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DIORGANOTIN HALIDE CARBOXYLATES, THIOCARBOXYLATES AND HALIDE HALOACETATES *

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Summary

Twenty-eight diorganotin halide acetates, thioacetates, haloacetates and carboxylates, eighteen not previously reported, have been synthesized by the reaction between the diorganotin oxides and acid halides, and by transacyloxylation reactions between diorganotin halide acetates and carboxylic acids. Infrared in the 2000—200 cm^{-1} range, proton and carbon-13 NMR and tin-119m Mössbauer data are interpreted in terms of acetoxy-bridged, trigonal bipyramidal tin in the solid phase with depolymerization occurring in solution where a dynamic equilibrium between diorganotin dihalide and dicarboxylate species is rapidly established. A new infrared absorption also appears at 100—125 cm^{-1} to higher frequency of the $\nu_{asym}(CO_2)$ which disappears on heating. A dimeric structure based upon four-membered Sn_2O_2 or Sn_2OX rings in which carboxylate group oxygen atoms bridge tin atoms of a second molecule leaving the C=O group free is proposed. The halide thioacetates are associated in the solid state but are monomeric in solution.

The question of intermolecular association in organotin compounds, of interest generally [1], is brought into sharp focus with the organotin chlorides and acetates. Data from gas phase studies of the methyltin halides [2—4] show no large deviations from tetrahedral geometry in the free molecules, while the crystal data show a progression of situations from the nearly tetrahedral geometry of triphenyltin chloride [5], through diphenyl- [6] and bis(chloromethyl)-tin dichloride [7] to that of dimethyltin dichloride [8] whose environment is substantially distorted toward the octahedral. We are clearly in an intermediate area, and the question of coordination number at the tin atom in the latter members of this series must be said at this writing to be indeterminate [1]. The same is found in the recently investigated diethyltin halides [9].

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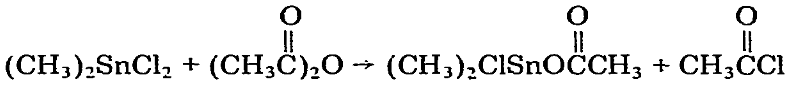
* Dedicated to Professor E.G. Rochow on the occasion of his 70th birthday.

The situation in the organotin acetates is analogous. The acetate moiety can behave as a bidentate chelating ligand or as a bridging group to give rise to associated oligomeric or polymeric chain structures in the solid. Binding in a unidentate fashion is found when a second donar group successfully competes for the coordination sites as in 2,2′-bipyridylbis(trifluoroacetato)divinyltin(IV) [10], when the chelating interaction would be weak or possibly impose a strained conformation on the molecule as in Cl_3SnCH_2Cl [4], or when the organic groups at the tin atom are too bulky to permit either chelation or bridging. Tricyclohexyltin acetate [11] may be an example of the last-named situation, but the stereochemically suggestive position and short distance of the second oxygen atom make this conclusion, and hence the assignment of the coordination number at the tin atom, ambiguous.

The simplest organotin carboxylate, trimethyltin formate, forms a structure of formoxy- and planar trimethyltin groups arranged alternately along a helical chain [12]. The carboxylate groups in trimethyltin acetate and trifluoroacetate also bridge in associated structures comprised of planar tin-carboxylate units [13]. Acetate groups in other examples bridge ditin units as in di-μ-acetatobis(diphenyltin) [13] and stannoxane units as in $\{[(n\text{-}C_4H_9)_2SnO_2CCCl_3]_2\}_2$ [16]. The structure of tribenzyltin acetate [17] exemplifies the crossover between the tendency for a bridged, one-dimensional polymer and the discrete, monomeric molecular form with an increase in steric bulk at the tin atom. The coordination number at the tin atom in this case is indeterminate.

Between these two situations lie the organotin halide acetates for which no X-ray crystal structure information is available [1]. The first compound of this type, dimethyltin chloride acetate, was prepared in 1960 by Okawara and Rochow by the action of acetic anhydride on dimethyltin dichloride [18]:



$$(CH_3)_2SnCl_2 + (CH_3\overset{O}{\overset{\|}{C}})_2O \rightarrow (CH_3)_2ClSnO\overset{O}{\overset{\|}{C}}CH_3 + CH_3\overset{O}{\overset{\|}{C}}Cl \qquad (1)$$

Later, the redistribution of dialkyltin dihalides and diacetates was used to prepare a variety of dialkyltin halide acetates [19—22].

$$R_2SnX_2 + R_2Sn(O_2CCH_3)_2 \rightarrow 2\ R_2XSnO_2CCH_3 \qquad (2)$$

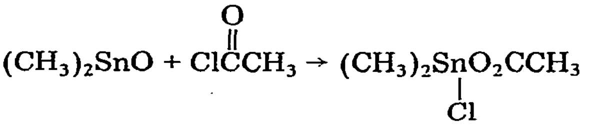
Another synthetically useful method is the reaction of tetraalkyl-1,3-dichlorodistannoxanes with acetic acid or acetic anhydride [23]:

$$2(R_2ClSn)_2O + 2\ CH_3CO_2H \rightarrow 2\ R_2ClSnO_2CCH_3 + H_2O \qquad (3)$$

$$(R_2ClSn)_2O + (CH_3CO)_2O \rightarrow 2\ R_2ClSnO_2CCH_3 \qquad (4)$$

Other, in general less convenient methods include the cleavage of tetra-n-butyl-1,2-diacetoxydistannane with bromine [24] to give di-n-butyltin bromide acetate, the reaction of di-n-butylchlorotin hydride with acetic acid [25] to give di-n-butyltin chloride acetate, and the cleavage of a methyl group from trimethyltin chloride by haloacetic acids [26,27] when heated together for several hours in a sealed tube.

Dimethyltin chloride acetate has also been prepared by the reaction of acetyl chloride with dimethyltin oxide [28]:



$$(CH_3)_2SnO + Cl\overset{\overset{O}{\|}}{C}CH_3 \rightarrow (CH_3)_2\underset{\underset{Cl}{|}}{Sn}O_2CCH_3 \qquad (5)$$

An analogous reaction between diethyltin oxide and benzoyl chloride gives only diethyltin dichloride and diethyltin dibenzoate [28]. Attempts to prepare dimethyltin chloride benzoate via a redistribution reaction were also unsuccessful [21].

We report in this paper the synthesis of twenty-eight diorganotin halide acetates, thioacetates, haloacetates, and carboxylates, eighteen of them reported here for the first time, and infrared, proton and carbon-13 nuclear magnetic resonance and tin-119m Mössbauer spectroscopic data which are interpretated in terms of the structures of these systems in the solid phase and in solution.

Experimental

Chemicals and spectra

Reagent grade chemicals were used as received, except for acetyl bromide, which was distilled in the presence of *N,N'*-dimethylaniline to remove hydrogen bromide, and used immediately. Melting points were measured on a Thomas-Hoover Capillary Melting Point Apparatus (Arthur H. Thomas Co.) and were uncorrected. Tin was analyzed as tin(IV) oxide through the action of nitric and sulfuric acids.

Infrared spectra were recorded on a Beckman IR-12 infrared spectrometer as Nujol mulls from 600—200 cm^{-1} and as KBr pellets from 2000—300 cm^{-1}. Solution infrared spectra were obtained between KBr plates in the region 2000—400 cm^{-1} and in polyethylene cells for the 600—200 cm^{-1} region.

^{119m}Sn Mössbauer spectra were recorded on a cam-drive, constant acceleration spectrometer previously described [29], using a $Ba^{119m}SnO_3$ source (New England Nuclear Corp.) as the zero of isomer shift.

^1H NMR spectra were recorded on a Varian A60-A spectrometer operating at an ambient probe temperature of ca. 39°C. Deuterochloroform was used as the solvent, and tetramethylsilane (TMS) as the internal standard.

Natural abundance, proton noise-decoupled carbon-13 spectra were recorded at 25.1 MHz on a modified Varian HA-100D spectrometer equipped for fast Fourier transform operation. Carbon-13 NMR data were collected and processed by a Digilab FTS/NMR-3 pulse and data system. Deuterochloroform was used as the solvent, and the samples, approximately 50% (wt/v), were contained in 8 mm o.d. tubes which held 2 mm o.d. coaxial inner cells containing C_6F_6, the external lock material. Probe temperatures were maintained at ca. 40°C during proton-decoupled experiments utilizing the Digilab 50-80 decoupler by a continuous flow of nitrogen circulated through cooling coils held in dry ice.

Carbon chemical shifts were measured in parts per million (ppm) relative to internal TMS, positive values being to high frequency. A resolution of ±1 Hz was achieved using 16384 (16 K) data points and a sampling frequency of 12000 s^{-1}.

