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SYNTHESIS AND SPECTROSCOPIC STUDIES OF SOME ORGANOTIN(IV) COMPOUNDS CONTAINING THE Sn–O BOND

G. DOMAZETIS, R. J. MAGEE and B. D. JAMES
Department of Inorganic and Analytical Chemistry, La Trobe University, Bundoora, Victoria 3083, Australia

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Abstract—The preparation of a number of organotin(IV) compounds, containing Sn–O bonds, is described. Their ^{13}C and ^{1}H NMR, IR spectra, and some molecular weight determinations, are presented. Structures are postulated based largely on the one bond coupling constant $^{1}J(^{119/117}Sn-^{13}C)$. Further evidence is obtained from ^{1}H NMR and IR spectra. For the compounds reported, IR spectra do not appear to provide unambiguous evidence because of difficulties in assigning and interpreting C=O, Sn–O and Sn–C stretch frequencies.

INTRODUCTION

Organotin(IV) complexes containing the Sn–O bond have been extensively studied. Organotin carboxylates, for example, have been shown to exist in either of two forms: polymeric 5-coordinate complexes in the solid, or monomeric 4-coordinate species in solution[1]. The structures of tribenzyltin acetate and tricyclohexyltin acetate have been shown by X-ray crystallography to be polymeric and monomeric respectively[2, 3] in the solid. Steric factors are held responsible for the differences observed. Organotin acetylacetonates and other β-diketonates have been studied via Mössbauer spectroscopy[4], and recently the distribution of the *cis* and *trans* isomers in solution have been studied with light scattering experiments[5]. The polymeric nature of solid oxides has been concluded from IR spectra[6], and the IR spectra of alkoxides have also been reported[7].

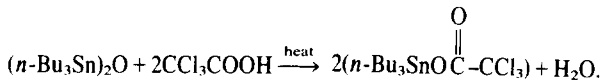
Here we report investigations into a number of organotin(IV) complexes containing oxygen ligands. Compounds have been prepared which provide an insight into the structural preferences of such complexes, and on the basis of their ^{13}C and ^{1}H NMR spectra, molecular weight data and IR spectra, we postulate some possible structures.

The preparations of the compounds studied are based on the following reaction schemes:

(1) Reaction of a triorganotin chloride with the sodium derivative of the ligand, e.g.

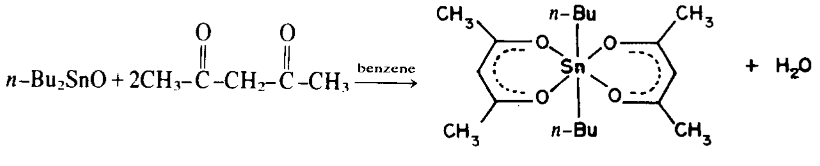
$$R_3SnCl + NaOCH_2CH_2NH{\cdot}R' \xrightarrow{n\text{-hexane}} R_3SnOCH_2CH_2NH{\cdot}R' + NaCl.$$

(2) Reaction with triorganotin oxide, e.g.



$$(n\text{-}Bu_3Sn)_2O + 2CCl_3COOH \xrightarrow{\text{heat}} 2(n\text{-}Bu_3SnO\overset{\overset{\displaystyle O}{\|}}{C}\text{-}CCl_3) + H_2O.$$

(3) Reaction with diorganotin oxide, e.g.



$$n\text{-}Bu_2SnO + 2CH_3\text{-}\overset{\overset{\displaystyle O}{\|}}{C}\text{-}CH_2\text{-}\overset{\overset{\displaystyle O}{\|}}{C}\text{-}CH_3 \xrightarrow{\text{benzene}}$$

(4) Reaction with triorganotin alkoxides, e.g.

$$n\text{-}Bu_3SnOCH_3 + HOCH_2C(CH_3)_2NH_2 \longrightarrow n\text{-}Bu_3Sn(L) + CH_3OH(L = O\text{-}CH_2C(CH_3)_2NH_2.)$$

EXPERIMENTAL

^{13}C NMR spectra were recorded from neat liquids or concentrated (saturated) solutions in $CDCl_3$, with TMS as internal standard, using a JEOL-FTR spectrometer operating at 25.15 MHz over 6250, 5000 and 2500 Hz sampling frequencies, with proton decoupling. Chemical shifts are accurate to ±0.1 ppm and coupling constants to ±2 Hz—except where peak overlapping occurs when precision limits are ±5 Hz. Assignments were made by comparisons with published spectra, by using the coupling satellite peaks, and where possible with off-resonance decoupling.

Mass spectra were obtained with a JEOL-D100 Mass spectrometer, and used to indicate parent ions where possible (using the ^{120}Sn isotope peak) and any impurities which may have been present.

^{1}H NMR spectra were recorded at ambient temperature with a Varian T-60 NMR spectrometer operating at 60 MHz. Samples were dissolved in $CDCl_3$ and TMS used as internal standard.

IR spectra were recorded down to 300 cm^{-1} with a Perkin–Elmer 457 Grating IR spectrophotometer, calibrated with polystyrene film. KBr pellets were used for solids and KBr plates for liquid film samples.

