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PREPARATION AND SPECTRAL STUDIES OF DIMETHYLCHLOROTIN CARBOXYLATES

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SUMMARY

Dimethylchlorotin carboxylates, $(CH_3)_2ClSnOOCR$ ($R=CH_3$, CF_3, C_2F_5, C_3F_7, CF_2Cl, CH_2Cl, $CHCl_2$, CCl_3, CH_2Br, CH_2I) are prepared by heating trimethyltin chloride with an excess of the appropriate acid at 100°. These compounds have been studied by ^1H and ^{19}F NMR, infrared, and Mössbauer spectroscopy. Based on this spectral data, in the solid state or in methylene chloride or chloroform, pentacoordinate tin is present. The solids are polymeric with bridging carboxylate units. In solution, the nonfluorinated carboxylate-containing compounds are very likely chelate monomers, while the remaining compounds retain polymeric character.

INTRODUCTION

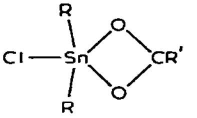
Dialkylchlorotin carboxylates ($R_2ClSnOOCR'$) have been prepared by a variety of methods including the reactions of dialkyltin dichlorides with carboxylic acids or salts of these acids[1]. Recently we reported[2] the syntheses of diorganochlorotin carboxylates in high yield via the reactions of triorganotin chlorides with carboxylic acids which involve the rather unexpected formation of methane[3]

$$(CH_3)_3SnCl+RCO_2H \rightarrow (CH_3)_2SnClO_2CR+CH_4$$

$$R=CH_3,\ CF_3,\ C_2F_5,\ C_3F_7,\ CF_2Cl,\ CH_2Cl,\ CHCl_2,\ CCl_3,\ CH_2Br,\ CH_2I$$

This is particularly interesting when the dialkylchlorotin product is compared with the trimethylsilyl perfluoroacetate obtained in 80% yield from the analogous reaction with trimethylchlorosilane and CF_3COOH[4] with hydrogen chloride as the only other product.

Some of the structural aspects of organotin compounds have been reviewed by Okawara and Wada[5]. Extensive work on the infrared as well as nuclear magnetic resonance and Raman spectra and X-ray data confirm that most compounds of the type R_3SnCO_2R' occur as polymeric solids (penta-coordinated tin) with planar trimethyl and bridging carboxylate groups[6–14]. In solution, or in the liquid phase, the compounds are monomeric. Formation of the polymeric structure is impeded by steric hindrance of bulky alkyl groups and also does not occur with thio- or dithioacetates. Thus, i-Pr_3SnOAc was found to exist as a monomeric liquid at 25° rather than as a five-coordinate polymer. Infrared spectral studies of halogen-substituted tributyltin acetates also indicate four-coordinate structures in solution[15]. In contrast, the structure of compounds of the type $R_2ClSnCO_2R'$ is thought to be five-coordinate and monomeric in solution, presumably with chelate carboxylate groups[16].



$R = C_2H_5, n\text{-}C_3H_7, H;\ R' = CH_3$

We have now prepared ten compounds of this type where R is methyl and R′ is a variety of haloalkyl groups and have attempted through available spectral techniques (vibrational, NMR and Mössbauer) to establish the structure of these materials. We report our conclusions below.

EXPERIMENTAL

Preparation of dimethylchlorotin carboxylates

A standard Pyrex glass high vacuum system was used for manipulating volatile materials and for separating the volatile products. All of the dimethylchlorotin carboxylates are prepared by sealing the reactants in a thick-walled Pyrex tube. *E.g.*, trimethyltin chloride (3.94 mmol) and an excess of trifluoroacetic acid (19.1 mmol) when heated at 100° for several hours form methane (3.94 mmol) quantitatively as measured by PVT techniques. The excess acid is removed under vacuum with concomitant heating when required. Essentially 100% conversion to the dimethylchlorotin trifluoroacetate (3.94 mmol) occurs. With the exception of the dimethylchlorotin monohaloacetates (~60% yield based on the amount of trimethyltin chloride converted), all preparations are essentially quantitative. Lower yields are due in part to the necessity for subliming the product from the reaction vessel.

