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SYNTHESIS AND SPECTROSCOPIC STUDIES OF ORGANOTIN COMPOUNDS CONTAINING THE Sn–S BOND

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Abstract—The preparation of a number of organotin(IV) compounds, containing Sn–S bonds, is described. Their ^{13}C and ^{1}H NMR and IR spectra are presented. In cases where either Sn–S or Sn–N may be expected, Mössbauer spectra show two sets of peaks consistent with these possibilities.

INTRODUCTION

Organo-tin compounds which contain the Sn–S bond are a class of derivatives whose structures span coordination states four to seven[1]. Organotin sulfides and thiolates, for example, are four-coordinate: thiolate derivatives being monomeric while the sulfides are polymeric (e.g. $[(\phi_2Sn)_2S]_3$). Inclusion of a ligand with a second donor site leads to a variety of structures which may contain unidentate, bidentate or bridging ligands.

The compounds studied range from sulfides and thiolates to those containing ligands of the type: (a) HS–RX where X = –SH, –CO$_2$H, –OH and –NH$_2$, (b) chelating ligands, (2-thiol pyridines), and (c) heterocyclic rings containing both S and N atoms. Spectroscopic studies permit deductions to be made regarding coordination state, steric interactions and some features of bonding for groups (b) and (c). We report here data on a number of new compounds and discuss structures based on ^{13}C NMR, Mössbauer, ^{1}H NMR and IR spectra.

RESULTS

1. ^{13}C NMR *spectra*

The data are shown in Table 1. The chemical shifts of the moiety bonded to tin may be reproduced satisfactorily by using the additivity parameters given in Ref. [2]. Additional terms (βSn–SR, βSnC, βSnR and βSnSpyr) were calculated by a procedure outlined in Ref. [3]. The table below lists some calculated and observed values. [βSnSR = 5.7 ± 0.6 (12),[‡] βSn–C = –1.1 ± 0.8 (24), βSnR = 1.9 ± 1.0 (5), βSnSpyr = 9.6 ± 0.6 (8)].

Compound	Calc. (αC)	Obs. (αC)
$Me_3SnS(n\text{-}C_3H_7)$	–4.9	–5.6
$Me_3Sn\text{-}SC_6H_4pCH_3$	–4.9	–4.9
$Et_2Sn(SCH_2CH(CH_3)S)$	13.3	12.1
$n\text{-}Bu_3SnS(n\text{-}C_4H_9)$	13.0	13.8
$n\text{-}Bu_2Sn(S\text{-}C_6H_4pCH_3)_2$	19.8	18.6
$n\text{-}Bu_3Sn(SpyrN \rightarrow O)$	18.4	19.0
$n\text{-}Bu_2Sn(SpyrNO_2)_2$	27.6	26.5

Values calculated for a set of 29 compounds containing a wide variety of ligands fitted the equation:

$$\delta C(\text{obs}) = 0.99\delta C\ (\text{calc}) + 0.22$$

with the coefficient of determination, $r^2 = 0.986$.

The chemical shifts of thiol ligands bound to the organotin moiety may be calculated by using the parameters in Ref. [4–6] and the βSnR term. Some representative values are listed below.

Compound	Calculated Shifts				Observed Shifts			
	αC	βC	γC	δC	αC	βC	γC	δC
$HSCH_2CH_2CH_2CH_3$	24.8	38.0	22.6	13.5	24.3	35.6	21.7	13.6
$Me_3SnSCH_2CH_2CH_3$	29.3	28.3	14.4		29.0	28.0	13.3	
$n\text{-}Bu_3SnSCH_2CH_2CH_2CH_3$	26.8	35.2	22.6	14.2	26.5	36.5	21.7	13.6
$n\text{-}Bu_3SnSCH_2CH_2OH$	30.1	70.0			29.5	64.1		
$n\text{-}Bu_3SnSC_6H_4pCH_3$	C(1) = 130.7				C(1) = 131.0			

The assignments for 2-thiol 5-nitropyridine and its di-*n*-butyl tin derivative were made with the aid of gated decoupling. The atoms C-2 and C-5 were not coupled to protons and thus were readily assigned, while long range C–H coupling enabled assignments of the remaining carbon chemical shifts to be made.

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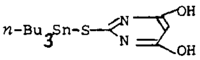
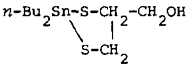
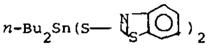
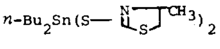
[‡] The numbers in parenthesis are the number of spectra used in the calculations.