Molecular weights were obtained with a Perkin–Elmer 115 vapor phase osmometer, or from the mass spectra of the compounds.

Microanalyses were performed by the Australian Microanalytical Service, Division of Applied Organic Chemistry, CSIRO, Melbourne. The starting materials Me_2SnO, Me_3SnCl and $(n\text{-}Bu_3Sn)_2O$ were obtained from Alfa Inorganics Inc. and used without further purification. Other compounds, n-Bu_3SnCl, n-Bu_2SnO, Et_2SnO and n-Bu_2SnCl_2 were prepared by published methods[8]. Unless otherwise stated, all ligands were also obtained commercially. Solvents were usually sodium-dried and when required, purified by standard procedures[9].

N-alkyl aminoalcohols were prepared from ethanolamine and the alkyl bromide (RBr) for $R = n$-propyl, n-butyl and n-hexyl[10]. The n-octyl derivative was obtained from the reaction of chlorohydrin with n-octylamine[11]. Boiling points and yields corresponded to those reported originally.

Preparation of complexes

(a) *Tri- and di-*n*-butyltin carboxylates.* Compounds were prepared by reacting the appropriate oxide with a stoichiometric quanitity of the acid. Tri-n-butyltin acetate was prepared in benzene. M.P.: 84.5°, lit.[8] 84.5–85.0°C. Di-n-butyltin diacetate, b.p.: 82–86°C at 0.2 torr.

(b) *Tri- and di-*n*-butyltin* (p-*ethoxy-benzoates*). These were prepared by refluxing the oxide and p-ethoxy benzoic acid, for 4 hr in benzene whilst removing the water with a Dean–Start trap. The benzene was vacuum distilled off to leave the product. n-$Bu_3SnO_2CC_6H_4p$-OC_2H_5, m.p.: 30.2–32.4°C. Calc. for $C_{12}H_{56}SnO_3$: C, 55.38; H, 7.99; Sn, 26.14. Found: C, 55.44; H, 7.78; Sn, 26.24. MWt. n-$Bu_2Sn(O_2CC_6H_4p$-$OC_2H_5)_2 = 565$ (from vapor phase osmometry), Calc. = 563.3. n-$Bu_3Sn(O_2CC_6H_4p$-$OC_2H_5) = 456$ (from mass spectrometry), Calc. = 455.4.

(c) *Complexes of β-diketones.* These were prepared similarly from the oxides and the ligand by refluxing in benzene, and removing the water formed, e.g. n-$Bu_2Sn(AcAc)_2$, b.p. 130–132°C/0.3 torr, lit.[12] 132°C/0.4 torr. Purity of these complexes was ascertained with mass spectrometry, ^1H NMR and ^{13}C NMR spectroscopy. MWt. n-Bu_3 $^{120}Sn(CH_3COCHCOC_6H_5) = 452$ (from mass spectrometry), Calc. = 451.43.

(d) *1,1,6,6 - Tetra - n - butyl - 1,6 - distanna - 2,5,7,10 - tetraoxocyclodecane.* This was obtained from dibutyltin oxide and ethylene glycol, as previously reported[13]. M.p. 218–222°, lit[13] 223–226°C. Calc. for $C_{20}H_{44}O_4Sn_2$: C, 40.96; H, 7.56; Sn, 40.57. Found: C, 41.06; H, 7.54; Sn, 40.8. MWt = 588 (from mass spectrometry), Calc. = 586.49.

(e) *Bis(diethyltin IV phenoxide)oxide.* Et_2SnO and phenol were refluxed in benzene in 1:2 molar ratios, for 2 hr. The benzene was removed and the product recrystallized from "wet" methylene chloride/petroleum ether (40–70°C). M.p.: 159.6–160.1°C. Calc. for $C_{20}H_{30}Sn_2O_3$: C, 43.22; H, 5.94. Found: C, 43.25; H, 5.42.

(f) *Tri-*n*-butyltin sulfonate* o*-benzoic acid.* 0.01 mol of $(n$-$Bu_3Sn)_2O$ and 0.02 mol of o-sulfobenzoic acid were mixed in 150 ml of benzene, and gently heated on a water bath at 80°C for 4 hr. The temperature was then raised to 100°C and water continuously removed with a Dean–Start trap. After 18 hr (0.36 g of water removed) 80 ml of benzene was removed, and the solution allowed to cool. Crystals of the product formed, and these were filtered off and dried. Yield = 41%. M.p. 143.0–145.6°C. Calc. for $C_{19}H_{32}SO_5Sn$: C, 46.46; H, 6.56, S, 6.53. Found: C, 46.38; H, 6.62; S, 6.3. MWt = 599 (from vapor phase osmometry), Calc. = 491.1.

(g) *Dimethylstannyl(IV) derivative of the* o*-sulfobenzoic acid dianion.* Equimolar quantities of dimethyltin oxide and o-sulfobenzoic acid were mixed in benzene and gently heated for 16 hr, water being removed with a Dean–Stark trap. The precipitate which formed was dissolved by adding anhydrous methanol and refluxing was continued for another 2 hr. The solvents were removed *in vacuo* and the resulting oil was dried in a vacuum desiccator to yield a white powder which is fairly soluble in methanol and ethanol, but insoluble in water and chloroform. It does not melt up to 300°C, and its low solubility makes it impossible to obtain acceptable ^{13}C NMR spectra. A mass spectrum was obtained with a probe temperature of 350°C. The ^1H NMR spectrum in a 10% CH_3OH/90% D_2O mixture yielded peaks of 0.9 ppm $[(CH_3)_2Sn]$ and at 7.7–8.0 ppm (aromatic ring). $^2J(^{119/117}Sn$–$CH)$ is about 100 Hz.

