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MÖSSBAUER AND NMR STUDIES OF INTRAMOLECULAR COORDINATION IN THIENYLTETRAORGANOTIN(IV) COMPOUNDS, AND THE X-RAY CRYSTAL STRUCTURE OF {*C,N*-[3-(2-PYRIDYL)-2-THIENYL]}TRI(*p*-TOLYL)TIN(IV)

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Summary

Tetraorganotin(IV) compounds containing the [3-(2-pyridyl)-2-thienyl] group (L), of formula R_3SnL (**1**: R = *p*-tolyl; **2**: R = Ph; **3**: R = *p*-ClC_6H_4; **4**: R = cyclo-C_5H_9; **5**; R = cyclo-C_6H_{11}) have been synthesized and their structures examined by ^{119m}Sn Mössbauer and NMR (^{119}Sn and ^{13}C modes) spectroscopic techniques, and in the case of compound **1** by X-ray analysis.

Compound **1** crystallises in the space group *C*2/*c* with *a* 20.85(1), *b* 9.521(1), *c* 26.69(1) Å; β 95.37(3)°; *V* 5274(3) Å^3; $Z = 8$. Its structure was solved by the heavy-atom method from 4251 observed Mo-K_α data and refined to $R = 0.068$. The coordination environment at tin in the compound is best described as a pseudo-trigonal bipyramid, involving a weak intramolecular Sn–N bond of distance 2.841(7) Å. This view is supported by the observation of partially-resolved Mössbauer spectra for compounds **1–5** (QS 0.57–0.96 mm s^{-1}) which is not evidenced, on the other hand, for (2-thienyl)SnR_3 compounds (**7**: R = *p*-tolyl; **8**: R = Ph), as well as by similar comparisons of data on ^{119}Sn chemical shifts (−176.3 ppm for **1** relative to −135.5 ppm for **8**) and one-bond coupling constants, $^1J(^{119}Sn-^{13}C(1))$, where C(1) = *ipso*-carbon of the aryl group or α-carbon of the cycloalkyl group (647.5 Hz for **1**, 726.6 Hz for **2** and 786.2 Hz for **3** relative to 536.9 Hz for **7**).

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Introduction

A prominent feature of organotin(IV) coordination chemistry is the acceptor property associated with mono-, di- and tri-organotin compounds containing strongly electron-withdrawing groups such as halide or pseudohalide attached to tin [1,2]. In contrast, tetraorganotin compounds, R_4Sn, show little tendency to expand their covalency beyond four. Thus spectroscopic studies in the solid state of R_4Sn compounds containing intramolecular donor sites attached to the α- or β-carbon atom [3] and in donor solvents of compounds containing relatively electronegative carbon moieties such as furyl [4,5], pyridyl [6–8], perhalogenoaryl [9–11] and thienyl [4,5] have generally not provided unequivocal evidence for higher-than-four coordination at the metal centre. However, for one class of tetraorganotins, namely the stannatrane derivatives represented by $Me_2Sn(CH_2CH_2CH_2)_2NMe$ and $MeSn(CH_2CH_2CH_2)_3N$, a multinuclear (^1H, ^{13}C, ^{119}Sn) NMR study has been reported [12] which strongly favours transannular N→Sn interactions in these compounds. The pentacoordinated structure of the triptych compound, $MeSn(CH_2CH_2CH_2)_3N$, has since been confirmed [13]. The literature also contains two references to isolable five-coordinated compounds in $Me_3SnCF_3 \cdot P(NMe_2)_3$ [14] and lithium 1,1-bis(η^1-cyclopentadienyl)-1-halo-2,3,4,5-tetraphenylstannole [15], but the structures of these have not been rigorously clarified.

Recently we succeeded in obtaining a unique six-coordinated tetraorganotin compound, bis{*C*,*N*-[3-(2-pyridyl)-2-thienyl]}diphenyltin(IV) [16]. The crystal structure of this compound revealed a pseudo-octahedral environment at tin (C_2 molecular symmetry), with the coordinating pyridyl nitrogens located *cis* to each other (Sn–N 2.560(2) Å, N–Sn–N 77.1(1)°) along with the phenyl groups (C–Sn–C 101.9(1)°), and the *ipso*-thienyl carbons arranged approximately *trans* to each other (C–Sn–C 144.4(1)°). In the present paper we describe the synthesis of a number of additional R_4Sn compounds containing the novel 2-(3-thienyl)pyridine ligand as one of the R groups, and discuss features of their ^{119m}Sn Mössbauer and NMR (^{13}C and ^{119}Sn) spectra which are indicative of weak Sn–N bonding interaction in a five-coordinated environment. In one case, viz. the title compound {*C*,*N*-[3-(2-pyridyl)-2-thienyl]}tri(*p*-tolyl)tin(IV), structural corroboration was obtained from a single crystal X-ray study.

Experimental

Preparation of {C,N-[3-(2-pyridyl)-2-thienyl]}tri(p-tolyl)tin (1)

To a solution of 2-(3-thienyl)pyridine (1 ml, 7.2 mmol) in dry ether (30 ml), 4.6 ml of a 15% n-BuLi solution in hexane was added dropwise at room temperature with stirring under nitrogen. The resulting brown solution was stirred for ca. 1 h, and then a solution of $(p\text{-tolyl})_3SnCl$ (2.55 g, 6.0 mmol) in dry ether (10 ml) was added dropwise. The reaction mixture was then refluxed for 4 h, after which the LiCl was filtered off and the filtrate concentrated. Dropwise addition of hexane to the filtrate caused immediate precipitation of **1** (2.4 g, 73% yield). Single crystals suitable for X-ray analysis were obtained by recrystallisation from toluene (m.p. 165–167°C, with decomposition). Anal. Found: C, 65.19; H, 4.96; N, 2.54. $C_{30}H_{27}NSSn$ calcd.: C, 65.34; H, 4.90; N, 2.62%. ^1H NMR ($CDCl_3$, 28°C): 7.90–7.85 (1H, m), 7.75–6.91 (17H, m), 2.40 (9H, s); Mass spectrum, *m/e* (rel.

intensity): 462 ($M^+ - C_7H_7$, 100); 393 ($M^+ -$ L, 2.1); 371 ($M^+ - 2C_7H_7$, 9.4); 280 ($M^+ - 3C_7H_7$, 23.9); 211 ($M^+ - 2C_7H_7 -$ L, 2.6); 161 (3-$C_5H_4NC_4H_3S^+$, LH^+, 18.8); 91 ($C_7H_7^+$, 65.6).