Table 1. ^{13}C NMR spectra

Compound	Chemical Shifts[a]				Coupling Const.[b]			Ligand Shifts[c]
	αC	βC	γC	δC	^1J	^2J	^3J	
Me$_2$SnS	4.8				398*			
(*n*-Bu$_3$Sn)$_2$S	17.8	28.8	27.3	13.7	335.1	20.5	63.5	
(Ø$_3$Sn)$_2$S[d]	139.1	136.6	128.6	129.4	566.4	43.9	58.6	
Me$_3$Sn-S(*n*-C$_3$H$_7$)	-5.58				354.0			28.0, 29.0, 13.3
Me$_3$Sn(S-C$_6$H$_4$*p*CH$_3$)	-4.85				353.0*			135.5, 134.5,130.5, 129.3
Et$_2$Sn-(SCH$_2$CH(CH$_3$)S)	12.1	10.2			373.1			46.7, 43.2, 23.6
n-Bu$_3$SnS(*n*-C$_4$H$_9$)	13.8	29.0	27.4	13.3	327.2*	26		26.5, 36.5, 21.7, 13.6
(*n*-Bu$_3$Sn)$_2$(SCH$_2$CH(CH$_3$)S)	20.7	28.8	27.2	13.8	-	-	-	46.9, 43.5, 23.9
	20.3	28.4	26.8					
n-Bu$_3$Sn-SCH$_2$CH$_2$OH	13.5	28.6	26.8	13.5	330.1	19.5	60	64.1, 29.5
n-Bu$_2$Sn[S(*n*-C$_4$H$_9$)]$_2$	17.6	28.5	26.9	13.7	385.7	23	-	26.9, 36.8, 21.9, 13.7
n-Bu$_2$Sn(SCH$_2$CH(CH$_3$)S)	20.6	28.3	26.6	13.6	-	25	70	46.8, 43.4, 23.8
n-Bu$_2$Sn(S-C$_6$H$_4$*p*CH$_3$)$_2$	18.6	27.9	26.4	13.4	365.0	26	-	
Ø$_3$Sn-S(*n*-C$_3$H$_7$)[d]	137.7	136.6	128.8	129.5	551	42.7	56.2	
Me$_3$Sn(SpyrNHCOCH$_3$)	7.0							168.9, 157.2, 138.8, 129.4, 124.5, 23.9(CH$_3$)
Me$_2$Sn(SpyrNHCOCH$_3$)$_2$	6.7							170.6, 158.9, 138.2, 131.7, 129.9, 125.6, 23.8(CH$_3$)
Me$_2$Sn(Cl)-SCH$_2$CH$_2$NH$_2$	3.8							44.6, 27.18
Me$_2$Sn(Spyr)$_2$	6.8				583			
n-Bu$_3$Sn(SpyrN→O)	19.0	28.8	27.2	13.8	361	-	63	154.2, 137.0, 128.2, 126.5, 119.3
n-Bu$_3$Sn(SpyrNO$_2$)	16.3	29.3	27.5	14.1	356	22	78	161.6, 151.3, 143.8, 130.3, 124.3
n-Bu$_3$SnS-CSN-C$_6$H$_4$	16.4	28.8	27.0	13.7	335.7	22	62.3	
	19.3	28.9	27.7	14.1	457.8	-	-	175.6, 166.5, 82.9
n-Bu$_2$Sn(SpyrN→O)$_2$	29.8	28.5	26.5	13.8	651.9	34.2	117	157.6, 137.2, 129.3, 128.2, 118.5
n-Bu$_2$Sn(SpyrNO$_2$)$_2$	26.5	28.4	26.3	13.6	522.5	34	-	173.0, 142.8, 140.8, 131.4, 124.6
 *n*-Bu$_2$Sn-S-CH$_2$-CH$_2$OH, S-CH$_2$	20.9	28.2	26.6	13.6	342	-	26.3	65.2, 51.6,37.2
	20.5	28.1					27.3	
	28.9	28.2	26.3	13.7	505	-	-	
	27.4	27.9	26.2	13.6	503.6	-	113	168.5, 149.9, 113.2, 16.5

[a] in ppm relative to TMS

[b] in Hz (^1J = ^{119}Sn-^{13}C peaks)

[c] in ppm; shifts are not generally assigned and are not given for every ligand

[d] the chemical shifts are given in the order: α(Sn-C), *o*-C *m*-C *p*-C

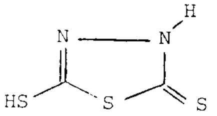
* average one-bond coupling constant

^{13}C Chemical Shifts and Coupling Constants
(i) 2-Thiol 5-nitropyridine

Shifts	(ppm)	Coupling Constants (Hz) H-3	H-4	H-6
C-2	136.6	—	—	—
C-3	134.3	177.0	—	—
C-4	129.1	—	172.4	4.3
C-5	184.8	—	—	—
C-6	137.7	—	~4	190.7
	(ii) Di-*n*-butyl tin derivative			
C-2	140.8	—	—	—
C-3	124.6	174.6	—	—
C-4	131.4	—	175.5	4.9
C-5	173.0	—	—	—
C-6	142.8	—	3.7	182.2

2. ^{119}Sn *Mössbauer spectra*

The data for six compounds are shown in Table 2. Compound 1, which appears to have the lowest isomer shift value reported for a di-*n*-butyl tin complex has been studied by single crystal X-ray crystallography[7]. Compound 2 provides an interesting contrast, and the implications are discussed below. Compounds 3–5 are of particular interest because of the possibility of both Sn–S and Sn–N bonding as a result of ligand tautomerism. Thus 2-thiolbenzothiazole may exist on either the thiol form or the thione form, while the ligand 1, 3, 4-thiazole-2, 5-dithiolate as been assigned the structure[8]:



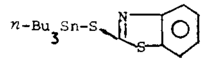
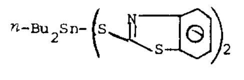
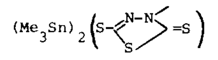
The IR spectrum of the ligand is compatible with this structure [ν(HN), ν(SH) and hydrogen bonding shown, while the band at 1501 cm^{-1} may be assigned to ν(S–C=N)]. The Mössbauer spectra of both compounds 4 and 5 consist of two sets of doublets consistent with both Sn–S and Sn–N bonded species.

The UV spectrum of compound 4 further supports the presence of two tautomers. The values obtained may be compared with those of 2-methylthiobenzothiazole (A), 3(N)-methylbenzothiazoline-2-thione (B)[9] and the tri-*n*-butyl tin derivative (table below). From UV spectrum of the tri-*n*-butyl tin derivative, a small amount of the thione form is probably present in the solution, while the thione form of 4 is estimated to make up *ca*. 30% of the total, from the ratio of the areas of the Mössbauer doublets.

A	B	U/V Spectra n-Bu$_3$SnL	n-Bu$_2$SnL$_2$
	332 (s)	331 (w)	330–320 (m)
	325 (s)	—	—
306 (s)	—	306 (s)	307(s)
294 (s)	—	295 (s)	295 (s)
279 (s)	—	287 (s)	287 (s)
246 (m)	247 (m)	251 (sh)	250 (sh)
238 (s)	235 (s)	244 (s)	—

Assignment of each doublet of compound 5 is difficult, and comparison of I.S. and Q.S. values with those of simpler compounds[10, 11] suggests that I.S. values of both Sn–N and Sn–S species differ by small amounts

Table 2. ^{119}Sn Mössbauer spectra (δ relative CaSnO$_3$: mm sec^{-1})

Compound	I.S. (±.01)	Q.S. (±.02)	Γ	I_1/I_2 [+]
1. n-Bu$_2$Sn(SpyrNO$_2$)$_2$	0.72$_5$	1.29	-	-
2. Me$_2$Sn(SpyrNHCOCH$_3$)$_2$	1.34	2.73	1.00	1.05
3. 	1.41	2.39	0.90	0.96
4.  [a]	1.48	3.00	0.94	1
	0.98	2.07	0.92	1
5.  [b]	1.33	3.45	0.88	1
	1.31	2.35	0.90	1
Alternate assignment	1.60	2.92	0.90	
	1.04	2.88	0.90	
6. Me$_2$Sn(Cl)SCH$_2$CH$_2$NH$_2$ [c]	1.27	2.83	1.08	1.13

[a] Ratio of areas of inner to outer doublet = 1:2.89.