Preparation of trimethyltin acetate

An excess of glacial acetic acid is added to a pyridine solution of trimethyltin chloride (2.5 mmol/cm^3). After stirring for several minutes, a white solid precipitated from solution. Pure trimethyltin acetate (1.9 mmol) was obtained by crystallization from water.

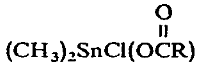
Methods

Elemental analyses of dimethylchlorotin perfluorocarboxylates and chlorodifluoroacetate were performed by Beller Mikroanalytisches Laboratorium, Göttingen, Germany. Other compounds were analyzed by Bernard Schecter of this department. Some chlorine analyses were determined using Volhard's method. The elemental and melting point data are given in Table 1. Melting points of the solid compounds were determined using a Thomas Hoover capillary melting point apparatus.

Infrared spectra were recorded using a Perkin–Elmer Model 621 grating spectrophotometer with a range of 4000–250 cm^{-1}. Spectra were calibrated from known peaks of a polystyrene film. Spectra of solids were obtained with pressed KBr

TABLE 1

ELEMENTAL ANALYSIS OF DIMETHYLCHLOROTIN CARBOXYLATES



$(CH_3)_2SnCl(O\overset{\overset{O}{\|}}{C}R)$

R	M.p. (°C)	C (%)	H (%)	Cl (%)	Sn (%)	F (%)
CF_3	118	16.21 (16.15)[a]	2.13 (2.02)	12.12 (11.93)	40.11 (39.94)	19.4 (19.18)
C_2F_5	103–104.5	17.26 (17.28)	1.90 (1.73)	10.41[b] (10.21)	33.81 (34.19)	27.1 (27.37)
C_3F_7	115	18.24 (18.13)	1.54 (1.51)	8.96[b] (8.93)	29.51 (29.59)	33.0 (33.49)
CF_2Cl	128–129	15.22 (15.31)	1.94 (1.93)	22.49 (22.63)	37.49 (37.83)	12.3 (12.11)
CH_3	187–188[c]					
CH_2Cl	129–130	17.52 (17.29)	2.93 (2.90)			
$CHCl_2$	130–131.5	15·60 (15.38)	2.52 (2.26)			
CCl_3	196	14.05 (13.85)	1.76 (1.74)			
CH_2Br	114–117	15.04 (14.90)	2.55 (2.50)			
CH_2I	127–128	13.55 (13.00)	2.60 (2.18)			

[a] Calculated values in parentheses. [b] Determined by Volhard method. [c] Lit.[17] 184–186°.

discs or with nujol mulls. Spectra of liquids or solutions in $CHCl_3$ or CH_2Cl_2 at several concentrations up to about 0.2 *M* were recorded from compensated KBr cells. High resolution ^{19}F NMR spectra were obtained with a Varian HA-100 spectrometer operating at 94.1 MHz and ^1H NMR spectra were recorded with an A-60 NMR spectrometer. Acetone-d_6 or $CHCl_3$ was used as a solvent and tetramethylsilane and/or trichlorofluoromethane as internal references. The Mössbauer spectra were determined at the University of British Columbia by using apparatus described previously[10]. Tin(IV) oxide was used as the reference and the spectra were recorded at −196°.

Reagents

CF_3CO_2H, $C_2F_5CO_2H$, $C_3F_7CO_2H$ and CH_2BrCO_2H were obtained from Aldrich Chemical Co.; CF_2ClCO_2H from Pierce Chemical Co.; CH_2ICO_2H from Eastman; CH_3CO_2H and CH_2ClCO_2H from J. T. Baker Chemical Co.; and $CHCl_2CO_2H$ and CCl_3CO_2H frpm Matheson, Coleman and Bell. Trimethyltin chloride was purchased from Alfa Inorganics.

