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Synthesis and spectral characterization of diorganotin(IV) complexes of thiohydrazides and thiohydrazone

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Abstract

2-Furanthiocarboxyhydrazide (Hfth), 4-hydroxyphenylthiocarboxyhydrazide (Hoth) and salicylaldehyde-2-furanthiocarboxyhydrazone (H_2L) form stable complexes of the compositions $Ph_2SnCl_2 \cdot Hfth$, $R_2Sn(LH)_2$ (where R = Ph or Bu and L = Hfth or Hoth), $Ph_2SnCl_2 \cdot H_2L$, $Ph_2Sn(HL)Cl$ and Bu_2SnL which have been characterised by elemental analysis and spectroscopic studies. All the complexes are octahedral except for Bu_2SnL which is five-coordinate with a distorted trigonal bipyramidal geometry around the tin atom.

Introduction

Transition metal complexes of thiohydrazides and thiohydrazones are known [1–4] but there have been no reports on diorganotin(IV) complexes of thiohydrazides and thiohydrazones. In view of this and of the biological applications of organotin compounds [5–7], we decided to synthesize some diorganotin(IV) complexes of 2-furanthiocarboxyhydrazide (Hfth), 4-hydroxyphenylthiocarboxyhydrazide (Hoth) and salicylaldehyde-2-furanthiocarboxyhydrazone (H_2L) The results are described below. The structures of the ligands are shown in Fig. 1.

Experimental

Hfth [8], H_2L [2], Hoth [9] and Ph_2SnCl_2 [10] were prepared as previously reported. Bu_2SnO (Aldrich) was used as received. The solvents dried by standard methods before use. Diphenyltin(IV) chloride adducts of Hfth and H_2L were prepared by stirring a mixture of a chloroform solution of diphenyltin(IV) chloride and a chloroform benzene solution of Hfth or H_2L (1/1 mol ratio), for about 4 h at

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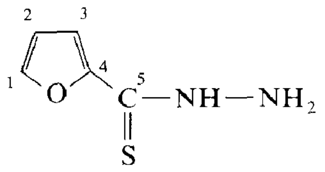
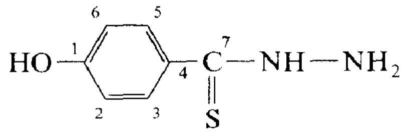
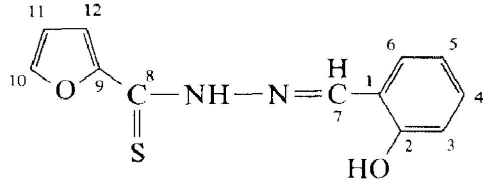


2-furanthiocarboxyhydrazide (Hfth)



4-hydroxyphenylthiocarboxyhydrazide (Hoth)



salicylaldehyde-2-furanthiocarboxyhydrazone (H_2L)

Fig. 1. Structure of ligands Hfth, Hoth and H_2L.

room temperature. The complexes, that separated during the stirring were filtered off with exclusion of moisture, washed thoroughly with a chloroform benzene mixture, and dried in vacuo over calcium chloride.

$Bu_2Sn(fth)_2$ and Bu_2SnL were prepared by refluxing benzene solutions or suspensions of Bu_2SnO and the respective ligand in 1/2 and 1/1 molar ratio,

Table 1

Analytical data for diorganotin(IV) complexes

Compound	Colour	Analysis (Found (calc.) (%))						M.p. (°C)
		C	H	Cl	N	S	Sn	
$Ph_2SnCl_2 \cdot Hfth$	Dirty yellow	41.89	3.01	14.87	5.44	6.06	23.93	174
		(41.01)	(3.29)	(14.62)	(5.77)	(6.59)	(24.43)	
$Ph_2SnCl_2 \cdot H_2L$	Yellow	48.20	3.09	12.12	4.69	5.91	19.72	136
		(48.84)	(3.39)	(12.04)	(4.75)	(5.43)	(20.13)	
$Ph_2Sn(HL)Cl$	Orange	51.68	3.25	6.92	5.11	4.93	20.94	183
		(52.06)	(3.43)	(6.42)	(5.06)	(5.78)	(21.46)	
$Ph_2Sn(fth)_2$	Brick red	47.91	3.67	–	10.21	10.89	20.76	110
		(47.71)	(3.60)		(10.09)	(10.54)	(21.40)	
$Ph_2Sn(oth)_2$	Light yellow	51.04	3.82	–	9.10	10.22	18.92	210
		(51.42)	(3.96)		(9.23)	(10.54)	(19.56)	
$Bu_2Sn(fth)_2$	Brown	42.02	5.28	–	10.78	12.18	22.96	210
		(41.97)	(5.44)		(10.87)	(12.47)	(23.06)	
$Bu_2Sn \cdot L$	Yellow	51.05	5.18	–	5.78	6.98	24.44	64
		(51.52)	(5.45)		(5.87)	(6.71)	(24.92)	
$Bu_2Sn(oth)_2$	Brown	46.82	5.70	–	9.88	10.97	20.54	170
		(46.70)	(5.64)		(9.88)	(10.29)	(20.97)	(dec.)