(h) *Tri-*n*-butyltin aminoalcohol derivatives* (n-$Bu_3SnOCH_2CH_2NHR$, *where* $R = n$-C_3H_7, n-C_4H_9, n-C_6H_{13}, n-C_8H_{17}). The preparation of tri n-butyltin(IV) [N-n-Propyl]ethanolamine is described, and is typical for these compounds.

0.1 mol of N-propyl ethanolamine was dissolved in 150 ml of n-hexane, and while stirring, 0.1 mol of freshly-cut sodium chips were added to the solution. After 1 hr, the reaction flask was warmed slowly until the solvent began to reflux. After a further 1 hr, when almost all the sodium had reacted, acetone was added until a clear red solution was obtained. This solution was cooled, and a 0.1 M solution of n-Bu_3SnCl in n-hexane, was added slowly, while the mixture was stirred thoroughly. Refluxing for 2 hr followed, precipitated NaCl was filtered off, to yield a pale red oil. This was distilled under vacuum (0.5 torr) and the fraction boiling at 128–130°C was collected. Yield = 46%. Calc. for $C_{17}H_{39}Sn\ O\ N$: C, 52.07; H, 10.01; N, 3.57. Found: C, 51.92; H, 9.80; N, 3.28. For $R = n$-C_4H_9, b.p.: 132–134°/0.15 torr. Yield 43%. $R = n$-C_6H_{13}, b.p.: 146–148°/0.5 torr. Yield 68%. $R = n$-C_8H_{17}, b.p.: 156–158°/0.3 torr. Yield 60%.

RESULTS

Chemical shifts and coupling constants for ^{13}C NMR spectra are recorded in Table 1. The one bond coupling constant $^1J(^{119/117}Sn$–$^{13}C)$ has been obtained for almost all the compounds, although peak overlapping prevents an accurate value for some aminoalcohol derivatives. The two and three bond coupling constant values are often obscured by peak overlapping between the β and γ carbon of the butyltin derivatives, but these values are not crucial for general structural deductions[14].

IR and ^1H NMR data are recorded in Table 2. ^1H NMR data are generally of little value in regard to the ethyl- and butyltin moieties in the molecules, but provide valuable information about the ligand. IR spectra are interesting because so many of the structural proposals in the past have been based on such data, but the value of the technique is curtailed by assignment difficulties. It is however useful in confirming certain observations, and such data is used where appropriate.

DISCUSSION

$^1J(Sn$–$C)$ *values and structure*

The one bond coupling constant is taken to indicate the nature of the Sn–C bond for the complex. According to Pople and Santry[15], of the three contributions to the value of coupling constants, the Fermi contact interaction is the dominant one. Molecular orbital calculations carried out on organomercury complexes[16] and organotin complexes[17] support this conclusion.

The contact contribution relates the coupling constant between atoms A and B to two basic contributions, the valence s-electron density of each atom and the mutual polarizability of the valence s-orbitals[15]. The magnitude of the one bond coupling constant $^1J(Sn$–$C)$ is viewed as an indication of the type of Sn–C bond present in the molecule. The Sn–C bond is influenced by the ligands attached to the tin atom, and atoms possessing high electronegativity values, will cause an increase in the coupling constant, in accordance with Bent's rule[18]. Change in the effective nuclear charge of the tin atom, and changes in the hybridization of the tin orbitals, will also be reflected in changes of the coupling constant.

From Mössabuer spectroscopy[4], it is suggested that in octahedral complexes such as *trans*-$Me_2Sn(Acac)_2$, most of the $5s$ electron character of tin is involved in the Sn–C bond. A rough relationship between size of the one bond coupling constant and the coordination number of Sn(IV) has been suggested[14].

Table 1.

