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Mössbauer Study of the Solid State Configuration of Triorganotin Derivatives with Intramolecular Coordination

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Triorganotin bromides with intramolecular nitrogen-to-tin coordination (I–VIII, Fig. 1) have been structurally investigated by Mössbauer and infrared spectroscopy. Mössbauer-Zeeman spectra have been measured for I and VIII in order to obtain the sign of the nuclear quadrupole splitting ΔE and the value of the asymmetry parameter η. Point-charge model values of ΔE and η have been calculated for environments of tin atoms in I–VIII which are plausible in view of the results of previous investigations. From trends of experimental ΔE in the series, and from the agreement between experimental and calculated Mössbauer parameters it is concluded that the compounds I–VIII all have trigonal bipyramidal structures with equatorial SnC_3 skeletons. In compound VIII only one of the two Me_2NCH_2 ligands intramolecularly coordinates to tin similar to the situation observed for VIII in solution at low temperature.

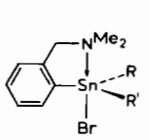
Introduction

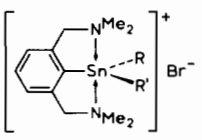
The triorganotin compounds I–VIII with intramolecular nitrogen-to-tin coordination have recently been synthesized [1–6]. It has been reported that the compound (2-$Me_2NCH_2C_6H_4$)$SnEt_2Br$ (V) shows an oligomycin-like activity, inhibiting the ATP-ase complex of whole, rat liver mitochondria [7].

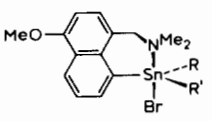
The crystal and molecular geometry of compound I [3], of the $(S)_C(S)_{Sn}$ diastereomer of [(S)-2-Me_2-$NCHMeC_6H_4$]PhMeSnBr, an analogue of compound III [5], of the naphthyl compound VII [6], as well as of the ionic triorganotin compound IV [4] have been determined. The latter compounds have distorted trigonal bipyramidal geometries around the tin atom with equatorial SnC_3 skeletons.

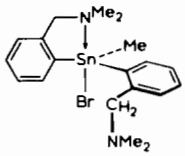
NMR studies have revealed that compounds I–VII have also a pentacoordinate structure in solution [1–6]. For compound VIII containing two 2-Me_2-$NCH_2C_6H_4$ groups a pentacoordinate structure with one Sn–N bond as well as a hexacoordinate structure with two Sn–N bonds is possible. ^{1}H NMR spectra showed that at low temperatures the tin atom is pentacoordinate in solution [2]. At higher temperatures this molecule appeared to be fluxional with the intramolecular rearrangement process involving a hexacoordinate intermediate. A hexacoordinate structure for VIII in the solid cannot be excluded a priori.

In this paper we report the Mössbauer parameters of the pentacoordinate compounds I–VII for which









(I), R = R′ = Ph (IV), R = R′ = Me (VI), R = R′ = Me (VIII)
(II), R = R′ = Me (V), R = R′ = Et (VII), R = Me; R′ = Ph
(III), R = Me; R′ = Ph

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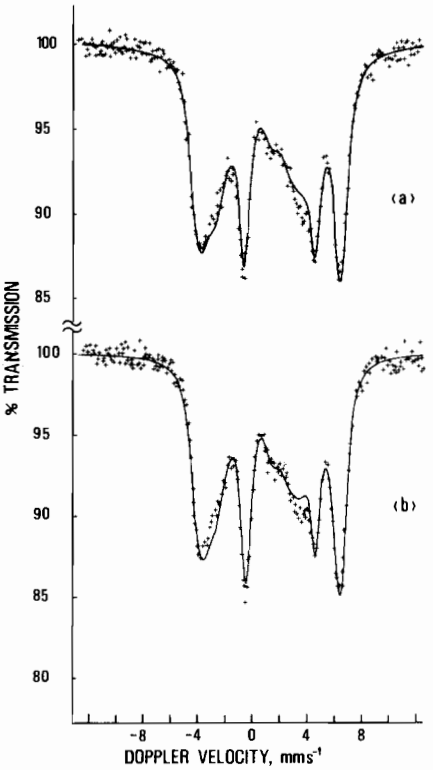

Fig. 1. Mössbauer-Zeeman spectra of (a) 2-$Me_2NCH_2C_6H_4$-$SnPh_2Br$ (I), and (b) (2-$Me_2NCH_2C_6H_4)_2SnMeBr$ (VIII). Full lines are computer fittings.

the structure in the solid is known, and the use of these data for the elucidation of the coordination geometry of VIII in the solid.

Experimental

The organotin compounds I–VIII have been prepared as previously reported [1, 2, 4].