Table 2

^1H NMR chemical shifts (δ ppm) for diorganotin(IV) complexes

Compound	Assignments
Hfth	3.43 (s, S*H*); 6.62–7.81 (m); 11.81 (s, N*H*) [a]
$Ph_2SnCl_2\cdot Hfth$	6.06–7.37 (m); 8.00 (s, NH_2)
$Ph_2Sn(fth)_2$	6.43–8.00 (m)
$Bu_2Sn(fth)_2$	6.55–7.54 (m)
Hoth	3.6 (s, O*H*) [a]; 10.0 (s, N*H*) [a]; 6.7–7.9 (m)
$Ph_2Sn(oth)_2$	3.48 (s, br, O*H*) [a]; 6.66–7.99 (m)
$Bu_2Sn(oth)_2$	3.48 (br, O*H*) [a]; 6.71–7.86 (m)
H_2L	6.70–8.00 (m); 8.91 (s, C*H*=N); 11.47 (s, N*H*) [a]; 13.52 (s, O*H*) [a]
$Ph_2SnCl_2\cdot H_2L$	4.00 (s, br, H-bonded O*H*) [a]; 11.34 (s, N*H*); 6.71–8.00 (m); 9.00 (C*H*=N)
$Ph_2Sn(HL)Cl$	3.33 (s, O*H*) [a]; 6.62–8.14 (m); 9.28 (C*H*=N)
$Bu_2Sn\cdot L$	6.38–7.43 (m); 9.33 (s, C*H*=N)

[a] These peaks disappear on D_2O exchange. s = singlet; m = multiplet; br = broad. The multiplets in the aromatic proton region also contain the NH_2 signal in the case of $R_2Sn(fth)_2$ and $R_2Sn(oth)_2$ (R = Bu, Ph).

respectively, for about 7 h. $Bu_2Sn(fth)_2$ crystallised out on removal of the most of solvent and cooling of the residual solution, but, Bu_2SnL was precipitated by addition of dry petroleum ether to the cooled and concentrated solution. The complexes thus obtained were filtered off, washed several times with petroleum ether and dried in vacuo over calcium chloride.

All the complexes were analysed for tin, chloride and sulfur by standard methods [11]. Nitrogen was determined microanalytically. The analytical data, colour and melting or decomposition temperatures of the complexes are shown in Table 1. The IR spectra were recorded on a Perkin–Elmer spectrophotometer model 783 as Nujol

Table 3

^{13}C NMR chemical shifts (δ, ppm) for diorganotin(IV) complexes [a]

Compound	Assignments
Hfth	168.71 (C(5)); 150.61 (C(1)); 144.49 (C(4)); 114.31 (C(2)); 112.25 (C(3))
$Ph_2SnCl_2\cdot Hfth$	181.77 (C(5)); 151.34 (C(1)); 146.67 (C(4)); 128.96–112.92 (Ph, C_2 and C_3 carbons)
$Ph_2Sn(fth)_2$	147.79 (C(5)); 146.05–112.01 (aromatic)
$Bu_2Sn(fth)_2$	156.30(C(5)); 144.50–112.24 (butyl + furan ring carbons)
H_2L	172.50 (C(8)); 162.00 (C(7)); 158.05 (C(2)); 153.40 (C(9)); 146.08 (C(10)); 132.36 (C(1)); 130.93 (C(6)); 119.40 (C(11)); 117.8 (C(3)); 116.7 (C(4), C(5)); 113.2 (C(12))
$Ph_2SnCl_2\cdot H_2L$	179.40 (C(8)); 166.00 (C(7)); 157.89–113.94 (aromatic carbons)
$Ph_2Sn(HL)Cl$	170.00 (C(8)); 167.60 (C(7)); 149.31–112.3 (aromatic carbons)
$Bu_2Sn\cdot L$	170.15 (C(8)); 163.84 (C(7)); 157.62–113.43 (aromatic carbons)
Hoth	183.50 (C(7)); 159.70 (C(1)); 129.7 (C(4)); 129.21 (C(3,5)); 114.80 (C(2,6))
$Ph_2Sn(oth)_2$	164.86 (C(7)); 157.71 (C(1)); 146.11–112.85 (ring carbon atoms)
$Bu_2Sn(oth)_2$	163.42 (C(7)); 159.55 (C(1)); 130.51–114.58 (ring carbons + butyl carbons)