RESULTS AND DISCUSSION

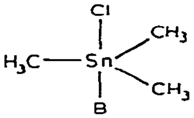
The reactions of trialkyltin chlorides with metal carboxylates have been used to prepare trialkyltin carboxylates[1]. However, we find that triorganotin chlorides react with carboxylic acids to give diorganochlorotin carboxylates[2] and alkane. Cleavage of the tin–carbon bond in tetraorganotin compounds has been used to prepare substituted organotin compounds[18,19], but dealkylation or dephenylation of triorganotin chlorides occurs only in a few cases[20]. However, in the reaction of tetraorganostannanes with hydrogen halides at higher temperature or for long periods at low temperature, diorganotin dihalides are formed[21-24].

$$R_4Sn + HX \rightarrow R_3SnX + RH$$

$$R_3SnX + HX \rightarrow R_2SnX_2 + RH$$

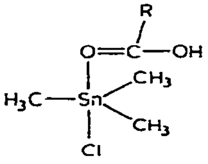
Recently Aubke *et al.*[25] reported that the reactions of HSO_3R (R = F, CF_3, Cl, Me, Et) with trimethyltin chloride yield $Me_2Sn(SO_3R)_2$ and methane and hydrogen chloride. They suggest the stepwise replacement of chloride by the acid anion followed by production of methane. However, under the conditions used in the present study, no HCl is obtained and a maximum of one mole of methane per mole of triorganotin chloride is produced regardless of the acid/tin compound ratio.

Triorganotin halides, in which the halogen atom sufficiently increases the acceptor strength of the molecule, have the tendency to interact with donor molecules to form trigonal bipyramidal adducts. The existence and structure (I) of penta-coordinated tin addition compounds, $(CH_3)_3SnCl \cdot B$[26-28] where B is $(CH_3)_2SO$, Ph_3PO or $CH_3C(O)N(CH_3)_2$, have been based on NMR spin-spin coupling values ($J(Sn-CH_3)$) and infrared studies.



(I)

The 1/2 molecular complexes of $SnCl_4$ and aromatic acids[29] have been isolated. For these compounds, Mössbauer studies have been used to lend support to the structure in which the carbonyl oxygen coordinates directly to the tin atom. Therefore, the reaction of trimethyltin chloride with carboxylic acids may occur via an adduct intermediate, such as II. Such an intermediate would favor formation of CH_4



(II)

rather than HCl. The Sn–Cl bond energy in $(CH_3)_3SnCl$ is about 85 kcal/mole, while that of the Sn–C bond in $(CH_3)_4Sn$ is about 55 kcal/mole[30]. Therefore, the Sn–C bond in $(CH_3)_3SnCl$ is expected to be weaker than the Sn–Cl bond and formation of CH_4 is not unexpected. McKennon and Lustig[3], in a reaction of another strong acid (difluorodithiophosphoric acid) with trimethyltin chloride also observe quantitative formation of methane. This reaction also was carried out in the absence of base.

However, we have found that in the presence of pyridine, trimethyltin chloride reacts with acetic acid to form trimethyltin acetate. Analogously, alkyltin chlorides form organostannyl arsenates[31] with arsenic acids in the presence of triethylamine according to:

$$R_{4-n}SnCl_n + n\,HOAs(O)R'_2 + n\,(C_2H_5)_3N \rightarrow n\,(C_2H_5)_3NHCl + R_{4-n}Sn(OAs(O)R'_2)_n$$

In these cases, the reactions could arise from nucleophilic attack by the acid anion at the positive tin center which would tend to weaken the Sn–Cl bond particularly when accompanied by the strong driving force provided by the formation of the quaternary ammonium chloride salt.

There is a marked difference in the behavior of $(CH_3)_3SnCl$ towards acids compared with that of $(CH_3)_3SiCl$[3,4] where HCl and not CH_4 is invariably formed. Again this is to be expected when it is noted that the bond energy for Si–C > Si–Cl while Sn–C < Sn–Cl.

