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TRIORGANOTIN(IV) DERIVATIVES OF FIVE MEMBERED HETEROCYCLIC 2-CARBOXYLIC ACIDS

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Abstract—A series of 20 complexes of general formula R_3SnL (R = CH_3, n-C_3H_7, n-C_4H_9, C_6H_5, c-C_6H_{11}; L = anion of thiophene 2-, thiophene 2-acetic, furoic 2- and pyrrole 2-carboxylic acids) has been prepared. All of these complexes are monomers except those of triphenyltin(IV) which are polymers and have been characterised by molecular weight determination, IR, ^{1}H-NMR and ^{119m}Sn Mössbauer studies. Tetrahedral and trigonal bipyramidal structures have been assigned and it has been found that none of the ring hetero atoms bond to tin(IV).

Fungicidal and bacteriocidal carboxylates of tributyltin(IV) with furoic and thiophene acids are known through patents.[1,2] Structural information about very few diorganotin(IV)[3] and tributyltin(IV)[4] compounds with furoic and pyrrole acids is available. A possible biological activity is expected from the triorganotin carboxylates reported in this paper since all the hetero atoms of the five membered carboxylic acids are free and are not bonded to tin(IV).

EXPERIMENTAL

Chemicals

Thiophene 2-carboxylic acid (ThioH), thiophene 2-acetic acid (ThioAH), furoic 2-carboxylic acid (FuH) and pyrrole 2-carboxylic acid (PyrH) were obtained from Aldrich Chemicals (England) and are used as such. Trimethyltin(IV) chloride and tributyltin(IV) chloride were procured from Alpha Products (USA) and Fluka Chemicals (Germany), respectively and are used as such while tripropyltin(IV) chloride,[5] triphenyltin(IV) chloride[6] and tricyclohexyltin(IV) chloride[7] were prepared by the reported methods.

Preparation of the sodium salt

Sodium hydroxide (BDH) (4.0 g, 0.1 mole) was added to a solution of ThioH (12.8 g, 0.1 mole) in ethanol (95%, 50 cm^3) and refluxed till a clear solution resulted (pH 7–7.2). After removing the excess alcohol by distillation, dry benzene (20 cm^3) was added to remove water azeotropically using a Dean and Stark trap. Thiophene 2-sodium carboxylate separated out and was filtered, washed several times with acetone and then with dry ether and dried *in vacuo*. Sodium salts of the remaining acids were prepared in a similar way.

Preparation of complexes

To a solution of triorganotin(IV) chloride (0.001 mole) in absolute alcohol (30 cm^3) was added the sodium salt of the acid (0.00104 mole). The reaction mixture was refluxed on a water bath for 3–4 h when a clear solution was produced. From the reaction mixture half of the alcohol was removed by distillation. On cooling some sodium chloride separated which was filtered through a sintered glass funnel (G-4) under reduced pressure. To the clear solution was added thiophene-free dry benzene (20 cm^3) followed by refluxing on a water bath using a Dean and Stark trap for 2 h. Sodium chloride that separates on cooling was filtered. Refluxing followed by cooling and subsequent filtration of the solution was repeated till the removal of sodium chloride was complete. After removing the solvents completely, the residue was dried *in vacuo*. All the compounds are solids except Nos 8, 12 and 18 (Table 1) which are liquids. Compound 12 solidifies on long standing whereas 18 becomes a semi-solid on keeping. Compounds 1–4 and 17–20 have been

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Table 1. Physical and analytical data of triorganotin(IV) derivatives