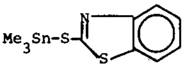
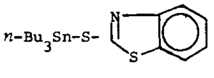
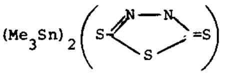
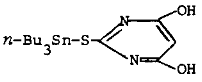
[b] Ratio of areas of inner to outer doublet = 1:1.01.

[c] The room temperature spectrum was recorded: I.S. = 1.26 (mm sec^{-1}), Q.S. = 2.77 (mm sec^{-1}), Γ = 0.74 (mm sec^{-1}), I_1/I_2 = 1.16.

[+] The ratio of the left to right hand peaks of the quadrupole doublet is a free fit. The value 1 indicates that the intensities were constrained to be the same.

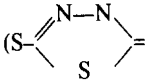
Table 3. IR spectra (in cm^{-1})

(a) *Organotin Thiolate Derivatives:*

Compound	ν(Sn-C) antisym.	symm	ν(Sn-S)	Some Ligand Modes
$Me_3SnS(n\text{-}C_3H_7)$	530 *v.s.*	510 *s*	-	
$Et_2Sn(SCH_2CH(CH_3)S)$	518 *m*	498 *s*	375 *s* 390 *s*	
$n\text{-}Bu_3SnS(n\text{-}C_4H_9)$	595 *s*	508 *m*	370 *m,sh*	
$n\text{-}Bu_3SnSC_6H_4pCH_3$	598 *m*	513 *w,sh*	390 *w*	
$(n\text{-}Bu_3Sn)_2(SCHCH(CH_3)S)$	595 *s,br*	509 *m,br*	375 *w* 390 *w*	
$Ø_3SnS(n\text{-}C_3H_7)$	263 *m*		350 *m*	
$n\text{-}Bu_2Sn[S(n\text{-}C_4H_9)]_2$	582 *s,br*	512 *w,br*	370 *w,sh*	
$n\text{-}Bu_2Sn(SCH_2CH(CH_3)S)$	595 *s*	510 *s*	392 *m* 374 *m*	
$n\text{-}Bu_3SnSCH_2CH_2OH$	597 *s*	509 *m*	390 *w*	ν(OH) = 3500
$Me_3SnSCH_2CH_2OH$	537 *m*	512 *w*	370 *w*	ν(OH) = 3388
Me_3SnSCH_2COOH	535 *m*	515 *m*	384 *m*	ν(OH) = 3450; ν(CO) = 1567
$Me_3SnSCH_2CH_2NH_2$	534 *s*	511 *w*	345 *w*	ν(NH_2) = 3358, 3280
$Me_2Sn(Cl)SCH_2CH_2NH_2$	562 *s*	530 *s*	394 *s*	ν(NH_2) = 3263, 3212, 3140; ν(Sn-Cl) = 331 *s*
$n\text{-}Bu_3Sn(SpyrNO_2)$	598 *m*	545 *m*	390 *m*	1583, 1568, 1518, 1465
$Me_3Sn(SpyrNHCOCH_3)$	545 *s*	512 *s*	343 *w*	ν(CO) = 1665; 1602, 1584, 1524, 1468
$Me_2Sn(SpyrNHCOCH_3)_2$	556 *m*	518 *m*	340 *w*	ν(CO) = 1682, 1690 *sh*; 1559, 1584, 1528, 1510, 1470; ν(NH) = 3307
	542 *m*	516 *m*	385 *w*	
	600 *s*	510 *m*	388 *s*	ν(CN) and ν(CS) = 1456
	530 *s*(?)	516 *w*	389 *m*(?)	
	-	-	-	ν(NH)/ν(OH) = 3400 (*br*); ν(CO) = 1600; δ(NH) = 1640

only, while Q.S. values differ considerably. Thus, the first assignment is the most probable.

3. IR *and* ^1H *spectra*

The data, shown in Tables 3 and 4, provide useful information on hydrogen bonding, and coordination by carbonyl and nitrogen groups. These aspects are discussed below. The assignments mostly are straight-forward except in the case of ν(Sn–C) values for (Me$_3$Sn)$_2$ . More bands are present than expected and these additional bands may be due either to different ν(Sn–C) values for each Me$_3$Sn moiety, or to ligand modes.

DISCUSSION

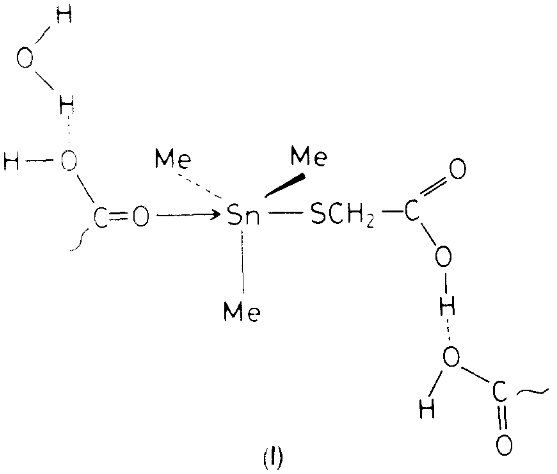
1. *Compounds with ligands* HS–R–X

(a) R'$_3$Sn-SCH$_2$CH$_2$OH (R' = n-Bu, Me) *and* Me$_3$Sn-SCH$_2$COOH. Like simple trialkyltinthiolate compounds, those with the –SC$_2$H$_4$OH ligand can be assigned four-coordinate structures from $^1J(^{119}Sn-^{13}C)$ and $^2J(^{119}Sn-CH)$ values. Hydrogen bonding is indicated by the ^{1}H NMR and IR spectra (Tables 3 and 4). Any Sn---O interaction is unlikely in view of the αC chemical shift values (Table 1).