The triphenyl- (**2**), tri(*p*-chlorophenyl)- (**3**), tricyclopentyl- (**4**) and tricyclohexyltin (**5**) analogues were similarly prepared: **2**, m.p. 118–120°C; yield, 80%; Found: C, 62.80; H, 4.34; N, 2.61. $C_{27}H_{21}NSSn$ calcd.: C, 63.40; H, 4.11; N, 2.74%. ^1H NMR ($CDCl_3$, 28°C): 7.93–6.44 (m); Mass spectrum, *m/e* (rel. intensity): 434 ($M^+ - C_6H_5$, 100); 440 ($M^+ - 2C_6H_5$, 1.1); 351 ($M^+ -$ L, 0.7); 280 ($M^+ - 3C_6H_5$, 23.3); 274 ($M^+ - C_6H_5 -$ L, 0.5); 197 ($M^+ -$ L $- 2C_6H_5$, 2.9); 160 (3-$C_5H_4NC_4H_2S$, L^+, 13.3).

3, m.p. 125–128°C; yield 50%; Found: C, 52.7; H, 3.14. $C_{27}H_{18}NSClSn$ calcd.: C, 52.7; H, 2.97. ^1H NMR ($CDCl_3$, 28°C): 8.40–8.23 (1H, m); 8.20–7.25 (17H, m). Mass spectrum, *m/e* (rel. intensity): 502 ($M^+ - p$-ClC_6H_4, 33.3); 453 ($M^+ -$ L, 100); 391 ($M^+ - 2p$-ClC_6H_4, 0.9); 342 ($M^+ -$ L $- p$-ClC_6H_4, 33.3); 280 ($M^+ - 3p$-ClC_6H_4, 21); 231 ($M^+ -$ L $- 2p$-ClC_6H_4, 50.9); 161 (3-$C_5H_4NC_4H_3S^+$, LH^+, 48).

4, m.p. 42–43°C; yield, 56%; Found: C, 59.78, H, 6.90; N, 2.86. $C_{24}H_{33}NSSn$ calcd.: C, 59.13; H, 6.78; N, 2.87%. ^1H NMR, ($CDCl_3$, 28°C): 8.36–8.31 (1H, m); 7.75–6.83 (5H, m); 1.81–1.42 (27H, m); Mass spectrum, *m/e* (rel. intensity): 417 ($M^+ -$ cyclo-C_5H_9, 100); 349 ($M^+ -$ 2cyclo-C_5H_9, 1.5); 327 ($M^+ -$ L, 1.7); 280 ($M^+ -$ 3cyclo-C_5H_9, 32.7); 258 ($M^+ -$ L $-$ cyclo-C_5H_9, 1.1); 189 ($M^+ -$ L $-$ 2cyclo-C_5H_9, 2.0); 161 (3-$C_5H_4NC_4H_3S^+$, LH^+, 7.6).

TABLE 1

DATA COLLECTION AND PROCESSING PARAMETERS

Molecular formula	$C_{30}H_{27}NSSn$
Molecular weight	552.30
Cell constants	*a* 20.85(1), *b* 9.521(1), *c* 26.69(1) Å, *β* 95.37(3)°, *V* 5274(3) Å^3, $Z = 8$
Density (exptl.)	1.380 g cm^{-3}
Density (calcd.)	1.391 g cm^{-3}
Space group	*C*2/*c*
Radiation	graphite-monochromatized Mo-K_α, λ 0.71069 Å
Absorption coefficient	10.63 cm^{-1}
Crystal size	0.36×0.28×0.24 mm
Mean μr	0.15 mm
Transmission factors	0.612 to 0.698
Scan type and speed	ω–2θ; 2.02–8.37 deg min^{-1}
Scan range	1° below $K_{\alpha 1}$ to 1° above $K_{\alpha 2}$
Background counting	stationary counts for one-half of scan time at each end of scan
Collection range	$h, k, \pm l$; $2\theta_{max}$ 52°
Unique data measured	4251
Observed data with $\vert F_o \vert > 3\sigma(\vert F_o \vert)$, *n*	3364
Number of variables, *p*	298
$R_F = \Sigma \Vert F_o \vert - \vert F_c \Vert / \Sigma \vert F_o \vert$	0.053
Weighting scheme	$w = [\sigma^2(F_o) + 0.001 \vert F_o \vert^2]^{-1}$
$R_G = [\Sigma w(\vert F_o \vert - \vert F_c \vert)^2 / \Sigma w \vert F_o \vert^2]^{1/2}$	0.068
$S = [\Sigma w(\vert F_o \vert - \vert F_c \vert)^2/(n-p)]^{1/2}$	1.495
Residual extrema in final difference map	+1.18 to −0.85 eÅ^{-3}

5, m.p. 88–90°C; yield, 60%; Found, C. 61.3; H, 7.20; N, 3.18. $C_{27}H_{39}NSSn$ calcd.: C, 61.2; H, 7.37; N, 2.65%. ^1H NMR ($CDCl_3$, 28°C): 8.40–8.23 (1H, m); 7.70–6.70 (5H, m); 2.33–0.83 (33H, m). Mass spectrum, *m/e* (rel. intensity): 446 (M^+ – cyclo-C_6H_{11}, 18.1); 363 (M^+ – 2cyclo-C_6H_{11}, 0.5); 280 (M^+ – 3cyclo-C_6H_{11}, 8.8), 203 (M^+ – L – 2cyclo-C_6H_{11}, 2.4); 161 (3-$C_5H_4NC_4H_3S^+$, LH^+, 100).