Nuclear magnetic resonance spectra

The ^{19}F NMR of some dimethylchlorotin carboxylates are listed in Table 2. The chemical shifts and coupling constants are in agreement with those reported for similar compounds[32]. The chemical shifts are essentially independent of the solvent used. No coupling between H–F or Sn–F is observed.

TABLE 2

^{19}F NMR SPECTRA OF DIMETHYLCHLOROTIN PERFLUOROCARBOXYLATES, $(CH_3)_2SnClOC(O)R$

R	$\varphi^*(CF_3)$	$\varphi^*(\alpha\text{-}CF_2)$	$\varphi^*(\beta\text{-}CF_3)$	*J (Hz)*
CF_3	75.5 (s)^a			
	75.8 (s)^b			
C_2F_5	83.2 (t)^a	120.8 (q)		1.3
	83.1 (t)^b	120.7 (q)		1.3
C_3F_7	80.9 (t)^a	118.2 (q)	126.9 (s)	8.7
	81.5 (t)^b	119.9 (q)	127.7 (s)	8.6
$CClF_2$	62.2 (s)^a			
	62.3 (s)^b			

[a] Solvent acetone. [b] Solvent chloroform.

Methyltin derivatives are particularly suitable for ^1H NMR studies because the proton–tin coupling constants are determined easily. In recent years, many NMR studies have been carried out on trimethyltin carboxylates[6,7] and dimethyltin diacetates[33], but none of the dimethylchlorotin carboxylates has been examined. Table 3 includes the proton chemical shifts and proton–tin coupling constants for dimethylchlorotin carboxylates determined during this work.

The observed chemical shifts can be explained as a function of the screening constants of the substituents while the coupling constant values reflect the differences in the state of hybridization[3,4] and the coordination number of the tin[35]. There is a systematic decrease in the screening constant of the CH_3 protons when methyl groups are successively displaced by the more electronegative chlorine atoms or acetyl groups on tin[28,34,36–38]. The Sn–CH_3 coupling constants, $J(^{117}Sn\text{–}CH_3)$ and $J(^{119}Sn\text{–}CH_3)$,

TABLE 3

PROTON NMR SPECTRA OF DIMETHYLCHLOROTIN CARBOXYLATES, $(CH_3)_2SnClO\overset{\overset{O}{\|}}{C}R$

R	$\delta(CH_3\text{–}Sn)$	$\delta(O\overset{\overset{O}{\|}}{C}CH_nX_{3-n})$	$J(^{119}Sn\text{–}CH_3)$	$J(^{117}Sn\text{–}CH_3)$
CH_3	1.075^{a}	1.975	86	83
	1.160^{b}	2.185	75	72.3
CH_2Cl	1.175^{a}	4.333	90	86.5
	1.205^{b}	4.210	77.5	74
$CHCl_2$	1.192^{a}	6.550	91	87
	1.265^{b}	6.060	77	73.5
CCl_3	1.209^{a}		92	88
	1.283^{b}		77	73.5
CH_2Br	1.100^{a}	3.891	88	83
	1.230^{b}	3.990	75.8	73.2
CH_2I	1.083^{a}	3.687	88	84
	1.185^{b}	3.820	77.5	73.8
CF_3	1.150^{a}		88	84
	1.250^{b}		72.8	69.5
C_2F_5	1.117^{a}		88	84
	1.250^{b}		74	71
C_3F_7	1.113^{a}		90	86
	1.250^{b}		74.5	71
$CClF_2$	1.200^{a}		92	88
	1.260^{b}		75	72

[a] Solvent acetone-d_6; int. ref. TMS. [b] Solvent $CHCl_3$. Recalibrated with $\delta(CHCl_3)$ 7.35.

