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THE MÖSSBAUER RECOIL-FREE FRACTION AND STRUCTURE

IV *. TRIPHENYLTIN DERIVATIVES OF METHIONINE, PENICILLAMINE AND CYSTEINE AND L-HISTIDINATOTIN(II)

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Summary

Tin-119 Mössbauer isomer shift, quadrupole splitting and resonance area data have been recorded in the temperature range 77–150 K for the four triphenyltin complexes, *O*-triphenylstannylmethionine (Ph_3Snmet), its methionine solvate, $Ph_3Snmet \cdot metH$, *O,S*-bis(triphenylstannyl)penicillamine ($(Ph_3Sn)_2pen$) and *O,S*-bis(triphenylstannyl)cysteine ($(Ph_3Sn)_2cys$) as well as L-histidinatotin(II) (HisSn). In the solid state, the structure of I comprises mainly discrete monomeric molecules with four-coordinated tin together with a small amount of a one-dimensional polymeric modification containing five-coordinated tin. The methionine solvate, $Ph_3Snmet \cdot metH$, also contains discrete monomeric molecules, which are involved in hydrogen-bonding with the methionine solvate molecules. Both $(Ph_3Sn)_2pen$ and $(Ph_3Sn)_2cys$ contain two chemically-distinct tin environments, one four-coordinate where the triphenyltin residue is bound to the thiol sulphur, and a five-coordinated site where bonding is to the carboxyl group. However, $(Ph_3Sn)_2pen$ appears to be monomeric in the solid, whereas $(Ph_3Sn)_2cys$ comprises a one-dimensional polymer. An essentially monomeric structure is proposed for HisSn, but with some moderately weak intermolecular association.

Introduction

The biological activity of organotin compounds derives principally from their ability to interact strongly with the thiol and imidazole functions of cysteine and histidine residues contained within proteinaceous systems. Practical aspects of the

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TABLE 1

ANALYTICAL AND SPECTROSCOPIC DATA FOR COMPLEXES I–V

Complex	Appearance	M.p. (°C)	Microanalysis data [a]				Tin-119 Mössbauer data [b]			Infrared data [g]	
			C	H	N	S	IS [c]	QS [c]	$-a$ ($\times 10^2$) [d]	$\nu(NH_2)$	$\nu(CO_2)$
Ph_3Snmet	White solid	121.5–123	55.45	5.06	2.81	6.44	1.12 [e]	1.35	2.20	3160 w	1610sh, 1580s,
(I)			(55.62)	(5.14)	(2.73)	(6.23)	1.14 [f]	2.89	1.90		1515s
$Ph_3Snmet \cdot metH$	White solid	209–211	52.03	5.45	4.33	9.92	1.13	1.59	2.20	3125w,	1610w, 1580ms,
(II)			(51.75)	(5.51)	(3.99)	(7.21)				3110sh	1510m
$(Ph_3Sn)_2pen$	White solid	187–189	58.12	4.64	1.65	3.78	1.26 [e]	1.31	2.01	3385w	1635m, 1580m
(III)			(57.99)	(4.83)	(1.21)	(1.76)	1.29 [f]	2.07	1.59		
$(Ph_3Sn)_2cys$	Yellow solid	128–130	57.04	4.26	1.70	3.90	1.35 [e]	1.36	1.97	3190vw,	1558br, 1550m
(IV)			(57.30)	(4.29)	(1.43)	(3.73)	1.31 [f]	3.12	1.26	3115vw	
HisSn	White solid	234–235 (dec.)	26.51	2.60	15.45	–	2.94	2.22	1.96	3105w	1625m, 1565m
(V)			(27.37)	(2.83)	(15.08)	–					

[a] Calculated values in parentheses. [b] Values at 77 K. [c] In mm s^{-1}. [d] In K^{-1}. [e] Peaks 2 and 3. [f] Peaks 1 and 4. [g] Recorded as Nujol mulls.

fungicidal and bacteriostatic activity of organotin compounds has been investigated widely [1–3], but few data are available concerning the chemical nature of such interactions. In this paper we report Mössbauer studies of the interaction of tin residues with some model molecules.

Experimental

(a) Triphenyltin derivatives

The synthesis of all the compounds were similar and therefore only a general method is described.

Triphenyltin hydroxide (5.51 g, 0.015 mol) was dissolved in dry benzene and mixed with the appropriate amino acid (0.015 mol) also dissolved in benzene. After the addition of a catalytic amount of dimethylformamide, the mixture was refluxed using a Dean and Stark water separater. After 3 h, the resulting precipitate was separated and dried in vacuo.

(b) Histidinatotin(II)

To a suspension of tin(II) dimethoxide (1.18 g, 10 mmol) in dry methanol was added a methanolic solution of L-histidine (1.55 g, 10 mmol), and stirred under argon at room temperature for 1 h. The resulting voluminous white solid was isolated as before.