Table 4. ^{1}H NMR spectra

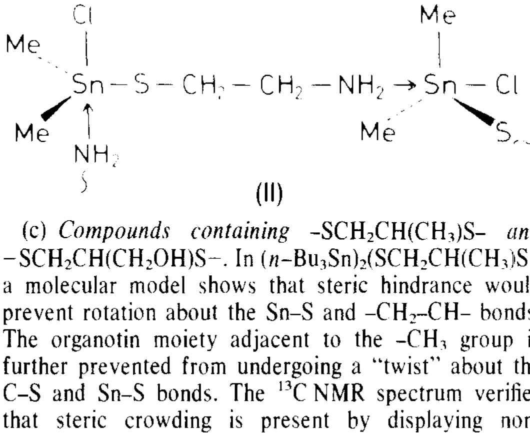
Compound	δSnMe (ppm)	$^2J(^{119}Sn-CH)$ (Hz)	$^2J(^{117}Sn-CH)$ (Hz)	Ligand Shifts (ppm)
Me_2SnS	0.87	63.4	59.7	
$Me_3Sn-S(n-C_3H_7)$	0.47	57.2	54.5	2.98(t), 2.0(q) 1.40(t)
$Me_3Sn-S(n-C_4H_9)$	0.33	55.6	53.0	
$Me_3Sn(SpyrNHCOCH_3)$	0.49	57	53	
$Me_3Sn(S-NCSC_6H_4)$	0.69	63.0	59.8	
$Me_2Sn(Cl)SCH_2CH_2NH_2$	1.39	78.0	73.8	
$Me_3SnSCH_2CH_2NH_2$	0.43	54.9	52.5	
$Me_3SnSCH_2CH_2OH$	0.44	56.0	53.2	2.98(s) = δ(OH)
$Me_3Sn-SCH_2COOH$	0.52	58.0	55.6	
$Me_3Sn-SCH_2-CH_2OH$	0.47	57.0	54.0	3.74, 2.83, 2.46
Me_3Sn-S	0.49	57.0	54.0	(complex pattern)

The structure of $Me_3Sn-SCH_2COOH$ is indicated to differ from the preceding compounds. While the ^2J(Sn-CH) and δ(SnMe) values are not appreciably different, the IR spectrum, however, shows a bridging carbonyl group. The mass spectrum, run at room temperature, contains a large number of di-tin fragments: [$(Me_3Sn-SCH_2COOSnMe_3)^+$, $(Me_3SnSCH_2COSnMe_3)^+$, $(Me_3SnSCH_2CO)_2^+$]. The presence of both symmetric and antisymmetric ν(Sn-C) modes rules out a trigonal bipyramid structure, and a distorted structure associated via [C=O→Sn] coordination (structure I) is indicated by these data.



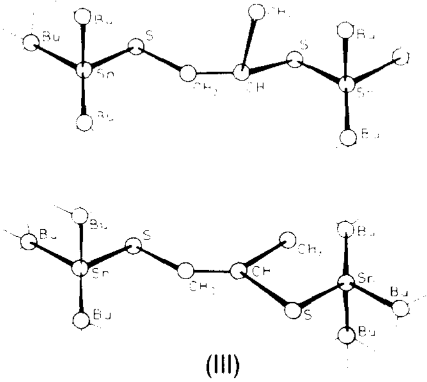
(I)

(b) $Me_3SnSCH_2CH_2NH_2$ and $Me_2Sn(Cl)SCH_2CH_2NH_2$. A four coordinate structure is deduced for the trimethyl tin compound with the $-NH_2$ group involved in hydrogen bonding. The chlorodimethyl tin compound differs quite markedly: it is largely insoluble in organic solvents, is only slightly soluble in D_2O and ethanol and has a relatively high melting point. Both the ^{1}H NMR and Mössbauer spectra indicate a five-coordinate structure, while the IR spectrum shows sharp ν(NH_2) bands typical of a coordinated group. That a Mössbauer spectrum can be observed at room temperature is indicative of an associated structure, such as that given in (II).



(II)

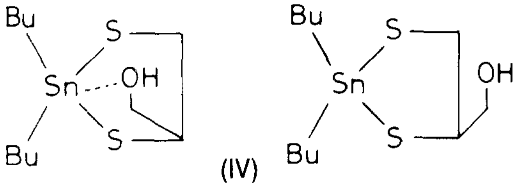
(c) *Compounds containing* $-SCH_2CH(CH_3)S-$ *and* $-SCH_2CH(CH_2OH)S-$. In $(n-Bu_3Sn)_2(SCH_2CH(CH_3)S)$, a molecular model shows that steric hindrance would prevent rotation about the Sn-S and $-CH_2-CH-$ bonds. The organotin moiety adjacent to the $-CH_3$ group is further prevented from undergoing a "twist" about the C-S and Sn-S bonds. The ^{13}C NMR spectrum verifies that steric crowding is present by displaying non-equivalent αC, βC and γC shift values. The large αC shift values (see Bu_3Sn-SR) suggests a strained structure (III) (αC similar to the di-n-butyl tin compound).



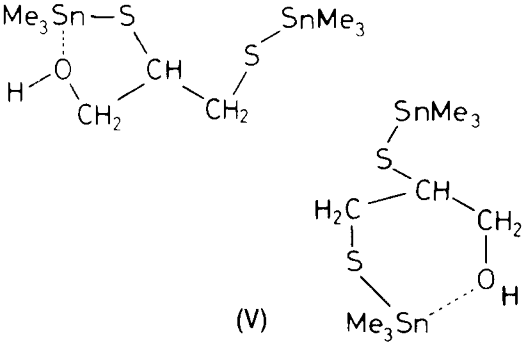
(III)

While $n-Bu_2Sn-SCH_2CH(CH_3)S$ shows an orthodox ^{13}C NMR spectrum, the compound n-Bu_2Sn-

$SCH_2CH(CH_2OH)S$ does not. The higher αC shift values of both compounds (see $Bu_2Sn(SR)_2$) is probably due to the strained five-membered ring. The spectrum of *n*-Bu_2Sn-$SCH_2CH(CH_2OH)S$ contains non-equivalent αC and βC chemical shifts. Steric crowding cannot account for this since the ring system is rigid and any barrier to motion of any type would result in non-equivalent *ligand* shift values, not those of the organotin moiety. The observed spectrum may be rationalized by postulating the presence of an equilibrium between two forms shown in (IV)—in which weak coordination can occur between tin and the oxygen atom.