Sr No.	Complex	Yield (%)	M.p. (°C)	Analysis (%) Found (Calc.)					Mol. wt		
				C	H	S	N	Sn	C^{a}	R^{b}	Calc.
1.	$(CH_3)_3$SnThio	85	158–9	33.4	3.7	10.9	—	40.6	253.0	270.0	290.7
				(33.0)	(4.1)	(11.0)		(40.8)			
2.	$(CH_3)_3$SnThioA	82	129–31	34.8	4.0	10.3	—	38.4	—	290.0	304.7
				(35.4)	(4.5)	(10.5)		(38.9)			
3.	$(CH_3)_3$SnFu	88	196–7	34.5	4.1	—	—	42.8	—	260.0	274.7
				(34.9)	(4.3)			(43.2)			
4.	$(CH_3)_3$SnPyr	75	139–40	35.2	4.3	—	5.4	43.0	—	259.0	273.7
				(35.0)	(4.7)		(5.1)	(43.3)			
5.	$(n\text{-}C_3H_7)_3$SnThio	80	89–90	44.5	6.0	8.6	—	31.5	326.1	330.2	374.7
				(44.8)	(6.4)	(8.5)		(31.6)			
6.	$(n\text{-}C_3H_7)_3$SnThioA	80	74–5	45.9	6.5	8.0	—	30.2	350.4	340.5	388.7
				(46.3)	(6.6)	(8.2)		(30.5)			
7.	$(n\text{-}C_3H_7)_3$SnFu	84	120–21	46.4	6.7	—	—	32.8	339.3	335.7	358.7
				(46.8)	(6.6)			(33.0)			
8.	$(n\text{-}C_3H_7)_3$SnPyr^{c}	85	—	46.7	6.5	—	3.4	33.0	318.5	320.0	357.7
				(46.9)	(6.9)		(3.9)	(33.1)			
9.	$(n\text{-}C_4H_9)_3$SnThio	75	63	48.4	6.7	7.8	—	28.3	390.5	380.5	416.7
				(48.9)	(7.1)	(7.6)		(28.4)			
10.	$(n\text{-}C_4H_9)_3$SnThioA	80	75	49.8	7.1	7.1	—	27.3	399.6	390.8	430.7
				(50.1)	(7.4)	(7.4)		(27.5)			
11.	$(n\text{-}C_4H_9)_3$SnFu	75	83–85	50.6	7.1	—	—	29.4	388.3	370.2	400.7
			(86–87)^{d}	(50.9)	(7.5)			(29.6)			
12.	$(n\text{-}C_4H_9)_3$SnPyr^{e}	75	59–61	50.7	7.4	—	3.15	29.4	379.1	375.6	399.7
				(51.0)	(7.7)		(3.50)	(29.7)			
13.	$(C_6H_5)_3$SnThio	80	114	57.7	3.7	6.6	—	24.5	459.1	450.8	476.7
				(57.9)	(3.8)	(6.7)		(24.9)			
14.	$(C_6H_5)_3$SnThioA	70	144–45	58.4	3.8	7.0	—	24.0	—	—	490.7
				(58.6)	(4.1)	(6.5)		(24.2)			
15.	$(C_6H_5)_3$SnFu^{f}	75	190	59.4	4.1	—	—	25.5	—	—	460.7
				(59.9)	(3.9)			(25.8)			
16.	$(C_6H_5)_3$SnPyr	80	160–62	60.5	3.7	—	3.44	25.5	—	—	459.7
				(60.0)	(4.1)		(3.04)	(25.8)			
17.	$(c\text{-}C_6H_{11})_3$SnThio	85	119–21	55.4	7.0	6.1	—	23.4	475.5	448.5	494.7
				(55.8)	(7.3)	(6.4)		(24.0)			
18.	$(c\text{-}C_6H_{11})_3$SnThioA	82	Semi-solid	56.2	7.1	5.9	—	23.1	—	470.0	508.7
				(56.6)	(7.5)	(6.3)		(23.3)			
19.	$(c\text{-}C_6H_{11})_3$SnFu	80	126–28	57.1	7.1	—	—	24.6	—	427.0	478.7
				(57.6)	(7.5)			(24.8)			
20.	$(c\text{-}C_6H_{11})_3$SnPyr	75	188–90	57.2	7.5	—	3.2	24.5	—	430.2	477.7
				(57.7)	(7.7)		(2.9)	(24.8)			

ThioH = thiophene 2-carboxylic acid; ThioAH = thiophene 2-acetic acid; FuH = furan 2-carboxylic acid; PyrH = pyrrole 2-carboxylic acid.