	Chemical shift, δ(ppm) vs TMS (±0.1)				Coupling Constant[+] Hz (±2)			Ligand Shifts, ppm[**]
Compound	Cα	Cβ	Cγ	Cδ	^1J	^2J	^3J	
n-Bu_3SnOCH_3	14.3	28.1	27.3	13.8	370	22	62	54.4 (OCH_3)
n-$Bu_3SnOCOCH_3$[a]	16.3	27.7	27.0	13.5	361	20	68	176.7 (C=O); 21.2 (CH_3)
n-$Bu_3SnAcAc$	18.8	27.9	26.9	13.6	410	*	76	190.5 (C=O); 101.8 (CH)
n-$Bu_3SnBzAc$	20.1	28.4	27.4	13.9	382	*	60	192.4, 182.7 (C=O); 96.8 (CH); 28.5 (CH_3)
n-$Bu_3SnOCOCCl_3$	17.3	27.4	26.8	13.4	342	24	62	165.3 (C=O); 91.9 (CCl_3)
n-$Bu_3SnO_2CC_6H_4OC_2H_5$[a]	16.2	27.8	26.9	13.4	366	*	102	170.7 (C=O)
n-$Bu_3SnO_3SC_6H_4CO_2H$[a]	20.3	27.8	26.9	13.7	400	*	70	171.8 (C=O)
n-$Bu_3SnOCH_2C(CH_3)_2NH_2$	15.6	28.3	27.3	13.7	376	*	82	73.5 (O-C): 51.3 ($C(CH_3)_2$); 8.9 (CH_3)
n-$Bu_3SnO(CH_2)_2NH(C_3H_7)$	14.8 16.5	28.4	27.5	13.8	360 370	*	*	65.2 (O-C): 57.5 (C-N); 54.3 (N-C); 52.5 (N-C-C)
n-$Bu_3SnO(CH_2)_2NH(C_4H_9)$	14.8 16.5	28.4	27.4	13.8	369 371	45	105	65.4 (O-C); 54.8 (C-N); 50.1 (N-C)
n-$Bu_3SnO(CH_2)_2NH(C_8H_{17})$	14.8 16.5	28.2	27.3	13.7	365 *	*	*	65.2 (O-C); 54.3 (C-N); 50.3 (N-C)
n-$Bu_3SnO(CH_2)_2NH(C_6H_{13})$	14.7 16.5	28.4	27.4	13.8	*	*	*	65.3 (O-C); 54.7 (C-N); 50.4 (N-C)
$(n$-$Bu_2Sn)_2(OCH_2CH_2O)_2$[a]	22.7	27.7	27.1	13.6	653	34	101	63.2 (O-C)
n-$Bu_2Sn(O_2CCH_3)_2$[a]	25.0	26.8	26.4	13.6	601	*	**	181.3 (C=O); 20.4 (CH_3)
n-$Bu_2Sn(AcAc)_2$	27.3	27.7	26.4	13.9	925	41	122	190.7 (C=O); 99.8 (CH); 27.7 (CH_3)
n-$Bu_2Sn(BzAc)_2$	27.9	27.3	26.4	13.8	901	*	*	192.9, 182.7 (C=O); 96.8 (CH); 28.5 (CH_3)
n-$Bu_2Sn(O_2CC_6H_4OC_2H_5)_2$[a]	25.5	26.8	26.4	13.5	598	20	98	175.6 (C=O)
$[(C_2H_5)_2SnOC_6H_5]_2O$[a]	17.6 15.6	9.7			632 617	43		161.1, 129.6, 118.5, 117.9 (C_6H_5)

[+] Coupling constants for ^1J are for $^{119}Sn-^{13}C$.

* Accurate values could not be obtained due to peak overlapping.

** Complete assignments for ligand shifts are not presented.

[a] Spectra obtained from 50% solution (otherwise saturated solution) in $CDCl_3$. Spectra for all other compounds were obtained from neat liquids.

It has also been shown that the size of the ^1J value for tetrahedral tributyl-tin complexes varies with the atom bonded to tin, in the order O > Cl > S[19]. This variation parallels the variation of electronegativity of these atoms, in accordance with Bent's rule[18].

A comparison of the ^1J values for some of the compounds reported in this work and the coordination number of related compounds of known structure is given in Table 3.

(i) *Carboxylates and β-diketonates*

(a) *Tributyltin derivatives.* The ^1J values for this series of compounds are close to that of tributyltin methoxide (370 Hz). The ν(C=O) frequencies are usually in the 1600 cm^{-1} region, as normally expected for associated species in the solid or neat liquid phases[1]. The compound $(n$-$C_4H_9)_3SnO_2CCl_3$, however, has a ν(C=O) frequency in the solid of 1650 cm^{-1}, suggesting that any interaction between the carbonyl group and tin is quite weak. Further, the ^1J value (in 30% solution) is 342 Hz, and this indicates that the compound exists as a monomeric species having 4-coordinate tin in both phases. On the basis of similar data, the compound $(n$-$C_4H_9)_3SnO_2CC_6H_4OC_2H_5$ also appears to be a 4-coordinate monomer (^1J = 366 Hz, 50% solution; *ν(C=O)* = 1635 cm^{-1}, solid). In this case also, the mass spectrum contains a molecular ion peak, which further argues against any association.

(b) *Dibutyltin derivatives.* The diacetate has ^1J = 601 Hz for a 50% solution (cf. 630 Hz, neat liquid[14]) and a ν(C=O) band at 1605 cm^{-1}. Its mass spectrum does not contain a parent ion peak of a monomer. These observations are consistent with the conclusions previously reported[14], namely that the compound is a dimer with bridging and non-bridging ligands. On the other hand, $(n$-$C_4H_9)_2Sn(O_2CC_6H_4OC_2H_5)_2$ is monomeric in dilute solution and ^1J = 598 Hz (50% solution in $CDCl_3$). It is thus expected to exist in solution as (I)—a monomer with chelating and non-chelating ligands[19]. The IR spectrum is complicated by peaks due to the ligand and assignments cannot reliably be made. IR spectroscopy is of little value for the deduction of the structure in this case.

