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STRUCTURAL STUDIES IN MAIN GROUP CHEMISTRY

III*. TIN-119*m* MÖSSBAUER INVESTIGATION OF SOME TIN–NITROGEN BONDED COMPOUNDS

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SUMMARY

The tin-119*m* Mössbauer data are presented for several classes of organotin–nitrogen bonded compounds, including *N*-stannylamines, -imines, -amides, and -carbamates. The structures of the *N,O*-bis(trialkylstannyl)carbamates are discussed. Those derivatives possessing the Sn–NR–C(O)X group are intermolecularly associated via carbonyl→tin coordination, the strength of the coordination varying with X in the manner $H \approx OSnR_3 > OR$.

In recent years tin-119*m* Mössbauer Spectroscopy has been shown to be a powerful technique for the structural elucidation of organotin compounds[2]. Investigations of tin–nitrogen bonded compounds have so far been confined to studies of organotin(IV) derivatives of amines[3], azole ring systems[4], and pseudohalides[5]. In the lower oxidation state, the tin(II) derivatives of imidazole, triazole[6] and *N*-phenylmethylcarbamate[7] have been studied. Because of the interesting structural possibilities, we have used Mössbauer spectroscopy to study triorganotin carbamates, and in addition some amino– and amido–tin derivatives.

RESULTS AND DISCUSSION

Tin-119*m* Mössbauer data for the tin–nitrogen bonded compounds are collected in Tables 1 and 2. Our data are in excellent agreement with those compounds for which data are already available [compounds (I)[3], (XI)[5] and (XV)[3]], although for compound (I) we have been able, using the narrow-line $Ba^{119m}SnO_3$ source, to discern a small quadrupole splitting not previously observed.

The isomer shifts for the triorganotin derivatives all fall in the narrow range

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* For Part II see ref. 1.

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TABLE 1

TIN-119*m* MÖSSBAUER DATA FOR SOME ORGANOTIN(IV)–NITROGEN COMPOUNDS

No.	*Compound*	δ (*mm/s*)	Δ (*mm/s*)	Γ_1 (*mm/s*)	Γ_2 (*mm/s*)
(I)	Me_3SnNEt_2[a]	1.25	0.92	1.19	1.29
(II)	$Me_3SnNPhSiMe_3$	1.33	1.45	1.27	1.13
(III)	$Me_3SnNPhCO_2SnMe_3$	1.29	3.72	1.86	1.71
(IV)	$Me_3SnN{=}CPh_2$	1.39	1.22	1.00	0.94
(V)	Bu_3SnNMe_2	1.43	1.08	1.62	1.50
(VI)	Bu_3SnNEt_2	1.36	0.93	1.73	1.03
(VII)	$Bu_3SnNPhCHO$	1.39	3.21	1.50	1.31
(VIII)	$Bu_3SnNNpCHO$	1.30	3.39	1.87	1.87
(IX)	$Bu_3SnNEtCO_2Et$	1.42	2.24	1.64	1.27
(X)	$Bu_3SnNPhCO_2Et$	1.53	2.68	1.80	1.22
(XI)	Ph_3SnN_3[b]	1.42	3.28	1.28	1.46
(XII)	$Ph_3SnN{=}PPhMe_2$	1.35		1.60	
(XIII)	$Ph_3SnN{=}PPh_3$	1.38		1.84	
(XIV)	$Me_2Sn(NMe_2)_2$	1.20	1.35	1.84	1.32
(XV)	$Sn(NMe_2)_4$[c]	0.77		1.66	

[a] Ref. 3 gives δ 1.13 mm/s, Δ 0. [b] Ref. 4 gives δ 1.40 mm/s, Δ 3.19 mm/s. [c] Ref. 3 gives δ 0.84 mm/s, Δ 0.