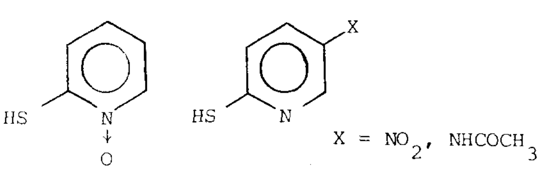

(IV)

The NMR spectra of $(Me_3Sn)_2SCH_2CH_2(OH)S$ display the expected non-equivalent MeSn chemical shifts with *J* values typical of a four-coordinate organotin-thiolate[12]. The Sn---O interaction postulated for the di-*n*-butyl tin compound is further indicated by the slightly higher δ(SnMe) value in the ^{13}C NMR spectrum—this is most likely due to the increase in the inductive effect of the $-CH_2OH$ group. Structures such as (v) are suggested.


(V)

2. *Compounds containing 2-thiol pyridines*

The ligands employed were (i), (HSpyrN→O), and (ii):



(i) (ii)

Ligand (i) is able to form a five-membered chelate ring, while (ii), if chelating, would form the less favoured four-membered ring. The crystal structure of the di-*n*-butyltin derivative of 2-thiol 5-nitropyridine ($HSpyrNO_2$) has been determined[7] and confirms the presence of a weak Sn---N interaction, consistent with a four-membered chelate ring. The ^{13}C NMR spectra confirm that ligand (i) forms the stronger five-membered chelate structure. $^1J(^{119}Sn-^{13}C)$ values for the tri-*n*-butyl- and di-*n*-butyltin complexes with ligand (i) suggest essentially distorted structures. This is a conclusion similar to that derived from Mössbauer spectra[13]. The additive model[3, 14] predicts a distorted octahedral structure with a C-Sn-C angle of *ca.* 130–140°.

The structure of *n*-$Bu_2Sn(SpyrNO_2)_2$ has been shown to contain two "chelating" ligands with long Sn---N bands[7]. The Mössbauer spectrum of this compound reveals unusually low I.S. and Q.S. values (Table 2). The I.S. indicates that the ligand exerts a pronounced electron withdrawal effect, leading to appreciable ionic bonding. The Q.S. value is considered to reflect σ-bonding imbalance, and the additivity model enables a distinction to be made between tetrahedral and octahedral geometries[15]. Effects of distortions can also be evaluated. The calculated Q.S. value for a distorted tetrahedral structure is 1.59 mm sec^{-1}, while for a distorted octahedral structure it is 3.02 mm sec^{-1}.

The effects of the Sn---N bonding on the pyridine ring may be evaluated qualitatively from the ^{13}C NMR spectrum. A comparison between the shifts and ^{1}J(C–H) values for the free ligand and those of the compound, is shown below. The relatively large upfield shift of 5–C is likely to result from a change in the π-electron density at this carbon, while that of the 2–C is due to a βSn–S effect. The π-electron change is most likely to be the result of some $p\pi$–$d\pi$ bonding between tin and nitrogen. Symmetry considerations indicate a distinct possibility of overlap between pyridine π-orbitals at nitrogen at the 5*d*(*xy*) and 5*d*(*yz*) orbitals of tin, along with some 5*d*(*xz*) orbitals and the lone pair at nitrogen.

$\Delta\delta$*(ppm)	^{1}J(C–H) lig.	^{1}J(C–H) cmpd.	ΔJ
2–C +4.20	—	—	—
3–C −9.70	177.0 Hz	174.6 Hz	−2.4 Hz
4–C +2.30	172.4 Hz	175.5 Hz	+3.1 Hz
5–C −11.90	—	—	—
6–C +5.10	190.7 Hz	189.2 Hz	−1.5 Hz

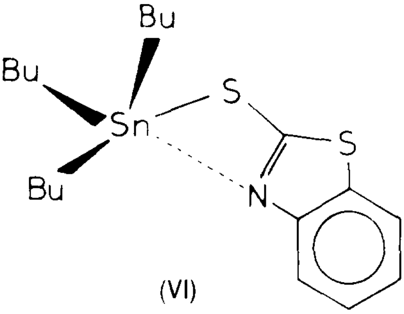
*$\Delta\delta$ = (δ compound− δ ligand)

The structures of trimethyl- and dimethyl tin complexes containing 2-thiol 5-acetaminopyridine ($HSpyrNHCOCH_3$) provide an interesting comparison with the 2-thiol 5-nitropyridine analogues. From the IR spectra, coordination by either NH or CO of the $-NHCOCH_3$ group can be eliminated. Instead, strong -NH---OO- hydrogen bonding is indicated by the mode ν(NH) = 3307 cm^{-1}. The Mössbauer spectrum of $Me_2Sn(SpyrNHCOCH_3)_2$ differs from that of *n*-$Bu_2Sn(SpyrNO_2)_2$. Although both ligands are expected to be chelating via the pyridine nitrogen, the differences in the Q.S. values are difficult to rationalize. One possibility is that there is a change in the geometry resulting from the hydrogen bonding indicated by the IR spectrum. A crystal and molecular structure determination would be necessary to resolve the ambiguity.

3. *Compounds containing heterocyclic ligands*

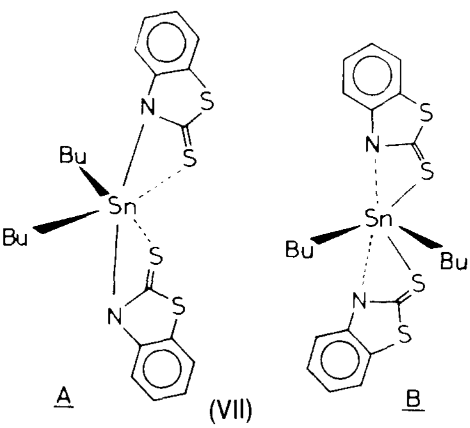
(a) 2-*mercaptothiazoles*. The ligands used were 2-mercapto-thiazoles, 2,5-dithiol-1,3,4-thiazole and 2-mercapto 4,6-hydroxypyrimidine. The predominant forms which exist are the thiones; thus the possibility of either Sn-S or Sn-N bond formation may be examined.