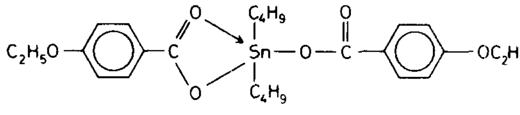


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Table 2.

Compound	ν(Sn-O) asym.	(cm^{-1}) sym.	ν(Sn-C) asym.	(cm^{-1}) sym.	ν(C=O) asym.	(cm^{-1}) sym.	^{1}H N.M.R. Chemical Shift, δ Rel. TMS (ppm)^a
$(CH_3)_2SnO$	575 vs	430 vs br	553 s	520 m	-	-	
$(C_2H_5)_2SnO$	570 vs	410 vs br	535 m	500 w	-	-	
n-Bu$_2$SnO	598 s	400 s br	570 s	-	-	-	
n-Bu$_3$SnOCH$_3$	618 m	410 w sh	597 m	518 vs	-	-	3.60 (OCH$_3$)
n-Bu$_3$SnO$_2$CCH$_3$		411 w		[495]* m	1570 s br	1410 s br	
n-Bu$_3$SnAcAc				512 w	1622 vs		5.45 (CH); 1.95 (CH$_3$)
n-Bu$_3$SnBzAc		410 w	542 m	510** w	1605 vs		7.8-7.4 (C$_6$H$_5$); 6.1 (CH); 2.10 (CH$_3$)
n-Bu$_3$SnO$_2$CCl$_3$		340 w		[495]* m br	1650 s br	1302 w	
					1680 s br		
n-Bu$_3$SnO$_2$CC$_6$H$_4$OC$_2$H$_5$			[600]* m	515 m	1635 s br		8.05, 6.90 (C$_6$H$_4$); 4.07 (OCH$_2$); 1-2, obscure (CH$_3$)
n-Bu$_3$SnO$_3$SC$_6$H$_4$CO$_2$H	622 s	390 w	575 s	558 m	1723 s		10.75 (CO$_2$H); 8.0-7.6 (C$_6$H$_4$)
n-Bu$_3$SnO(CH$_2$)$_2$NH(C$_4$H$_9$)		410 w sh	598 m	510 m			
(*n*-Bu$_2$Sn)$_2$(OCH$_2$CH$_2$O)$_2$	600 s	340 m [400]†† m br					
n-Bu$_2$Sn(O$_2$CCH$_3$)$_2$				[492]* m	1605 vs	1430 m br	2.04 (O$_2$CCH$_3$)
n-Bu$_2$Sn(AcAc)$_2$		410 s		550 s	1582 vs		
n-Bu$_2$Sn(BzAc)$_2$		416 m		541** m	1590 vs		7.9-7.4 (C$_6$H$_5$); 6.0 (CH); 2.18 (CH$_3$)
$[(C_2H_5)_2SnOC_6H_5]_2O$	608† s	[300]^b w	568 s	550 s br			
$(CH_3)_2SnSO_3(C_6H_4)CO_2$	613 s 712 s	[296] w [443] s	571 s	567 m	1540 s br	1590 br sh	8.0, 7.6 (C$_6$H$_4$); 0.9 (CH$_3$); J(Sn^{119}-CH$_3$) = 100 Hz

* Values in parentheses are tentative assignments. For carboxylate derivatives, the CO$_2$ scissoring mode is also found in this region.

** Free BzAcH ligand shows two bands at 555 and 570 cm^{-1}.

† There is also a band at 755 cm^{-1} (s) which can be assigned to a Sn-O-Sn vibration.

†† This mode might also be the ν(Sn-O)sym., but assignment as due to O→Sn is more probable.

a The butyltin portion of the ^{1}H NMR spectrum consists of broad, overlapping peaks at 1-2 p.p.m.

b Tentative assignment. This mode could be either the ν(Sn-O)sym. or due to O→Sn.

Table 3. Comparison of ^{1}J value and coordination number for some organotin compounds

Present Compound	$^1J(^{119}Sn-^{13}C)$	Related Compound	Coordn. No.	Ref.
n-Bu$_2$SnCl$_2$	402	$(CH_3)_2SnCl_2$*	4^a	31
n-Bu$_3$SnO$_2$CCl$_3$	342	$(C_6H_{11})_3SnO_2CCH_3$	4	3
n-Bu$_3$SnO$_2$CCH$_3$	361	$(C_6H_5CH_2)_3SnO_2CCH_3$	4-5^b	2
n-Bu$_2$Sn(O$_2$CCH$_3$)$_2$	601	*n*-Bu$_2$Sn(O$_2$CCH$_3$)$_2$	5	30
$\{[(C_2H_5)_2SnOC_6H_5]_2O\}_2$	632,617	[(*n*-Bu$_2$SnO$_2$CCCl$_3$)$_2$O]$_2$	5^c	32
n-Bu$_3$SnO$_3$SC$_6$H$_4$CO$_2$H	400	$(CH_3)_3Sn(O_3SC_6H_5)H_2O$	5^d	29
n-Bu$_2$Sn(Acac)$_2$	925	(CH$_3$)$_2$Sn(Acac)$_2$**	6	1

a - structure is considerably distorted.

b - coordination number may be considered as 5. One O atom coordinates to a neighbouring Sn atom, with the distance Sn----O = 2.65 Å.

