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STUDIES OF ORGANOTIN CHEMISTRY
I. PREPARATION AND PROPERTIES OF NEW, SOLUBLE FORMS OF TRIMETHYLTIN FORMATE AND ACETATE

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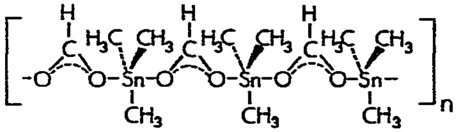
INTRODUCTION

Trimethyltin formate was prepared by Okawara, Webster and Rochow[1] by the reaction of trimethyltin hydroxide with formic acid. A striking property of the substance was its virtual insolubility in organic solvents, surprising in view of the great solubility of compounds such as trimethyltin chloride. On the basis of infrared studies, they advanced the novel suggestion that trimethyltin formate was an ionic compound, consisting of planar trimethyltin cations and formate anions. The original interpretation has since been modified, and the current view, as summarized by Poller[2], is as follows: Planar trimethyltin groups are linked together by formate bridges into infinite linear chains, as in (I), in which five-coordinate tin is an essential feature. Such a structure would, of course, account for the insolubility of the compound.



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In the course of investigations of the chemical behavior of organotin compounds, we have succeeded in converting the "classical" formate to a *soluble* form of markedly different properties.

We describe in this paper the preparation, infrared (both solution and solid) and NMR spectra of soluble trimethyltin formate and similar data for a soluble form of trimethyltin acetate.

The structure of trialkyltin carboxylates has been the subject of a number of recent studies[1-8]. Investigation of the simplest members of this class has heretofore been restricted to the solid state by solubility limitations. We anticipate that the removal of this restriction will lead to an increased understanding of the nature of the rather complex interactions which evidently operate in alkyltin carboxylates.

EXPERIMENTAL

Trimethyltin formate[1] and trimethyltin acetate[9] were prepared in their normal insoluble forms and purified according to the published procedures. Trimethyltin hydroxide for these reactions was obtained by the method of Luijten[10]. Other reagents were commercially available.

Microanalyses were carried out by Alfred Bernhardt Mikroanalytisches Laboratorium, Mülheim; Pascher Mikroanalytisches Laboratorium, Bonn; and Schwartzkopf Microanalytical Laboratory, Woodside. Molecular weights were determined with the Mechrolab Osmometer by Schwartzkopf and by the Microanalytical Laboratory of this Department.

Proton NMR data were obtained using Varian A-60, HR-100 and HA-100 spectrometers. Internal TMS was used with the HR-100 instrument, external TMS with the A-60 instrument and $CHCl_3$ was used as the lock for the HA-100. Accurate determination of the chemical shift and the spin–spin couplings were determined using a Hewlett–Packard Model 521C frequency counter and Model 241A Hewlett–Packard Oscillator. Differential temperature NMR data were obtained using a Varian V4343 variable temperature probe and the HA-100 spectrometer.

Infrared spectra to 400 cm^{-1} were determined using Perkin Elmer 421 and 337 spectrophotometers. Spectra to 200 cm^{-1} were measured using the 421 spectrophotometer equipped with caesium bromide interchange.

Conversion of insoluble to soluble trimethyltin formate

Initially, conversion was carried out in an autoclave at high pressure, starting with the insoluble form under cyclohexane solution. Subsequently, it was discovered that the conversion could be effected in essentially quantitative yield when the insoluble form was heated in a sealed ampoule with cyclohexane at 90° for 12–24 h. The solid is completely in solution when the tube is removed from the oven, and large, well formed needles form on cooling. An analytical sample was prepared by recrystallization from chloroform/pentane, followed by sublimation; after sublimation, the material was still soluble. (Found: C, 22.95, 23.21; H, 4.55, 4.85; O, 15.54, 15.53. $C_4H_{10}O_2Sn$ calcd.: C, 23.01; H, 4.79; O, 15.33%.) Molecular weight calcd., 208.7; found: 768 (3.610 mg/835.6 mg CCl_4); 775 (17.025 mg/1076.1 mg CH_2Br_2); 730 (8.880 mg/1601.3 mg CH_2Br_2; 320 (4.602 mg/ml benzene); 212 (1.300 mg/211.3 mg ethanol).