From ^{13}C NMR data, triorganotin capounds appear to be 4-coordinate but little else can be deduced. Diorganotins appear to be either 5-coordinate with interchanging cheltating/non-chelating ligands, or very distorted octahedral compounds[12]. The IR spectra contain the bands due to the ν(C–H) and ν(C–S) modes[16]. The only clear-cut evidence of the existance of both thiol and thione forms is obtained from the Mössbauer and UV spectra. It is apparent that for tri-*n*-butyl tin 2-mercaptobenzothiazole, the presence of only one resolvable doublet (Fig. 1) suggests that the compound exists as the Sn–S form (VI) with a very small amount of the Sn–N form. The spectrum of di-*n*-butyltin bis(2-mercaptobenzothiazole) on the other hand (Fig. 2) shows that the predominant form is the Sn–S species, with a significant amount of the Sn–N form present.



(VI)

The predominant form of the bis(2-mercaptobenzothiazole) complex may be deduced as distorted octahedral (structure VIIB). The I.S. and Q.S. values of the thione form (structure VIIA) suggest a *cis* octahedral structure (calculated Q.S. $\simeq 2.1$ mm sec^{-1}, observed 2.07 mm sec^{-1}). In view of the unusual I.S. and Q.S. values observed for *n*-$Bu_2Sn(SpyrNO_2)_2$, the bonding in the thione form may involve π-interactions. In any event, a structure is difficult to postulate from spectral data alone.



(VII)

(b) *Bis(trimethyl tin)1,3,4-thiazole-2,5-dithiolate.* The Mössbauer and IR spectra may be used in deducing a likely structure for this compound. The absence of bands arising from -SH and -NH stretching modes confirms that the Me_3Sn– moieties are bonded to S and N atoms. Comparison of the IR spectrum of the ligand and that of the trimethyl tin compound shows pronounced shifts to lower wavelengths on compound formation. In particular, two strong bands at 1500 and 1449 cm^{-1} in the ligand spectrum, associated with S–C–N stretching modes, shift to 1415 and 1322 cm^{-1}, while the 1262 cm^{-1} band is greatly reduced in intensity and appears at 1195 cm^{-1}. Such shifts would be consistent with Sn–N and Sn–S interactions[16] and the Mössbauer spectrum can be interpreted by postulating structure VIII in which both tins are five-coordinated. Intermolecular coordination is likely in view of the calculated Q.S. value of 3.5 mm sec^{-1} for such a structure (see observed 3.45 mm sec^{-1}).

(c) *Tri-N-butyl tin 2-mercapto-4,6-hydroxypyrimidine.* The αC shift value for this compound is surprisingly similar to that of *n*-Bu_3 Sn(SpyrN→O), but the ^1J value is much higher. This suggests that the Sn–S form of this compound is five-coordinate with possibly

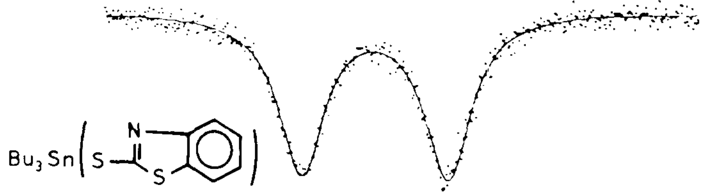


Fig. 1.

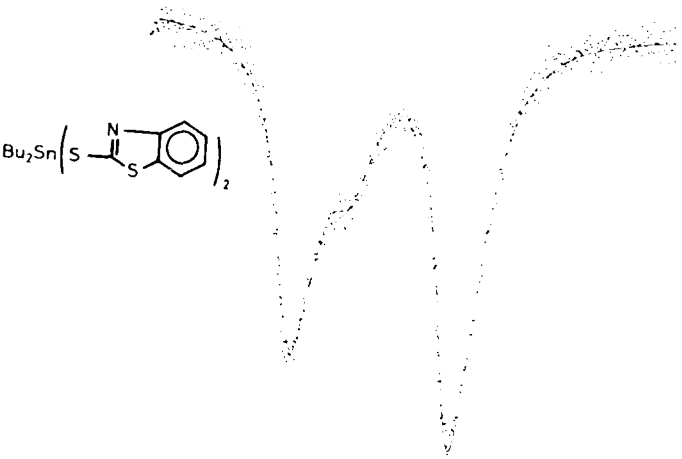
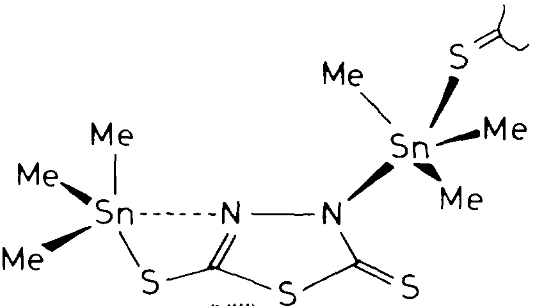
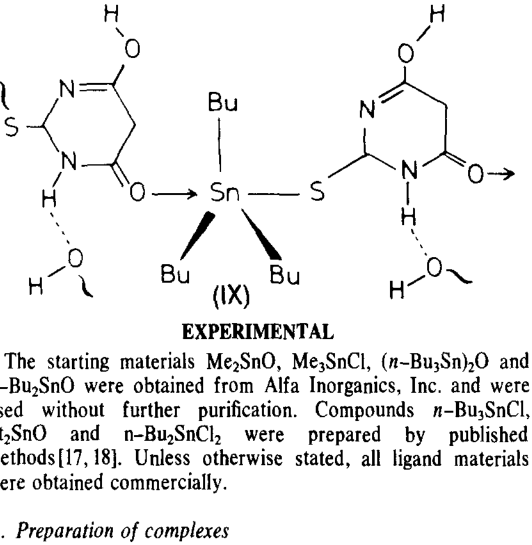


Fig. 2.



(VIII)

an intermolecular Sn←O coordination. The IR spectrum contains a broad band centred at 3400 cm^{-1} (hydrogen bonded OH or NH groups) and a ν(C=O) value which is indicative of coordinated carbonyl groups. It is likely that Sn–N and Sn–O bonded species are also present. The IR spectrum of the di-*n*-butyl tin complex also is very complicated and suggests the presence of different species. The predominant form of the tri-*n*-butyl tin complex is suggested as structure IX. It is unfortunate that difficulties in growing crystals suitable for X-ray study have hampered the determination of this structure.