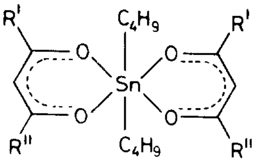
c - structure contains unusual Sn----O distances.

d - the water molecule coordinates to Sn, while the SO$_3$ group is unidentate. H----O bonding occurs between neighbouring H$_2$O molecules.

* $^1J(^{119}Sn-^{13}C)$ = 480 Hz for this compound.

** $^1J(^{119}Sn-^{13}C)$ = 966 Hz for this compound (ref. 14).

The β-diketonate derivatives exhibit ^1J values (*ca.* 900 Hz) and the ν(C=O) and ν(Sn–C) values expected[20] for the 6-coordinate species (II).



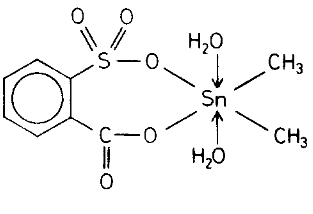
$R' = CH_3$; $R'' = CH_3, C_6H_5$

II

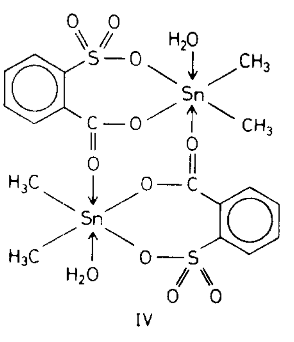
(ii) *Complexes containing the* o-*sulfobenzoic acid ligand*

The ligand favours coordination by both SO_3 and CO_2 groups to form a seven-membered ring with very little strain. It should then be an indicator of the tendency for organotin compounds to form complexes of higher coordination number.

The tributyltin complex has been shown to be 4-coordinate about the tin[19], hydrogen bonding seemingly being responsible for this low coordination number. The dimethyltin complex with this ligand, however, appears to be 6-coordinate in a *ca.*90/10 water/methanol solvent mixture since the $^2J(^{119/117}Sn–CH_3)$ value is about 100 Hz. The mass spectrum has a strong peak at m/z = 518 which exhibits the polyisotopic cluster characteristic of an ion containing two tin atoms—and this may be assigned to the species$[(CH_3)_2Sn(O_3SC_6H_4CO_2)Sn(CH_3)_2.H_2O]^+$. Also peaks at m/z = 350$[(CH_3)_2Sn(O_3SC_6H_4CO_2)^+]$, m/z = 255$[(CH_3)Sn(O_2CC_6H_4)^+]$ and m/z = 230$[(CH_3)_2SnSO_3^+]$ indicate that the compound contains Sn–O–S and Sn–O–C entities. Coordinated water in the solid is indicated by a strong IR peak at 3360 cm^{-1}. The IR peaks at 1590 and 1540 cm^{-1} may be due to bridging and non-bridging C=O groups. Other peaks at 571 and 567 cm^{-1} may be assigned to the non-linear Sn–C stretch[1], that at 443 cm^{-1} may be due to a coordinate Sn ← O interaction and the one at 296 cm^{-1} can be assigned to a Sn–O stretch[1]. On the basis of these results, it seems reasonable then, that the compound may exist as (III) in solution and as (IV) in the solid.



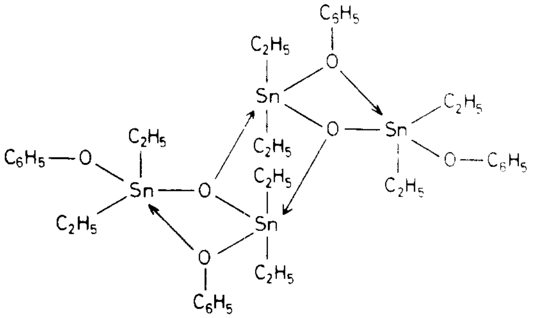
III



IV

(iii) *Bis(diethyltin phonoxide)oxide*

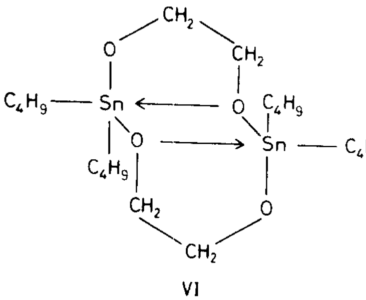
$(Et_2SnOC_6H_5)_2O$ is dimeric in solution[21], and the ^1J value is indicative of pentacoordinate tin. Two α carbon shift values are recorded, while the phenoxide ligands shows equivalent shift valves. This may indicate the presence of *cis* and *trans* ethyl groups about the tin atoms, suggesting structure (V) in solution. The phenoxide ligand would presumably interchange leading to equivalence. It is not possible however, to rule out the possibility of a distorted hexacoordinate tin structure, but the ^1J value would indicate that this is rather unlikely.