Syntheses

Two synthetic methods were used in the preparation of the diorganotin halide carboxylates listed in Table 1: by reaction between diorganotin oxides and acid halides, and by transacyloxylation reactions between diorganotin halide acetates and carboxylic acids. A description of each method used in a typical preparation is given below.

Di-n-butyltin chloride acetate. Di-n-butyltin oxide (3.00 g, 12 mmol) was suspended in carbon tetrachloride and acetyl chloride (0.94 g, 12 mmol) added with stirring. The mixture was heated and allowed to reflux ca. 0.5 hour, during which time all the suspended di-n-butyltin oxide dissolved. The solution was cooled, the carbon tetrachloride solvent removed by rotary evaporation, and the product recrystallized from hexane, m.p. 63—64°C (lit. [25] 64—65°C).

Di-n-butyltin chloride monochloroacetate. Di-n-butyltin oxide (3.00 g, 12 mmol) was suspended in toluene and acetyl chloride (0.94 g, 12 mmol) added. The temperature of the mixture was slowly increased, but kept below the boiling point of toluene, until all the di-n-butyltin oxide had dissolved. The solution was cooled and monochloroacetic acid (1.14 g, 12 mmol) was added. The acetic acid released during the transacyloxylation reaction was removed by azeotropic distillation and the remaining toluene was removed by rotary evaporation. The product was recrystallized from hexane, m.p. 68—69.5°C.

Results

Infrared spectra and assignments

Diorganotin halide acetates. Solid-state infrared spectral data for the diorganotin halide acetates in the range of 2000—200 cm^{-1} are given in Table 2 *. Assignments are based upon the spectrum of sodium acetate [30—33]. The infrared spectrum of dimethyltin chloride acetate has also been previously reported [20,26,34].

The most prominent bands arise from the $\nu_{asym}(CO_2)$ and $\nu_{sym}(CO_2)$ modes which occur as very strong, broad absorptions in the ranges 1560—1551 and 1422—1408 cm^{-1}, respectively. Other bands associated with the carboxylate group are the CO_2 scissor vibration which is a strong band at 689—679 cm^{-1}, the CO_2 out-of-plane deformation which is a medium band at 618—612 cm^{-1}, and the in-plane CO_2 deformation which is a weak band at 498—484 cm^{-1}. The lowest CO_2 deformation frequency has been assigned to the out-of-plane motion based upon the bending frequencies of acetone [35,36].

A medium to strong band that occurs in the 287—271 cm^{-1} range is assigned to the ν(Sn—O) mode. While only few far infrared studies have been made on organotin carboxylates, bands in the 300—250 cm^{-1} region, which are absent in the infrared spectra of sodium formate and acetate, have been assigned to the ν(Sn—O) mode for triorganotin formates [37] and acetates [38—40] and dialkyltin diacetates [41].

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* Tables 2—9 and 14 have been deposited as NAPS document No. 03431 (21 pages). Order from NAPS, c/o Microfiche Publications, P.O. Box 3513, Grand Central Station, New York, N.Y. 10017. Remit in advance, U.S. funds only $ 5.25 for photocopies or $ 3.00 for microfiche. Outside the U.S. and Canada add postage of $ 3.00 for photocopy and $ 1.00 for microfiche.

Both the ν_{sym}(Sn—C) (606—577) and ν_{asym}(Sn—C) (630—616 cm^{-1}) vibrations are observed for all the dialkyltin halide acetates studied. These modes in phenyltin compounds are found in the 382—261 and 249—225 cm^{-1} regions, respectively [42—45]. The ν_{asym}(Sn—C) mode in diphenyltin chloride acetate is not observed, and probably coincides with the strong ν(Sn—O) band which overlaps it at 294 cm^{-1}. A shoulder appears at 280 cm^{-1} for diphenyltin bromide acetate, which may arise from the ν_{asym}(Sn—C) mode. The ν_{sym}(Sn—C) vibrations for the diphenyltin compounds are assigned to 238 and 224 cm^{-1} for the chloride and bromide compounds, respectively. Assignment of this band is not unambiguous since a band in the same region has been assigned to ν_{sym}(Sn—O) for trimethyltin formate and acetate [46].

Tin—halogen stretching vibrations are easily observable as intense bands in the 335—326 and 242—227 cm^{-1} regions for ν(Sn—Cl) and ν(Sn—Br), respectively.

Phenyl ring assignments for the diphenyltin halide acetates are based on comparison with other phenyltin compounds [45,46].

Dialkyltin halide haloacetates. Solid-state infrared spectral data for the dimethyltin chloride and bromide haloacetates and di-n-butyltin chloride haloacetates are given in Tables 3 and 4, respectively. Complete assignments have not been attempted, but literature values for the sodium haloacetate salts [31] and the triorganotin haloacetates [38,40,48] allow some assignments to be made with confidence.

The $\nu_{asym}(CO_2)$ and $\nu_{sym}(CO_2)$ modes yield broad, very strong bands in the frequency ranges 1651—1580 and 1408—1358 cm^{-1}, respectively. While $\nu_{asym}(CO_2)$ and $\nu_{sym}(CO_2)$ show a marked dependence on increasing halogenation, ν_{asym}(Sn—C) and ν_{sym}(Sn—C) show little variation, appearing in the ranges 586—580 and 528—522 cm^{-1}, respectively for the dimethyltin compounds. The ν_{asym}(Sn—C) mode appears at 603—595 cm^{-1} in the di-n-butyltin compounds. The CO_2 bending vibrations were assigned to the following: a strong band in the 718—682 cm^{-1} range to the CO_2 scissor vibration, a weak to medium intensity band in the 639—615 cm^{-1} range to the CO_2 out-of-plane deformation, and the CO_2 in-plane deformation to a medium to strong band at 514—497 cm^{-1}. This latter band probably overlaps the ν_{sym}(Sn—C) absorption for the di-n-butyltin compounds, which is also found in this region (cf. Table 2).

The tin—halide stretching vibrations are again easily identifiable as a strong band at 350—314 cm^{-1} for ν(Sn—Cl) and at 241—236 cm^{-1} for the ν(Sn—Br) mode.

The assignment of the carbon—halogen stretching vibrations is more difficult. Strong bands in the 849—788 cm^{-1} frequency range for the chloroacetate derivatives probably arise from the ν(C—Cl) mode, but assignments for the dimethyltin compounds are not unambiguous since a strong absorption arising from the Sn—CH_3 rocking mode also occurs in this region (cf. Table 2). This band is absent in the di-n-butyltin compounds, making assignments somewhat less difficult. The ν(C—Br) mode is easily identified as a strong band at 727 cm^{-1} for dimethyltin chloride bromoacetate and at 702 cm^{-1} for di-n-butyltin chloride bromoacetate.

The ν(Sn—O) mode is found as a weak to medium intensity band in the

TABLE 1

DIORGANOTIN HALIDE CARBOXYLATES

Compound	Preparative [a] method	Recrystallisation solvent	Yield (%)	M.p. (°C)		Sn (Found (calcd.)) (%)
				found	Lit. (°C)	
$(CH_3)_2ClSnO_2CCH_3$	1	acetone	80	186—189	184—189 [18] 187—188 [27]	48.20 (48.79)
$(CH_3)_2ClSnO_2CH_2Br$	2	hexane/$CHCl_3$	80	136—138		35.24 (36.84)
$(CH_3)_2ClSnO_2CCH_2Cl$	2	hexane/$CHCl_3$	76	123—126	126.5—128 [21] 129—130 [27]	43.16 (42.74)
$(CH_3)_2ClSnO_2CCHCl_2$	2	CCl_4	80	123—125	130—131 [27]	37.84 (38.02)
$(CH_3)_2ClSnO_2CCCl_3$	2	$CHCl_3$	55	186	196 [27]	34.13 (34.25)
$(CH_3)_2ClSnO_2CC_6H_5$	1	hexane	67	73—76		36.06 (35.71)
$(CH_3)_2ClSnSC(O)CH_3$	2	pentane	64	62—63		45.80 (45.77)
$(CH_3)_2BrSnO_2CCH_3$	1	acetone	90	191—193		40.76 (41.25)
$(CH_3)_2BrSnO_2CCH_2Cl$	2	toluene	82	122—124		37.24 (36.84)
$(CH_3)_2BrSnO_2CCHCl_2$	2	CCl_4	72	72—75		33.48 (33.28)
$(CH_3)_2BrSnO_2CCCl_3$	2	$CHCl_3$	81	175—176		30.21 (30.35)
$(CH_3)_2BrSnO_2CC_6H_5$	2	hexane		76—78		32.47 (33.93)
$(n\text{-}C_4H_9)_2ClSnO_2CCH_3$	1	hexane	93	63—64	56—57.5 [20], 60—61 [22], 61 [23] 63—65 [25]	
$(n\text{-}C_4H_9)_2ClSnO_2CCH_2I$	2	hexane	88	68—69.5		25.89 (26.18)
$(n\text{-}C_4H_9)_2ClSnO_2CCH_2Br$	2	hexane	90	60—62		29.58 (29.21)
$(n\text{-}C_4H_9)_2ClSnO_2CCH_2Cl$	2	hexane	93	68—69.5		32.79 (32.80)