Related preparations. For purposes of comparison with compounds **1** and **2**, the corresponding unsubstituted 2-thienyltin derivatives, (2-thienyl)tri(*p*-tolyl)tin(IV) (m.p. 208–210°C) and (2-thienyl)triphenyltin(IV) (m.p. 208–211°C) were synthesized similarly from 2-lithiothiophene in 60–80% yields, and gave satisfactory elemental analyses.

The microanalyses were performed by the Microanalytical Service, University College, London (UK). The ^{119}Sn NMR spectra were recorded on a JEOL-FX60Q

TABLE 2

FRACTIONAL ATOMIC COORDINATES (×10^5 for Sn and S; ×10^4 for other atoms) AND TEMPERATURE FACTORS [a] (Å^2 ×10^4 for Sn and S; ×10^3 for C atoms)

Atom	x	y	z	U_{eq}
Sn	9032(2)	22497(5)	12107(2)	547(2)
S	20491(9)	16056(24)	21615(7)	782(7)
N	1251(3)	–195(6)	689(2)	75(2)
C(1)	1691(3)	1084(7)	1589(3)	61(2)
C(2)	2536(4)	150(10)	2205(3)	94(4)
C(3)	2433(3)	–669(10)	1809(3)	87(3)
C(4)	1944(3)	–139(7)	1450(3)	64(3)
C(5)	1745(3)	–806(7)	965(3)	67(3)
C(6)	2030(5)	–2021(8)	779(4)	100(4)
C(7)	1813(6)	–2556(10)	328(4)	117(5)
C(8)	1315(5)	–1906(11)	39(4)	113(5)
C(9)	1049(4)	–750(11)	248(3)	105(4)
C(10)	–25(3)	1296(7)	1267(2)	58(2)
C(11)	–471(3)	1984(8)	1519(3)	78(3)
C(12)	–1081(3)	1457(9)	1563(3)	82(3)
C(13)	–1283(3)	244(8)	1345(3)	67(3)
C(14)	–837(4)	–478(9)	1100(3)	87(3)
C(15)	–217(4)	27(8)	1062(3)	83(3)
C(16)	–1962(4)	–346(10)	1376(4)	99(4)
C(17)	878(3)	4151(7)	1665(2)	56(2)
C(18)	795(3)	4121(8)	2178(3)	68(3)
C(19)	797(3)	5362(10)	2442(3)	80(3)
C(20)	877(4)	6658(10)	2230(3)	81(3)
C(21)	937(4)	6661(9)	1733(3)	91(4)
C(22)	950(5)	5438(8)	1445(3)	77(3)
C(23)	892(5)	8019(10)	2529(4)	124(5)
C(24)	1041(3)	2993(7)	473(2)	56(2)
C(25)	520(4)	3302(9)	137(3)	75(3)
C(26)	603(4)	3805(9)	–354(3)	92(3)
C(27)	1212(5)	4021(8)	–507(3)	85(3)
C(28)	1728(4)	3716(8)	–167(3)	85(3)
C(29)	1645(3)	3217(8)	314(3)	72(3)
C(30)	1298(6)	4557(11)	–1038(4)	126(5)

[a] Equivalent isotropic temperature factor U_{eq} defined as one-third of the trace of the orthogonalised U_{ij} tensor

TABLE 3

MOLECULAR DIMENSIONS OF{*C,N*-[3-(2-PYRIDYL)-2-THIENYL]}TRI(*p*-TOLYL)TIN(IV) (1) WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

Bond distances (Å)			
Sn–C(1)	2.153(6)	Sn–C(10)	2.155(6)
Sn–C(17)	2.183(6)	Sn–C(24)	2.136(6)
S–C(1)	1.710(7)	S–C(2)	1.715(9)
N–C(5)	1.343(9)	N–C(9)	1.322(11)
C(1)–C(4)	1.346(10)	C(2)–C(3)	1.316(12)
C(3)–C(4)	1.423(10)	C(4)–C(5)	1.467(10)
C(5)–C(6)	1.412(11)	C(6)–C(7)	1.344(14)
C(7)–C(8)	1.381(15)	C(8)–C(9)	1.374(15)
C(10)–C(11)	1.365(10)	C(10)–C(15)	1.372(10)
C(11)–C(12)	1.383(10)	C(12)–C(13)	1.343(11)
C(13)–C(14)	1.369(11)	C(13)–C(16)	1.533(11)
C(14)–C(15)	1.392(11)	C(17)–C(18)	1.394(9)
C(17)–C(22)	1.374(10)	C(18)–C(19)	1.376(12)
C(19)–C(20)	1.374(13)	C(20)–C(21)	1.344(12)
C(20)–C(23)	1.520(14)	C(21)–C(22)	1.397(12)
C(24)–C(25)	1.375(9)	C(24)–C(29)	1.384(10)
C(25)–C(26)	1.420(11)	C(26)–C(27)	1.385(13)
C(27)–C(28)	1.372(12)	C(27)–C(30)	1.534(13)
C(28)–C(29)	1.394(11)	Sn–N	2.841(7)
Bond angles (deg)			
C(1)–Sn–C(10)	113.6(2)	C(1)–Sn–C(17)	102.9(2)
C(10)–Sn–C(17)	104.0(2)	C(1)–Sn–C(24)	116.2(2)
C(10)–Sn–C(24)	113.7(2)	C(17)–Sn–C(24)	104.5(2)
C(1)–S–C(2)	91.9(4)	C(5)–N–C(9)	118.7(7)
Sn–C(1)–S	121.3(4)	Sn–C(1)–C(4)	128.2(5)
S–C(1)–C(4)	110.3(5)	S–C(2)–C(3)	111.9(6)
C(2)–C(3)–C(4)	112.6(8)	C(1)–C(4)–C(3)	113.3(6)
C(1)–C(4)–C(5)	122.1(6)	C(3)–C(4)–C(5)	124.5(7)
N–C(5)–C(4)	115.9(6)	N–C(5)–C(6)	119.3(7)
C(4)–C(5)–C(6)	124.8(7)	C(5)–C(6)–C(7)	120.5(9)
C(6)–C(7)–C(8)	120.2(10)	C(7)–C(8)–C(9)	116.3(10)
N–C(9)–C(8)	125.0(8)	Sn–C(10)–C(11)	119.4(5)
Sn–C(10)–C(15)	125.0(5)	C(11)–C(10)–C(15)	115.6(6)
C(10)–C(11)–C(12)	122.9(7)	C(11)–C(12)–C(13)	121.8(7)
C(12)–C(13)–C(14)	116.1(7)	C(12)–C(13)–C(16)	123.0(7)
C(14)–C(13)–C(16)	120.9(7)	C(13)–C(14)–C(15)	122.6(8)
C(10)–C(15)–C(14)	120.9(7)	Sn–C(17)–C(18)	122.7(5)
Sn–C(17)–C(22)	119.5(5)	C(18)–C(17)–C(22)	117.8(6)
C(17)–C(18)–C(19)	119.4(7)	C(18)–C(19)–C(20)	123.6(8)
C(19)–C(20)–C(21)	115.8(8)	C(19)–C(20)–C(23)	123.2(8)
C(21)–C(20)–C(23)	121.0(8)	C(20)–C(21)–C(22)	123.4(8)
C(17)–C(22)–C(21)	119.9(8)	Sn–C(24)–C(25)	120.5(5)
Sn–C(24)–C(29)	122.6(5)	C(25)–C(24)–C(29)	116.9(6)
C(24)–C(25)–C(26)	121.2(7)	C(25)–C(26)–C(27)	121.1(7)
C(26)–C(27)–C(28)	117.3(8)	C(26)–C(27)–C(30)	120.8(8)
C(28)–C(27)–C(30)	121.9(9)	C(27)–C(28)–C(29)	121.5(8)
C(24)–C(29)–C(28)	122.1(7)	N–Sn–C(1)	65.8(2)
N–Sn–C(10)	87.8(2)	N–Sn–C(17)	166.6(2)
N–Sn–C(24)	76.0(2)	Sn–N–C(5)	108.0(4)
Sn–N–C(9)	133.6(4)		