increase with increasing electronegativity of the substituents and with the coordination number of tin. For the trimethyltin carboxylates[34], $J(^{119}Sn\text{–}CH_3)$ occurs around 59 Hz, thus in the vicinity observed for four-coordinated systems, *e.g.*, tetramethyltin, J 54.0 Hz and trimethyltin chloride, J 58.5 Hz. Therefore, these carboxylates exist as monomers in nonpolar solvents[6,7]. In established penta-coordinated tin compounds, such as the pyridine adduct of trimethyltin chloride[35,39], or trimethyltin chloride in D_2O, the $Sn\text{–}CH_3$ coupling increases to 67.0 and 70.7 Hz, respectively. For dimethyltin diacetate, which contains six-coordinated tin based on COO– vibration frequencies in the infrared spectrum[33], the $^{119}Sn\text{–}CH_3$ coupling constant is 82.5 Hz. Thus, the magnitude of the coupling constant can be used as a diagnostic tool in predicting the coordination number of tin in the dimethylchlorotin derivatives.

Since the $^{119}Sn\text{–}CH_3$ coupling constants for these new dimethylchlorotin carboxylates fall in the range 73–77 in $CHCl_3$ solution, the structure is one in which the tin atom is penta-coordinated[40] as was suggested for $R_2Sn(Cl)O_2CCH_3$[16] (R = Et, n-Pr, n-Bu); while in acetone-d_6 ($J(^{119}Sn\text{–}CH_3)$ 88 Hz), the tin must be six-coordinated resulting from the coordination of the carbonyl oxygen of acetone.

The linear relationship between the degree of *s*-character in the tin orbitals directed toward carbon and the coupling constants have been studied in detail by Homes and Kaesz[34] and Van der Kelen[28]. Interpolation from the function[34] relating $J(^{119}Sn\text{–}CH_3)$ to the apparent *s*-character of the tin-atom orbital in the Sn–C bond indicates 39% *s*-character for the J value of 77 Hz in $CHCl_3$ solution and 43% *s*-character for 88 Hz in acetone-d_6 solution which supports the above penta- and hexacoordinated models for the dimethylchlorotin carboxylates.

Proton nuclear magnetic resonance measurements on the dimethylchlorotin carboxylates also show several other important features: the chemical shifts of $(CH_3)_2$-Sn protons show very little change in the deshielding of the methyl protons with increasing electron withdrawing ability of the R groups. The inductive effect predominates in the series $R=CH_3$, CH_2Cl, $CHCl_2$, CCl_3 since there is a regular decrease of the screening constant of RCOO– protons with increasing number of halo substituents. Also, the inductive effect shows in the chemical shifts of RCOO– protons in the series CH_2Cl, CH_2Br, CH_2I. In this series, the tin–proton coupling constants show an irregular change, while they are essentially unaffected by increasing the number of chlorine substituents. The anisotropy effect must be the main contributing factor in the series $R=CF_3$, CF_2Cl, CCl_3.

Infrared spectra

The completely rigorous assignment of the bands to their respective normal

TABLE 4

INFRARED AND RAMAN SPECTRA OF $(CH_3)_2SnClO_2CCH_3$, $(CH_3)_2SnCl_2$ AND NaO_2CCH_3

	$(CH_3)_2\overset{Cl}{\overset{\vert}{Sn}}O\overset{O}{\overset{\Vert}{C}}CH_3$		$(CH_3)_2SnCl_2$		$NaO\overset{O}{\overset{\Vert}{C}}CH_3$[41]
	IR[a,b]	*Raman*[c]	*Raman*[46] (*in 9 M HCl*) $[(CH_3)_2SnCl]^+$	*IR*[43,b]	*IR*
$\nu_a(CH)$	3014 vw	3022 w	3025		2989
$\nu_s(CH)$	2923 w	2930 m	2930		2936
	2852 vw				
$\nu_a(CO_2)$	1550 s	1572 vw			1578
	1450 s	1453 vw			1443
$\delta_a(CH_3)$	1430 s	1432 vvw			1430
$\delta_a(CH_3)$	1403 s	1413 vvw		1410	1414
$\nu_s(CO_2)$		1352 vvw			
	1210 w	1214 m			
$\delta(CH_3\text{–}Sn)$	1196 vw	1202 w	1204	1204	
	1047 vw				1042
CH_3 rock	1015 m				1009
$\nu(C\text{–}C)$	950 vw	954 w			924
	815 sh			786	
$Sn\text{–}CH_3$ rock	794 s			745	
COO scissor	685 s				646
COO out of plane bend	613 w				615
$\nu_a(Sn\text{–}C)$	576 m	577 w	577	567	
$\nu_s(Sn\text{–}C)$	527 w	532 vvs	518	575	
COO rock	493 w	500 w			460
$\nu(Sn\text{–}Cl)$	324 s	319 s	325		
	285 w	282 w			
		271 w			
		200 w			
		149 m			