TABLE 1 (continued)

$(n\text{-}C_4H_9)_2ClSnO_2CCHCl_2$	2	hexane	92	75.5—77		29.87 (29.95)
$(n\text{-}C_4H_9)_2ClSnO_2CCCl_3$	2	hexane	84	92.5—94		27.38 (27.55)
$(n\text{-}C_4H_9)_2ClSnO_2CC(CH_3)_3$	1			(B.p. 106—109/0.25 Torr)		32.83 (32.12)
$(n\text{-}C_4H_9)_2ClSnO_2CC_6H_5$	1	pentane	66	40—41.5 (B.p. 96—99/0.25 Torr)		30.03 (30.47)
$(n\text{-}C_4H_9)_2ClSnSC(O)CH_3$	1					35.54 (34.56)
$(n\text{-}C_4H_9)_2BrSnO_2CCH_3$	1	hexane	92	64	67—68.5 [24]	
$(n\text{-}C_8H_{17})_2ClSnO_2CCH_3$	1	pentane	32	73.5—75		27.08 (27.00)
$(n\text{-}C_8H_{17})_2BrSnO_2CCH_3$	1	pentane	67	70—71.5		24.40 (24.52)
$(C_6H_5)_2ClSnO_2CCH_3$	1	pentane	79	92—95		31.76 (32.31)
$(C_6H_5)_2BrSnO_2CCH_3$	1	pentane	21	86—89		28.44 (28.82)

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[a] 1: reaction between R_2SnO and $R'COX$; 2: reaction between $R_2XSnO_2CCH_3$ formed in situ, and $R'CO_2H$.

range 293—253 cm^{-1}. The frequency of this vibration increases with increasing halogenation for the dimethyltin compounds, although observation of the effect is less certain for the di-n-butyltin compounds.

Solution infrared spectra of dialkyltin halide acetates and haloacetates. The prominent absorption bands of dimethyltin halide haloacetates in solution are given in Table 5, and those of di-n-butyltin chloride haloacetate and di-n-butyltin bromide acetate are given in Table 6.

The tin—carbon asymmetric and symmetric stretching vibrations are relatively unchanged from the solid-state (cf. Tables 2 and 3). Compared to their positions in the solid-state, however, the tin—halogen stretching frequencies increase by 10—35 cm^{-1}.

Significant changes also occur in the positions of the carbonyl stretching vibrations. The $\nu_{asym}(CO_2)$ modes increase, and $\nu_{sym}(CO_2)$ decrease from the solid-state to the solution phase. The shift to higher frequencies for the $\nu_{asym}(CO_2)$ mode is greatest for the acetate compounds (41—47 cm^{-1}), and relatively smaller for the haloacetate compounds, although in some cases precise measurement was difficult owing to asymmetry in the shape of the absorption band. In the dimethyltin halide chloroacetates and dichloroacetates the $\nu_{asym}(CO_2)$ absorption is split into two bands, No comparable splitting was observed in dimethyltin chloride bromoacetate, or in the corresponding di-n-butyltin chloride compounds, although the band showed some asymmetry in shape.

In solution all the compounds exhibited a higher frequency band generally 100—200 cm^{-1} higher than $\nu_{asym}(CO_2)$ that was absent in the solid state infrared spectra. Shifts in $\nu_{asym}(CO_2)$ with increasing halogenation were accompanied by a comparable shift in this higher frequency absorption band.

Dialkyltin halide benzoates and thioacetates. Data for the dialkyltin halide benzoates are given in Table 7. Assignments and the numbering of the phenyl ring vibrations are based upon the spectra of the alkali metal salts of benzoic acid [49], and the observed frequencies and band intensities closely parallel those found there. The $\nu_{asym}(CO_2)$ and $\nu_{sym}(CO_2)$ modes are found at 1575—1566 and 1380—1366 cm^{-1}, respectively. The asymmetric carbonyl vibrations in the dimethyltin compounds are split; in dimethyltin chloride benzoate the splitting is unresolved and the band is asymmetric in shape, but in dimethyltin bromide acetate it is clearly split. In CCl_4 solution, on the other hand, only one absorption peak is observed.

Characteristic benzene ring vibrations in benzoic acid include a strong band at 1609—1616 cm^{-1} arising from a ν(C—C) mode, a strong band at 725—720 cm^{-1} assigned to a benzene ring deformation, and a weak ν(C—C) mode at 1308—1305 cm^{-1}. Carbon—hydrogen deformation vibrations are found at 1179—1178, 1076—1071, and 1028—1025 cm^{-1}. The very sharp band at 1452—1451 cm^{-1} observed for all the compounds probably arises from a C—C skeletal vibration, although no comparable band is reported for the alkali metal salts [49]. A medium intensity band at 1135—1134 cm^{-1} is also absent in the spectra of the alkali metal salts; however, a medium intensity band at 1134 cm^{-1} is reported in the Raman spectra of lithium and sodium benzoate [49].

The symmetrical deformation and CO_2 out-of-plane rock are found at 700—691 and 568—550 cm^{-1}, respectively. The later lies between the ν_{asym}-

(Sn—C) and ν_{sym}(Sn—C) modes at 615—591 and 534—518 cm^{-1}, respectively, all three of which are broadened and in some cases overlap.

The ν(Sn—Cl) vibrations are found in the 359—324 range and ν(Sn—Br) in dimethyltin bromide benzoate at 237—236 cm^{-1}. The positions of ν(Sn—Cl) are shifted by 20—30 cm^{-1} to higher frequencies in solution, however, there is no shift in ν(Sn—Br).

Surprisingly few spectral changes occur on dissolving the compounds. As was observed for the dialkyltin halide acetates, a new, sharp, high frequency band appears at 1701—1697 cm^{-1}. The only other significant changes occur in the spectra of the dimethyltin compounds, in which a band at 946 cm^{-1} in the solid-state disappears, and the ν(Sn—Cl) mode shifts to higher frequencies. The most notable observation, however, is that the $\nu_{asym}(CO_2)$ and $\nu_{sym}(CO_2)$ modes in the halide acetates show only very small shifts, as compared to the acetates.

Table 8 gives the infrared spectral data for the dimethyl- and di-n-butyltin chloride thioacetates. The data for the metal salts of thioacetic acid are lacking, but a number of bands can be assigned with confidence by comparison with the infrared spectra of thioacetic acid [50], thioacetate esters [51] and trialkyltin thioacetates [52].

The carbonyl stretching vibration is seen as a broad, intense band at 1612—1600 cm^{-1}, the ν(C—S) mode as a strong band at 965—963 cm^{-1}, and ν(OC—C) the strong band at 1139—1133 cm^{-1}. A strong band is also observed at 657—654 cm^{-1}, and is assigned to the out-of-plane skeletal deformation of the thiocarboxylate group. Both the ν_{asym}(Sn—C) and ν_{sym}(Sn—C) modes are found in the 610—500 region and ν(Sn—Cl) at 340—321 cm^{-1}.

The band observed at 273—266 cm^{-1} may arise from the ν(Sn—O) stretch of the weakly coordinated tin—oxygen bond, since a comparable band is also found in the trialkyltin thioacetates [52] in which tin—oxygen coordination is believed to exist.

As with the dialkyltin halide benzoates, no spectral changes occur on dissolving the thioacetates.

Di-n-butyltin chloride trimethylacetate. The data for di-n-butyltin chloride trimethylacetate as the neat liquid and in carbon tetrachloride solution are listed in Table 9. The $\nu_{asym}(CO_2)$ stretch is split, as in the sodium salt [31] and occurs at higher frequencies, like other dialkyltin halide acetates, in solution. A strong absorption, attributable to a carbonyl out-of-plane bend at 627 cm^{-1}, obscures the asymmetric tin—carbon stretch, but the symmetric vibration is observed at 515 cm^{-1} as a weak band. The tin—chloride stretch absorbs as a strong band at 330 cm^{-1}.

The spectrum of di-n-butyltin chloride trimethylacetate in carbon tetrachloride solution is nearly identical to that of the neat liquid, except that the tin—chlorine stretching vibration increases in frequency by 23 cm^{-1}.

