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Organotin(IV) derivatives of mercaptosuccinic and thiodiacetic acids

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Di- and tri-organotin(IV) complexes of general formula R_2SnAH, $(R_3Sn)_2AH$, R_2SnB, $(R_3Sn)_2B$ (A = dianion of mercaptosuccinic acid; B = dianion of thiodiacetic acid; R = Me, Et, nPr, nBu, nOct in R_2Sn and nBu in R_3Sn) have been synthesized and characterized by elemental analysis, IR and ^1H and ^{13}C NMR spectroscopy. These data support the preferential binding of sulphur over carboxylate by tin(IV) in R_2SnAH and $(R_3Sn)_2AH$. R_2SnAH complexes are assigned pentacoordinated bridged polymeric trigonal bipyramidal geometry whereas $(R_3Sn)_2AH$ complexes are monomeric with trigonal bipyramidal geometry at tin arising from a bidentate carboxylate group at one tin atom and from weak bonding via $Sn \leftarrow O{=}C$ at the other tin atom. In R_2SnB and $(R_3Sn)_2B$, tin(IV) binds to two carboxylate groups in a unidentate and a bidentate manner respectively, resulting in tetracoordinated and pentacoordinated structures. Potential uses of these compounds are discussed.

Keywords: Organotin(IV), mercaptosuccinic acid, thiodiacetic acid, complexes, structures, Sn–S bonding

INTRODUCTION

A large number of industrial applications of organotin mercaptides and mercaptoesters as polymer additives, stabilizers and catalysts have been described mainly in the patent literature.[1–4] Biocidal activity has been reported for organotin(IV) derivatives of 2-mercaptobenzothiazole and 2-mercaptobenzoxazoles.[5,6] Cyclic dialkyltin(IV) dicarboxylates incorporating polyolefins have been prepared and used as stabilisers.[7] Various di-n-butyltin dicarboxylate preparations are used to eliminate roundworms, cecal worms and tape worms in poultry.[8] Alkyltin derivatives of iminodiacetic acid have been used as dentrificial agents.[9] Organotin compounds of *N*-methyliminodiacetic acid inhibit the growth of *E. coli* and *Staphylococcus aureus*.[10] Recently the interaction of the dimethyl ester of meso-2,3-dimercaptosuccinic acid with cadmium (Cd^{2+}) and zinc (Zn^{2+}) ions in rabbit liver metallothionein has been reported. The rabbit liver metallothionein is more susceptible to oxidation at physiological pH after the removal of metal ions.[11]

Cyclic diorganotin dicarboxylates of mercaptosuccinic and 2,2′-thiodiacetic acid reported in the present paper may act as potential biocides and also may be useful in the polymer industry since the mercaptosuccinates contain one free carboxylate (COOH) group which may interact with the metal ions present in physiological systems, just as *in vivo*, in the presence of certain diorganotin compounds the thiol groups bind to metal to form a stable chelate which destroys enzyme activity.[12] The activity of these compounds may be due to R_2Sn moieties which may possibly be released into the cells. Cyclic di-n-butyltin(IV) thiodiacetate (complex **8** below) has been used as a covalent template in the synthesis of macrocyclic keto ethers due to the presence of a reactive Sn—O bond.[13] The macrocyclic keto ethers may be used as antibiotics or ion carriers and may selectively bind metal ions. The reactive Sn—O bond in these complexes may also be responsible for interaction with other metal ions present in living systems and thus may interfere with these systems.

EXPERIMENTAL

Materials and methods

The oxides of dimethyl-, di-n-butyl, di-n-octyl and bis(tri-n-butyl)-tin oxides were obtained from Alfa Products, USA. Diethyl- and di-n-propyl-tin oxides were prepared by a known method.[14] Mercaptosuccinic and thiodiacetic acids were purchased from Fluka and E. Merck respectively and used as such.