instrument operating at 22.24 MHz under nuclear Overhauser-suppressed conditions [17]; the field frequency lock was to external D_2O. ^1H and ^{13}C NMR spectra were recorded on a JEOL JNM-FX100 spectrometer operating at 99.55 MHz for ^1H and 25.00 MHz for ^{13}C. Complete proton decoupling irradiation was used to record the ^{13}C spectra in $CDCl_3$, with the solvent also providing the internal lock. All spectra were recorded at ambient temperatures, concentrated solutions being used for the ^{13}C data and the concentrations specified in Table 6 for the ^{119}Sn spectra. ^{119m}Sn Mössbauer spectra were obtained at 80 K by use of the constant-acceleration microprocessor spectrometer described previously [18]. The broad, partially resolved, resonance lines obtained for compounds **1–5** were each fitted as a Lorentzian doublet by a least-squares fitting programme [19]. The Mössbauer data are tabulated in Table 5. Mass spectra were recorded on an AE1 MS 3074 double beam mass spectrometer under the following conditions: electron energy, 70 eV; pressure, 1–3 torr; current, 300 μA; source temperature, 150–170°C.

X-Ray analysis

Diffraction measurements on the title complex, **1**, were made on a Nicolet R3m four-circle diffractometer (graphite-monochromatized Mo-K_α radiation, λ 0.71069 Å). The crystal class, orientation matrix, and accurate unit-cell parameters were determined by standard procedures [20]. Intensities were recorded at 22°C, and data collection and processing parameters are summarized in Table 1. Absorption corrections were applied by fitting a pseudo ellipsoid to azimuthal scans of selected strong reflections [21]. The structure was solved by the heavy-atom method. All non-hydrogen atoms were refined anisotropically. The 18 ring hydrogens were placed in positions calculated on the basis of sp^2-hybridization (C–H 0.96 Å) of their respective parent C atoms, and were assigned isotropic temperature factors. Some methyl hydrogens were located by Fourier synthesis and the methyl groups were refined as rigid groups. All calculations were performed on a Data General Corporation Nova 3/12 minicomputer with the SHELXTL programme package [22]. Analytic expressions of neutral-atom scattering factors incorporating the real and imaginary components of anomalous dispersion were employed [23]. Blocked-cascade least-squares refinement [24] converged to the R values and other parameters listed in Table 1. Fractional atomic coordinates and temperature factors of the non-hydrogen atoms are given in Table 2, and bond distances and angles in Table 3. Tables of hydrogen parameters, anisotropic temperature factors, torsion angles and structure factors are available from the authors.

Results and discussion

The crystal structure of the title compound, **1**, consists of a packing of discrete molecules as shown in Fig. 1. A stereoview of an individual molecule is shown in Fig. 2, which reveals along with the bond angle data (Table 3) a configuration intermediate between a tetrahedron and a trigonal bipyramid. The distortion towards the higher coordination geometry is especially evident upon comparing the bond angles of **1** with those of the distorted tetrahedral tetrakis(2-thienyl)tin molecule [25]. Thus, in the latter the bond angles are all opened to 112.6° [25], while in **1**, two sets of C–Sn–C bond angles may be discerned, viz. 102–104° and

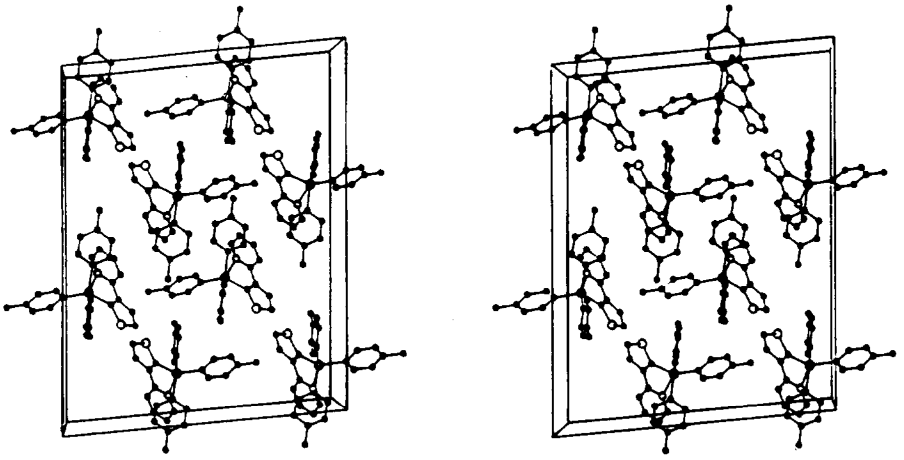

Fig. 1. Stereo-drawing showing the molecular packing in 1. The unit cell lies at the upper left corner, with *a* pointing from left to right, *b* towards the reader, and *c* downwards.