[a] For original spectrum in NaCl region, see Okawara[43]. [b] KBr disc. [c] Neat solid.

modes is impossible for these complex compounds. However, some assignments can be made by referring to the spectra of the corresponding sodium salts[41,42], the trimethyltin carboxylates[6,8,43], the dimethyltin diacetates[33], and methyltin chlorides[43–47]. Particularly pertinent to this work is the Raman spectrum of $[(CH_3)_2SnCl]^+$ (C_{2v}) as given for $(CH_3)_2SnCl_2$ in HCl solution[46]. Corresponding peaks can be found in the infrared and Raman spectra of dimethylchlorotin acetate (taken as representative). Many of the remaining bands may be identified by comparing with the spectrum of $NaOC(O)CH_3$ as shown in Table 4.

The characteristic absorptions due to carbonyl asymmetric and Sn–C asymmetric and symmetric stretching frequencies and Sn–Cl vibrations are listed in Table 5. The fact that both asymmetric and symmetric stretches are observed for Sn–C indicates the presence of a nonlinear C–Sn–C moiety. Since it is difficult to assign

TABLE 5

CHARACTERISTIC ABSORPTIONS OF DIMETHYLCHLOROTIN CARBOXYLATES $(CH_3)_2SnClO_2CR$

R	$\nu_a(CO_2)$	$\nu_a(Sn–C)$	$\nu_s(Sn–C)$	$\nu(Sn–Cl)$
CH_3	1550[a]	576	527	324
	1548[b]	575	525	324
	1598[c]	560	523	[f]
	1572[d]	577	532	319
CH_2Cl	1598[a]	580	508	340
	1600[b]	580	510	338
	1635[c]	580	530	340
$CHCl_2$	1624[a]	580	524	348
	1643[c]	548	528	345
	1632[d]	586	528	350
CCl_3	1635[a]	583	530	340
	1635[b]	586	535	335
	1650[c]	568	525	347
CH_2Br	1590[a]	585	528	340
	1590[b]	585	528	340
	1620[c]	580	527	[f]
CH_2I	1550[a]	573	503	316
	1553[b]	573	510	316
	1610[c,e]	573	527	[f]
CF_3	1691[a]	580	521	345
	1690[b]	581	524	347
	1692[c]	567	526	350
	1670[d]	578	526	347
C_2F_5	1686[a]	586	524	360
	1690[b]	588	525	360
	1690[c]	570	526	348
C_3F_7	1655[a]	588	525	355
	1668[b]	590	524	355
	1685[c]	568	530	348
	1671[d]	581	527	334
CF_2Cl	1688[a]	545	517	349
	1687[b]	555	527	340
	1680[c]	564	526	350

[a] KBr discs. [b] Nujol mull. [c] CH_2Cl_2 solution. [d] Raman. [e] $CHCl_3$ solution. [f] Not observed.