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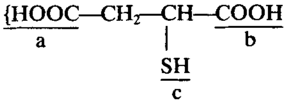
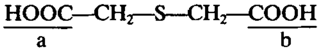
$$AH_3 + R_2SnO/(R_3Sn)_2O \rightarrow R_2SnAH/(R_3Sn)_2AH + H_2O$$
$$BH_2 + R_2SnO/(R_3Sn)_2O \rightarrow R_2SnB/(R_3Sn)_2B + H_2O$$



$$\{\underset{a}{\underline{HOOC-CH_2}}-\underset{\underset{c}{\underline{SH}}}{\underset{|}{CH}}-\underset{b}{\underline{COOH}}$$

AH₃



$$\underset{a}{\underline{HOOC-CH_2}}-S-\underset{b}{\underline{CH_2-COOH}}$$

BH₂

Scheme 1

Physical measurements

Elemental analyses were carried out by Microanalytical Service, R.S.I.C., Panjab University, Chandigarh, India. Tin was estimated as SnO_2. Infrared spectra of complexes **1–6** below were recorded on a Pye–Unicam P 321 spectrophotometer in the 4000–200 cm^{-1} range and complexes **7–10** were recorded on a Perkin–Elmer 1430 spectrophotometer in the 4000–400 cm^{-1} region. The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AC 200 MHz spectrometer using TMS as an internal standard.

Preparation of sodium salts

Mercaptosuccinic or thiodiacetic acid (0.1 mol) and sodium hydroxide (0.2 mol) were dissolved in distilled ethanol (95%, 50 cm^3) and refluxed until a clear solution was obtained (pH 7–7.2). After removing the excess of ethanol by distillation, dry benzene (20 cm^3) was added to remove water azeotropically using a Dean and Stark trap. The sodium salt separated and was filtered and washed several times with dry acetone and ether and dried in vacuum.

Preparation of ethyl ester

The ester of mercaptosuccinic or thiodiacetic acid was prepared by refluxing (0.1 mol) of acid in absolute ethanol (20 cm^3) and 2–3 drops of sulphuric acid for 3 h. The solution was filtered and poured into excess water. Finally the ester was extracted with diethyl ether and dried over anhydrous sodium sulphate.

Preparation of complexes

Mercaptosuccinic acid or thiodiacetic acid (0.1 mol) was dissolved in a mixture of dry benzene (30 cm^3) and absolute ethanol (10 cm^3) and dialkyltin or trialkyl tin oxide (0.1 mol) was added to the solution. The reaction mixture was then refluxed azeotropically over a water bath using a Dean–Stark trap. Dialkyltin(IV) oxide went into solution within 10–15 min to give a clear solution. Refluxing was further continued for 3–4 h and the contents were then cooled and solvent was removed under reduced pressure. Complexes **1–5** and complex **10** were obtained as white solids whereas a viscous liquid resulted in case of complexes **6–9**. The solid complexes were recrystallized from absolute ethanol whereas viscous liquids were washed with chloroform.

RESULTS AND DISCUSSION

Di- and tri-organotin(IV) complexes of mercaptosuccinic acid (AH_3) and thiodiacetic acid (BH_2) have been prepared in 1:1 molar ratio (Scheme 1).

The ligands AH_3 and BH_2 have three and two bonding sites, a, b, c and a, b respectively, available for coordination to tin(IV) which have been further identified with the help of IR, ^{1}H and ^{13}C NMR studies.

Complexes **1–5** are soluble in ethanol, methanol and dimethyl sulphoxide but insoluble in benzene, carbon tetrachloride, chloroform, ethyl acetate, petroleum ether and hexane, whereas complexes **6–10** are soluble in these solvents. Physical and analytical data are given in Table 1.

Infrared spectra

Spectral data of liquids (esters, complexes **6–9**) have been recorded neat and of solids **1–5** and **10** in KBr. The stretching frequencies of interest are of COO, C–S, S–H, Sn—O, Sn—C and Sn—S (Table 2).