A high frequency band near 1705 cm^{-1} for both the neat liquid and carbon tetrachloride solution is also observed, similar to those described above.

NMR spectra and assignments

^{1}H NMR data. Table 10 lists the ^{1}H NMR data for the dimethyltin halide carboxylates. The general increase in chemical shifts of the acetate group protons with increasing halogen substitution is expected on the basis of simple

TABLE 10

^1H NMR DATA FOR $(CH_3)_2XSnO_2CR'$

R'	$\delta(Sn—C—H)$ [a]	$\delta(O_2C—C—H)$ [a]	$\lvert ^2J(^{119}Sn—C—^1H)\rvert$ [b]
X = Cl			
CH_3	1.08	2.09	76.0
CH_2Br	1.13	3.87	75.5
CH_2Cl	1.16	4.14	75.1
$CHCl_2$	1.18	5.96	74.1
CCl_3	1.20		73.8
C_6H_5	1.13		76.1
X = Br			
CH_3	1.18	2.10	74.0
CH_2Cl	1.22	4.11	74.8
$CHCl_2$	1.30	5.99	73.3
CCl_3	1.33		72.6
C_6H_5	1.29		70.5
$(CH_3)_2ClSnSC(O)CH_3$	1.06	2.04	71.8

[a] Ppm relative to internal TMS. [b] In Hz.

electron withdrawal. The methyltin protons are similarly affected by halosubstitution, but in a much less drastic way. Comparable shifts have been observed for trimethyltin haloacetates [29,38].

The two-bond $\lvert ^2J(^{119}Sn—C—^1H)\rvert$ couplings for the dimethyltin halide haloacetates decrease with increasing halogen substitution on the acetate group. The data for the dimethyltin chloride haloacetates vs. group electronegativities [52], χ_i, can be fit to a straight line with a correlation coefficient of 0.985 and a standard deviation of the calculated values of J from the measured values of 0.16. The equation of the calculated line is found to be $J(^{119}Sn) = -3.84\ \chi_i + 83.61$. A least-squares fit of the ^{119}Sn J values vs. the Taft inductive factor σ^* [53] also gives a straight line, but in this case the correlation coefficient is only 0.974 with a standard deviation of 0.21. The equation of the calculated line is $J(^{119}Sn) = -0.90\ \sigma^* + 76.09$.

Similar plots of the ^{119}Sn data vs. group electronegativities and Taft inductive factors for the dimethyltin bromide haloacetates give unsatisfactory results. The correlation coefficients are less than 0.9, probably owing to the exceptionally high J values found for the monochloroacetate compound.

^{13}*C NMR data.* Carbon-13 NMR data are listed in Table 11 for the di-n-butyltin chloride haloacetates and the dimethyltin halide benzoates, but not for the dimethyltin halide haloacetates owing to their limited solubilities. The results for the di-n-butyltin compounds parallel the ^1H NMR data for the analogous dimethyltin compounds. The general increase in the acetate α-carbon chemical shifts with increasing halosubstitution is expected on the basis of electron withdrawal, and the n-butyltin carbon atoms are similarly affected. A least-squares fit of the shifts of the carbon atoms bonded to tin (C(1)) vs. group electronegativities gives a straight line with a correlation coefficient of 0.903 and a standard deviation of 5.8. The equation of the calculated line is $\delta(^{13}C(1)) = 53.9\ \chi_i + 544.4$. A significantly better fit is obtained by using the Taft inductive factors (a correlation coefficient of 0.959 and standard deviation of 3.8 is

TABLE 11

^{13}C NMR DATA FOR R_2XSnO_2CR'

Compound	δ(C(1)) [a]	δ(C(2)) [a]	δ(C(3)) [a]	δ(C(4)) [a]	δ(C_α) [a]	δ(O_2C) [a]	^1J [b]	^2J [c]	^3J [d]
$(n\text{-}C_4H_9)_2ClSnO_2CCH_3$	25.56	26.27	25.80	13.03	19.63	178.87	506	34	92
$(n\text{-}C_4H_9)_2ClSnO_2CCH_2I$	26.25	26.25	26.64	13.47		178.12	492	36	92
$(n\text{-}C_4H_9)_2ClSnO_2CCH_2Br$	26.40	26.67	26.25	13.99	25.66	176.20	488	34	91
$(n\text{-}C_4H_9)_2ClSnO_2CCH_2Cl$	26.51	26.71	26.27	13.46	40.82	175.81	485	34	92
$(n\text{-}C_4H_9)_2ClSnO_2CCHCl_2$	26.85	26.64	26.25	13.44	64.57	172.50	474	36	91
$(n\text{-}C_4H_9)_2ClSnO_2CCCl_3$	27.07	26.61	26.22	13.44	90.37	169.16	468	36	89
$(n\text{-}C_4H_9)_2ClSnO_2CC_6H_5$	26.28	26.76	26.27	13.47	129.26	175.78	507		
$(n\text{-}C_4H_9)_2BrSnO_2CC_6H_3$	26.46	26.12	27.16	13.47	20.14	181.02	482	34	88
$(CH_3)_2ClSnO_2CC_6H_5$	6.24				128.91	174.72	568		
$(CH_3)_2BrSnO_2CC_6H_5$	10.82				128.63	175.16	500		

[a] Ppm relative to internal TMS. [b] $|^1J(^{119}Sn-^{13}C)|$ in Hz. [c] $|^2J(^{119}Sn-C-^{13}C)|$ in Hz. [d] $|^3J(^{119}Sn-C-C-^{13}C)|$ in Hz.

obtained for the calculated line of equation $\delta(^{13}C) = 14.1\sigma^* + 647.3$).

The magnitudes of the $|^1J(^{119}Sn—^{13}C)|$ values are much larger than those of the two bond $|^2J(^{119}Sn—C—^1H)|$ couplings, and are much more sensitive to changes in bonding and structure in organotin compounds [55,56]. The $|^1J(^{119}Sn—^{13}C)|$ values decrease with increasing halosubstitution on the acetate group. Their plot against Taft inductive factors gives a better fit to a straight line, with a correlation coefficient of 0.980 and standard deviation of 2.7 as compared to the correlation coefficient of 0.950 and standard deviation of 4.2 against group electronegativity. The resulting equations for each line are $J(^{119}Sn) = -14.3\sigma^* + 503.2$ and $J(^{119}Sn) = -56.4\chi_i + 611.7$, respectively.

^{119m}Sn Mössbauer spectra. Table 12 lists the ^{119m}Sn Mössbauer data taken at 77 K. All the spectra show well-resolved doublets. The isomer shifts (*IS*) and quadrupole splittings (*QS*) in each series of haloacetates show a general increase with increasing halosubstitution on the acetate group, a trend previously observed for analogous series of triorganotin haloacetates [29,57,58]. A pronounced saturation effect in the variation of quadrupole splitting with group electronegativity was observed for the tri-n-butyltin haloacetates [29]. The same effect is also observed for di-n-butyltin chloride haloacetates, as illustrated by Fig. 1, but is less severe for the dimethyltin compounds.