$\nu_s(CO_2)$ frequencies in the 1400–1300 cm^{-1} region in which C–H deformations also appear, these are omitted even though separation of $\nu_a(CO_2)$ and $\nu_s(CO_2)$ is used to detect the types of carboxyl groups by some authors[48,49]. The $\nu_a(CO_2)$ frequencies increase generally with increasing electron withdrawing ability in the substituted carboxylate groups. The nujol mull spectra are essentially the same as spectra obtained from samples in KBr discs. In comparison of solution and solid state spectra, the ν_a(Sn–C), ν_s(Sn–C), ν(Sn–Cl) vibrations do not show significant changes.

However, the carbonyl vibrations do shift to higher energies for the nonfluorinated carboxylates (R=CH_3, CH_2Cl, $CHCl_2$, CCl_3, CH_2Br, CH_2I), *e.g.*, for $(CH_3)_2ClSnO_2CCH_3$ the band for the asymmetric carbonyl shifts to 1598 from 1550 cm^{-1}. For $(CH_3)_3SnO_2CCH_3$[7,10], with $\nu_a(CO_2)$ at 1658 cm^{-1} in $CHCl_3$ solution shifted from 1570 cm^{-1} in the solid, the shift is that expected when changing from a monomeric ester form in solution to a bridged polymeric species (penta-coordinate) in the solid. Also, from the spin–spin coupling constant[50], $J(^{119}Sn–CH_3)$ 58.2, for $(CH_3)_3SnO_2C(CH_3)$ in $CDCl_3$ solution, the tin is four-coordinated which indicates a normal ester. Because of the analogous infrared shift and the $Sn–CH_3$ coupling constants in the 75 Hz region for the nonfluorinated carboxylates in $CHCl_3$, it is likely that a monomeric non-ester acetoxy form is present, and tin has a coordination number of five. Cryoscopic measurements of molecular weight of $(C_2H_5)_2ClSnO_2CCH_3$ show that it is monomeric in nonpolar solvents (benzene)[16]. An infrared shift for $\nu_a(CO_2)$ to higher energy is also observed (1550 to 1600 cm^{-1}) suggesting a non-ester type of acetoxy group. This would support a monomeric chelate structure for the new compounds. Preliminary molecular weight determinations in $CHCl_3$ are inconclusive, although they do point to monomeric structures in solution, *e.g.*, the experimental values exceed theoretical for monomeric species by about 25% for $(CH_3)_2ClSnO_2CCH_2I$ and $(CH_3)_2ClSnO_2CHCl_2$, but they are concentration independent.

All bands in the solution infrared spectra change proportionately with concentration which suggests that no monomer–polymer equilibrium exists.

For the compounds which have fluorine-containing carboxylate groups it should be noted that essentially no shift occurs in $\nu_a(CO_2)$ in going from solid to CH_2Cl_2 solution with the exception of the C_3F_7 compound. This suggests that the structure for compounds with R=CF_3, C_2F_5, and CF_2Cl is not greatly different in solution. NMR data point to penta-coordinated systems in solution and Mössbauer to five-coordinated tin in the solids (see next section). Molecular weight determinations on $CF_3CO_2SnCl(CH_3)_2$ in $CHCl_3$ were: 10 mg/cm^3, 919; 30 mg/cm^3, 927; and 60 mg/cm^3, 914. The formula weight for $CF_3CO_2SnCl(CH_3)_2$ is 297.5. Based on the experimental molecular weight, the compound must be at least trimeric or perhaps polymeric in chloroform solution. Similar results are obtained for the C_3F_7 case where experimental molecular weight values ranging between 761 and 1433 were obtained (monomeric=396). This then confirms the existence of these compounds in the solid state as polymeric structures with bridging COO– groups.