The melting point taken in a conventional (Gallenkamp) apparatus using a sealed capillary was poorly defined, with softening beginning at 135° and liquification complete near 148°. Observed microscopically on a Kofler hot stage, the behavior was extremely complex, with sublimation and several apparent phase changes beginning around 100°. For comparison, the m.p. of "insoluble" trimethyltin formate was sharp at 147–148° (Gallenkamp apparatus; literature[1], 151°).

Preparation of soluble trimethyltin acetate

The procedure was exactly as described for the formate; the acetate was completely in solution when removed from the oven at 90°, and formed long needles on cooling to room temperature. The crystals were removed by filtration and air dried. (Found: C, 26.68; H, 5.25; O, 13.26. $C_5H_{12}O_2Sn$ calcd.: C, 26.96; H, 5.39; O, 14.37%.) Molecular weight calcd., 222.7; found: 252 (9.977 mg/ml CH_2Br_2).

Melting was sharp at 191–192° in a sealed capillary (Gallenkamp apparatus). For comparison, the "insoluble" acetate melted at 194–195° (literature[9], 196.5–197.5°).

RESULTS AND DISCUSSION

The previously known *insoluble* trimethyltin formate has been converted in high yield to a new, *soluble* form. This is accomplished by the simple process of heating the insoluble formate with cyclohexane in a sealed tube to about 100° for several hours. The solubility of the new form in chloroform at room temperature is of the order of 200 mg/ml. It is a remarkable fact that both forms are sublimable in high vacuum *without interconversion*. The soluble form is appreciably more volatile, however.

Molecular weight data for the soluble formate show that it is monomeric in the donor solvent ethanol. In solvents such as carbon tetrachloride or dibromomethane, however, the degree of association lies between three and four.

There is also no question as to the existence of trimethyltin acetate in both "soluble" and "insoluble" forms. It has often been stated that lower trimethyltin acylates, specifically the acetate, are insoluble in the solvents generally used in infrared spectroscopy[1,3]. The form discussed here is amply soluble for both infrared and NMR measurements; the solubility in chloroform is of the order of 50 mg/ml at room temperature. It should be noted, however, that the normal procedure for preparation of the acetate[9] involves recrystallization from light petroleum (boiling range 111–136°C); it is certainly possible that during prolonged heating prior to crystallization, a partial conversion to the soluble form would occur.

Infrared spectra

Arguments as to the structure of trialkyltin carboxylates, in both the solid state and in solution, have been largely based on the 1700–1400 cm^{-1} and 600–500 cm^{-1} regions of the infrared spectrum. In the original study[1] of insoluble trimethyltin formate, a strong doublet was observed at 1590–1615 cm^{-1} and a strong band at 1378 cm^{-1}. Notwithstanding the resemblence of these bands to those of sodium formate[11,12], it was concluded[6] that the spectrum was consistent with a bridging role for the RCOO moiety, as in (I). One would expect these bridges to be disrupted in solution, and it has been found[3] that triethyltin acetate, with bands at 1572 cm^{-1} and 1412 cm^{-1} as a solid, absorbs in carbon tetrachloride solution at 1655 cm^{-1} and 1302 cm^{-1}; the latter bands were considered to arise from a "free" carboxylate molecule, with structure analogous to that of an organic ester. The heavy metal atom was presumed[3] to reduce the frequencies below the normal organic ester range[13]. In more concentrated solutions, disruption of the solid structure is incomplete, and association can be detected by molecular weight[5,21] and infrared measurements[3,4,5,8].

