_{12}\text{Cl}_{12}^{2-}$ group, and the lack of agreement of the calculated and theoretical analytical data may well be due to the difficulties inherent in analyses of such compounds. In any event, the infrared spectrum of the product shows many more bands than the free $\text{B}_{12}\text{Cl}_{12}^{2-}$ ion²², which clearly has not retained its I_h symmetry. Instead of the bands at 1030 , 536 , and 518 cm^{-1} , as found for $\text{Ag}_2\text{B}_{12}\text{Cl}_{12}$, this product shows bands at 1040 , 1002 , 950 , 925 , 824 , 535 , 480 , 425 , and 325 cm^{-1} , all arising from the $\text{B}_{12}\text{Cl}_{12}$ unit. When the product is exposed to air, its spectrum gradually changes with the disappearance of the bands at 950 , 925 , 824 , 480 , 425 , and 325 cm^{-1} , to resemble more closely that of the $\text{B}_{12}\text{Cl}_{12}^{2-}$ ion. The interaction with $\text{B}_{12}\text{Cl}_{12}^{2-}$ of $(\text{CH}_3)_2\text{Sn}^{2+}$ is therefore similar to that¹¹ of $(\text{CH}_3)_3\text{Sb}^{2+}$.

These results therefore strengthen our previous conclusions^{1,11}. In all of the organometallic compounds we have investigated, $[(\text{CH}_3)_3\text{SnX}$, $(\text{CH}_3)_2\text{SnX}_2$ or $(\text{CH}_3)_3\text{SbX}_2]$ the infrared spectra consistently show the marked changes in the spectral features of the anionic group, arising from interaction with the organometallic species. The decomposition of the dimethyltin derivatives of fluoro anions into the corresponding Lewis acids and dimethyltin difluoride emphasizes the considerable strength of this interaction. It is improbable that such similar spectroscopic features of the solid state should occur in so wide a variety of compounds, purely as a consequence of crystalline site effects. Certainly, the relatively low symmetry of $(\text{CH}_3)_3\text{Sn}^+$ or $(\text{CH}_3)_3\text{Sb}^{2+}$ ions could cause considerable polarization of the anionic group. However, the spectroscopic evidence for compounds such as $(\text{CH}_3)_3\text{SbCO}_3$, or $(\text{CH}_3)_3\text{SnNO}_3$ leads to a more convincing explanation in terms of coordination involving some degree of covalent bonding. Such a model explains convincingly all the evidence available for organotin and organoantimony compounds and compounds such as trimethyllead acetate. However, spectroscopic studies²³ of

thallium(III) derivatives, R_2TlX , provide no evidence of co-ordinative interactions between R_2Tl^+ and X^- , and the very sharp distinction between these and the related R_3PbX compounds is not readily understood.

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SUMMARY

The preparation and infrared spectra of dimethyltin difluoride, dimethyltin sulfate, of pyridine and dimethyl sulfoxide adducts of dimethyltin sulfate and dimethyltin dichloride are described. Dimethyltin carbonate, obtained as an intimate mixture with silver chloride, is similarly described. In all these cases, the infrared spectra show a lowering of the symmetry of the anionic group, presumably by interaction with $(CH_3)_2Sn$. Such interaction is also shown by the fact that attempts to prepare $(CH_3)_2SnX_2$ where $X = BF_4^-, PF_6^-, AsF_6^-, SbF_6^-$ gave mixtures containing large amounts of dimethyltin difluoride. The latter was the only solid product in the reaction of $(CH_3)_2SnCl_2$ with Ag_2SiF_6 . These results strengthen previous conclusions, and some further discussion of the nature of these interactions is given.

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