(IX)

EXPERIMENTAL

The starting materials Me_2SnO, Me_3SnCl, $(n\text{-}Bu_3Sn)_2O$ and $n\text{-}Bu_2SnO$ were obtained from Alfa Inorganics, Inc. and were used without further purification. Compounds $n\text{-}Bu_3SnCl$, Et_2SnO and $n\text{-}Bu_2SnCl_2$ were prepared by published methods[17, 18]. Unless otherwise stated, all ligand materials were obtained commercially.

A. *Preparation of complexes*

1. *Organotin sulfides and thiolates.* Me_2SnS: M.p. 146–147°C (*cf.* 144.5–151°C,[19]); $(\phi_3Sn)_2S$:M.p. 135–136°C (*cf.* 145–147°C[19]); $n\text{-}Bu_3SnS(n\text{-}C_4H_9)$: B.p. 175–177°/13 torr[20]; $\phi_3Sn\text{–}S\text{–}C_6H_4pCH_3$: B.p. 102–104°C (*cf.* 103–105°C[21]); $n\text{-}Bu_2Sn[S(n\text{-}C_4H_9)]_2$: B.p. 210–213°C; $n\text{-}Bu_2Sn(S\text{–}C_6H_4pCH_3)_2$ (decomposes on heating).

Microanalyses on the organotin thiolates showed that they were of satisfactory purity.

2. *Organotins containing ligands HS–RX.* (a) $(n\text{-}Bu_3Sn)_2(SCH_2CH(CH_3)S)$. To a solution of 1,2-propanedithiol (2.16 g, 0.02 mol) in benzene was added freshly cut sodium chips (0.92 g, 0.04 mol). When the reaction had ceased, a solution of $n\text{-}Bu_3SnCl$ (13.02 g, 0.04 mol) in benzene/ethanol (60:40) was added and the mixture stirred and warmed for 1 hr. The precipitated NaCl was removed, the solvent distilled off and the product purified by vacuum distillation (180–195°C/13 torr). Yield 45%. *Anal.* Calc. for $C_{27}H_{60}S_2Sn_2$: C = 47.23; H = 8.75; S = 9.3%. Found: C = 46.58; H = 8.62; S = 8.6%.

(b) $n\text{-}Bu_2Sn(SCH_2CH(CH_3)S)$. Prepared by warming together $n\text{-}Bu_2SnO$ and 1,2-propanedithiol to give a clear oil. B.p. 188–190°C/13 torr. Yield 75%. *Anal.* Calc. for $C_{11}H_{24}S_2Sn$: C = 38.94; H = 7.35; S = 18.9%. Found: C = 39.16; H = 7.08; S = 19.8%.

(c) $Me_3SnSCH_2CH_2NH_2$. Equimolar quantities of Me_3SnCl and 1-thiol 2-aminoethane hydrochloride were dissolved in water, and an equal volume of $CHCl_3$ added. The mixture was stirred vigorously to mix the two phases, and aqueous NaOH added until the aqueous phase was pH 10. The mixture was stirred for another 2 hr and the $CHCl_3$ layer separated. This was then washed with water three times, dried with anhydrous $MgSO_4$, filtered and the solvent removed. The resulting oil was dried *in vacuo*. On standing, it slowly turns light-orange and a solid is deposited after one month. It was characterized by IR, ^1H NMR and mass spectra on a fresh sample.

(d) $n\text{-}Bu_3SnSCH_2CH_2NH_2$. Prepared from $n\text{-}Bu_3SnOMe$ and $HSCH_2CH_2NH_2$; the product decomposes on heating and slowly decomposes on standing. *Anal.* Calc. for $C_{14}H_{33}NSSn$: C = 45.89; H = 9.07%. Found: C = 44.80; H = 8.50%.

(e) $Me_2Sn(Cl)SCH_2CH_2NH_2$. Prepared as previously described[22].

(f) $Et_2Sn(Cl)SCH_2CH_2NH_2$. As for (e); m.p. 177–178°C (dec).

(g) $n\text{-}Bu_3Sn\text{–}SCH_2CH_2OH$. Prepared by warming $(n\text{-}Bu_3Sn)_2O$ and $HSCH_2CH_2OH$ and distilling the product. B.p. 108–110°C/0,7 torr (153°C/4 torr[23]).

(h) $Me_3SnSCH_2CH_2OH$. Prepared similarly from $(Me_3Sn)_2O$ and $HSCH_2CH_2OH$ in ethanol. The colourless oil slowly turns into a white solid on standing.

(i) Me_3SnSCH_2COOH. Prepared from Me_3SnCl and $HSCH_2COOH$ by a method similar to (c) above. A white solid slowly forms on standing.

3. *Organotins containing 2-thiol pyridines.* The ligands 2-thiol 5-nitropyridine ($HSpyrNO_2$) and 2-thiol 5-acetamino pyridine ($HSpyrNHCOCH_3$) were prepared according to published procedures[24, 25]. Yields and m.ps., were similar to those reported, except for the final step in the preparation of 2-thiol 5-nitropyridine. A reasonable yield could be obtained only when ethanol was freshly distilled from magnesium ethoxide. Even small traces of water reduced the yield substantially.

(a) $n\text{-}Bu_3Sn(SpyrNO_2)$. A solution of 2-thiol 5-nitropyridine (1.56 g, 0.01 mol) in acetone was added dropwise to $n\text{-}Bu_3SnOMe$ (3.21 g, 0.01 mol) in acetone, and the mixture stirred for 1 hr. The solvent was evaporated in an air stream and the red oil kept in a vacuum at room temperature for 12 hr. Yield 67%. *Anal.* Calc. for $C_{17}H_{30}N_2O_2SSn$. C = 45.84; H = 6.78; S = 7.20. Found: C = 46.25; H = 7.25; S = 6.9%.