Mössbauer spectra have been measured on sample absorbers at ~77K, with a $Ca^{119}SnO_3$ source, 10 mCi (R.C., Amersham). The source was moving at constant acceleration (triangular and sawtooth waveforms). Apparatus and procedures, including computer data reduction, have been previously described [8]. The Mössbauer–Zeeman spectra of compounds I and VIII have been measured at 4.2 K in a transverse magnetic field of 6 Tesla (data obtained by Nuclear Physics Division, AERE Harwell are shown in Fig. 1). The measured Mössbauer parameters are reported in Table I.

Point-charge model calculations [9] of ΔE and η (see Table I) have been performed according to published procedures [9, 10], employing a computer program written by Dr. T. C. Gibb (University of Leeds). For trigonal bipyramidal structures the following values of partial quadrupole splittings, p.q.s. (mm s^{-1}) have been used [10] (tba and tbe superscripts refer to trigonal bipyramidal apical and equatorial, respectively): $\{Br\}^{tba}$ 0.00; $\{Alk\}^{tbe}$ −1.13; $\{Ph\}^{tbe}$ −0.98; $\{N\}^{tba}$ +0.01 (*i.e.* this corresponds to the value of apical piperidine [10]). These p.q.s.'s are in $\frac{1}{2}e^2|Q|\{L\}$ units [10], and have also been used in the calculation for the actually observed solid state structure of I (see Table I).

The point-charge model equations for the principal components of the E.F.G. tensor [9, 10], in regular trigonal bipyramidal structures (Fig. 2, A) are as follows*: for I (R = R′ = Ph, L = Br), $V_{zz} = 2\{N\}^{tba} -$

TABLE I. Experimental and Calculated Mössbauer Parameters.

Code[a]	δ[b]	$\Delta E_{exp.}$ [$\eta_{exp.}$][c]	$\Delta E_{calcd.}$ [$\eta_{calcd.}$][d]
I	1.32	−2.74 [0.18]	−2.90 [0.15][e]
			−2.96 [0.00]
II	1.37	3.10	−3.27
III	1.35	2.81	−3.12
IV	1.37	3.31	−3.29
V	1.46	3.11	−3.29
VI	1.36	2.99	−3.27
VII	1.36	2.89	−3.12
VIII	1.34	−2.90 [0.12]	−3.12 [0.14]
			+0.14 [0.00] [f]
			−3.26 [0.90] [f]
			+3.40 [0.93] [f]

[a]See introduction for the structures. [b]Isomer shift, mm s^{-1}, with respect to R. T. $CaSnO_3$. [c]Nuclear quadrupole splitting, mm s^{-1}; asymmetry parameter, $\eta = (V_{xx} - V_{yy})/V_{zz}$. Full widths at half height of the resonant peaks are ~0.8 mm s^{-1} for a sample thickness of ~0.5 mg $^{119}Sn/cm^2$. Signs of ΔE and values of η are obtained from Mössbauer-Zeeman spectra, see Fig. 1. The largest standard error of δ and ΔE for our apparatus is ±0.01 mm s^{-1} with the values of $|x - x_{av}|$ being typically 0.02 mm s^{-1}. This has been determined by measuring more than 40 absorbers, at least 5 spectra for each run, repeated for different samples sometimes with intervals of several years. [d]Data obtained by using the point-charge model formalism assuming a regular trigonal bipyramidal structure (Fig. 2, A) unless otherwise stated. Assuming a regular trigonal bipyramidal structure for compounds II–VII $\eta_{calcd.}$ is 0.14. [e]Calculated using input polar coordinates θ and ϕ from crystallographic angles at Sn [3]. [f]Calculated for the octahedral isomers (B), (C) and (D) shown in Fig. 2. See text. Other possible isomers yield values comparable to those of (B, C, D): interchanging Br with one N, the following ΔE [η] are in fact obtained: (B), +0.17 [0.18]; (C), −3.28 [0.88]; (D), + 3.41 [0.95].

*The subsequent identifications of radicals R and R′ refer exclusively to Fig. 2A; substituted phenyl and naphthyl groups are indicated as Ph, since their p.q.s. s are assumed to coincide with that of Ph.

TABLE II. Relevant Infrared Absorptions[a] for I–VIII[b] in the 600–200 cm^{-1} Region.