TABLE 2

TIN-119*m* MÖSSBAUER SPECTRA OF *N,O*-BIS(TRIALKYLTIN)CARBAMATES

No.	*Compound*	δ_1 (*mm/s*)	δ_2 (*mm/s*)	δ_3 (*mm/s*)	δ_4 (*mm/s*)
(XVI)	$Pr_3SnNNpCO_2SnPr_3$	−0.37	0.31	2.30	3.25
(XVII)	$Bu_3SnNMeCO_2SnBu_3$	−0.33	0.46	2.27	3.25
(XVIII)	$Bu_3SnNEtCO_2SnBu_3$	−0.28	0.44	2.14	3.37
(XIX)	$Bu_3SnNPhCO_2SnBu_3$	−0.33	0.31	2.41	3.22
(XX)	$Bu_3SnNNpCO_2SnBu_3$	−0.29	0.35	2.16	3.25

1.25–1.53 mm/s. However, the quadrupole splittings range from zero to 3.72 mm/s. Quadrupolar interactions arise when the electric field at the tin nucleus deviates from cubic symmetry. The two principal origins of such perturbations are (*i*) electronic imbalances in the σ-framework of approximately tetrahedral or octahedral geometries, which produce small ($<$ 1.4 mm/s), often unresolvable splittings and (*ii*) changes in coordination number at tin causing gross deviations from cubic symmetry, which produce large (2.2–3.9 mm/s) splittings[8], although secondary effects, *e.g.* π-bonding may not have negligible contributions. Colligative measurements have indicated monomeric character for the stannylamines[9] and -phosphinimines[10], which have quadrupole splittings of ca. 1 mm/s and zero respectively. The fairly large half-height peak widths of the two phosphinimines may indicate unresolved splittings. The *N*-stannylketimine, (IV), and the silylstannylamine, (II), exhibit similar small splittings. Thus it is evident that the quadrupole splittings in these four-coordinate derivatives arise from the small changes induced in the σ-framework by the differing ligand electronegativities. In contrast, triphenyltin azide, for which a structure involving azide groups bridging planar Ph_3Sn moieties increasing the coordination number at tin to five has been proposed, exhibits a quadrupole splitting of 3.28 mm/s.

A priori the reactive Sn–X bonds of R_3SnX (X = H, OR, $OSnR_3$) compounds may react with the multiply-bonded isocyanate N=C=O system in two possible ways to give Sn–N (A) or Sn–O (B) bonded structures[11,*].

$$R_3SnX + R'{-}N{=}C{=}O \rightarrow \underset{(A)}{R_3Sn{-}NR{-}C(O)X} \quad \text{or} \quad \underset{(B)}{R_3Sn{-}O{-}C({=}NR)X} \qquad (1)$$

Since on hydrolysis the adducts yield the *N*-proto derivatives, the tin–nitrogen bonded structure (A) was preferred. The formulation of the triorganotin hydride/isocyanate adducts as *N*-stannylformamide derivatives is corroborated by NMR, UV and IR spectroscopy[12], and in the latter, the lowering of the carbonyl stretching frequency from the parent formamide to that of the adducts by ca. 60 cm^{-1} is indicative of strong carbonyl→tin coordination, rather than a mass effect due to the heavy organotin residue. This has been demonstrated by infrared[13] and X-ray crystallographic studies[14] on (triphenylstannyl)-*N*-phenyl-*N*-benzoylhydroxylamine in which the carbonyl group is *intra*molecularly coordinated to tin, causing the infrared vibration to be lowered by ca. 80 cm^{-1}. Triorganotin derivatives of organic residues, $R_3SnX{-}Y$, which possess in the residue X–Y a second group Y capable of coordination to the metallic centre may adopt either the *cis*- (C) or *trans*-R_3SnXY (D) configuration.