Mössbauer spectra

The ^{119}Sn Mössbauer isomer shifts and quadrupole splittings provide a good tool for the study of the coordination in tin compounds. The isomer shift of the ^{119}Sn resonance is related to the density of 5*s* electrons at the tin nucleus and the quadrupole

TABLE 6

MÖSSBAUER DATA FOR $(CH_3)_2SnClO_2CR$

Compound R	δ *(mm/sec)*[a]	Δ *(mm/sec)*[a]	$\rho\ \frac{\Delta}{\delta}$
CH_3	1.34	3.58	2.67
CH_2Cl	1.38	3.75	2.72
$CHCl_2$	1.45	3.91	2.70
CCl_3	1.45	3.96	2.73
CH_2Br	1.39	3.79	2.73
CF_3	1.44	3.85	2.67
C_2F_5	1.45	3.90	2.69
C_3F_7	1.40	3.83	2.74
CF_2Cl	1.42	3.84	2.70

[a] Values reproducible to 0.03 mm/sec.

splitting gives a measure of the deviation from cubic symmetry of the electron distibution about the tin atom. In Table 6 are found the ^{119}Sn Mössbauer data recorded at 80 K for some of the dimethylchlorotin carboxylates. The spectrum of each compound was a well-resolved doublet. The isomer shift (δ) values, relative to SnO_2, fall in the region 1.34–1.45 mm/sec and the quadrupole splitting (Δ) values in the range 3.58–3.96 mm/sec. As is the case for dialkyltin dicarboxylates, no noticeable Mössbauer effect is present at ambient temperature[51]. Although room temperature Mössbauer effects reportedly reflect the presence of polymeric structures[52,53], the dicarboxylates still doubtlessly are polymeric even though the association is probably weak. The δ values for $(CH_3)_2ClSnO_2CR$ are slightly higher than those for tetraorganotin compounds and are similar to those of $(CH_3)_3SnO_2CCH_3$[10,14], $(CH_3)_3SnCN$[54] and $(CH_3)_3SnSCN$[54], which have been shown to have a polymeric structure with bridging CO_2 or CN or SCN groups and trigonal bipyramidal configuration around the tin atom[12,55,56]. The observed Δ values are quite large and similar to those for compounds having trigonal bipyramidal structures, *e.g.*, trimethyltin acetates[6,7,10], $(CH_3)_3SnF$[54], and $(CH_3)_3SnCN$[54]. Based on our Mössbauer data, all of the dimethylchlorotin carboxylates are penta-coordinate, and very likely polymeric in the solid state (*i.e.*, $\Delta > 3.6$ mm/sec, whereas for four-coordinated R_3SnO_2CR' compounds, $\Delta \sim 2.3$ mm/sec)[11].

CONCLUSION

Dimethylchlorotin carboxylates can be easily made by the reaction of trimethyltin chloride with appropriate acids. These compounds have been studied by a variety of spectroscopic methods in the solid state and in solution which cause us to argue as follows:

(1) Based on $J(^{119}Sn\text{-}CH_3)$ values obtained on solutions in $CHCl_3$ and on quadrupole splitting values for the solids, the compounds contain penta-coordinated tin. The position of $\nu_a(CO_2)$ in the infrared spectra (solid or solution) is far removed from the usual organic ester frequency (1740 cm^{-1}) which suggests bridge or chelate COO– groups in penta-coordinated compounds.

(2) For the nonfluorinated carboxylates, solution in $CHCl_3$ or CH_2Cl_2 is accompanied by a shift to higher frequencies of $\nu_a(CO_2)$ which indicates a change of structure. Molecular weights done on our compounds are not convincing but the closely related molecule $(C_2H_5)_2ClSnO_2CCH_3$, for which a similar frequency shift occurs, is monomeric in solution. This is strong evidence for chelate monomers in solution and for COO– bridged polymeric structures in the solid.

(3) For the fluorinated carboxylates, $\Delta\nu_a(CO_2)$ is essentially zero when solution in $CHCl_3$ or CH_2Cl_2 occurs which indicates no change in structure. Molecular weight determinations on $(CH_3)_2ClSnO_2CCF_3$ point convincingly to polymers in solution (C_3F_7 is somewhat less certain) and thus to COO– bridged polymeric solids, hence eliminating penta-coordinate chelate monomers in the solid.

(4) Comparison of our Mössbauer data with that of compounds of known structure also strongly points to a polymeric solid state for all of the dimethylchlorotin carboxylates.

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