[a] Cryoscopically.

[b] Rast method.

[c] Liquid complex.

[d] Literature value, P. Dunn and T. Norris, *Austral. Defence Sci. Serv. Defence Stand. Labs*, Report 269, Feb. 1964.

[e] Compound solidifies on prolonged standing.

[f] Decomposes.

recrystallized from ethanol while 5–7 and 9–12 from pet-ether (60–80°C). The triphenyltin(IV) derivatives (13–16) could not be recrystallized because of their insolubility in common organic solvents but were washed with pet-ether (40-60°) to remove Ph_3SnCl.

Physical measurements

Melting points were determined in open capillaries and are uncorrected. Elemental analysis was carried out by microanalytical service, Calcutta University, Calcutta. Tin was estimated as SnO_2.[8] Molecular weights were determined both cryoscopically in benzene and by Rast's method (in molten camphor, 175°C). Infrared spectra were recorded on Pye–Unicam $Sp_{3\text{-}300}$ spectrophotometer in KBr and in neat polythene strips in 4000–200 cm^{-1} range. ^{1}H-NMR spectra were recorded on Tesla BS487C (80 MHz) using TMS as internal standard. The ^{119m}Sn Mössbauer spectra were recorded at 77 K on a Ranger Engineering constant acceleration spectrometer equipped with an NaI scintillation counter using $Ca^{119m}SnO_3$ as the source and $Ca^{119m}SnO_3$ was the reference material for zero velocity at room temperature. The velocity calibration was based on β-tin and natural iron foils. The resultant spectra were fitted using standard least squares techniques assuming a Lorentzian shape.

RESULTS AND DISCUSSION

All the complexes except triphenyltin(IV) derivatives are soluble in common organic solvents. The analytical data are given in Table 1. Molecular weight determination of all the complexes except those of triphenyltin(IV) complexes by Rast and cryoscopic methods indicates a monomeric nature of the compounds. Insoluble nature of the triphenyltin(IV) complexes indicates polymeric structures.

The assignments of important infrared bands are shown in Table 2 both for ligands and complexes. A band around 2900–2500 cm^{-1} in the spectra of acids disappears in the spectra of their respective sodium salts and complexes which indicates deprotonation of the carboxylic group. A lower ν(N–H) in the PyrNa as compared to PyrH supports the presence of hydrogen bonding in the PyrH. A higher ν(N–H) value in complexes 4, 8 and 12 or its unchanged value in 16 and 20 show non-participation of nitrogen atom in bonding to tin.

The $\Delta\nu$ value $[\Delta\nu = \nu(COO)_{asym} - \nu(COO)_{sym}]$ which is useful in drawing structural inferences in the case of metal carboxylate[9] is used to determine the nature of bonding of the carboxylate to tin(IV). In the seven complexes 8, 12, 13 and 17–20, Table 2, the $\Delta\nu$ value is higher by 90–65 cm^{-1} than in the sodium salts and indicates either asymmetric or a unidentate bonding of the carboxylate group to tin(IV)[10] while in the remaining complexes the carboxylate group behaves in a bidentate manner since $\Delta\nu$ value is comparable to the sodium salt of the acids.[11] However, polymeric triphenyltin(IV) complexes have asymmetrically bonded bridging bidentate carboxylate group since $\nu(COO)_{asym}$ and $\nu(COO)_{sym}$ fall in the range of bridging carboxylates.[12] Observation of both $\nu(Sn\text{–}C)_{asym}$ and $\nu(Sn\text{–}C)_{sym}$ modes in the infrared spectrum of all the compounds studied rules out the planar arrangement for the SnC skeleton. The assignment of ν(Sn–C) and ν(Sn–O) are consistent with the values reported in literature.[11]