113–116°, the first being those subtended at tin by C(17) with each of the other *ipso*-carbons. Equally noteworthy is the appreciably longer Sn–C(17) bond distance relative to other Sn–C$_{ipso}$ bonds in the molecule (Table 3). If these trends are interpreted in terms of a pseudo-trigonal bipyramidal structure, then the pyridyl nitrogen and the tolyl *ipso*-carbon, C(17), would occupy approximately apical positions consistent with the C(17)–Sn–N bond angle of 166.6(2)°; the corresponding angles involving other *ipso*-carbons are generally less than half of this value. However, the absence of a well-defined trigonal plane comprising the atoms C(1),

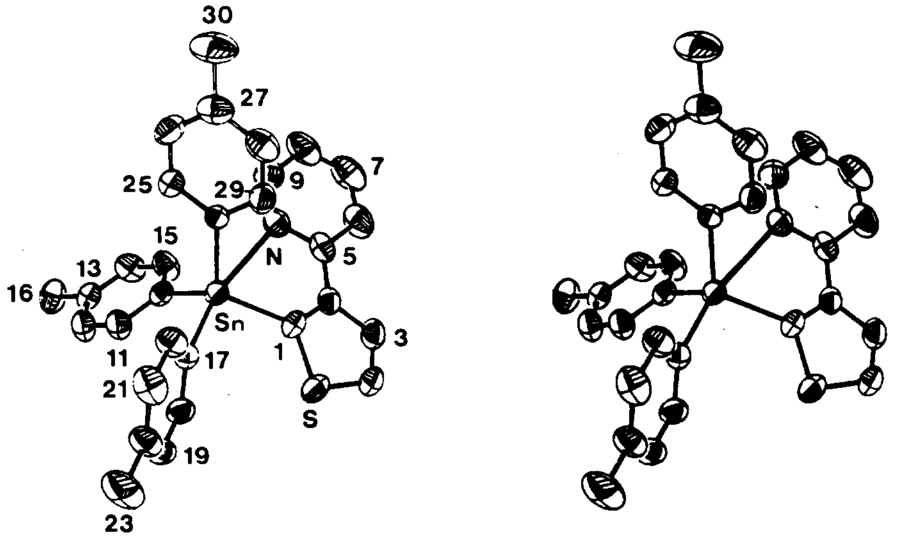

Fig. 2. ORTEP plot (35% thermal ellipsoids) with atom labelling of {*C*,*N*-[3-(2-pyridyl)-2-thienyl]}tri(*p*-tolyl)tin(IV) (1).

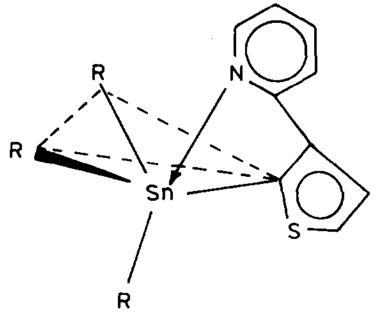

Fig. 3. Schematic representation of the structural form assumed by compounds **1**–**5**.

C(10) and C(24) (Fig. 3) is implied in the sum of only 343.5(4)° for the "equatorial" angles, and the displacement of Sn from this quasi basal plane by 0.51(1) Å towards C(17). The coordinative approach of the pyridyl nitrogen is facilitated by a torsional twist of −6.2(1)° between the thienyl and pyridyl rings. The Sn atom is seen to lie in the plane of the pyridyl ring (sum of angles subtended at N by C(5), C(9) and Sn equals 360.3(11)°); the bisector of the C(5)–N–C(9) angle, however, makes an appreciable angle of 13(1)° with the Sn–N bond. The ligand 'bite' angle is 65.8(2)°, which is smaller than the corresponding value of 70.3(1)° in the pseudo-octahedral bis{*C*,*N*-[3-(2-pyridyl)-2-thienyl]}diphenyltin(IV) molecule, **6** [16]. There is also a lesser torsional twist (−2.6(3)°) between the thienyl and pyridyl rings in the latter instance. These differences, which presumably reflect the different steric demands for coordination of the ligand in the two cases, lead to the observed difference in the Sn–N bond lengths: 2.841(7) Å for **1** versus 2.560(2) Å for **6**. The longer Sn–N bond distance in **1** represents a weak interaction as judged on the basis of Sn–N bond lengths previously reported for a range of di- and triorganotin(IV) compounds. A tabulation of the available data is given in Table 4 for selected cases, including the compound $[Ph_2SnCl_2 \cdot pyz]_n$ [26] which shows two independent Sn–N bond lengths (2.782(11) and 2.965(11) Å) in the polymeric chain, the latter distance being the longest ascribed to Sn←N complexation. It is seen that in all cases the values exceed the sum of atomic radii of Sn and N (2.10 Å) [27], suggesting that the Sn–N bond has a low degree of covalent character [28]. Interestingly, for both **1** and **6** there is no evidence for orientational disorder of the thienyl groups such as is encountered in tetrakis(2-thienyl)tin [25] and $(3\text{-thienyl})_3SnBr \cdot Ph_3PO$ [29], implying that the pyridyl substituents in the first two cases lead to coordinative "anchoring" of the thienyl units at tin.