Carbonyl–carboxyl region. We show in Fig. 1 the concentration dependence of the carbonyl–carboxyl region of the spectrum of soluble trimethyltin formate in chloroform solution. The spectrum is strongly concentration dependent, and it is reasonable to suppose that different species (or aggregates) are present at low and high concentrations. At low concentration (Fig. 1a) there is a strong absorption at 1650 cm^{-1} which we assign to the carbonyl stretching mode of an unassociated formate group. The weak shoulder near 1600 cm^{-1} shifts to lower frequency and increases in intensity at the expense of the 1650 cm^{-1} band as the concentration is increased; ultimately, the 1580 cm^{-1} band is dominant, with the 1650 cm^{-1} band appearing as a relatively weak band (Fig. 1d). We assign the 1580 cm^{-1} band to the

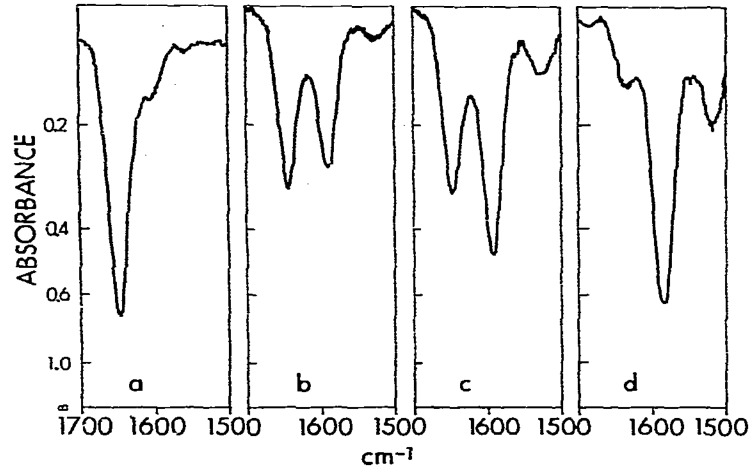
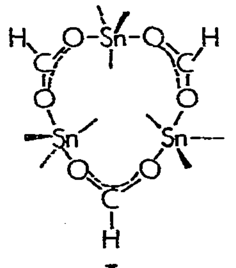


Fig. 1. Effect of concentration on the infrared spectrum of trimethyltin formate in chloroform; a. 16.1 mg/ml, 0.5 mm cell; b. 26.5 mg/ml, 0.1 mm cell; c. 80.5 mg/ml, 0.1 mm cell; d. 161 mg/ml, 0.025 mm cell.

asymmetric carbonyl stretching mode of an associated formate group. The sequence of spectra in Fig. 1 strongly suggests an equilibrium between associated and unassociated forms. Indeed, these results closely parallel the observations of Van der Kerk *et al.*, for trimethyltin laurate[3]; these workers, in common with others[4,5] have assumed that the associated form, predominant at higher concentrations, has a *linear* structure. We suggest, however, that the associated form may have a *cyclic* structure [such as (II)]. Such cyclic associated forms are compatible with much of



I

the earlier data, *both in solution and in the solid state*. As will be discussed more fully, it is tempting to attribute a cyclic form to soluble trimethyltin formate, while retaining the conventional view that insoluble trimethyltin formate possesses a linear structure.

It is of interest to examine the carbonyl–carboxyl region of soluble trimethyltin formate in the non-polar solvent cyclohexane (Fig. 2). Although the solubility in cyclohexane is much lower than in chloroform, the same two bands appear, although shifted slightly to 1665 cm^{-1} and 1590 cm^{-1}. The spectrum of Fig. 2a was obtained on a warmed, supersaturated solution, and the relatively high abundance of the unassociated (1665 cm^{-1}) species, as compared to chloroform as solvent (Fig. 1d), may be explained as a temperature phenomenon[4]. In the saturated though very dilute cyclohexane solution (Fig. 2b), the relative abundances of associated and unassociated formate can again be gauged from the intensities of the two bands; it is signifi-