Details of the analytic and spectroscopic data for all the complexes are collected in Table 1.

The Mössbauer instrumentation has been described previously [4]. Samples were finely ground to eliminate preferential orientation effects prior to loading in the variable-temperature cryostat (Oxford Instruments Ltd). Spectra were recorded at various temperatures in the temperature range 77–150 K, accumulating in a minimum of 10^6 counts per channel, and subsequently fitted to Lorentzian line shapes by usual least-squares methods.

Results and discussion

The complexes, *O*-triphenylstannylmethionine, Ph_3Snmet (I), its methionine solvate, $Ph_3Snmet \cdot metH$ (II), *O,S*-bis(triphenylstannyl)penicillamine, $(Ph_3Sn)_2pen$ (III), *O,S*-bis(triphenylstannyl)cysteine, $(Ph_3Sn)_2cys$ (IV), were prepared by azeotropic dehydration of the appropriate ratio of triphenyltin hydroxide and the amino acid in boiling benzene in the presence of dimethylformamide;

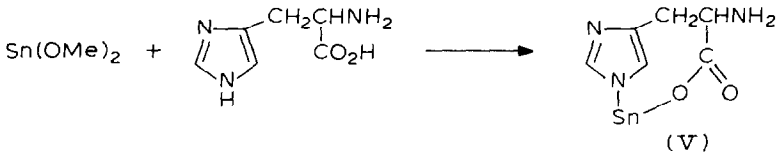
$$Ph_3SnOH + MeSCH_2CH_2CH(NH_2)CO_2H \rightarrow MeSCH_2CH_2CH(NH_2)CO_2SnPh_3 \quad (I)$$

$$Ph_3SnOH + 2MeSCH_2CH_2CH(NH_2)CO_2H \rightarrow MeSCH_2CH_2CH(NH_2)CO_2SnPh_3 \cdot MeSCH_2CH_2CH(NH_2)CO_2H \quad (II)$$

$$2Ph_3SnOH + HSCMe_2CH(NH_2)CO_2H \rightarrow Ph_3SnSCMe_2CH(NH_2)CO_2SnPh_3 \quad (III)$$

$$2Ph_3SnOH + HSCH_2CH(NH_2)CO_2H \rightarrow Ph_3SnSCH_2CH(NH_2)CO_2SnPh_3 \quad (IV)$$

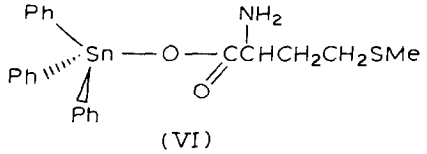
Histidinatotin(II), hisSn (V), was obtained from tin(II) methoxide and histidine in methanol;



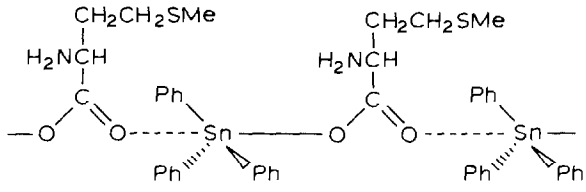
(V)

The triphenyltin complexes I–V are sharply melting amorphous white or yellow solids, which are only sparingly soluble in benzene and chloroform and practically insoluble in all other solvents. The tin(II) complex (V) is an infusible, insoluble white solid. Spectroscopic data are listed in Table 1.

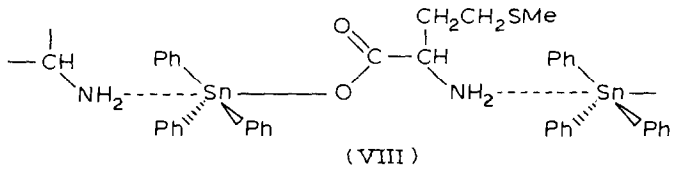
The tin-119 Mössbauer spectrum of triphenylstannylmethionine (I) is quite unusual, and comprises two quadrupole split resonances, but with different relative intensities. Although the isomer shifts of both are similar, the major resonance has a quadrupole splitting of 1.35 mm s^{-1}, whilst the weaker resonance has a much larger splitting of 2.84 mm s^{-1}. Consistent with previous interpretations of quadrupole splitting data, the former value is indicative of a four-coordinated [C_3SnO] environment for tin, whilst the higher value would indicate five-coordination, but with some distortion of the equatorial [SnC_3] moiety from ideal trigonal bipyramidal geometry. The recoil-free fraction temperature coefficient, $-a$, values for the major (four-coordinate) and minor (five-coordinate) components are 2.20 and 1.90 K^{-1}, respectively, i.e. the tin atoms in the latter environment are more tightly bound. Thus, we interpret these data in terms of a lattice comprising largely isolated monomers, VI, with a small amount of a one-dimensional polymer produced either by carboxyl bridging, VII, as observed in most triorganotin carboxylates [5,6], or by amino-group bridging as in the structure of trimethyltin glycinate [7].