TABLE 12

^{119m}Sn MÖSSBAUER DATA FOR R_2XSnO_2CR' AT 77 K

Compound	*IS* [a]	*QS* [b]	Γ_1	Γ_2	(*QS*/*IS*)
$(CH_3)_2ClSnO_2CCH_3$	1.39	3.52	1.46	1.41	2.53
$(CH_3)_2ClSnO_2CCH_2Br$	1.39	3.81	1.16	1.06	2.74
$(CH_3)_2ClSnO_2CCH_2Cl$	1.44	3.84	1.32	1.33	2.67
$(CH_3)_2ClSnO_2CCHCl_2$	1.44	3.87	1.34	1.37	2.69
$(CH_3)_2ClSnO_2CCCl_3$	1.49	3.94	1.04	1.10	2.64
$(CH_3)_2ClSnO_2CC_6H_5$	1.35	3.49	1.03	1.10	2.59
$(CH_3)_2ClSnSC(O)CH_3$	1.44	3.08	1.10	1.06	2.14
$(CH_3)_2BrSnO_2CCH_3$	1.44	3.58	1.07	1.03	2.49
$(CH_3)_2BrSnO_2CCH_2Cl$	1.52	3.87	1.02	1.09	2.55
$(CH_3)_2BrSnO_2CCHCl_2$	1.63	3.93	1.03	1.17	2.41
$(CH_3)_2BrSnO_2CCCl_3$	1.48	3.98	0.96	1.01	2.69
$(CH_3)_2BrSnO_2CC_6H_5$	1.40	3.57	0.89	0.98	2.55
$(n\text{-}C_4H_9)_2ClSnO_2CCH_3$	1.42 [c]	3.58 [a]	1.09	1.20	2.52
$(n\text{-}C_4H_9)_2ClSnO_2CCH_2I$	1.60	3.84	1.11	1.00	2.40
$(n\text{-}C_4H_9)_2ClSnO_2CCH_2Br$	1.63	3.95	1.19	1.15	2.42
$(n\text{-}C_4H_9)_2ClSnO_2CCH_2Cl$	1.59 [c]	3.91 [a]	1.10	1.13	2.46
$(n\text{-}C_4H_9)_2ClSnO_2CCHCl_2$	1.58 [c]	3.90 [a]	1.06	1.16	2.47
$(n\text{-}C_4H_9)_2ClSnO_2CCCl_3$	1.62 [c]	3.90 [a]	1.04	1.16	2.41
$(n\text{-}C_4H_9)_2ClSnO_2CC_6H_5$	1.59	3.53	1.08	1.12	2.22
$(n\text{-}C_4H_9)_2ClSnSC(O)CH_3$	1.60	3.22	0.93	1.11	2.01
$(n\text{-}C_4H_9)_2BrSnO_2CCH_3$	1.56	3.67	1.07	1.19	2.35
$(n\text{-}C_8H_{17})_2ClSnO_2CCH_3$	1.50	3.59	1.00	1.03	2.39
$(b\text{-}C_8H_{17})_2BrSnO_2CCH_3$	1.54	3.63	1.04	1.12	2.36
$(C_6H_5)_2ClSnO_2CCH_3$	1.38	3.37	1.27	1.36	2.44
$(C_6H_5)_2BrSnO_2CCH_3$	1.44	3.44	1.03	1.05	2.39
$(CH_3)_3SnO_2CCH_3$ [d]	1.31	3.57	1.10	1.16	2.73
$(n\text{-}C_4H_9)_3SnO_2CCH_3$ [d]	1.38	3.71	1.33	1.05	2.69
$(CH_3)_3SnSC(O)CH_3$	1.34	2.86	1.28	1.14	2.13
$(n\text{-}C_4H_9)_3SnSC(O)CH_3$	1.48	2.39	1.20	1.05	1.61

[a] ±0.06 mm/s. [b] ±0.12 mm/s. [c] ±0.03 mm/s. [d] Reference 52.

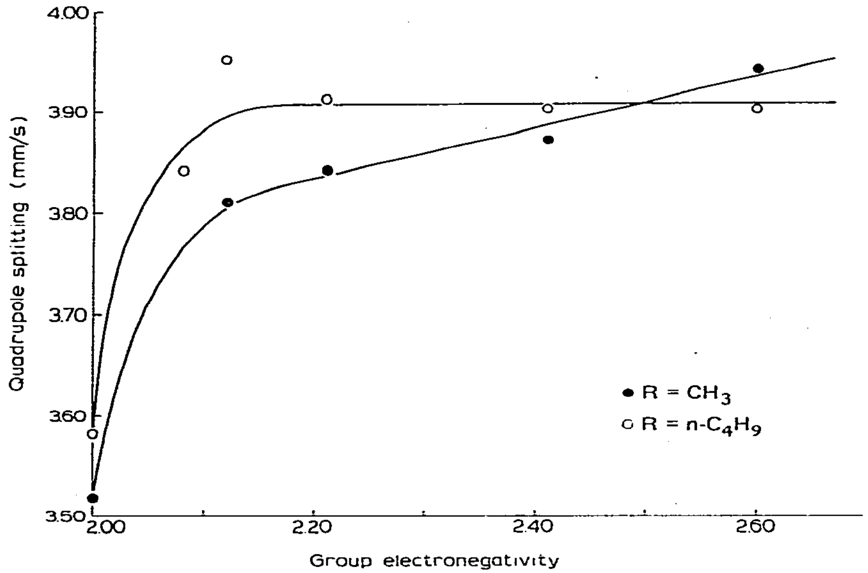


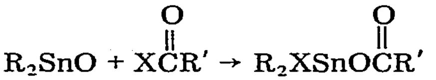
Fig. 1. The QS of $R_2ClSnO_2CCH_nX_{3-n}$ vs. the group electronegativity of CH_nX_{3-n}.

Discussion

Preparation of diorganotin halide carboxylates. Reactions of diorganotin oxides with metallic and organometallic halides [59—62] and with thionyl chloride [63] are well-known, and in general may be written as:

$$R_2SnO + E{-}X \rightarrow R_2XSnOE \qquad (6)$$

The reaction of dimethyltin oxide with acetyl chloride to give dimethyltin chloride acetate [28], shown in eq. 5, is an example. The reaction of acid halides with diorganotin oxides is a convenient method for the preparation of diorganotin halide carboxylates:



$$R_2SnO + X\overset{\overset{\displaystyle O}{\|}}{C}R' \rightarrow R_2XSnO\overset{\overset{\displaystyle O}{\|}}{C}R' \qquad (7)$$

Although only diethyltin dichloride and diethyltin dibenzoate could be isolated from the reaction of diethyltin oxide and benzoyl chloride [28], in this study the action of benzoyl halides with dimethyl- and di-n-butyltin oxides yielded dialkyltin halide benzoates. Acetyl chloride acts on di-n-butyltin sulfide to give di-n-butyltin chloride thioacetate.

Other carboxylic acid derivatives were obtained through exchange reactions of the type of eq. 8, in which HO_2CR' is a higher boiling carboxylic acid, and

$$R_2XSnO_2CCH_3 + HO_2CR' \rightarrow R_2XSnO_2CR' + HO_2CCH_3 \qquad (8)$$

the acetic acid formed was removed by distillation. However, as noted in earlier studies [64,65] relative volatility is not always the controlling factor in these transformations. Although thioacetic acid (b.p. 93°C) is more volatile, for example, it readily liberates acetic acid (b.p. 118°C) from dimethyltin chloride acetate. Thioacetic acid also displaces acetic acid from tri-n-butyltin acetate [66], suggesting that tin—sulfur is favored over tin—oxygen bonding. This is also demonstrated by the preparation of organotin mercaptans in aqueous alkaline solution [67], while organotin alkoxides react rapidly with water.

The structure and bonding of triorganotin carboxylates have been extensively discussed [68], however, diorganotin halide carboxylates have not been as thoroughly investigated. The results of infrared, ^{119m}Sn Mössbauer, ^{1}H and ^{13}C NMR measurements for the diorganotin halide carboxylates are now discussed.

Diorganotin halide acetates and haloacetates

Triorganotin carboxylates are pentacoordinated in the solid-state through bridging carboxylate groups, unless the substituents at tin are bulky, or the carboxylate group is branched at the α-carbon [69], and X-ray crystallographic data [1] confirms this suggestion originally put forward on the basis of infrared studies [70]. The $\nu_{asym}(CO_2)$ mode for trimethyltin acetate [34] at 1576 cm^{-1} is typical of these associated organotin carboxylates [68]. The frequency separations of the $\nu_{asym}(CO_2)$ and $\nu_{sym}(CO_2)$ modes have also been used to infer the type of carboxylate structure present [71—73]. These separations from Table 2 are all in the range 150—128 cm^{-1}, indicative of the expected bridged carboxylate structure shown in Fig. 2a. Similar conclusions for organotin haloacetates are precluded owing to shifts in the carbonyl stretching frequencies with halosubstitution. All the acetate and haloacetate derivatives listed in Tables 2, 3 and 4 exhibit both ν_{asym}(Sn—C) and ν_{sym}(Sn—C) modes, indicating a nonlinear C—Sn—C moiety consistent with the proposed structure.

The increase in ν_{asym} and lowering of $\nu_{sym}(CO_2)$ modes with increasing halogenation on the acetate group has also been observed for the triorganotin haloacetates [27,29,34,38,57,58,72,74,75]. Many factors are involved in determining this frequency, such as inductive, resonance, and field effects, which alter the force constant of the carbonyl group, as well as phase changes, mass and angle effects, vibrational coupling, and changes in the force constants of the adjacent bonds. Substituting increasingly electronegative groups on the α-carbon atom would tend to increase the $\nu(CO_2)$ frequency, while the mass effect would be expected to decrease it, and these factors have been principally associated with these changes [37,74].

The Mössbauer *IS* should be lowered by the progressive substitution of increasing electron withdrawing groups [76]. Table 12, however, shows a small, but monotonic increase of *IS* values with successive halosubstitution. In addition, while the values of the dialkyltin chloride acetates are smaller than those of the corresponding bromide acetates as is predicted, the *IS* values of the diorganotin halide acetates are larger than those of the corresponding trialkyltin acetates, opposite to what is predicted.