TABLE 3

ASSIGNMENTS OF THE MÖSSBAUER SPECTRA OF THE *N,O*-BIS(TRIALKYLTIN)CARBAMATES

A. Peaks (1)& (4) and (2) & (3)

Compound	$\delta(1,4)$ (*mm/s*)	$\delta(2,3)$ (*mm/s*)	$\Delta(1,4)$ (*mm/s*)	$\Delta(2,3)$ (*mm/s*)
(XVI)	1.49	1.31	3.72	1.99
(XVII)	1.48	1.36	3.61	1.81
(XVIII)	1.50	1.39	3.54	1.70
(XIX)	1.44	1.36	3.55	2.10
(XX)	1.48	1.25	3.55	1.81

B. Peaks (1) & (3) *and* (2) & (4)

Compound	$\delta(1,3)$ (*mm/s*)	$\delta(2,4)$ (*mm/s*)	$\Delta(1,3)$ (*mm/s*)	$\Delta(2,4)$ (*mm/s*)
(XVI)	0.97	1.83	2.67	3.04
(XVII)	0.97	1.83	2.60	2.83
(XVIII)	0.93	1.85	2.41	2.83
(XIX)	1.06	1.76	2.74	2.91
(XX)	0.93	1.80	2.45	2.91

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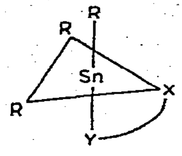
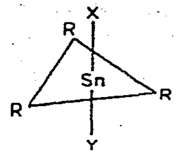
[*] In the case of the adduct of triethyltin hydride and hexyl isocyanate, addition to the N=C bond takes place in the reverse sense to give the $Et_3Sn{-}C(O){-}NH(C_6H_{13})$[12].

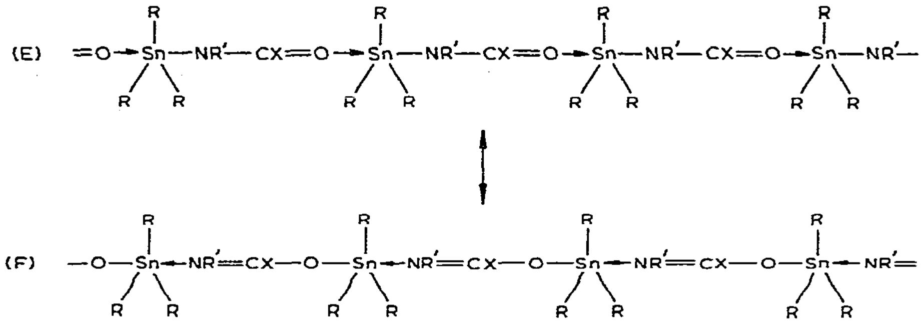


(C)



(D)

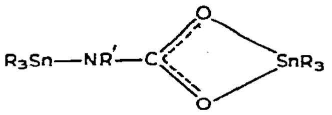
Model compounds of each type for which both structural and Mössbauer data are available, show that derivatives with the *cis* configuration have quadrupole splittings of ca. 2 mm/s[13], whilst the *trans* configuration gives rise to splittings well in excess of 3 mm/s[4,15]. The two *N*-(tributylstannyl)formamide derivatives, (VII) and (VIII), exhibit quadrupole splittings of 3.2–3.4 mm/s, consistent with *inter*molecular coordination, as in (E). Davies and Bloodworth[11] have postulated a rapid interconvertibility of the amido (A) and imido (B) forms of the adducts of the trialkyltin alkoxides and bis(trialkyltin) oxides with isocyanates via *inter*molecular coordination, *viz.*:



(2)

Ethyl-*N*-ethyl- and *N*-phenyl-*N*-(tributylstannyl)carbamate, (IX) and (X), exhibit quadrupole splittings of 2.24 and 2.68 mm/s respectively, supporting a model of rather weak *inter*molecular interaction, which is also indicated by the infrared carbonyl stretching frequency which is lowered by only 20–40 cm^{-1}.