(VI)



(VII)

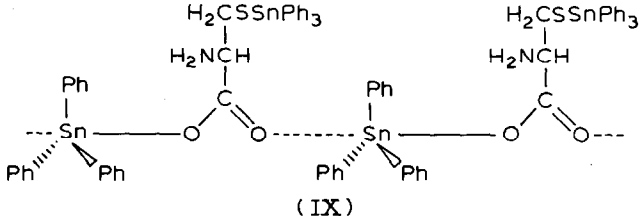


(VIII)

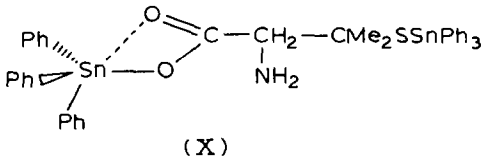
The methionine solvate, $Ph_3Snmet \cdot metH$, exhibits only one quadrupole-split resonance with very similar isomer shift, quadrupole splitting, and temperature

coefficient values as the monomeric component, VI, and hence it would appear that in this case, the formation of a one-dimensional polymeric form is precluded. However, in the infrared, the positions of the $\nu(NH_2)$ vibration is shifted from 3180 cm^{-1} in free methionine to a doublet at 3125 and 3110 cm^{-1} (cf. 3160 cm^{-1} in Ph_3Snmet), the $\nu(CO_2)$ band is moved from 1515 to 1510 cm^{-1} indicating that the solvating methionine molecule is held by a network of hydrogen bonds involving the amino and carbonyl groups.

Both $(Ph_3Sn)_2pen$ and $(Ph_3Sn)_2cys$ exhibit two sets of resonances in their Mössbauer spectra, corresponding to the two chemically different tin environments expected in these molecules. The resonances with the smaller splittings in both are similar to that in Ph_3SnSPh [8] and are assigned to the four-coordinate $[Ph_3SnS]$ environment, with the larger splitting resonances to the carboxyl-bound Ph_3Sn environment. The quadrupole splitting observed for the carboxyl-bound tin in $(Ph_3Sn)_2pen$ is significantly smaller (2.07 mm s^{-1}) than that in $(Ph_3Sn)_2cys$ (3.12 mm s^{-1}), which is close to that observed in triphenyltin acetate (3.36 mm s^{-1}), a five-coordinated one-dimensional polymer [6]. The splitting for the analogues site in $(Ph_3Sn)_2cys$ is lower even than that in triphenyltin *o*-(2-hydroxy-5-methylphenylazo)benzoate (2.38 mm s^{-1}), where steric crowding precludes association, leaving the tin in a distorted *cis*-$[SnC_3O_2]$ trigonal bipyramidal environment [5]. The recoil-free fraction temperature coefficients for the carboxyl tin atoms in both $(Ph_3Sn)_2pen$ and $(Ph_3Sn)_2cys$ (1.59 and 1.26 K^{-1}, respectively) are lower than those for the thiol-bound tin atoms in the same molecules (2.01 and 1.97 K^{-1}, respectively). These two latter values are quite consistent with significant freedom of motion of these tin atoms, whereas the motion of the carboxyl-bound tin atoms is significantly lower. Polymeric triphenyltin acetate exhibits an $-a$ value of 1.91 K^{-1} [6], but the value for monomeric triphenyltin *o*-(2-hydroxy-5-methylphenylazo)benzoate is only 1.59 K^{-1} [5]. Some caution, therefore, needs to be applied in the interpretation of the temperature coefficient data. However, it would appear likely that $(Ph_3Sn)_2$)cys has a polymeric chain structure IX, analogous to that of triphenyltin acetate, whilst a monomeric structure (X) similar to that of triphenyltin *o*-(2-hydroxy-5-methylphenylazo)benzoate is proposed for $(Ph_3Sn)_2pen$. The difference in structure may be accounted for by the steric crowding resulting from the methyl substitution at the thiolato carbon atom.



(IX)



(X)

The isomer shift of histidinatotin(II) (2.94 mm s^{-1}) confirms its bivalent nature, whilst the recoil-free fraction temperature coefficient (1.96 K^{-1}) is much higher

than that of tin(II) formate (0.84 mm s^{-1}), a two-dimensional sheet polymer, and tin(II) oxide (0.23 mm s^{-1}), but much lower than that in stannocene (3.13 mm s^{-1}), crystals of which comprise discrete monomers [9]. We therefore propose an essentially monomeric structure for this compound, but with some moderately weak intermolecular association.

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