The observed ^{119m}Sn Mössbauer data may be interpreted, following our previous study of the trialkyltin acetates [29], as follows: the population of the empty 5*d*-orbitals of the tin atom by electrons from a carbonyl oxygen atom of a second molecule in an intermolecular association would be expected to lower the *IS* relative to the value found in a monomer with a free, organic ester structure. The subsequent weakening of the Lewis base strength of the carbonyl by the inductive pull of the halomethyl group in the $X_nH_{3-n}CCO_2$-group could thus account for the observed incremental increase in *IS* in the associated system. We previously predicted that halosubstitution at the tin atom, with its concomitant increase in Lewis acidity of the tin atom, would result in an increase in *IS* [29], and this is confirmed by the present data. Another consequence of this suggestion is a strengthening of the intermolecular tin—carbonyl oxygen bond with a concomitant lowering of the $\nu(CO_2)$ frequency, which for the dimethyltin chloride and bromide acetates are ca. 20 cm^{-1} lower than those of trimethyltin acetate [34,71].

The ratios of *QS* to *IS* (ρ), are greater than 2.1 for all the acetate and haloacetates studied, reflecting higher than four coordination at tin [75]. The observation of a spectrum at ambient temperatures for dimethyltin chloride acetate is indicative of a polymeric lattice structure [76] *. The *QS* data for dimethyl- and di-n-butyltin halide acetates are the same as those of the trimethyl- and tri-n-butyltin acetates.

The proposed structure for diorganotin chloride halide acetate shown in Fig. 2a contains bridging acetoxy groups in the axial positions, with the two organic groups and the halogen atom in the equatorial positions. Another associated, pentacoordinated structure is also possible, with the acetoxy groups bridging from axial to equatorial positions with halogen in the axial position. Distinguishing these two isomers on the basis of infrared or Mössbauer data is at present impossible [78].

The $\nu_{asym}(CO_2)$ modes shift to higher frequencies (cf. Tables 5 and 6) on dissolving, the greatest increases being for the acetates (ca. 40—50 cm^{-1}), suggesting that depolymerization occurs in solution. The dialkyltin chloride acetates which are monomeric in solution, show similar increases [23], and the $\nu_{asym}(CO_2)$ frequency of trimethyltin acetate which is monomeric in dilute solution increases from 1570 to 1658 cm^{-1}, the latter value typical of an ester-type structure [77]. However, the chelated structure shown in Fig. 2b has also been proposed for the halide acetates in solution [23,27], and for monomeric dialkyltin diacetates which show carbonyl bands at ca. 1600 cm^{-1} in solution, where bis-chelated, hexacoordinated structures have been suggested [41]. The chelated structure shown in Fig. 2b is analogous to that of the solid sulfur derivative, dimethyltin chloride *N,N*-dimethyldithiocarbamate [1].

The $\nu_{asym}(CO_2)$ absorption bands of the dimethyltin halide mono- and dichloroacetates in solution show splittings with frequency differences of ca. 24—37 cm^{-1}, indicating that rotational isomerism of the acetoxy chloromethyl group occurs in these compounds. Rotational isomerism, inferred from splittings with frequency differences of ca. 25 cm^{-1}, has been claimed for tri-n-butyltin chloroacetates [74,80], however, the corresponding bands in di-n-butyltin chloride haloacetates are unsplit.

The NMR $|^2J(^{119}Sn—C—^1H)|$ couplings for methyltin compounds of coordination numbers four to six show a steady increase, presumably arising through

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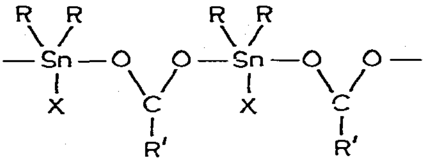
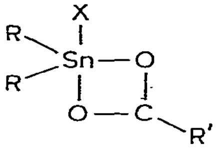
[*] The recent observation of ambient-temperature tin-119m Mössbauer spectra for certain molecular solids such as tetraphenyltin (m.p. 229°C) [78] does not affect our conclusion which is based upon a variety of physical evidence and upon close analogies with other associated tin(IV)-oxygen and -sulfur solids whose structures are known [1].



a. Solid-state structure



b. Solution structure

Fig. 2. Proposed structures of diorganotin halide carboxylates.

increased concentration of *s*-character in the tin—carbon bond [81]. An inductive pull through the C—CO_2—Sn system should enhance this concentration of *s*-character in the tin—carbon bonds, and lead to an increase in tin—proton coupling constant values with halogen substitution as has been seen for trimethyltin haloacetates [29].

The $|^2J(^{119}Sn—C—^1H)|$ values for dimethyltin halide haloacetates fall in the range 69—76 Hz, usually attributed to pentacoordinated tin, and have been interpreted [27] in terms of the chelated acetoxy structure shown in Fig. 2b. The results in Table 10, however, show a decrease in magnitude with increasing halosubstitution, a trend that is opposite to that found for the dimethyltin haloacetates. The coupling constants likewise show a monotonic decrease with increasing halosubstitution in the di-n-butyltin chloride compounds.

We attribute this decrease to a breaking of the chelated acetoxy structure. The inductive effect of halosubstitution would decrease the Lewis basicity of the carboxylate carbonyl oxygen. As the carbonyl oxygen becomes less effective in coordinating to the tin atom, the coupling constants decrease in magnitude.

It has been noted that the carbon-13 chemical shifts and tin—carbon coupling constants for di-n-butyltin chloride acetate are merely the average of the values for neat di-n-butyltin chloride acetate and diacetate [56]. Comparison of the ^{1}H NMR parameters listed in Table 10 with data for neat dimethyltin dihalides [81] and diacetates [41] individually suggests that a dynamic equilibrium exists in solution (eq. 9) in which the halide and acetoxy groups exchange rapidly

$$2\ R_2XSnO_2CR' \rightleftharpoons R_2SnX_2 + R_2Sn(O_2CR')_2 \qquad (9)$$

between dimethyltin moieties. When solutions of either dimethyltin bromide acetate or chloride trichloroacetate are mixed with dimethyltin chloride acetate, the ^{1}H NMR parameters quickly become the average of those for the individual solutions.

The solution infrared spectra for all the acetate and haloacetate compounds show an additional band at ca. 100—125 cm^{-1} to higher frequencies than the $\nu_{asym}(CO_2)$ mode, which is absent in the solid-state spectra. The shifts in these higher frequency absorptions with increasing halosubstitution parallel the shifts in the $\nu_{asym}(CO_2)$ mode, suggesting that the band is associated with a carboxylate vibration. This higher frequency band was investigated in more detail for di-n-butyltin chloride acetate, where it is invariant with concentration, while the $\nu_{asym}(CO_2)$ absorption at ca. 1600 cm^{-1} shows the expected increases in intensity. The $\nu_{asym}(CO_2)$ mode is unaffected by addition of triethylamine; however, at a mole ratio of base above 1/10, the high frequency band disappears. Further addition of triethylamine precipitates the bis-adduct of di-n-butyltin dichloride. Addition of 1,10-phenanthroline to solutions of dimethyltin chloride acetate also precipitates the adduct with dimethyltin dichloride, results which confirm the equilibrium depicted in eq. 9. As the temperature of a cyclohexane solution of di-n-butyltin chloride acetate is raised, the higher frequency band disappears reversibly. In contrast, no variation is observed in the $\nu_{asym}(CO_2)$ mode.

Figure 3 illustrates some of the carboxylate structures possible. Organotin compounds with a bridging structure (Fig. 3a) generally exhibit the $\nu_{asym}(CO_2)$ mode in the range 1560—1540 vs. 1660—1640 cm^{-1} for the free ester structure (Fig. 3d). Compounds containing a dimeric structure (Fig. 3b) which has been proposed for the neat liquid dialkyltin diacetates [41], have the $\nu_{asym}(CO_2)$ mode in the same range as the bridging structures. Structures with a chelating acetate group (Fig. 3c) would be expected to have the $\nu_{asym}(CO_2)$ absorption at frequencies between those of the bridging and the free ester-type structures.