The title complex, **1**, yielded a partially-resolved ^{119m}Sn Mössbauer spectrum at 80 K which was fitted as a Lorentzian doublet with a quadrupole splitting of 0.57 mm s^{-1}. A similar curve-fitting programme was used to obtain the quadrupole splittings for the analogous complexes, **2**–**5** (Table 5). The Mössbauer spectra for compounds **1** and **4** are illustrated in Fig. 4. On the other hand, unresolved spectra were obtained for $(2\text{-thienyl})_2Sn(p\text{-tolyl})_2$, $(2\text{-thienyl})Sn(p\text{-tolyl})_3$ and $(2\text{-thienyl})SnPh_3$, even with extended spectral accumulation (Table 5). Although the Mössbauer literature on tetraorganotins abounds in anomalies of resolvable and non-resolvable spectra [30] which caution against structural conclusions, it is in-

TABLE 4. COMPARISION OF TIN-NITROGEN LIGAND BOND LENGTHS IN {*C*,*N*-[3-(2-PYRIDYL)-2-THIENYL]}TRI(*p*-TOLYL)TIN(IV) (**1**), WITH THOSE IN SELECTED ORGANOTIN(IV) COMPOUNDS CONTAINING NITROGEN DONOR LIGANDS

No	Compound	Sn–N (Å)	Ref.
1	$Me_3SnCl \cdot py$	2.26	41
2	$(p\text{-}ClC_6H_4)_2SnCl_2 \cdot 4,4'\text{-}Me_2bipy$		42
	cis-isomer	2.294(6); 2.322(6)	
	trans-isomer	2.406(8)	
3	$(p\text{-tolyl})_2SnCl_2 \cdot bipy$	2.306(3); 2.374(6)	18
4	$Ph_2SnCl_2 \cdot bipy$	2.344(6); 2.375(6)	43
5	$ClSn(CH_2CH_2CH_2)_3N$	2.372(29)	12
6	$Cl_2Sn(CH_2CH_2CH_2)_2NMe$	2.44	13
7	n-Pr(Et)Sn(quin)$_2$ [a]	2.542(5); 2.597(6)	44
8	$Ph_2SnCl_2 \cdot SC_7H_5N$	2.548(2)	45
9	$[3\text{-}(2\text{-py})\text{-}2\text{-}C_4H_2S]_2SnPh_2$ (**6**)	2.560(2)	16
10	$MeSn(CH_2CH_2CH_2)_3N$	2.62	13
11	$Ph_3SnSC_5H_4N$	2.62(2) [b]	46
12	$[3\text{-}(2\text{-py})\text{-}2\text{-}C_4H_2S]Sn(p\text{-tolyl})_3$ (**1**)	2.841(7)	[c]
13	$(Ph_2SnCl_2 \cdot pyz)_n$ [d]	2.965(11); 2.782(11)	26

[a] Hquin = 2-methylquinolin-8-ol. [b] Reported as intermolecular Sn–N distance. [c] This work. [d] pyz = pyrazine.

TABLE 5. ^{119m}Sn MÖSSBAUER DATA [a] (mm s^{-1}) AT 80 K

Compound	IS [b]	QS	Γ_1	Γ_2	Ref.
$[3\text{-}(2\text{-py})\text{-}2\text{-}C_4H_2S]Sn(p\text{-tolyl})_3$ (**1**)	1.07	0.57	0.88	0.93	[c]
$[3\text{-}(2\text{-py})\text{-}2\text{-}C_4H_2S]SnPh_3$ (**2**)	1.11	0.63	1.07	1.30	[c]
$[3\text{-}(2\text{-py})\text{-}2\text{-}C_4H_2S]Sn(p\text{-}ClC_6H_4)_3$ (**3**)	1.13	0.59	1.15	1.03	[c]
$[3\text{-}(2\text{-py})\text{-}2\text{-}C_4H_2S]Sn(cyclo\text{-}C_5H_9)_3$ (**4**)	1.29	0.92	1.02	1.10	[c]
$[3\text{-}(2\text{-py})\text{-}2\text{-}C_4H_2S]Sn(cyclo\text{-}C_6H_{11})_3$ (**5**)	1.35	0.96	1.11	0.98	[c]
$[3\text{-}(2\text{-py})\text{-}2\text{-}C_4H_2S]_2SnPh_2$ (**6**)	1.03	0.73	1.03	1.14	16
$(2\text{-}C_4H_3S)SnPh_3$	1.16	0	1.14 [d]		[e]
$(2\text{-}C_4H_3S)Sn(p\text{-tolyl})_3$	1.21	0	1.09 [d]		[e]
$(2\text{-}C_4H_3S)_2Sn(p\text{-tolyl})_2$	1.10	0	1.19 [d]		[e]

[a] Error ±0.05 mm s^{-1}. [b] Relative to $CaSnO_3$ or $BaSnO_3$. [c] This work. [d] Γ_{av} of the single peak. [e] V.G. Kumar Das and K.M. Lo, unpublished results.

TABLE 6. ^{119}Sn NMR DATA

Compound	Solvent (conc. w/w)	δ [a] (ppm)	Ref.
$[3\text{-}(2\text{-py})\text{-}2\text{-}C_4H_2S]Sn(p\text{-tolyl})_3$ (**1**)	$CDCl_3$ (0.12/1.5)	−176.3	[b]
$[3\text{-}(2\text{-py})\text{-}2\text{-}C_4H_2S]SnPh_3$ (**2**)	$CDCl_3$ (0.08/1.3)	−181.6	[b]
$[3\text{-}(2\text{-py})\text{-}2\text{-}C_4H_2S]Sn(p\text{-}ClC_6H_4)_3$ (**3**)	$CDCl_3$ (0.08/1.3)	−180.0	[b]
$[3\text{-}(2\text{-py})\text{-}2\text{-}C_4H_2S]Sn(cyclo\text{-}C_5H_9)_3$ (**4**)	$CDCl_3$ (0.4/1.5)	−57.8	[b]
$[3\text{-}(2\text{-py})\text{-}2\text{-}C_4H_2S]Sn(cyclo\text{-}C_6H_{11})_3$ (**5**)	$CDCl_3$ (0.11/1.3)	−105.9	[b]
$[3\text{-}(2\text{-py})\text{-}2\text{-}C_4H_2S]_2SnPh_2$ (**6**)	$CDCl_3$ (0.1/1.5)	−245.5	16
$(3\text{-}C_4H_3S)Sn(p\text{-tolyl})_3$	$CDCl_3$ (10) [c]	−157.8	29
$(3\text{-}C_4H_3S)_2Sn(p\text{-tolyl})_2$	$CDCl_3$ (0.1/1.5)	−146.3	[d]
$(2\text{-}C_4H_3S)SnPh_3$	$CDCl_3$ (0.08/2.0)	−135.5	[b]
$(2\text{-}C_4H_3S)_2Sn(p\text{-tolyl})_2$	$CDCl_3$ (0.07/1.5)	−138.0	[d]
$(2\text{-}C_4H_3S)_2SnPh_2$	$CDCl_3$ (0.13/1.5)	−140.8	[d]
$(2\text{-}C_4H_3S)_2SnMe_2$	$CDCl_3$ (0.4/1.5)	−62.7	[d]
$(2\text{-}C_4H_3S)_4Sn$	$CDCl_3$ (7) [c]	−147.0	3
Ph_4Sn	$CDCl_3$ (saturated)	−128.1	36
$(cyclo\text{-}C_5H_9)_4Sn$	$CDCl_3$ (0.13/1.5)	−18.3	[e]