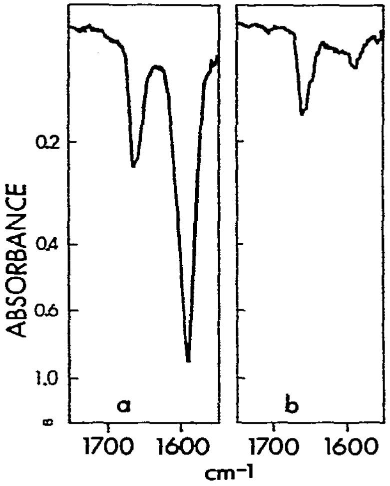


Fig. 2. Effect of concentration on the infrared spectrum of trimethyltin formate in cyclohexane; a. warmed supersaturated solution; b. saturated solution at room temperature.

cant, however, that the proportion of the associated species is greater than in chloroform, even though the total concentration in chloroform (Fig. 1a) is greater. We infer that the unassociated form is favored in chloroform solution, either by the polarity of the medium or by some more specific interaction.

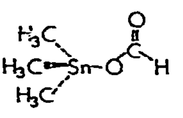
TABLE 1

INFRARED SPECTRA OF TRIMETHYLTIN FORMATES

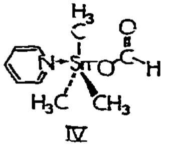
$(CH_3)_3SnOCOH$ (soluble)			*$(CH_3)_3SnOCOH$ (insoluble)*		
$CHCl_3$[a]	*KBr*	*Nujol*	*KBr*	*Nujol*	*KBr*[d]
	3000 w		3000 m		
	2930 m		2940 m		
	2860 m		2870 m		
	2790 vw		2800 vw		
	2710 w	2720 vw	2725 w		
	2370 w	2375 vw	2380 w		
1650 s					
1595 m[b]	1592 s			1600 m	1615 s
		1580 s, br	1580 s, br	1575 s	1590 s
	1565 s				
1370 m–w	1368 s		1372 s		1378 s
	1355 s	1355 s	1360 s	1360 m	1363 s
	1198 w	1202 w	1205 w	1202 vw	1205 m
	1190 m	1195 m	1195 m	1195 w	1195 m
	770 s	780 s	780 s, br	775 m	790 sh 770 s
550 m	562 s	555 s	555 s	550 s	552 s
513 w					
430 mw	425 vw	425 vw			
[c]	[c]	305 m	[c]	[c]	

[a] $CHCl_3$ absorbs 800 cm^{-1}–600 cm^{-1}. [b] Not present in dilute solution (see DISCUSSION). [c] Spectrum below 400 cm^{-1} not available. [d] From ref. 1.

Tin–carbon stretching region. It is well established that an $Sn(CH_3)_3$ group involving a tetrahedral tin atom should give rise to two Sn–C stretching vibrations, while only one infrared active stretching band is expected for a planar $Sn(CH_3)_3$ group. Soluble trimethyltin formate (like the insoluble form[1]) in the *solid* state exhibits a single Sn–C stretching band at 555 cm^{-1} (Table 1). In *solution*, however, (Fig. 3a) a second band at 513 cm^{-1} clearly indicates the presence of non-planar $Sn(CH_3)_3$ groups. We assume that the non-planar species in question, which we represent as (III), gives rise also to the unassociated formate vibration at 1650 cm^{-1}.



III



IV

Studies of complex formation. Confirmation for the presence in solution of unassociated, tetrahedral trimethyltin formate molecules is provided by the spectra of Fig. 3, in which the effect of adding pyridine to a chloroform solution is shown. It is well established that trialkyltin halides interact with bases such as pyridine or dimethyl sulfoxide to form five-coordinate complexes in which the tetrahedral arrangement of the free halide has been converted to a trigonal bipyramidal structure containing a planar SnC_3 unit[14,15,16]. It is evident from Fig. 3 that the intensity of the symmetric Sn–C stretching mode at 513 cm^{-1} decreases as the pyridine concentration increases; at high pyridine concentrations only the asymmetric 543 cm^{-1} vibration remains. This behavior parallels that observed[15] in the dimethylacetamide/trimethyltin chloride system, and we conclude that pyridine is converting the soluble formate (III) to the complex (IV).