The $\nu_{asym}(CO_2)$ frequencies for the acetate derivatives of the Group IV

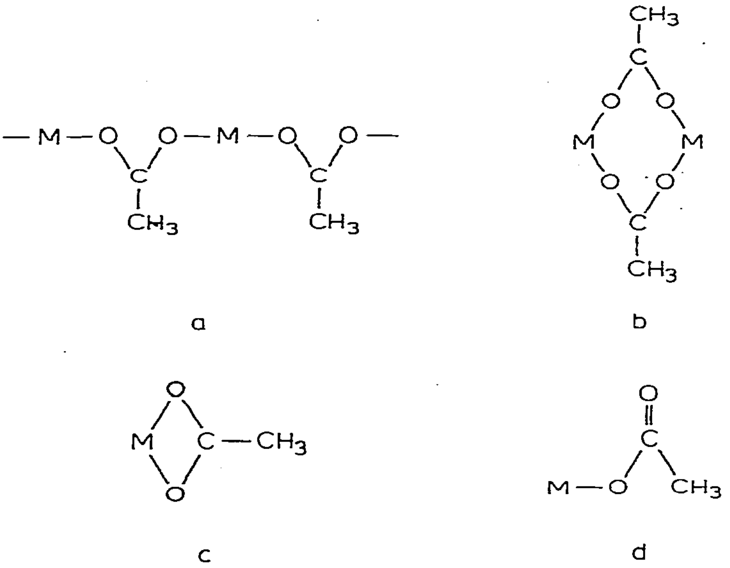


Fig. 3. Possible organometal acetate structure.

elements, M, recorded under conditions in which all the derivatives possess an ester-type structure, decrease with increasing atomic weight of M, as shown in Table 13. The mass effect does not predominate in increasing the halosubstitution on the acetate group, however, and other effects must also be considered.

Changes in the degree of M—O bond ionicity have been discussed [83], however, this assumes that only electronic effects occur, ignoring the rotational isomerism that has been observed for the mono- and di-haloacetate compounds. [73,80]. For the compounds listed in Table 13, only the rotational isomers of the *cis* derivatives should be observed, since steric considerations would rule out the *trans* configuration. With the carbonyl oxygen in the *cis* position, interaction with M would be possible, and the carbonyl frequencies should decrease in the order of Lewis acidities Sn > Ge > Si.

Trimethyltin acetate [76] is monomeric, in dilute solution, with $\nu_{asym}(CO_2)$ at 1650 cm^{-1}. As the concentration is increased, a band at 1580 cm^{-1} attributable to the associated form grows. This band disappears upon heating, while the 1650 cm^{-1} band arising from the monomer grows. The same effect also occurs upon addition of trimethylamine. The tin—proton coupling constants for trimethyltin acetate in dilute solution suggest tetracoordinated tin.

The question of interaction of the carbonyl oxygen in the presumably tetracoordinated, monomeric tin compound is complex, however. While the infrared and NMR data indicate no appreciable interaction, the ^{119m}Sn Mössbauer and X-ray data for tricyclohexyltin acetate disagree. Solid tricyclohexyltin acetate consists of discrete monomers with an intramolecular tin—carbonyl oxygen distance of only 2.95 Å [12]; but the $\nu_{asym}(CO_2)$ mode in the solid [12] (1645 cm^{-1}) is nearly identical to that for trimethyltin acetate in dilute solution [76]. However, the Mössbauer *QS* value of 3.27 mm/s [84], ($\rho = 2.08$), is suggestive of considerable interaction.

The carbonyl oxygen in trimethyl- and tricyclohexyltin acetate is prevented from being directed away from the tin atom by steric requirements. In tin(IV) acetate [85,86], the butyltin tricarboxylates [87], and dimethyltin oxalate monohydrate [88], on the other hand, at least one carbonyl oxygen cannot be coordinated to tin, and all exhibit an additional higher frequency carboxylate absorption band as discussed above for our compounds.

Molecular model studies of di-n-butyltin chloride acetate and trimethylacetate suggest that rotation to the *trans* isomer is possible for the former but not for the latter. However, the higher frequency band is also observed for the

TABLE 13

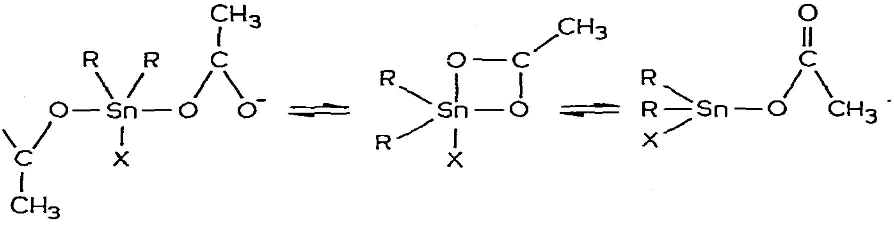
$\nu(CO_2)$ FREQUENCIES FOR THE ACETATE DERIVATIVES OF GROUP IV ELEMENTS $(CH_3)_3MO_2CCH_3$ (cm^{-1})

M	$\nu_{asym}(CO_2)$	$\nu_{sym}(CO_2)$	Reference
Si	1725	1267	31
Ge	1692	1280	3
Sn	1650 [a]	1380	77

[a] Recorded in dilute solution in which the compound is monomeric.

latter, exhibiting the same temperature dependence as in the acetate. Rotational isomerism alone then cannot explain these results.

An equilibrium involving an uncoordinated carboxylate oxygen, eq. 10, can

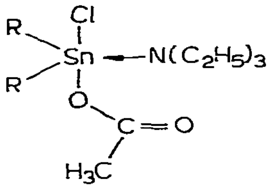


(10)

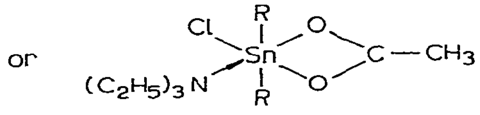
(I) (II) (III)

be ruled out since increasing the temperature would be expected to shift the equilibrium toward the right and result in an increase in the intensity of the higher frequency band. However, the opposite is observed.

Addition of a Lewis base such as triethylamine which would coordinate with the tin atom producing either of the species IV or V. IV would exhibit an



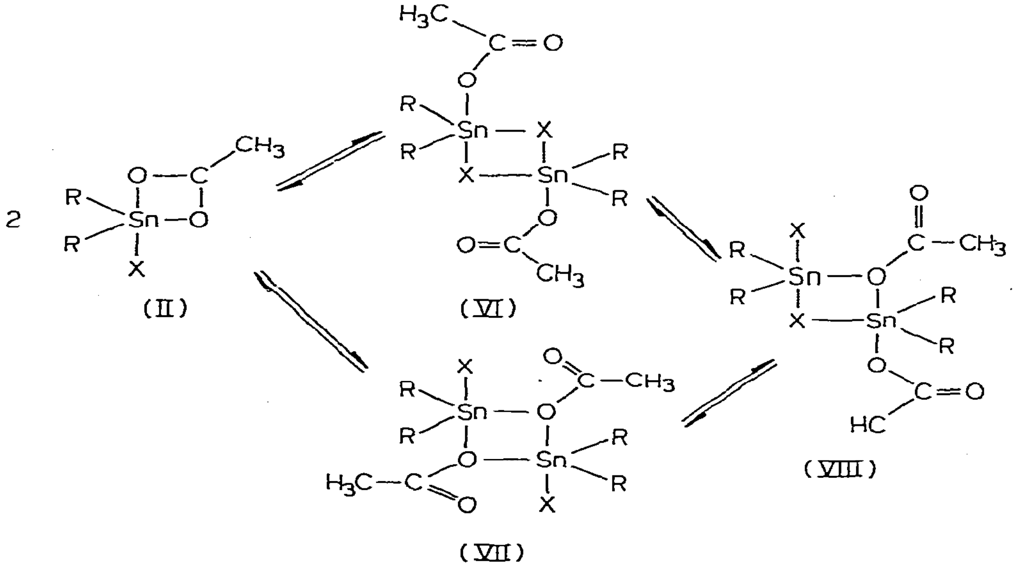
(IV)



(V)

enhanced uncoordinated carboxylate oxygen band, again contrary to what is observed. Production of the second species is complicated by the fact that addition of even a small excess of triethylamine precipitates the bis-adduct of R_2SnX_2.

Association to give dimers must be considered. Possible dimeric equilibrium structures are shown in eq. 11.



(11)

Molecular weight data for diethyl- and di-n-propyl-tin chloride acetate, as determined cryoscopically in benzene, are about 5% higher than the monomeric molecular weights [23], but those for dimethyltin chloride monoiodo- and dichloro-acetate in chloroform [27] exceed the calculated values by about 25%.

The dimeric structures VII and VIII in the scheme are based upon a four-membered Sn_2O_2 or Sn_2OX ring for which, in at least the former case, there is ample structural data in support [1]. In each case there is an acetate group with the carboxylate oxygen both bonded to a tin atom and coordinated to the tin atom of the second molecule in the dimer. This arrangement, which leaves the carbonyl group free, is seen in the X-ray crystal structures of the dimeric $\{[(H_2C{=}CH)_2SnO_2CCF_3]_2O\}_2$ [15] and $\{[(n\text{-}C_4H_9)_2SnO_2CCCl_3]_2O\}_2$ [16], molecules which include such a tricoordinated carboxylate oxygen and free carbonyl group. Such a system would be expected to exhibit a higher carbonyl stretching vibration than for a typical free-ester group, and strong absorptions at ca. 1700 and 1715 cm^{-1}, respectively, have been recorded for these two examples as well as at 1715 cm^{-1} for the dimeric $\{[(n\text{-}C_4H_9)_2SnO_2CCH_n\text{-}Cl_{3-n}]_2O\}_2$ [89]. Since the dynamic equilibria shown in Scheme 1 involve only dimers, their relative positions should be unaffected by concentration changes, but the addition of the Lewis base triethylamine would shift the system to the bis-adduct of the monomer, which precipitates. Heating would also drive the system to the monomeric form.