[a] Spectra recorded in DMSO-(d_6) except $Ph_2Sn(fth)_2$ (in $CDCl_3$). The numbering of carbon is shown in Fig. 1.

Table 4

^{119}Sn NMR chemical shifts (δ, ppm) and Mössbauer spectral data for diorganotin(IV) complexes

Complex	$\delta(^{119}\mathrm{Sn})$	Isomer shift, δ(mm sec^{-1})	Quadrupole splitting, ΔEq(mm sec^{-1})	Coordination number
$Ph_2SnCl_2 \cdot Hfth$	−372.4	0.842	1.87	6
$Ph_2SnCl_2H_2L$	−280.6	0.753	1.765	6
$Ph_2Sn(fth)_2$	−279.9	1.298	1.979	6
$Ph_2Sn(HL)Cl$	−295.8	1.110	2.085	6
$Bu_2Sn \cdot L$	−134.8	1.282	2.846	5
$Bu_2Sn(oth)_2$	−269.3	1.179	1.794	6
$Ph_2Sn(oth)_2$	−316.8	1.186	2.102	6
$Bu_2Sn(fth)_2$	−210.0	1.084	1.848	6

Table 5

Selected infrared spectral bands (cm^{-1}) for the ligands and diorganotin(IV) complexes

Compound	ν(NH)	$\nu(NH)_2$	ν(C=N)	Thioamide bands			ν(N–N)
				[β(NH) + ν(CN)]	[ν(CN) + β(NH)]	[ν(C=S)/ ν(C–S)]	
Hfth (Nujol)	3240	3180,3140	–	1535	1300	810	995
$Ph_2SnCl_2 \cdot Hfth$	3260	3160,3140	–	1555	1345	770	1005
$Ph_2Sn(fth)_2$	–	3160,3100	–	1570	1385	725	1015
$Bu_2Sn(fth)_2$	–	3120,3140	–	1575	1385	735	1020
Hoth (nujol)	3260	3140	–	1520	1300	840	980
Hoth (MeCN)	3320	3270	–	1520	1220	845	1035
$Ph_2Sn(oth)_2$	–	3120,3180	–	1570	1365	720	1010
$Bu_2Sn(oth)_2$	–	3110,3170	–	1565	1360	720	1015
$H_2L(CHCl_3)$	3350	–	1620	1465	1280	880	970
$Ph_2SnCl_2 \cdot H_2L_2$	3380	–	1590	1540	1355	840	1005
$Ph_2Sn(HL)Cl$	–	–	1590	1495	1320	805	1015
$Bu_2Sn \cdot L$	–	–	1580	1570	1370	720	1010

mulls (Table 5). Mössbauer spectra * were recorded at 78 K by use of $Ba^{119}SnO_3$ source maintained at room temperature and the isolated isomeric shift values are with respect to this source (Table 4). The spectra were least square fitted with assumption of a Lorenzian line shape. The ^{1}H and ^{13}C NMR spectra in $CDCl_3$ and DMSO-d_6 were recorded on a Jeol FX 90Q spectrometer. ^{119}Sn NMR spectra were recorded with solutions in CD_3CN. The positions and assignments of the various signals in the ^{1}H, ^{13}C and ^{119}Sn NMR spectra are given in Tables 2, 3 and 4, respectively.

Results and discussion

The analytical data show that Hfth forms a 1/1 adduct and also a 1/2 deprotonated complex with Ph_2SnCl_2, and only a 1/2 deprotonated complex with

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* Mössbauer spectra were obtained from BARC, Bombay.

Bu_2SnO, whereas H_2L forms a 1/1 adduct and deprotonated complexes with both Ph_2SnCl_2 and Bu_2SnO. Hoth forms only 1/2 deprotonated complexes with Bu_2SnO and Ph_2SnCl_2. All the complexes are insoluble in CCl_4, CH_2Cl_2 and C_6H_6, but soluble in acetone, chloroform, acetonitrile, DMF and DMSO, and with a few exceptions, in EtOH and MeOH.