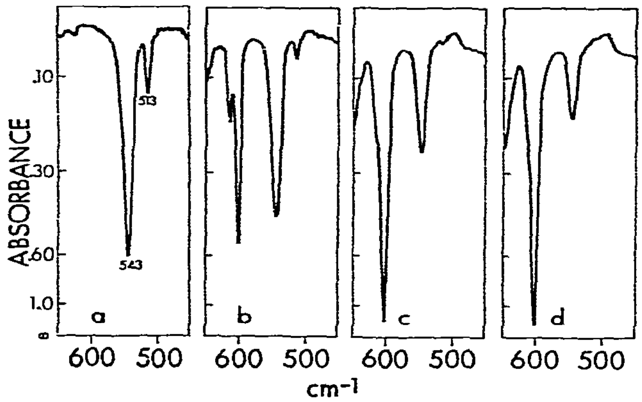


Fig. 3. Effect of pyridine on SnC_3 stretching vibrations of trimethyltin formate in chloroform solution; a. no pyridine added, 0.083 *M* formate; b. 0.33 *M* pyridine, 0.069 *M* formate; c. 1.0 *M* pyridine, 0.042 *M* formate; d. 2.0 *M* pyridine, 0.028 *M* formate.

It was of interest to observe the effect of complex formation on the carbonyl–carboxyl region of the spectrum. The base triethylamine was selected for this purpose, because pyridine absorbs in the region of interest. The results are shown in Fig. 4. The most significant result is the increase in intensity of a band at 1600 cm^{-1} with

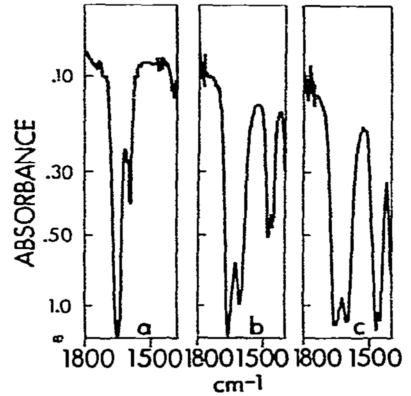


Fig. 4. Effect of triethylamine on carbonyl vibrations of trimethyltin formate in chloroform solution; a. no triethylamine added, 0.065 *M* formate; b. 0.099 *M* triethylamine, 0.065 *M* formate; c. 0.34 *M* triethylamine, 0.065 *M* formate.

increasing amine concentration. The 1600 cm^{-1} band cannot in this case be attributed to an "associated" trimethyltin formate species, in view of the findings concerning the configuration of the SnC_3 portion of the molecule (we consider it unlikely that a trialkyltin derivative is capable of six-coordination). We therefore suggest that the 1600 cm^{-1} band is due to a species like (IV), although the ionic character of the tin–formate bond and the geometry of the formate group may well differ from the conventional representation of the formula. Thus, the 1600 cm^{-1} frequency is intermediate between that of the unassociated species (III) (1650 cm^{-1}) and that of symmetrical or ionic formates such as (I) (1580 cm^{-1}).