I	II	III	IV	V	VI	VII	VIII	Assignments[c,d]
				565 vw		545 m		
	550s		560 s	530 m	540 s			$\nu_{as}(SnC_2^{alk})$
	530 ms		535 ms	505 mw	515 m			$\nu_s(SnC_2^{alk})$
		540 ms				525 m	530 m	$\nu(SnC^{alk})$
			490 ms	490 mw	495 m	495 mw		
					470 m	470 m		out-of plane skeletal bending (naphthyl)
460 s	455 s	450 s	475 ms	470 m		460 m 450 m	460 m	y(subs. phenyl)
430 m	430 s	435 m	425 mw	425 vw			435 m	
360 vvw	360 w	360 vvw	385 mw	380 mw	380 mw	380 w	360 w	
				310 mw	315 w	315 w		
280 s	276 ms	280 mw	270 m	280 ms		260 m	296 mw	t,t' (subs. phenyl and naphthyl),
272 s		260 m		270 ms			254 m	corresp. to ν_{as} and $\nu_s(SnAr)$;
					240 m	245 (sh)		u(subs. phenyl); (+ν(SnN) ?)
225 w	234 mo	240 mw	230 m	230 vvw[e]		230 mw	230 mw	

[a] s strong, m medium, w weak, v very, sh shoulder. [b] The structures are shown in the introduction. [c] Aryl group vibrations, *cf.* ref. 11. [d] $\nu_{as,s}(SnC_2)$ and ν(SnC) for Sn–C^{alk} bonds, see ref. 12. [e] Further bands at 217, 211, 205 vvw cm^{-1}.

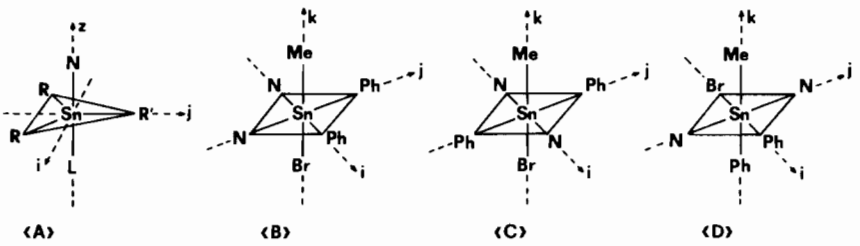

Fig. 2. Principal EFG axes for (A) compounds (I–VIII) in an idealized regular trigonal bipyramidal configuration, and (B–D) for compound (VIII) in presumed regular octahedral structures; (B): a *fac*-R_3 isomer; (C, D): two *mer*-R_3 isomers.

$3\{Ph\}^{tbe}$, $V_{ii} = V_{jj} = -\{N\}^{tba} + 1.5\{Ph\}^{tbe}$ (= V_{xx}, V_{yy}); for II and VI (R = Me, R' = Ph, L = Br), $V_{zz} = 2\{N\}^{tba} - 2\{Alk\}^{tbe} - \{Ph\}^{tbe}$, $V_{ii} = V_{yy} = -\{N\}^{tba} - \{Ph\}^{tbe} + 2.5\{Alk\}^{tbe}$, $V_{jj} = V_{xx} = -\{N\}^{tba} + 2\{Ph\}^{tbe} - 0.5\{Alk\}^{tbe}$; for III, VII and VIII (R = Ph, R' = Me, L = Br), $V_{zz} = 2\{N\}^{tba} - 2\{Ph\}^{tbe} - \{Alk\}^{tbe}$, $V_{ii} = V_{xx} = -\{N\}^{tbe} - \{Alk\}^{tbe} + 2.5\{Ph\}^{tbe}$ $V_{ii} = V_{yy} = -\{N\}^{tba} + 2\{Alk\}^{tbe} - 0.5\{Ph\}^{tbe}$; for IV and V (R = Alk, R' = Ph, L = N), $V_{zz} = 4\{N\}^{tba} - 2\{Alk\}^{tbe} - \{Ph\}^{tbe}$, $V_{ii} = V_{yy} = -2\{N\}^{tba} - \{Ph\}^{tbe} + 2.5\{Alk\}^{tbe}$, $V_{jj} = V_{xx} = -2\{N\}^{tba} + 2\{Ph\}^{tbe} - 0.5\{Alk\}^{tbe}$.

Subsequently, the values $\eta = (V_{xx} - V_{yy})/V_{zz}$, and $\Delta E = \frac{1}{2} e Q V_{zz}(1 + 1/3\,\eta^2)^{1/2}$, have been obtained [9].

In the case of compound VIII ΔE and η have also been calculated for the possible octahedral isomers B, C and D (Fig. 2) as well as for other possible isomers. P.q.s.'s employed are [9]: ([Alk] – [hal]) –1.03, ([Ph]) [hal]) – 0.95, ([N] – [hal]) – 0.01 (*i.e.*, the value of piperidine [9]), $\frac{1}{2} e^2 |Q|$ ($[L]^{oct} - [hal]^{oct}$) units. Point-charge model equations for $V_{\alpha\alpha}$ are (omitting the subtractive term [hal] for brevity): (B), $V_{KK} = V_{ZZ} = 2$ [Alk] – 2 [N] – 2 [Ph], $V_{ii} = V_{jj} =$ [Ph] + [N] – [Alk] (= V_{xx}, V_{yy}); (C), $V_{kk} = V_{xx} = 2$ [Alk] – 2 [Ph] – 2 [N], $V_{ii} = V_{zz} = 4$ [N] – [Alk] – 2 [Ph], $V_{jj} = V_{yy} = 4$ [Ph] – [Alk] – 2 [N] and (D), $V_{kk} = V_{zz} = 2$ [Alk] + [Ph] – 2 [N], $V_{ii} = V_{xx} =$ [Ph] – [Alk] – 2 [N], $V_{jj} = V_{yy} = 4$ [N] – [Alk] – 2 [Ph]. The results are reported in Table I.