[a] Relative to Me_4Sn. [b] This work. [c] Concentration in w/v %. [d] V.K. Kumar Das, K.M. Lo and S.J. Blunden, unpublished results. [e] V.G. Kumar Das, G.C. Ong and S.J. Blunden, unpublished results.

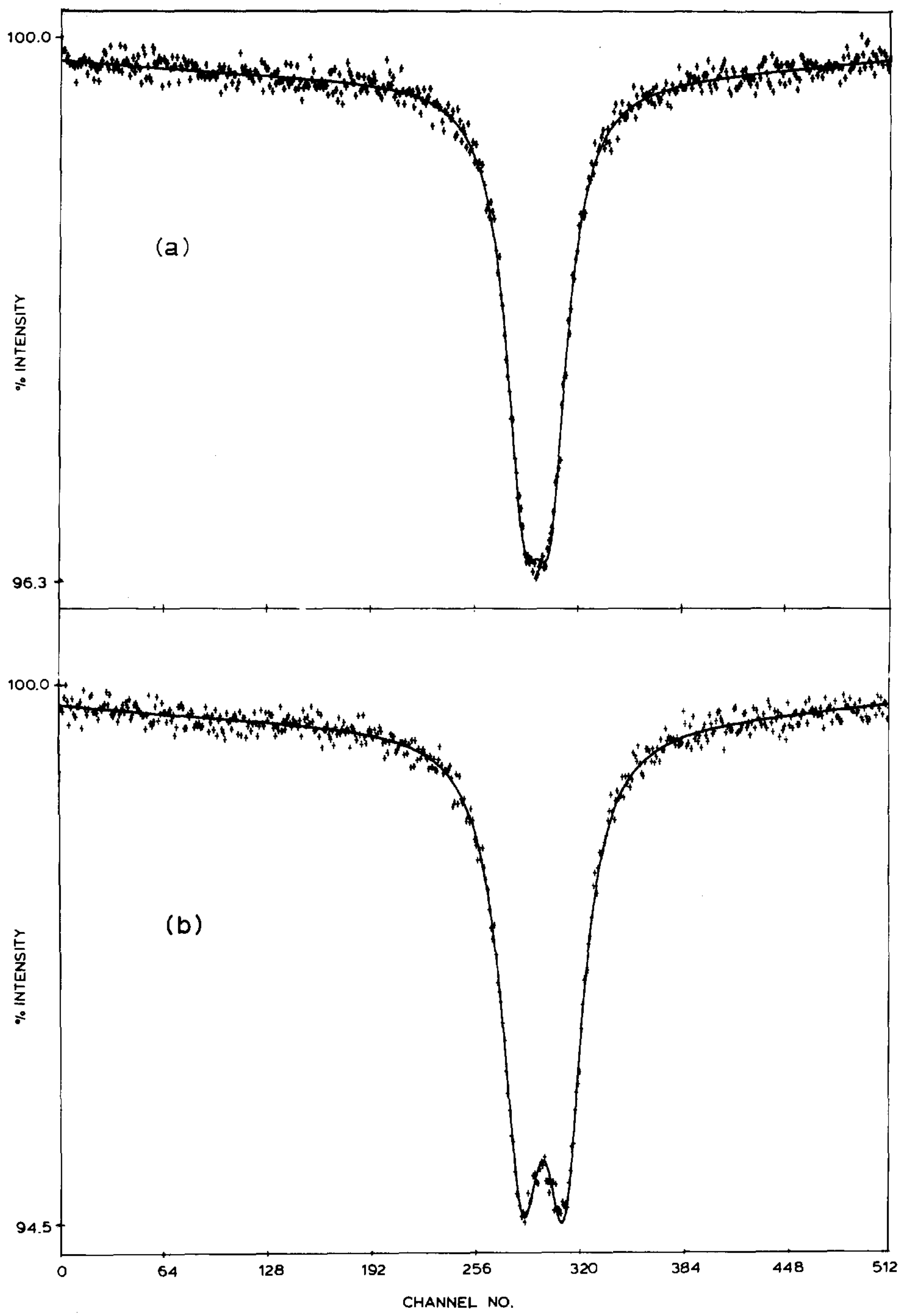

Fig. 4. Mössbauer spectra at 80 K of (a) compound 1, (b) compound 4.