Trimethyltin acetate. Table 2 gives complete infrared data and Fig. 5 shows

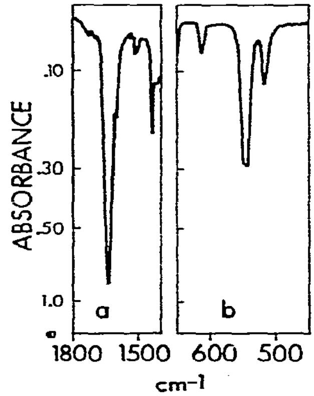


Fig. 5. Infrared spectrum of trimethyltin acetate in chloroform solution; a. carbonyl stretching region; b. SnC_3 stretching region.

the infrared spectrum of a chloroform solution of trimethyltin acetate in the two regions of interest. The relatively low intensity of the associated carboxylate band (Fig. 5a) indicates that the degree of association of the acetate is less than that of the formate (compare Fig. 1), as one would expect on steric grounds. Fig. 5b shows unambiguously the two tin–carbon stretching vibrations of the tetrahedral trimethyltin group. At higher concentrations (not shown), the "associated" 1580 cm^{-1} band

TABLE 2

INFRARED SPECTRA OF TRIMETHYLTIN ACETATES

$(CH_3)_3SnOCOCH_3$ *(soluble)*			$(CH_3)_3SnOCOCH_3$ *(insoluble)*		
$CHCl_3$	*KBr*	*Nujol*	*$CHCl_3$*	*KBr*	*Nujol*
	2990 w			3010 m	
	2910 w			2930 m	
	2815 vw			2830 wm	
				2710 vw	
				2370 vw	
1678 s, sh		1677 w			
1658 vs			1650 vs		
1625 wm	1600 m, sh	1608 ms	1615 m		
		1585 s, sh		1600 s, sh	1595 m, sh
	1570 vs	1570 vs		1575 vs, br	1565 s
1438 vvw, sh	1425 vs	1425 vs	1430 wm	1425 vs	1420 s
1388 m		1383 ms	1380 s		1380 wm
	1367 w	1370 m		1370 ms	1368 wm
	1355 w 1345 w	1360 m		1360 m	1355 wm
		1348 wm	1335 m	1348 m	1345 w
1318 vs			1315 vs		
	1210 wm	1206 w		1210 m	1205 w
	1197 wm	1193 w		1195 m	1192 w
1050 vw	1052 vvw		1052 vw	1050 w	
1015 w	1020 w 948 vw	1015 w	1018 m	1020 m	1015 w
	785 s	775 ms		780 s	773 s
	675 s	665 ms		670 s	668 s
	618 w	608 vw	618 wm	613 wm	615 vw
544 ms	558 s	548 ms	580 w 553 s	553 s	553 s
515 w			523 m		
		490 w		495 m	495 wm
425 vw		425 vw	425 vw	425 vw	425 vw

reaches an intensity about equal to that of the "unassociated" 1650 cm^{-1} band. The spectral changes thus parallel those of soluble trimethyltin formate.

NMR spectra

An initial conclusion of rather fundamental importance made possible by NMR is that the soluble formate here described is indeed a *formate*, and not, for example, the isomeric and as yet unknown trimethyltincarboxylic acid. The NMR spectrum of our material exhibited absorptions at 1.9 τ and 9.4 τ in an area ratio close to 1:9. The 9.4 τ peak was clearly due to methyl groups on tin in view of the characteristic ^{119}Sn and ^{117}Sn satellites, as well as its location in a region where trimethyltin resonance commonly occurs. The low field absorption could result from either a formate or carboxylic acid proton. The acid structure was ruled out by the lack of exchange of the low field proton with small amounts of added D_2O; the formate structure was confirmed by the observation of ^{13}C satellites of the 1.9 τ peak with $J(^{13}C\text{–}H) = 199$ cps (saturated chloroform solution), a reasonable value for formates[17].

A particular advantage of methyltin derivatives is the ease with which proton–tin spin–spin coupling constants can be determined. The coupling constants $J(^{119}\text{Sn–CH}_3)$ and $J(^{117}\text{Sn–CH}_3)$* provide invaluable information about the hybridization[18] and coordination number[19] of the tin atom. Thus, in tetramethyltin, J is 54.0 cps, while in trimethyltin chloride, J is 58.5 cps, reflecting a redistribution of *s*-character while retaining an approximately tetrahedral coordination for tin. In the pyridine adduct of trimethyltin chloride, known to contain five-coordinate tin with a planar trimethyltin group[14], J rises to 67.0 cps for a pyridine solution of trimethyltin chloride[19], and to 70.0 cps for a tetramethylene sulfoxide solution[15]. Thus J can be used to distinguish between four- and five-coordinate tin.