V

(iv) 1,1,6,6 - *tetra* - n - *butyl* - 1,6 - *distanna* - 2,5,7,10 - *tetraoxacyclodecane*, $(n\text{-}Bu_2Sn)_2(OCH_2CH_2O)_2$

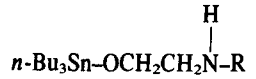
The molecular weight in dilute solution and the IR spectrum of the solid have been reported for this compound[13] and its composition as a di-tin monomer is established. The ^1J value of 653 Hz indicates 5-coordinate tin in solution. The IR spectrum contains a broad peak at 400 cm^{-1} which suggests a Sn ← O interaction. The mass spectrum contains a molecular ion peak at *m/z* = 586, thus showing that the compound exists as the di-tin entity both in dilute solution and in the solid. Whilst further weak association may occur in the solid, structure (VI) is proposed for the complex in solution. The equivalence of the ligand carbon shifts indicates rapid interchange of the coordinated oxygens.



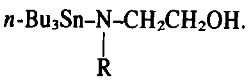
VI

(v) *Tri*-n-*butyltin aminoalcohol complexes*

These complexes provide an interesting study. ^{13}C NMR data shows the presence of two α-carbon shift values in neat samples, and these agree well with values expected for Sn–O and Sn–N type compounds. In all cases, peak intensities and coupling satellite peaks have been the same for both α-C peaks. (This confirms that impurities could not possibly account for these values, as microanalysis rules out the presence of such large amounts of imputities.) It would appear that at the temperature of the ^{13}C NMR probe, two species (one O-bonded and one N-bonded) exist in the product, i.e.



$n\text{-}Bu_3Sn\text{-}OCH_2CH_2\overset{\displaystyle H}{\underset{}{N}}\text{-}R$



$n\text{-}Bu_3Sn\text{-}\underset{\displaystyle R}{N}\text{-}CH_2CH_2OH.$

The compound $n\text{-}Bu_3Sn\text{-}OCH_2C(CH_3)NH_2$ does not, however, show this type of spectrum. Presumably, steric factors prevent the formation of the Sn–N bonded species in this case.

IR spectroscopy

Since IR spectroscopy has been very useful in determining the configurations of organotin compounds, it was instructive to investigate its utility in the study of these particular complexes. One obvious limitation is the complexity of the spectra due to the butyl groups and large ligands employed. The areas of interest are the carbonyl stretch frequencies of the carboxylates and β-diketonates, located at 1700–1550 cm^{-1}[1, 23–25], the Sn–O stretch frequencies, including also the oxides and alkoxides, and the Sn–C frequencies located in the 600–500 cm^{-1} region. The assignments given in Table 2 are based on values found in the literature, from comparisons with the spectra of the starting materials, and sometimes by comparing with the spectrum of a similar, but simpler, compound.

For the compound $n\text{-}Bu_3SnOCH_3$, the ν(Sn–O) bands have been assigned[7] to those at 618 cm^{-1} (asym) and 410 cm^{-1} (sym), but a similar assignment cannot be made for $n\text{-}Bu_3SnOCH_2CH_2NH(n\text{-}C_4H_9)$ since no band can be found in the 610–640 cm^{-1} region, although a weak feature is observed at 410 cm^{-1}. The oxides[24, 26] display bands at *ca.* 580 cm^{-1} and *ca.* 410 cm^{-1} whilst the β-diketonates[1] and carboxylates[24] show one *ca.* 410 cm^{-1}. A vibration of the Sn–O–Sn grouping is assigned[26] to the 755 cm^{-1} band for the dimer $[(C_2H_5)_2SnOC_6H_5]_2O$. Assignments of Sn–C stretching frequencies are made in the 500–600 cm^{-1} region[1, 27], but at times ligand vibrations obscure this region or no bands are visible at all.

The presence of two bands in the 500–600 cm^{-1} region in the IR spectra[6, 28] of the oxides suggests that these compounds exist as distorted polymers. The band near 410 cm^{-1} may be due to a tin–oxygen coordinate bond, thus indicating that the polymeric structure is built up via $Sn \leftarrow O$ bonds between monomeric units.

All our compounds that could have involved some interaction between tin and the carbonyl oxygen, exhibited a shift of the C=O frequency to *ca.* 1600 cm^{-1}. The *o*-sulfobenzoic acid derivative of tributyltin however, did not, and this we feel, is clear evidence for a SO_3–Sn bond instead of COO–Sn. Examination of Table 2, will show however, that a clear correlation between C=O stretch frequency and coordination to tin is not possible. Thus $n\text{-}Bu_3SnAcAc$ has a strong band at 1622 cm^{-1}, which is of higher frequency than that for $n\text{-}Bu_3SnO_2CCH_3$ (1570 cm^{-1}), even though the former is expected to be more strongly coordinated to tin than the latter. (^{13}C NMR does make this distinction by showing a larger ^1J value for the acetylacetonate complex.) The $n\text{-}Bu_2Sn(AcAc)_2$ and $n\text{-}Bu_2Sn(O_2CCH_3)_2$ compounds show a reversal of the C=O stretching frequency, yet the benzoylacetonate complex has the same ν(C=O) frequency as the diacetate. This indicates that factors other than the strength of the Sn---OC interactions may be operating in some cases[33]. Thus, for the compounds studied, it is prudent to employ the C=O stretch region only to indicate the presence or otherwise of an interaction between C=O groups and tin.