The ^{1}H-NMR spectra of the ligands and soluble complexes are given in Table 3. The carboxylic acid proton signal in the acids disappears in the spectra of all the complexes. However in pyrrole 2-carboxylic acid the two protons of the COOH and the NH groups appear as a broad multiplet which may be due to strong hydrogen bonding. The N–H resonance appears as a broad highfield signal in the spectra of all the pyrrole derivatives which is indicative of the non-participation of the nitrogen atom of the ligand to tin(IV). Integrations tally with the expected ratio. In the derivatives of triphenyltin(IV), the signals for protons of the rings (acid) overlap with those of the aromatic protons and are thus difficult to distinguish. Since a multiplet is observed for CH_3 protons in all the trimethyltin(IV) complexes so a *cis* or a *mer* trigonal bipyramidal structure may be present. However, the possibility of a distorted planar Me_3Sn skeleton cannot be ruled out.

The quadrupole splitting parameter (QS) is very useful for interpreting Mössbauer data.[13] A higher QS value in the range 3.69–3.82 mm s^{-1} for complexes 1, 5 and 9, Table 4, is consistent with five coordination. The ratio ρ = QS/IS also favours a five coordinated structure.[15] Ph_3SnThio which is a monomer has much lower QS value and involves monodentate carboxylate. Both properties are consistent with four coordination for tin as reported for other tri-organotin carboxylates.[16]

CONCLUSIONS

All the four Cy_3Sn, n-Pr_3SnPyr, n-Bu_3SnPyr and Ph_3SnThio complexes are monomers with a unidentate carboxylate which bonds to tin(IV) tetrahedrally. Mössbauer parameters of Ph_3SnThio further support a four coordinate structure. Me_3Sn-, 1–4, n-Pr_3Sn-, 5–7, and n-Bu_3Sn-, 9–11,

Table 2. IR spectral data (cm^{-1}, KBr/neat in polythene strips)

Sr No.	Compound	ν(Sn–O)	ν(Sn–C)	$\nu(\mathrm{COO})_{\mathrm{asym}}$	$\nu(\mathrm{COO})_{\mathrm{sym}}$	$\Delta\nu$	ν(N–H)
	ThioH	—	—	1685s,b	1285s	400	—
	ThioNa	—	—	1550s,b	1340s	210	—
	ThioAH	—	—	1700vs	1225s	475	—
	ThioANa	—	—	1565vs	1350m,sp	215	—
	FuH	—	—	1690vs	1300s	390	—
	FuNa	—	—	1590vs	1370s	220	—
	PyrH	—	—	1670vs	1320s,sp	350	3360s
	PyrNa	—	—	1565vs	1380s	185	3260s
1.	$(CH_3)_3$SnThio	420w,sh	540–500bs	1575vs	1365vs	210	—
2.	$(CH_3)_3$SnThioA	405w, 340m,sp	545s, 475w	1570vs	1355s,sp	215	—
3.	$(CH_3)_3$SnFu	455m,sp	545s,sp, 515sh	1600vs,sp	1365s,sp	235	—
4.	$(CH_3)_3$SnPyr	470s,sp, 400s	550s, 505sh	1575vs,b	1365vs,sp	210	3420s,sp, 3310vs,sp
5.	$(n\text{-}C_3H_7)_3$SnThio	415w,sp	590w, 500m,sp	1575vs	1360vs,sp	215	—
6.	$(n\text{-}C_3H_7)_3$SnThioA	475w,sp, 425w,sp	600m,sp, 505w	1580vs,b	1380sh	200	—
7.	$(n\text{-}C_3H_7)_3$SnFu	450ms,sp, 385w,sp	590m,sp, 500w,sp	1600vs,sp	1365vs,sp	245	—
8.	$(n\text{-}C_3H_7)_3$SnPyr^a	480m,sp, 385w,sp	595m,sp, 510w,b	1610vs,sp	1350s,sp	260	3490sh, 3290vs,sp
9.	$(n\text{-}C_4H_9)_3$SnThio	425m,sp	600s,sp, 510s,sp	1580vs,b	1355vs,b	225	—
10.	$(n\text{-}C_4H_9)_3$SnThioA	435w,b, 390w	550w,sp, 505w	1595vs,sp	1380s,sp	215	—
11.	$(n\text{-}C_4H_9)_3$SnFu	455m,sp	595w,b, 540m,sp	1600vs,sp	1360s,sp	240	—
12.	$(n\text{-}C_4H_9)_3$SnPyr^a	490m,sp	605ms,b, 515w,b	1605s,sp	1355s,b	250	3270s,sp
13.	$(C_6H_5)_3$SnThio	340w,b	265w, 245sh	1620vs	1320s,sp	300	—
14.	$(C_6H_5)_3$SnThioA	320w,sp	270w, 230sh	1570vs	1330sh	240	—
15.	$(C_6H_5)_3$SnFu	325w,sp	265m,sp, 250w	1585s,sp	1355ms,sp	230	—
16.	$(C_6H_5)_3$SnPyr	315m,sp	285sh, 275m,sp	1615s,sp	1340s,sp	275	3250vs,b
17.	$(c\text{-}C_6H_{11})_3$SnThio	320m,sp, 280sh	480w,sp, 410m,sp	1620s,sp	1360s,sp	260	—
18.	$(c\text{-}C_6H_{11})_3$SnThioA	280sh	480w, 410m,sp	1645s,sp	1335s,sp	310	—
19.	$(c\text{-}C_6H_{11})_3$SnFu	270sh, 250sh	480w,sp, 410w,sp	1605s,sp	1350s,sp	255	—
20.	$(c\text{-}C_6H_{11})_3$SnPyr	310m,sp, 280w,sp	485m,sp, 415w,sp	1610vs,sp	1350vs,sp	260	3230s,b