We shall see that the trends in coupling constants are entirely consistent with the hypothesis set forth on the basis of infrared results: that the soluble formate exists in solution as an associated and perhaps cyclic form containing five-coordinate tin, in equilibrium with an unassociated or monomeric form in which tin is four-coordinate [*cf.* (II) and (III)].

Table 3 gives the NMR results for trimethyltin formate. We draw attention initially to entries 1–4 of Table 3, in which the concentration is varied in $CDCl_3$ solution at constant temperature. Values of J range from 62.7 cps at the lowest concentration to 67.4 cps at the highest. This range falls between the approximate limits suggested in the previous discussion for four- and five-coordinate tin. It is reasonable to suppose that we are observing the averaged coupling constants of four- and five-

TABLE 3

PROTON MAGNETIC RESONANCE PARAMETERS FOR SOLUBLE TRIMETHYLTIN FORMATE

Solvent (ml)	Conc. (mg/ml)	Temp. (°C)	$J(^{119}Sn\text{–}CH_3)$ (cps)	$J(^{117}Sn\text{–}CH_3)$ (cps)	$\tau(CH_3\text{–}Sn)$ (ppm)	$\tau(H\text{–}COO)$ (ppm)
1. $CDCl_3/CHCl_3$	48.0	33.5	62.7	59.9	9.44	1.89
2. $CDCl_3$	52.6	33.5	63.9	60.4	9.42	1.90
3. $CDCl_3$	68.2	33.5	66.7	63.8	9.44	1.92
4. $CDCl_3$	150.0	33.5	67.4	64.4	9.45	1.91
5. $CDCl_3$	48.0	40	62.0	59.2	9.44	1.89
6. $CDCl_3$	48.0	50	60.5	57.7	9.43	1.87
7. $CDCl_3$	48.0	−30	68.7	65.8	9.50	1.96
8. $\left\{\begin{matrix}\left.\begin{matrix}CDCl_3\\CHCl_3\end{matrix}\right\}0.75\\C_5D_5N\ 0.25\end{matrix}\right.$	36.0[a]	33.5	67.3	64.4	9.70	
9. $\left\{\begin{matrix}CDCl_3 & 0.5\\C_6H_6 & 0.1\\C_5D_5N & 0.4\end{matrix}\right.$	80.0[b]	−40	68.5	65.5	9.56	
10. $\left\{\begin{matrix}DMSO\text{-}d_6 & 0.75\\CHCl_3 & 0.25\end{matrix}\right.$	110.0[c]	33.5	69.9	67.0	9.24	
11. DMSO-d_6	200[d]	33.5	70.4	67.6	[e]	[f]
12. Acetone-d_6	210	33.5	66.4	63.5	9.96	2.37

[a] Molar ratio pyridine-d_5/formate = 18 : 1. [b] Molar ratio pyridine-d_5/formate = 7 : 1. [c] DMSO = dimethyl sulfoxide; Molar ratio DMSO-d_6/formate = 20 : 1. [d] Molar ratio DMSO/formate = 7.4 : 1. [e] $J(^{13}CH_3)$ = 130 cps. [f] Peak broadened to about 100 cps; this phenomenon is under investigation.

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* Hereafter we refer only to the ^{119}Sn coupling constant, which we denote simply as J.

coordinate trimethyltin formate species in rapid equilibrium. This supposition is confirmed by the marked *increase of coupling constants with concentration.* The proportion of the associated, five-coordinate form relative to the four-coordinate monomer will increase at higher concentration; this is reflected in the higher average coupling constant.