CONCLUSION

^{13}C NMR spectroscopy provides a useful technique for elucidating structures of organotin compounds. From the results presented here, and those in Ref.[14], ^1J values for tetracoordinate tin compounds lie around 360 Hz, pentacoordinate trialkyltin compounds between 450 and 500 Hz, pentacoordinate dialkyltin compounds between 550 and 600 Hz, and hexacoordinate dialkytin compounds at about 900 Hz. Studies on the complexes containing Sn–O bonds reported here have indicated that the structures assumed contain 4- or 5-coordinate tin in most cases. Only the β-diketonate complexes contained hexacoordinate tin. Steric factors appear to be predominantly responsible for this state of affairs in these compounds. ^1J values give a better indication of the coordination state of tin for these compounds than does IR spectroscopy.

REFERENCES

1. A. K. Sawyer, *Organotin Compounds*, Vol. 2 pp. 253–295. Marcel Dekker, New York (1971).
2. N. W. Alcock and R. E. Timms, *J. Chem. Soc* (A), 1873 (1968).
3. N. W. Alcock and R. E. Timms, *J. Chem. Soc.* (A) 1876 (1968).
4. G. M. Bancroft and J. K. Shan, *Can. J. Chem.* **52**, 1361 (1974).
5. N. Asting and W. H. Nelson, *Inorg. Chem.* **16**, 148 (1977).
6. D. H. Lohmann, *J. Organometal. Chem.* **4**, 382 (1965).
7. F. K. Butcher, W. Gerrard, E. F. Mooney, R. G. Rees and H. A. Willis, *Spectrochim. Acta* **20**, 51 (1964).
8. G. J. M. van der Kerk and J. G. A. Luijten, *J. Appl. Chem.* **6**, 49 (1956).
9. D. D. Perrin, W. L. F. Armarego and D. R. Perrin, *Purification of Laboratory Chemicals*. Pergamon Press, Oxford (1966).
10. J. S. Pierce, J. M. Salsbury and J. M. Fredericksen, *J. Am. Chem. Soc.* **64**, 1691 (1942).
11. J. R. Reasenberg and S. D. Goldberg, *J. Am. Chem. Soc.* **67**, 933 (1945).
12. R. C. Mehrotra and V. D. Gupta, *J. Organometal. Chem.* **4**, 237 (1965).
13. W. J. Considine, *J. Organometal. Chem.* **5**, 263 (1966).
14. T. N. Mitchell, *J. Organometal. Chem.* **59**, 189 (1973).
15. J. A. Pople and D. P. Santry, *Mol. Phys.* **8**, 1 (1964).
16. T. Iwayanagi, T. Ibusuki and Y. Saito, *J. Organometal. Chem.* **128**, 145 (1977).
17. G. Barbieri, R. Benassi and F. Taddei, *J. Organometal. Chem.* **129**, 27 (1977).
18. H. A. Bent, *Chem. Revs.* **61**, 275 (1961).
19. G. Domazetis, R. J. Magee and B. D. James, *J. Organometal. Chem.* **148**, 339 (1978).
20. M. M. McGrady and R. S. Tobias, *J. Am. Chem. Soc.* **87**, 1909 (1965).
21. W. J. Considine and J. J. Ventura, *J. Org. Chem.* **28**, 221 (1963).
22. T. Tanaka, *Organometal. Chem. Rev.* **A5**, 1 (1970).
23. K. Nakamoto, *Infrared Spectra of Inorganic and Coordination Compounds*, 2nd Edn, p. 222 and pp. 247–256. Wiley, New York (1970).
24. R. E. Hester, *J. Organometal. Chem.* **23**, 123 (1970).
25. J. R. Dyer, *Applications of Absorption Spectroscopy of Organic Compounds*, p. 46. Prentice-Hall, Englewood Cliffs (1965).

26. B. Kushlefsky, I. Simmons and A. Ross, *Inorg. Chem.* **2**, 187 (1963).
27. Y. Kawasaki, T. Tanaka and R. Okawara, *Bull. Chem. Soc. Jap.* **37**, 903 (1964).
28. W. P. Neumann, *The Organic Chemistry of Tin*, pp. 216–219. Wiley, New York (1970).
29. P. G. Harrison, R. C. Phillips and J. A. Richards, *J. Organometal. Chem.* **114**, 47 (1976).
30. R. Okawara and M. Wada, *Adv. Organometal. Chem.* **5**, 137 (1967).
31. A. G. Davies, H. J. Milledge, D. C. Purley and P. J. Smith, *J. Chem. Soc.* A, 2862 (1970).
32. R. Graziani, G. Bombieri, E. Forsellini, P. Furlan, V. Peruzzo and G. Tagliavini, *J. Organometal. Chem.* **125**, 43 (1977).
33. Factors such as distortions in the solid geometry due to crystal packing, variation of the atomic masses involved in the vibrating system and bulk of the ligand may influence ν(C=O). See discussion by A. J. Bloodworth in *Organometallic Derivatives of the Main Group Elements* (Edited by B. J. Aylett), M.T.P. International Review of Science, Inorganic Chemistry Series One, Vol. 4. pp. 275–295. Butterworths, London (1972).