The infrared spectra of the compound I–VIII have been measured in the region 4000–200 cm^{-1} with Perkin-Elmer 577 and 580 instruments in CsI discs or

as Nujol mulls between CsI and polyethylene windows. The IR absorption peaks in the 600–200 cm^{-1} region are given in Table II.

Discussion

Little structural information is obtained from the IR spectra of I–VIII. The far IR data in the 600–200 cm^{-1} region (Table II) confirm the bending of the $C_{alk}SnC_{alk}$ skeleton in the dialkyl compounds II and IV–VI as evidenced by the occurrence of both the $\nu_{as}(SnC_2)$ and $\nu_{sym}(SnC_2)$. No information concerning the Sn–Br and Sn–N bonds can be extracted from the spectra. In fact, the ν(SnBr) would occur below 200 cm^{-1} analogous to assignments made for adducts of R_nSnBr_{4-n} [13]. Moreover, vibrations arising from N-to-Sn coordination bonds would be predicted to occur in the same region of the t,t′, u phenyl and naphthyl modes (Table II, *cf.* ν(Sn–N) calcd. 242–253 and ν(Sn–N) found 270 cm^{-1} for $SnCl_4(NMe_3)_2$ [14]) or at lower wavenumbers as the mass of the groups covalently bound to tin increases.

The Mössbauer isomer shifts, δ, reported in Table I, for the compounds I–VII, which have a known structure in the solid, are in the range characteristic of triorganotin halides and their adducts [9]. The minor changes detected along the I–VII series exactly reflect the respective inductive effects of groups bound to Sn in the structures shown for these compounds in the introduction. Experimental nuclear quadrupole splittings ΔE confirm the observed common trigonal bipyramidal type of structure for the compounds I–VII. In fact, the electrical charge is expected to be concentrated in the SnR_3 trigonal plane, whereas the principal component of the electric field gradient tensor, V_{zz} [9], is directed roughly along the NSnBr in I–III and VI, VII and NSnN directions in IV and V. V_{zz} would then bear a positive sign, thus reflecting a negative charge deficiency along these bonds. On the basis of the respective electron donating powers of the various organic ligands in the trigonal planes, and assuming a near equivalence of axial Br and N in this respect, it is predicted that the larger charge imbalance between the trigonal plane and the axial bonds occurs for II and IV–VI which contain alkyl substituents. These compounds would consequently show the larger absolute ΔE values in the series. Moreover, the lesser imbalance, and lower ΔE, would be pertinent to I, while III and VII would be in an intermediate situation. The absolute experimental ΔE values exactly follow this expected trend (Table I).

These qualitative conclusions are supported by the results of the point-charge model calculation as well as by the information concerning the sign of ΔE, and the value of η as obtained from Mössbauer-Zeeman spectra. It clearly appears from Table I that values calculated on the assumption of trigonal bipyramidal structures, Fig. 2, A, are fully consistent with the experimental data, not only with respect to the absolute values which are well within the limiting accepted difference of 0.4 mm s^{-1} [15], but also to the sign of ΔE and the values of η in the case of I. Besides, η of I can be reproduced by taking into account the true molecular structure [3].

As regards the structure of VIII in the solid, looking only at the magnitude and sign of ΔE (both the experimental and calculated values) the trigonal bipyramidal structure (Fig. 2, A) and the octahedral meri-isomer (Fig. 2, C) are equally probable. However, this uncertainty is completely removed by the agreement between experimentally determined and calculated Mössbauer–Zeeman η values of 0.12 and 0.14, respectively, which unequivocally points to a trigonal bipyramidal structure having the most electronegative substituents in the axial positions [16]. A polymeric structure resulting from intermolecular Sn–N bond formation as well as an ionic structure involving two intramolecular Sn–N bonds can be excluded on the basis of the solubility behaviour of VIII [2]. Therefore, it is concluded that VIII has a pentacoordinate structure in the solid with only one of the two Me_2NCH_2 ligands intramolecularly coordinated to Sn similar to that observed for VIII in solution at low temperatures [2].

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