Diorganotin halide benzoates. The infrared, ^{119m}Sn Mössbauer, ^1H and ^{13}C NMR results for dialkyltin halide benzoates in general parallel those of the diorganotin halide acetates. In the solid state, the benzoate may act as a bridging group between dialkyltin halide units in a linear polymer. The carbonyl stretch at ca. 1570 cm^{-1} and the *QS* values of ca. 3.5 mm/s are very similar to those of the diorganotin halide acetates.

Unlike in the diorganotin halide acetates, however, the $\nu_{asym}(CO_2)$ modes do not shift to higher frequencies on solution, and except for the appearance of the higher frequency absorption band at ca. 1700 cm^{-1}, the solution infrared spectra are nearly identical to the solid state spectra. We interpret the higher frequency band in the same way as above.

The $\nu_{asym}(CO_2)$ mode of solid triphenyltin benzoate is found at 1620 [47], and at 1565 and ca. 1640 cm^{-1} in tri-n-propyl- [83] and tri-n-butyltin benzoate [83,90], respectively, which are liquids. Since there is no shift towards higher frequencies in the $\nu_{asym}(CO_2)$ mode on solution, it is likely that structures adopted in both states contains chelated benzoate groups.

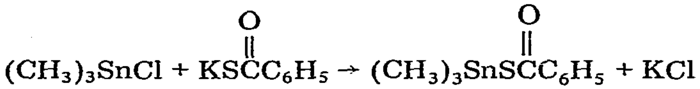
Again, two bond tin—proton NMR coupling constants measured for the dimethyltin halide benzoates are the average of those for dimethyltin dihalide [91] and dimethyltin dibenzoate [21], suggesting an equilibrium as in eq. 9.

Dialkyltin chloride thioacetates. Dialkyltin chloride thioacetates have considerably different physical properties from their oxygen analogues. Dimethyltin chloride thioacetate is a low melting point crystalline solid and di-n-butyltin chloride thioacetate is a liquid at room temperature.

The infrared spectra of solid dimethyltin chloride thioacetate and of di-n-butyltin chloride thioacetate as a liquid film are similar to those in solution. The $\nu(C{=}O)$ mode is found in the range 1612—1604 cm^{-1}, similar to the dialkyltin halide acetates, but ca. 50 cm^{-1} lower than observed for trialkyltin thioacetates [52,92]. Although the $\nu(C{=}O)$ mode for the sodium salt of thioacetic acid has not been assigned, a qualitative comparison may be made with that of sodium thiobenzoate [51], which is found at 1557 cm^{-1}. Trimethyltin thioacetate is monomeric in solution [52], and its two bond tin—proton coupling constant values are in the range of those attributable to tetracoordinated tin. While both the $\nu_{asym}(Sn—C)$ and $\nu_{sym}(Sn—C)$ modes are present, no bands attributable to the $\nu(C{=}S)$ mode are observed.

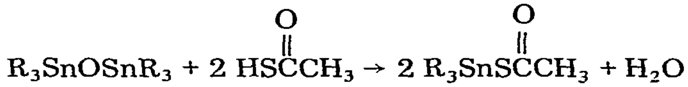
Proton NMR data are in the range of those expected for pentacoordinated tin, but exchanges as in eq. 9 may also be occurring. Evidence in support of a pentacoordinated structure comes from the Mössbauer *QS* data which for the trialkyltin thioacetates are in the range of those found for tetracoordinated tin [52], but for the dimethyl- and di-n-butyltin chloride thioacetate are >3.00 mm/s. Unfortunately, no Mössbauer data are available for other organotin—sulfur compounds of similar structure. The Mössbauer spectrum of the disulfur analogue, dimethyltin chloride, *N,N*-dimethyldithiocarbamate, whose chelating structure has been confirmed by X-ray crystallography [79] has not been measured.

Trialkyltin thioacetates. Trimethyltin thioacetate has been prepared by the action of the potassium salt of thioacetic acid on trimethyltin chloride [92]:

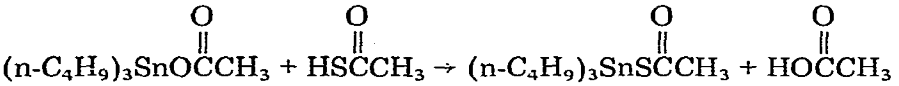


$$(CH_3)_3SnCl + KS\overset{\overset{O}{\|}}{C}C_6H_5 \rightarrow (CH_3)_3SnS\overset{\overset{O}{\|}}{C}C_6H_5 + KCl \qquad (12)$$

and the n-butyl derivative by the action of thioacetic acid on bis(tri-n-butyltin)-oxide [92] (eq. 13) or on tri-n-butyltin acetate [65] (eq. 14).

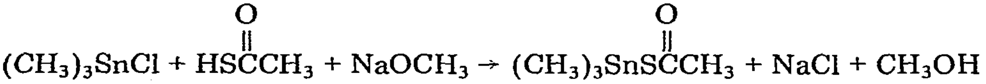


$$R_3SnOSnR_3 + 2\ HS\overset{\overset{O}{\|}}{C}CH_3 \rightarrow 2\ R_3SnS\overset{\overset{O}{\|}}{C}CH_3 + H_2O \qquad (13)$$



$$(n\text{-}C_4H_9)_3SnO\overset{\overset{O}{\|}}{C}CH_3 + HS\overset{\overset{O}{\|}}{C}CH_3 \rightarrow (n\text{-}C_4H_9)_3SnS\overset{\overset{O}{\|}}{C}CH_3 + HO\overset{\overset{O}{\|}}{C}CH_3 \qquad (14)$$

We have prepared the trimethyltin compound in high yield using sodium methoxide (eq. 15). The tri-n-butyl derivative was synthesized by the method depicted in eq. 13.



$$(CH_3)_3SnCl + HS\overset{\overset{O}{\|}}{C}CH_3 + NaOCH_3 \rightarrow (CH_3)_3SnS\overset{\overset{O}{\|}}{C}CH_3 + NaCl + CH_3OH \qquad (15)$$

The infrared spectra are given in Tàble 14 * for the neat compounds and their solutions. The spectra of tri-n-butyltin thioacetate as a liquid film and in solution, and the trimethyltin thioacetate in solution are all very similar. The $\nu(C{=}O)$ modes are observed as intense absorption bands at ca. 1660 cm^{-1}; that for trimethyltin thioacetate is broad and split, at 1603 and 1575 cm^{-1}. This latter band has been previously reported [52] to occur at the same frequency observed in solution, 1667 cm^{-1}, however, no mention was made of whether the solid was dispersed in potassium bromide or in Nujol. It was found in this investigation that when trimethyltin thioacetate was run in Nujol, the sharp band at ca. 1660 cm^{-1} appears together with a weaker band at ca. 1600 cm^{-1}.

The *QS* value in Table 12 for trimethyltin thioacetate is significantly greater

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* See footnote on p. 136.

than that for tri-n-butyltin thioacetate, which is monomeric and tetracoordinated [1], but is similar to the value found for the tri-n-butyltin compound in frozen pyridine solution, in which there is higher coordination at tin [93]. The infrared and Mössbauer data for solid trimethyltin thioacetate suggest that its structure contains a chelating thioacetoxy group.

The less Lewis acidic tin in trimethyltin thioacetate is tetracoordinated in solution, the $\nu(C{=}O)$ mode moving to higher frequencies. The $|J(^{119}Sn{-}C{-}^{1}H)|$ value of 58.0 Hz is confirmatory.

A recent report [94] opens up a new dimension on these studies. During the annealing of a sample of $(C_6H_5)_3SnO_2CCCl_3$ [58] at room temperature for five years a solid state monomer-polymer phase transition occurred. This new associated form could also be produced directly by changing the solvent of reaction from methanol [58] to ethanol. The $\nu_{asym}(CO_2)$ mode absorbs at 1700 cm^{-1} in the monomer (*QS* 2.97 mm/s) and at 1618 cm^{-1} in the polymer (*QS* 3.90 mm/s) in the solid state, but the latter dissolves as the monomer in dilute carbon tetrachloride.

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