TABLE 7

CARBON-13 NMR DATA FOR SOME THIENYLTIN(IV) COMPOUNDS [a,b,c]

Compound	$C_i(C_\alpha)$	$C_o(C_\beta)$	$C_m(C_\gamma)$	$C_p(C_\delta)$	C(1)	C(2)	C(3)	C(4)	C(5)	C(6)	C(7)	C(8)	C(9)
[3-(2-py)-2-C_4H_2S]Sn(p-tolyl)$_3$(**1**)	137.2	136.9	128.9	137.8	147.4	125.5	133.9	141.3	152.4	121.7	138.6	118.9	148.6
	(647.5)	(41.7)	(56.4)	(11.7)	[d]	(45.5)	(29.0)	[d]					
[3-(2-py)-2-C_4H_2S]$SnPh_3$(**2**)	137.3	136.8	128.0	128.2	137.3	125.5	134.2	147.4	152.1	121.7	142.3	118.8	147.7
	(726.6)	(39.6)	(43.2)	(11.7)	[d]	(45.4)	(32.2)	[a]					
[3-(2-py)-2-C_4H_2S]Sn(p-ClC_6H_4)$_3$(**3**)	138.2	137.9	128.4	129.3	134.8	125.5	135.0	147.6	152.0	122.2	139.9	119.1	151.8
	(786.2)	(45.3)	(57.3)	[d]	[d]	(49.6)	(39.3)	[d]					
[3-(2-py)-2-C_4H_2S]Sn(cyclo-C_3H_9)$_3$(**4**)	27.1	31.2	26.3		147.2	126.3	131.7	140.4	154.4	121.0	154.4	119.8	148.3
	(396.7)	(14.7)	(57.4)		[d]	(31.7)	(15.9)	[d]					
[3-(2-py)-2-C_4H_2S]Sn(cyclo-C_6H_{11})$_3$(**5**)	30.3	32.2	29.5	27.2	147.5	126.5	131.7	139.2	154.6	120.9	136.5	119.8	148.2
	(374.8)	(15.9)	(62.3)	(< 7)	[d]	(31.7)	(13.4)	[d]					
[3-(2-py)-2-C_4H_2S]$_2SnPh_2$(**6**)	135.5	136.3	127.6	137.1	144.9	124.9	132.2	145.7	152.3	121.3	146.5	118.7	147.6
	(794.9)	(43.2)	(56.6)	(< 10)	[d]	(50.8)	(32.2)	[d]					
(2-C_4H_3S)Sn(p-tolyl)$_3$(**7**)	134.5	136.9	129.4	138.8	133.8	129.5	131.8	137.2					
	(536.9)	(41.7)	(52.0)	(11.7)	[d]	(54.2)	(20.6)	(38.8)					
(2-C_4H_2S)$SnPh_3$(**8**)	137.4	137.0	128.8	129.4	132.4	128.3	132.1	137.3					
	[d]	(39.1)	(53.7)	(11.0)	[d]	(44.2)	(19.5)	(33.1)					

[a] In concentrated $CDCl_3$ solution. [b] *i (ipso), o (ortho), m (meta), p (para)* refer to aryl carbon atoms; α, β, γ, δ refer to carbon atoms of the cycloalkyl ring; C(1)–C(9) refer to carbon atoms of the heterocyclic moiety (see Fig. 2). [c] Coupling constants (in parentheses) reported are for $^{n}J(^{119}Sn-^{13}C)$. [d] Coupling constants cannot be estimated from data.

structive that only compounds **1**–**6**, off the thienyltin compounds listed in Table 5, which contain the pyridyl substituent, display partially-resolved spectra.

The ^{119}Sn NMR spectrum of **1** in $CDCl_3$ at 30°C shows a single sharp resonance at -176.3 ppm (relative to Me_4Sn). This value differs marginally from the average values noted for tetrakis(2-thienyl)tin and the range of mixed thienylaryltins listed in Table 6. A much lower frequency shift ($\Delta\delta > 100$ ppm) is, however, noted for compound **6** which contains two pyridyl-substituted thienyl groups. Whereas on the basis of $\delta(^{119}Sn)$, a non-tetrahedral environment at tin in solution can be confidently predicted [31,32] for **6**, a similar conclusion for **1** appears to be less secure. For compound **4**, the ^{119}Sn signal appears at -57.8 ppm; the high frequency shift relative to **1** in this case is explicable [33] in terms of the reduced electronegativity of the cyclopentyl group relative to aryl. For tetracyclopentyltin, $\delta(^{119}Sn)$ is -18.3 ppm. More informative, however, from the standpoint of structural assignments, are the ^{13}C NMR spectral data secured for the compounds, particularly the one-bond couplings, $^1J(^{119}Sn-^{13}C_{ipso,\alpha})$. Studies on n-butyl- [34,35] and aryl-tin(IV) [36,37] compounds have demonstrated that the time-averaged one-bond couplings, $^1J(^{119}Sn-^{13}C)$, provide a sensitive measure of the state of hybridization at tin and increase with coordination number in these compounds. Further, a recent study [37] indicates that the magnitudes of these coupling constants in the series of complexes, $(p\text{-}ZC_6H_4)_3SnClL$ ($Z = CH_3$, H, Cl; L = neutral, monodentate oxygen donor), strongly reflect the acceptor strength sequence, $(p\text{-}ClC_6H_4)_3Sn > (C_6H_5)_3Sn > (p\text{-}tolyl)_3Sn$, deduced from infrared and Mössbauer spectral evidence. In the present context, it is instructive that $^1J(^{119}Sn-^{13}C_{ipso})$, where C_{ipso} refers to the *ipso*-carbon of the aryl group bonded to tin, has the value of 786.2 Hz for **3**, 726.6 Hz for **2** and 647.5 Hz for **1** (Table 7). The value for **3** is close to that observed for **6** (794.9 Hz). In contrast, for (2-thienyl)Sn(p-tolyl)$_3$, ^1J has the value 536.9 Hz. Similarly, for compound **4**, ^1J has the value of 396.7 Hz which compares favourably with the values of 386.7 and 399.9 Hz noted for $(cyclo\text{-}C_5H_9)_3SnCl \cdot Ph_3PO$ and $[(cyclo\text{-}C_5H_9)_3Sn(DMSO)_2]^+ [BPh_4]^-$ respectively [38]; tetracyclopentyltin, on the other hand, has the value 328.0 Hz. Although dynamic behaviour in solution cannot be entirely precluded, we consider these data to be fairly diagnostic of intramolecular N→Sn interactions in the compounds **1**–**6**. A more rigorous assessment of the higher-than-four coordination status of tin in these compounds, however, must await ^{15}N NMR spectral measurements [39,40], particularly of the one-bond couplings, $^1J(^{119}Sn-^{15}N)$, which provide evidence for spin-transfer.

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