The variation of J with temperature is given in entries 1 and 5–7 of Table 3. Values decrease from 68.7 cps at $-30°$ to 60.5 cps at $+50°$. These results are consistent with a temperature-dependent equilibrium, with the associated form favored by low temperatures. Indeed, J at $-30°$ approaches the limiting value expected for five-coordinate tin, and the proportion of monomer present must be low.

The influence of pyridine-d_5 is shown in Table 3, entry 8. The dominant species, as in the case of the infrared studies, is the pyridine adduct (IV). J has the value 67.3 cps, which should be compared with 65.2 cps for pyridine-trimethyltin chloride[19]. Both values represent averages of complexed and free species, as a small equilibrium concentration of the latter would be present. As the temperature of the pyridine-containing solution is lowered, (entry 9, Table 3), J increases to 68.5 cps, in accord with the expected stabilization of the adduct (IV).

Solutions of soluble trimethyltin formate in the strongly coordinating solvent dimethyl sulfoxide are measured in entries 10 and 11 of Table 3. In these cases, J is about 70 cps and there is evidently an insignificant amount of four-coordinate tin present.

The results of a less extensive NMR study of trimethyltin acetate are given in Table 4. The J values suggest that very little five-coordinate tin is present in solution even at $-30°$, in marked contrast to the formate case. Infrared and molecular weight studies also indicated very little association for the acetate. The pyridine complex, from its smaller J value, appears to be less stable than that of the formate, a reasonable conclusion on steric grounds.

TABLE 4

PROTON MAGNETIC RESONANCE PARAMETERS FOR SOLUBLE TRIMETHYLTIN ACETATE[a]

Solvent	*Temp. (°C)*	*$J(^{119}Sn\text{–}CH_3)$ (cps)*	*$J(^{117}Sn\text{–}CH_3)$ (cps)*	*$\tau(CH_3\text{–}Sn)$ (ppm)*	*$\tau(CH_3\text{–}COO)$ (ppm)*
$CDCl_3$	33.5	58.5	56.0	9.47	7.99
$CDCl_3$	50.0	58.2	55.7	9.50	7.98
$CDCl_3$	-30	58.1[b]		9.46	7.95
$CDCl_3/C_5D_5N$[c]	33.5	65.8	63.1	9.54	8.18

[a] All measurements on solutions which were initially saturated at room temp.; estimated solubility is 50 mg/ml at room temperature. [b] Signal broadened by precipitation of solid; ^{117}Sn–^{119}Sn satellites not resolvable under these conditions. [c] $CDCl_3$ 0.75 ml; pyridine-d_6 0.25 ml; estimated molar ratio pyridine-d_6/acetate = 10.5 : 1.

CONCLUSIONS

A soluble form of trimethyltin formate has been prepared and studied by infrared and NMR spectroscopy. The hypothesis has been advanced that this form exists in solution in a cyclic, associated form in equilibrium with free monomer. The spectroscopic evidence is in accord with this hypothesis.

It is well known that linear inorganic polymers tend to form small cyclic systems[20]; the driving force is the increase in entropy accompanying the change. Thus, there is precedent for the proposal that a linear formate is converted under our conditions to a cyclic form.

We must also suppose that the cyclic form postulated in solution persists in the solid state. The results of X-ray crystallographic examination of the two forms will be of interest, as this method alone can establish conclusively the essential structural differences between the two forms.

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SUMMARY

The previously known insoluble trimethyltin formate has been converted to a new, soluble form by heating in a sealed tube with cyclohexane at 100°. Trimethyltin acetate undergoes a similar transformation. The effects of concentration, temperature, and added complexing agents on the infrared and NMR spectra are reported. The results imply an equilibrium in solution between monomeric and associated forms. It is suggested that the associated forms may have a cyclic structure, in contrast to the linear polymeric structure usually attributed to the insoluble form.

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