In the spectra of R_2SnAH and $(R_3Sn)_2AH$ complexes, vibrations (2900–2600 cm^{-1}) associated with the OH group of the COOH group of AH_3 appeared, showing that at least one COOH group is not involved in coordination to tin. The ethyl ester of AH_3 showed a strong sharp S—H absorption at 2580 cm^{-1},[15] which is absent in complexes

Table 1 Physical and analytical data of organotin(IV) complexes of mercaptosuccinic and thiodiacetic acid

No.	Complex	Colour	M.p. (°C)	Yield (%)	Elemental analysis (%): Found (Calcd) C	H	Sn
1	$[(CH_3)_2SnAH]^a$	White	170–171	80	26.3(24.96)	3.48(3.37)	38.56(40.00)
2	$[(C_2H_5)_2SnAH]^a$	White	120–122	82	29.61(29.56)	3.51(4.31)	35.43(36.5)
3	$[(C_3H_7)_2SnAH]^a$	White	105–106	87	34.7(34.0)	5.20(5.10)	31.94(33.65)
4	$[(C_4H_9)_2SnAH]^a$	White	155–156	85	37.33(35.9)	5.76(5.33)	26.88(28.76)
5	$[(C_8H_{17})_2SnAH]^a$	White	175–177	88	47.9(48.7)	8.05(7.71)	22.96(24.07)
6	$[(Bu_3Sn)_2AH]$	Colourless	L	87	—	—	30.74(32.63)
7	$[(C_3H_7)_2SnB]$	Colourless	L	80	—	—	32.53(33.65)
8	$[(C_4H_9)_2SnB]$	Colourless	L	79	—	—	26.98(28.76)
9	$[(C_8H_{17})_2SnB]$	Colourless	L	76	—	—	23.87(24.07)
10	$[(Bu_3Sn)_2B]^a$	White	90–92	85	44.9(46.19)	8.00(7.97)	31.54(32.63)

Abbreviations: AH, dianion of mercaptosuccinic acid; B, dianion of thiodiacetic acid; L, viscous colourless liquid washed with chloroform.

[a] Crystallized from absolute ethanol.

For structures of the ligands see Conclusions.

1–6 suggesting coordination of sulphur to tin. A strong band at 1025 cm^{-1} in the case of the ethyl ester of AH_3, assigned to the stretching frequency of the C—S bond,[16] shifts downfield in complexes **1–6**, further suggesting bonding of sulphur to tin. The presence of an Sn—S absorption band in the

Table 2 Infrared spectral data[a] of organotin(IV) complexes of mercaptosuccinic and thiodiacetic acid

No.	Complex	$\nu(COO)_{asym}$	$\nu(COO)_{sym}$	$\Delta\nu$	ν(C—S)	ν(Sn—C)	ν(Sn—O)	ν(Sn—S)
	AH_3	1690sb	1180s	510	1080s	—	—	—
	ANa_2	1570s	1390s	180	—	—	—	—
	AEt_2	1725s	1165s	560	1025s	—	—	—
	BH_2	1695sb	1215s	480	920s	—	—	—
	BNa_2	1595s	1380s	215	925s	—	—	—
	BEt_2	1740s	1295s	445	935s	—	—	—
1	$[(CH_3)_2SnAH]$	1710s	1200s	510	995s	555m	498m	390m
		1555s	1395s	160				
2	$[(C_2H_5)_2SnAH]$	1710s	1200s	510	1000s	610m	490s	390s
		1545s	1385s	160				
3	$[(C_3H_7)_2SnAH]$	1710s	1205s	515	925s	595m	495s	385s
		1555s	1390s	165				
4	$[(C_4H_9)_2SnAH]$	1735s	1180s	555	1015m	595m	500m	380m
		1580s	1375s	205				
5	$[(C_8H_{17})_2SnAH]$	1730s	1210s	525	950m	550m	480sh	385m
		1580s	1380s	200				
6	$[(Bu_3Sn)_2AH]$	1650s	1180s	470	995m	600m	510m	395m
		1560s	1380s	180			460m	
7	$[(C_3H_7)_2SnB]$	1740s	1225m	515	940m	595w	470s	
		1640m	1300w	340				
8	$[(C_4H_9)_2SnB]$	1740s	1215m	525	935m	590sh	490s	
		1640m	1295m	345				
9	$[(C_8H_{17})_2SnB]$	1740s	1220w	520	915s	605sh	490w	
		1585m	1300w	285				
10	$[(Bu_3Sn)_2B]$	1580s	1385s	195	940w	610s	470m	

Abbreviations: AH_3, mercaptosuccinic acid: ANa_2, sodium salt; AEt_2, ethyl ester; BH_3, thiodiacetic acid; BNa_2, sodium salt; BEt_2, ethyl ester; sh, shoulder; s, strong; w, weak; m, medium.