^1H NMR spectra

The appearance of a signal from an SH proton indicates that thioenolisation of Hfth takes place in DMSO-d_6 solution. In the spectra of the deprotonated complexes of Hoth and Hfth the signal due to the NH proton disappears indicating that the deprotonation involves the removal of this proton through thioenolisation.

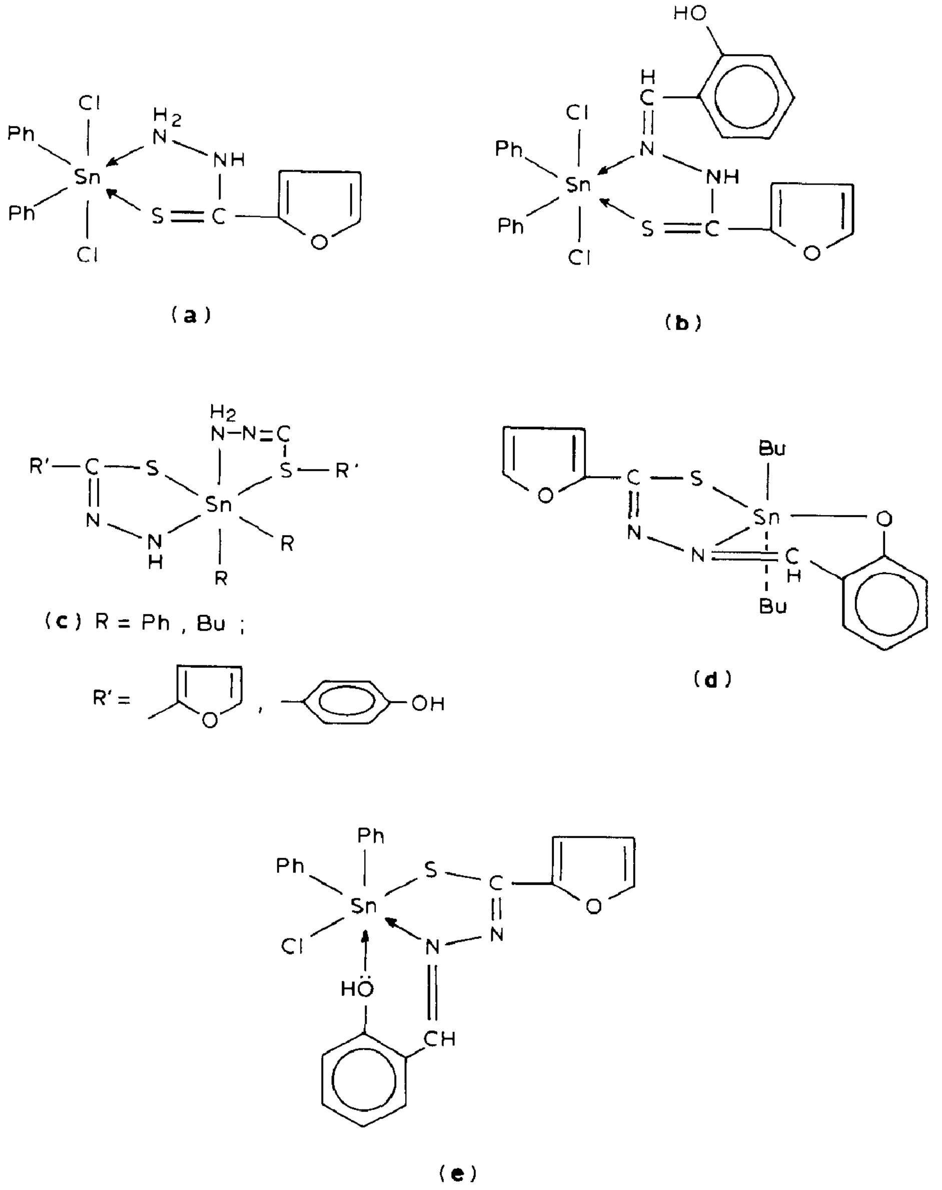

Fig. 2. Suggested structures of the complexes a–e.

The resonance signal for the NH proton appears at about the same position for $Ph_2SnCl_2 \cdot H_2L$ as for H_2L, indicating that the NH group is not involved in complexation (Fig. 2). The absence of the NH proton signal and presence of an OH proton signal in the case of $Ph_2Sn(HL)Cl$ is suggestive of the monobasic nature of the ligand. The disappearance of the signals due to both the NH and OH protons and the deshielding of azomethine proton by 0.42 ppm suggest the ligand is tridentate in Bu_2SnL.