$\Delta\nu = \nu(\mathrm{COO})_{\mathrm{asym}} - \nu(\mathrm{COO})_{\mathrm{sym}}$.

[a] In polythene strips.

s = strong, b = broad, m = medium, w = weak, sp = sharp, sh = shoulder.

Table 3. ^{1}H-NMR data (δ, $CDCl_3/CCl_4$)[a]

Sr		Ring protons					
No.	Compound	H^3	H^5	H^4	R–Sn–R		
	ThioH	7.70 (d, 1H)	7.48 (d, 1H)	6.98 (t, 1H)	—		
	ThioAH	7.05 (bd, 1H)	6.5–6.875 (m, 2H)	—	—		
	FuH	7.60 (d, 1H)	7.43 (t, 1H)	6.55 (t, 1H)	—		
	PyrH	6.85 (t, 1H)	6.63 (t, 1H)	6.05 (q, 1H)	—		
1.	$(CH_3)_3$SnThio	7.75 (d, 1H)	7.53 (d, 1H)	7.32–7.03 (m, 1H)	1.3–0.43 (m, 9H)		
2.	$(CH_3)_3$SnThioA	7.15 (m, 1H)	6.85 (m, 2H)	—	0.58 (s, 9H)		
3.	$(CH_3)_3$SnFu	7.45 (s, 1H)	7.05 (t, 1H)	6.43 (m, 1H)	1.08–0.53 (m, 9H)		
4.	$(CH_3)_3$SnPyr	6.68 (m, 1H)	6.35 (bm, 1H)	6.03 (m, 1H)	1.33–0.28 (m, 9H)		
5.	$(n\text{-}C_3H_7)_3$SnThio	7.75 (d, 1H)	7.50 (d, 1H)	7.10 (t, 1H)	1.73 (m, 6H)	1.38 (m, 6H)	1.04 (t, 9H)
6.	$(n\text{-}C_3H_7)_3$SnThioA	7.08 (m, 1H)	6.80 (m, 2H)	—	1.63 (m, 6H)	1.25 (m, 6H)	0.78 (t, 9H)
7.	$(n\text{-}C_3H_7)_3$SnFu	7.45 (s, 1H)	6.95 (d, 1H)	6.40 (m, 1H)	1.88 (m, 6H)	1.48 (m, 6H)	1.08 (t, 9H)
8.	$(n\text{-}C_3H_7)_3$SnPyr	6.73 (m, 1H)	6.33 (bm, 1H)	6.03 (q, 1H)	1.65 (m, 6H)	1.18 (m, 6H)	1.03 (t, 9H)
9.	$(n\text{-}C_4H_9)_3$SnThio	7.63 (d, 1H)	7.43 (t, 1H)	7.05 (t, 1H)	1.73–1.13 (m, 18H)		0.93 (t, 9H)
10.	$(n\text{-}C_4H_9)_3$SnThioA	7.08 (m, 1H)	6.80 (t, 2H)		2.05–1.08 (m, 18H)		0.73 (t, 9H)
11.	$(n\text{-}C_4H_9)_3$SnFu	7.43 (m, 1H)	6.93 (m, 1H)	6.38 (m, 1H)	1.93–1.23 (m, 18H)		0.88 (t, 9H)
12.	$(n\text{-}C_4H_9)_3$SnPyr	6.73 (s, 1H)	6.30 (bm, 1H)	6.03 (d, 1H)	2.0–1.05 (m, 18H)		0.93 (t, 9H)