[a] Complexes **1–6** in 4000–200 cm^{-1} region; complexes **7–10** in 4000–400 cm^{-1} region.

Table 3 ^1H NMR data (scale, δ ppm) of organotin(IV) complexes of mercaptosuccinic and thiodiacetic acid

				Sn—R	
No.	Complex	—CH—	—CH_2—	—CH_2—	CH_3
	AH_3	2.96–2.87(t, 1H)	2.70–2.49(d, 2H)	—	—
	BH_2	—	3.35(s, 4H)	—	—
1	$[(CH_3)_2SnAH]^a$	2.92–2.87(t, 1H)	2.66–2.50(d, 2H)	—	0.73(s, 6H)
2	$[(C_2H_5)_2SnAH]^a$	3.03–2.96(t, 1H)	2.63–2.58(d, 2H)	1.31–1.21(m, 4H)	0.98–0.85(t, 6H)
3	$[(C_3H_7)_2SnAH]^a$	3.03–2.95(t, 1H)	2.57–2.45(d, 2H)	1.86–1.65(m, 8H)	1.41–1.25(t, 6H)
4	$[(C_4H_9)_2SnAH]^a$	3.10–3.02(t, 1H)	2.69–2.59(d, 2H)	1.40–1.29(m, 12H)	0.94–0.88(t, 6H)
5	$[(C_8H_{17})_2SnAH]^a$	3.02–2.95(t, 1H)	2.60–2.58(d, 2H)	1.64–1.27(m, 28H)	1.19–0.87(t, 6H)
6	$[(Bu_3Sn)_2AH]^b$	2.96–2.75(t, 1H)	2.39–2.50(d, 2H)	1.57–1.31(m, 36H)	1.29–0.90(t, 18H)
7	$[(C_3H_7)_2SnB]^b$	—	3.36–3.25(d, 4H)	1.60–1.26(m, 8H)	1.25–1.18(t, 6H)
8	$[(C_4H_9)_2SnB]^b$	—	3.32–3.21(d, 4H)	1.60–1.28(m, 12H)	1.26–1.19(t, 6H)
9	$[(C_8H_{17})_2SnB]^b$	—	3.39–3.32(d, 4H)	1.65–1.26(m, 28H)	1.23–1.19(t, 6H)
10	$[(Bu_3Sn)_2B]^b$	—	3.38(s, 4H)	1.64–1.22(m, 36H)	0.92–0.85(t, 18H)

Abbreviations: s, singlet; d, doublet; t, triplet; m, multiplet. Coupling constants were not recorded.
[a] Spectra recorded in $^6DMSO-d_6$. [b] Spectra recorded in $CDCl_3$.

Table 4 ^{13}C spectra data (scale, δ ppm) of organotin(IV) complexes of mercaptosuccinic and thiodiacetic acid

$$\overset{1}{Sn—CH_2}—\overset{2}{CH_2}—\overset{3}{CH_2}—\overset{4}{CH_2}—\overset{5}{CH_2}—\overset{6}{CH_2}—\overset{7}{CH_2}—\overset{8}{CH_3}$$