^{13}C NMR spectra

A peak due to $>C=S$ carbon atom in Hfth and Hoth, observed at δ 168.71 and 183.50 ppm, respectively, is shifted markedly downfield in the case of the adduct, $Ph_2SnCl_2 \cdot$ Hfth as a result of a drift of electrons from the metal via sulfur. A pronounced shielding is observed for the $>C=S$ carbon in deprotonated complexes, perhaps as a result of the change in environment around $>C=S$ from HNC=S to N=CS upon the removal of proton upon thioenolisation. The peaks at δ 172.50 and 162.00 ppm observed for $>C=S$ and CH=N carbon atoms of H_2L show downfield shifts of 6.9 and 4.00 ppm, respectively, indicating that in $Ph_2SnCl_2 \cdot H_2L$ the tin is bonded through the sulfur and azomethine nitrogen atoms. The $>C=S$ signal for $Ph_2Sn(HL)Cl$ is shifted upfield. The upfield shift for the $>C=S$ signal and in that from the phenolate carbon in Bu_2SnL correspond to a larger shielding of these carbon atoms on deprotonation compared with that for the ligand.

^{119}Sn NMR spectra

The ^{119}Sn NMR spectra of the complexes show only one signal in the range δ -210 to -372.4 ppm as expected for six-coordinated organotin(IV) complexes [12] having a *cis*-disposition of the phenyl groups. The value of δ (^{119}Sn) -134.8 ppm for Bu_2SnL is consistent with its five-coordinate trigonal bipyramidal structure [13].

^{119}Sn Mössbauer spectra

The isomer shift values (δ, 0.842–1.298 mm sec^{-1}) and large quadrupole splitting values (ΔEq, 1.765–2.102 mm sec^{-1}) are typical of diorganotin(IV) complexes in an octahedral environment [14–16]. The large quadrupole splittings are suggestive of distorted octahedral nature of the complexes bonded to the non-identical donor atoms of the ligand. The lower isomer shift value (1.282 mm sec^{-1}) for Bu_2SnL than for Bu_2SnCl_2 (1.60 mm sec^{-1}) is consistent with a penta-coordinate geometry for the former [17]. The higher quadrupole splitting (2.846 mm sec^{-1}) indicates that the charge distribution around the tin nucleus is highly asymmetric and the geometry considerably distorted (18).

Infrared spectra

The IR data (Table 5) show that the position of the ν(NH) band remains practically unchanged on going from the free ligand to $Ph_2SnCl_2 \cdot$ Hfth and $Ph_2SnCl_2 \cdot H_2L$ but that this band is absent for all the deprotonated complexes, indicating that nitrogen of the imino group is not involved in bonding in the adducts and proton of this group is involved in the formation of deprotonated complexes via thioenolisation. The ν(NH) band due of primary amine group (NH_2) undergoes a smaller shift, indicating coordination through this group in the complexes of Hfth and Hoth [4,19]. A broad band at 3160 cm^{-1} for H_2L, assigned to

ν(OH), is absent in the case of Bu_2SnL owing to the loss of the OH proton and the presence of a new band due to ν(C–O–Sn) at 1530 cm^{-1} suggests bonding to tin through phenolate oxygen.

The thioamide bands I and II [20] and the ν(N–N) band undergo larger shifts indicating that thioamide sulfur and hydrazinic nitrogen are involved in bonding. Bonding through the thione sulfur in the adducts is further evidenced by smaller shifts in the ν(C=S) band. The shift in the thioamide bands is more pronounced in the case of deprotonated complexes formed via thioenolisation [20,21]. The bonding through thiolato sulfur is supported by the absence of a band in ν(C=S) region and the presence of a new ν(C–S) band at much lower frequency [22]. A shift towards lower frequency of ν(C=N) band in the H_2L complexes further is consistent with bonding through the azomethine nitrogen [22], as already indicated by a higher frequency of ν(N–N) [23].

The far infrared spectral bands of diorganotin(IV) complexes in the 280–320, 290–320, 310–450, 345–355 cm^{-1} regions are tentatively assigned to ν(Sn–C), ν(Sn–N), ν(Sn–S) and ν(Sn–Cl) modes, respectively.

On the basis of the spectra the structures shown in Fig. 2 are suggested for the complexes.

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