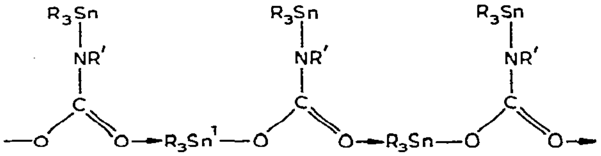
The Mössbauer spectra of the adducts of bis(trialkyltin) oxides and isocyanates exhibited four peaks (Table 2), except for *N*,*O*-bis(trimethylstannyl)-*N*-phenylcarbamate (III) for which only a doublet with a quadrupole splitting of 3.72 mm/s was observed. The *N*,*O*-bis(trialkyltin)carbamates, $R_3Sn^1{-}NR'{-}C(O){-}O{-}Sn^2R_3$, possess two different types of tin, for which two quadrupole split resonances are expected. The four observed lines may therefore be grouped in three possible ways. The assignments, $\delta(1)$ & $\delta(2)$, and $\delta(3)$ & $\delta(4)$, may be ruled out since it would place one of the isomer shifts in the region usually associated with tin in its lower oxidation state[16]. Isomer shift and quadrupole splitting data resulting from the remaining possibilities is given in Table 3. Assignment *B* results in isomer shifts of ca 1.0 and 1.8 mm/s which are both well outside the range of isomer shifts of the other compounds discussed above and other R_3SnX derivatives[17]. Hence the most probable choice appears to be assignment *A*, for which the isomer shifts are in the expected range and the two quadrupole splittings are ca. 3.5 and ca. 2 mm/s. This would require one of the tin atoms to possess a *trans*-R_3SnX_2 configuration, and hence any *intra*molecularly coordinated structure such as



may be ruled out, since the expected quadrupole splitting for neither tin should exceed ca. 2 mm/s.

Observation of the carbonyl stretching region in the infrared indicates strong carbonyl→tin coordination. The Mössbauer data is consistent with the previous model [eqn. (2), X = $OSnBu_3$], where peaks 1 and 4 may be assigned to Sn^1 and peaks 2 and 3 to Sn^2. Tributyltin alkoxides such as Bu_3SnO-t-Bu and $Bu_3SnOCPh_3$ in which steric hindrance prevents any association have quadrupole splitting of ca. 2 mm/s[17], and hence Sn^2 must remain essentially four-coordinate when R = Pr or Bu. For the methyl derivative (III), however, the coordination number of all tin atoms must be raised to five via extra coordination, reflecting the ease with which the Me_3Sn moiety assumes a planar configuration[18].

An alternative structure, (G), may also be considered for the *N*,*O*-bis(trialkyltin)carbamates.



(G)

In this structure the quadrupole splitting expected for the five-coordinate Sn^1 atoms will be ca. 3.5 mm/s, a value observed for the *O*-trialkyltin carbamates and the closely related trialkyltin acetates[17]. The value for the four-coordinate tin–nitrogen bonded Sn^2 atoms is however not expected to exceed ca. 1.5 mm/s. However, this structure may not be unequivocally ruled out.

The strength of the carbonyl–tin coordinate bond of the $R_3Sn{-}NR'{-}C(O)X$ adducts is thus dependent on the group X, and, using the magnitude of the Mössbauer quadrupole splitting as a measure of the distortion from tetrahedral to trigonal bipyramidal, varies in the order $H \approx OSnR_3 > OR$.

EXPERIMENTAL

All manipulations were performed in an inert atmosphere. Compounds (I), (V), (VI), (XIV) and (XVI) were prepared from the organotin chloride and the lithium amine[9]. Compounds (IX) and (X) were prepared from tributyltin ethoxide and the appropriate isocyanate[11], whilst compounds (III) and (XVI)–(XX) were similarly obtained from the bis(trialkyltin) oxide and the isocyanate[19]. The silylstannylamine (II) was synthesised by the addition of trimethyltin chloride to the lithium derivative of *N*-(trimethylsilyl)aniline (from (trimethylsilyl)aniline[20] and butyllithium in ether at

−80°). *N*-(Trimethylstannyl)diphenylketimine (IV) was prepared according to Chan and Rochow[21]. The organotin formamides, (VII) and (VIII) were synthesised by the addition of tributyltin hydride to the appropriate aryl isocyanate[12]. Triphenyltin azide was prepared from the corresponding chloride and sodium azide[22]. The triorganotin phosphinimines, (XII) and (XIII), were prepared from triphenyltin azide and the phosphine at ca. 200° [11].

Tin-119*m* Mössbauer data were collected at 77 K *vs.* a $Ba^{119m}SnO_3$ source, and refined using least squares.

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