Sn—R

					Sn—R							
No.	Complex	—CH_2—	—CH—	—COO—	C_1	C_2	C_3	C_4	C_5	C_6	C_7	C_8
	AH_3	37.14	38.39	172.58 170.83	—	—	—	—	—	—	—	—
	BH_2	32.71	—	170.45	—	—	—	—	—	—	—	—
1	$[(CH_3)_2SnAH]^a$	39.00	41.19	176.08 169.24	12.69	—	—	—	—	—	—	—
2	$[(C_2H_5)_2SnAH]^a$	42.76	41.48	176.03 169.97	13.25	8.12	—	—	—	—	—	—
3	$[(C_3H_7)_2SnAH]^a$	39.50	41.55	176.04 169.22	24.96	18.72	17.95	—	—	—	—	—
4	$[(C_4H_9)_2SnAH]^a$	39.71	42.76	176.00 169.78	25.79	22.15	21.89	13.03	—	—	—	—
5	$[(C_8H_{17})_2SnAH]^a$	39.79	41.87	176.07 169.87	32.59	30.86	28.27	28.19	24.44	21.95	21.62	14.18
6	$[(Bu_3Sn)_2AH]^b$	37.51	41.37	176.38 170.05	27.61 27.64	26.33 26.97	14.05 16.64	14.05 16.64	— —	—	—	—
7	$[(C_3H_7)_2SnB]^b$	33.37	—	174.52 169.63	26.35	19.85	13.17	—	—	—	—	—
8	$[(C_4H_9)_2SnB]^b$	33.41	—	174.83 169.68	27.43	26.39	25.38	13.94	—	—	—	—
9	$[(C_8H_{17})_2SnB]^b$	33.78	—	179.34 169.59	32.22	31.64	29.42	28.96	27.59	25.79	21.08	13.91
10	$[(Bu_3Sn)_2B]^b$	34.44	—	174.85 174.75	27.85	26.44	26.29	13.16	—	—	—	—

[a] Spectra recorded in DMSO-d^6. [b] Spectra recorded in $CDCl_3$.

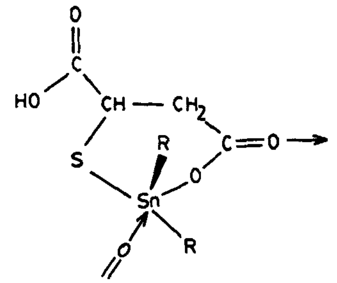


Figure 1 R = CH_3, C_2H_5, n-C_3H_5, n-C_4H_9, n-C_8H_{17}

390–380 cm^{-1} region[17] supports the coordination of sulphur to tin.

The presence of two $\nu(COO)_{asym}$ and two $\nu(COO)_{sym}$ values in complexes **1–5**, which are comparable with the ethyl ester and sodium salt of AH_3, suggests that one carboxylate is free while the other carboxylate is bonded to tin in a bidentate manner. Since the $\nu(COO)_{asym}$ vibration is present in the range 1540–1580 cm^{-1} in complexes **1–5**, this shows the bridging bidentate nature of the carboxylate group.[18,19]

In complex 6, pentacoordinated trigonal bipyramidal geometry at both tin atoms is supported by (1) the presence of one $\nu(COO)_{asym}$ stretch in the range of the sodium salt of AH_3, thus revealing the bidentate nature of the carboxylate group coordinated to tin, and (2) the lowering of the other $\nu(COO)_{asym}$ stretch, which is attributed to weak bonding between tin (IV) and carboxyl, viz. Sn←O=C—OH in addition to tin(IV)–sulphur bonds.

Two broad bands at 2860 and 2690 cm^{-1} observed in BH_2 are absent in the case of complexes **7–10**, indicating deprotonation of the carboxyl groups. The unidentate and asymmetrical bonding nature of the two carboxylate–tin atom bonds in complexes **7–9** is revealed by the presence of two values for $\nu(COO)_{asym}$ and $\nu(COO)_{sym}$ in the range of the ethyl ester vibrations of BH_2. In complex **10**, the presence of a single strong band due to $\nu(COO)_{asym}$ and $\nu(COO)_{sym}$ stretching and a comparable $\Delta\nu$ value to that of BNa_2 indicates the bidentate and symmetrical bonding of the carboxylate group to two tin atoms.