(b) $n\text{-}Bu_2Sn\ (SpyrNO_2)_2$. A solution of 2-thiol 5-nitropyridine (1.56 g, 0.01 mol) in acetone was added slowly to a suspension of $n\text{-}Bu_2SnO$ (1.25 g, 0.005 mol) in 60 cm^3 absolute ethanol maintained at 60°C. Stirring was continued until the solution was almost clear. After a further hour, the hot solution was filtered and half the solvent removed. On cooling, bright yellow crystals formed. M.p. 143°C. Yield 80%. *Anal.* Calc. for $C_{18}H_{24}N_4O_4S_2Sn$: C = 39.78; H = 4.45; S = 11.80; N = 10.31; Sn = 21.89%. Found: C = 39.84; H = 4.54; S = 11.7; N = 10.12; Sn = 21.3%.

(c) $Me_3Sn(SpyrNHCOCH_3)$. A solution of 2-thiol 5-acetaminopyridine (0.3 g, 1.8 mmol) in acetone/carbon tetrachloride (2:1) was added to a solution of Me_3SnCl (0.36 g, 18 mmol) in carbon tetrachloride, and the mixture stirred for $\frac{1}{2}$ hr. A solution of NaOH (0.07 g) in water was slowly added and vigorous stirring continued for a further 2 hr, after which time the CCl_4 layer was separated off. Evaporation of the solvent yielded a yellow–brown product which was recrystallized from diethyl ether. M.p. 138–140°C. *Anal.* Calc. for $C_{10}H_{16}N_2OSSn$: C = 36.26; H = 4.86; S = 9.68%. Found: C = 35.88; H = 5.14; S = 9.5%.

(d) $Me_2Sn(SpyrNHCOCH_3)_2$: To a solution of 2-thiol 5-acetaminopyridine (0.84 g; 5.0 mmol) in 50 cm^3 of ethanol was added slowly solid Me_2SnO (0.41 g, 2.5 mmol). The mixture was stirred and warmed slightly until a clear solution formed. The alcohol was removed and the product obtained was recrystallized from ethanol/diethyl ether. M.p. 200–201°C. Yield 83%. *Anal.* Calc. for $C_{16}H_{20}N_4O_2S_2Sn$: C = 39.94; H = 3.77; Sn = 25.6%. Found: C = 39.68; H = 4.43; Sn = 24.7%.

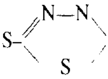
(e) $n\text{-}Bu_3Sn(SpyrN\rightarrow O)$ and (f) $n\text{-}Bu_2Sn(SpyrN\rightarrow O)_2$. Prepared from the organotin oxide and 2-thiol pyridine N-oxide ($HSpyrN\rightarrow O$) by procedure (d) above.

4. *Organotins containing heterocyclic ligands with both* S *and* N *atoms.* (a) $n\text{-}Bu_3Sn\text{–}S\text{–}CSNC_6H_4$. Prepared from $(n\text{-}Bu_3Sn)_2O$ and 2-mercaptobenzo-thiazole (1:2 molar ratio) in absolute alcohol. Yield 67%. *Anal.* Calc. for $C_{17}H_{31}NS_2Sn$: C =

50.03; H = 6.85; S = 14.0%. Found: C = 50.22; H = 6.92; S = 14.1%.

(b) n-$Bu_2Sn(S\text{-}CSNC_6H_4)_2$. Prepared as (a) from n-Bu_2SnO and 2-mercaptobenzothiazole. M.p. 75.7–77.0°C. Yield 82%. *Anal.* Calc. for $C_{22}H_{26}N_2S_4Sn$: C = 46.73; H = 4.63; S = 22.69%. Found: C = 46.46; H = 5.10; S = 20.1%.

(c) n-$Bu_2Sn(S\text{-}C_3HSNCH_3)_2$. 2-mercapto 4-methylthiazole was prepared from ammonium dithiocarbamate and chloroacetone[26]. The compound was prepared as in (a). M.p. 85–86.5°C. Yield 86%.

(d) $(Me_3Sn)_2(S$–  =S). 1,3,4-thiazole 2,5-dithiol was dissolved in ethanol and freshly-cut sodium added followed by Me_3SnCl (1:2 molar ratio). After 1 hr the NaCl was filtered off and the solvent evaporated in a stream of air until crystals formed. These were filtered off then dried *in vacuo*. M.p. 184.6°C. Yield 45%. *Anal.* Calc. for $C_8H_{18}N_2S_3Sn_2$: C = 20.19; H = 3.18; S = 20.21. Found: C = 19.95; H = 3.51; S = 20.5%. Molecular weight (mass spectrum) = 478. Calc. = 475.92.

(e) N-$Bu_3Sn(SC_4N_2O_2H_3)$. Prepared from $(n\text{-}Bu_3Sn)_2O$ and 2-mercapto 4,6-hydroxypyrimidine in absolute alcohol. M.p. 210°C (dec). Yield 77%. *Anal.* Calc. for $C_{16}H_{30}N_2O_2SSn$: C = 44.37; H = 6.97; N = 6.47; Sn = 27.40%. Found: C = 43.76; H = 7.29; N = 5.04; Sn = 26.6%%.

B. *Spectra*

^{13}C NMR spectra were recorded from neat liquids or concentrated (saturated) solutions in $CDCl_3$ or D_6-acetone, 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 ± 0.10 ppm and coupling constants to ± 2 Hz except where peak overlapping occurs when precision limits are ± 5 Hz. Assignments were made by comparison with published spectra, by using the coupling satellite peaks (and where possible with off-resonance decoupling) and by using additivity parameters.

^1H NMR spectra were recorded at ambient temperature in $CDCl_3$ or D_6-acetone solutions with a Varian T-60 NMR spectrometer operating at 60 MHz, and a Perkin–Elmer R-32 instrument operating at 90 MHz. TMS was used as internal standard.

Mössbauer spectra were taken at liquid nitrogen temperature using a conventional constant acceleration drive as described previously[27].

IR spectra were obtained using a Perkin–Elmer 457 instrument calibrated with polystyrene film. For solid samples KBr pressed disks were employed and for oils a liquid film was pressed between KBr plates. The 600–250 cm^{-1} regions for oil samples were recorded from thin films on polypropylene disks.

C. *General*

Molecular weights were obtained with a Perkin–Elmer 115 vapor phase osmometer, or from the mass spectra of the compounds. Mass spectra were obtained with a JEOL–D100 mass spectrometer.

Microanalyses were performed by the Australian Microanalytical Service, Division of Amdel, Fishermens Bend, Melbourne, Vic.

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