13.	$(C_6H_5)_3$SnThio[a]	7.78 (m, 4H)	7.55 (m, 2H)	7.35 (m, 10H) 6.95 (m, 2H)			
14.	$(C_6H_5)_3$SnThioA[b]	—	—	—	—		
15.	$(C_6H_5)_3$SnFu[b]	—	—	—	—		
16.	$(C_6H_5)_3$SnPyr[a]	7.90	7.60	6.78 (bm,5H) 7.30 (m, 7H)	—		
17.	$(c\text{-}C_6H_{11})_3$SnThio	7.83 (m, 1H)	7.55 (d, 1H)	7.13 (m, 1H)	2.43–1.13 (m, 33H)		
18.	$(c\text{-}C_6H_{11})_3$SnThioA	7.25 (bs, 1H)	6.80 (bs, 2h)		2.65–1.00 (m, 33H)		
19.	$(c\text{-}C_6H_{11})_3$SnFu	7.50 (bs, 1H)	7.18 (bs, 1H)	6.45 (bs, 1H)	2.65–1.00 (m, 33H)		
20.	$(c\text{-}C_6H_{11})_3$SnPyr	6.65 (m, 1H)	6.38 (m, 1H)	6.03 (m, 1H)	2.25–1.25 (m, 33H)		

s = singlet; d = doublet; t = triplet; q = quarter; b = broad; m = multiplet.

[a] Soluble in $CDCl_3 + DMSO(D_6)$.

[b] Insoluble in $CDCl_3$ and CCl_4.

Table 4. ^{119m}Sn Mössbauer spectral data (80 K, mm s^{-1})

	Complex	IS ± 0.03 (SnO$_2$)	QS ± 0.06	Line width 1	Line width 2	ρ
1.	$(CH_3)_3$SnThio	1.42	3.69	1.04	1.08	2.598
5.	$(n\text{-}C_3H_7)_3$SnThio	1.54	3.76	1.21	1.14	2.440
9.	$(n\text{-}C_4H_9)_3$SnThio	1.54	3.82	1.36	1.11	2.480
		1.48[a]	3.78	—	—	2.554
13.	$(C_6H_5)_3$SnThio	1.33	2.54	1.21	1.69	1.909

[a] Literature value, D. W. Allen, J. S. Brooks, R. Formstone, A. J. Crowe and P. J. Smith, *J. Organomet. Chem.* 1978, **156**, 359.

derivatives are monomers with a bidentate carboxylate in a five coordinate structure. Mössbauer data of three complexes Me$_3$SnThio, n-Pr$_3$SnThio and n-Bu$_3$SnThio further support a trigonal bipyramidal structure for these complexes. Three remaining Ph$_3$Sn-, 14–16, derivatives, which are polymers, have a five coordinate carboxylate bridged structure.

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