The presence of one tin–carbon (Sn—C) absorption band in the region 600–500 cm^{-1} reveals the linear configuration of the R—Sn—R moiety in complexes **1–6**. Absorption bands in the 510–480 cm^{-1} region are attributed by ν(Sn—O) in all the complexes which have been supported by a recent X-ray study.[20]

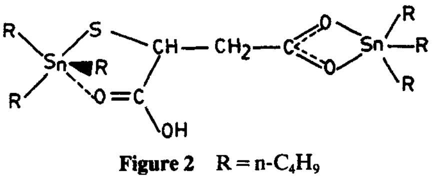


Figure 2 R = n-C_4H_9

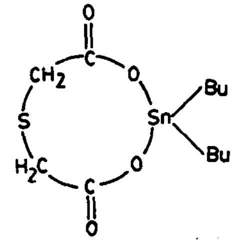


Figure 3 R = n-C_3H_7, n-C_4H_9, n-C_8H_{17}

^{1}H NMR spectra

The ^{1}H NMR spectra of ligands and complexes **1–5** have been recorded in DMSO-d_6 and complexes **6–10** in $CDCl_3$ (Table 3). a single resonance is observed at 8.07 ppm due to the formation of the complex, DMSO-d_6 . . . H_3A, in the spectra of AH_3 while that of COOH is missing. The —SH proton signal present at 3.65 ppm in the spectra of AH_3 disappears in complexes **1–6**, which confirms the participation of sulphur in bonding to tin(IV). The positions of a doublet and a triplet due to —CH_2 and —CH— protons in complexes **1–6** undergo negligible change compared with that in AH_3.

A single resonance is observed in BH_2 at 10.05 ppm due to two acidic protons which disappear in the spectra of complexes **7–9**, confirming complex formation. The presence of a singlet at 3.35 ppm in BH_2 due to two —CH_2— groups is changed into a doublet in complexes **7–9**, demonstrating their magnetic non-equivalence, which may be due to asymetric bonding of two carboxylates to tin(IV) in these complexes. A singlet is observed in complex **10** due to two —CH_2— groups directly attached to carboxylates, which reveals their magnetic equivalence.

The presence of a single methyl resonance in

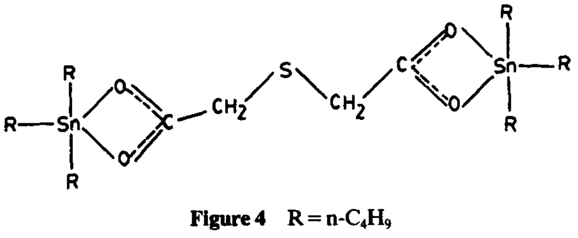


Figure 4 R = n-C_4H_9

complex **1** reveals the *trans* configuration of the two methyl groups. In complexes **2–10** the presence of triplets due to methyl protons and multiplets due to —CH_2— protons of the Sn—R moiety confirms the formation of the complexes. The number of protons calculated from the integration curves agrees with the expected molecular formulae.

^{13}C NMR data

The ^{13}C NMR spectra of ligands and complexes **1–5** have been recorded in DMSO-d_6 and those of complexes **6–10** in $CDCl_3$ (Table 4). The number of signals found corresponds with the magnetically non-equivalent carbon atoms. The position of one carboxylate carbon is shifted downfield and the other carboxylate carbon undergoes no change in complexes **1–6**, which indicates the participation of only one carboxylate group in coordination to tin(IV). The presence of only one signal due to two carboxylate groups in BH_2 reveals their magnetic equivalence; on complex formation this is resolved into two signals, which apparently shows the asymmetric nature of the two carboxylates in complexes **7–9**. The presence of two sets of values for butyl carbons in complex 6 reveals the magnetic non-equivalence of butyl groups since the two tin atoms bearing the butyl groups are in different environments. The presence of one set of values for the butyl groups in complex **10** suggests that the two tin atoms may be in the same environment, thus accounting for the magnetic equivalence of the butyl carbons. The identification of alkyl carbons in all the complexes confirms complexation.

CONCLUSIONS

The spectral data of R_2SnAH, $(R_3Sn)_2AH$ and $(R_3Sn)_2B$ complexes support five-coordinated trigonal bipyramidal structures (Figs 1, 2 and 4). A tetrahedral structure (Fig. 3) is favoured for the complexes **7–9** with unidentate carboxylates bonded asymmetrically to tin.

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