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Syntheses and spectra of triphenyltin heteroarenethiolates Crystal structures of triphenyltin 1-methyltetrazole-5-thiolate and triphenyltin benzoxazole-2-thiolate

Carla V. Rodarte de Moura[a], Ana P.G. de Sousa[a], Rosalice M. Silva[a,*], Anuar Abras[b], Manfredo Hörner[c], Adailton J. Bortoluzzi[c], Carlos A.L. Filgueiras[d], James L. Wardell[e]

[a]*Departamento de Quimica, Universidade Federal de Minas Gerais, 31270-901, Belo Horizonte, MG, Brazil*
[b]*Departamento de Fisica, Universidade Federal de Minas Gerais, 31270-901, Belo Horizonte, MG, Brazil*
[c]*Departamento de Quimica, Universidade de Santa Maria, 97119-000, Santa Maria, RS, Brazil*
[d]*Instituto de Quimica, Departamento de Quimica, Universidade Federal do Rio de Janeiro, C.P. 68563, 21945-970, Rio de Janeiro, RJ, Brazil*
[e]*Department of Chemistry, University of Aberdeen, Meston Walk, Old Aberdeen AB24 3UE, UK*

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Abstract

Reactions between Ph_3SnCl and the sodium salts of 5-mercapto-1-methyltetrazole (MTS-H), 2-mercaptobenzoxazole (MBZ-H), 2-mercaptobenzothiazole (MBT-H) and 2-mercapto-1-methylimidazole (MMI-H) gave Ph_3Sn(MTS) (**5**: R=Ph, R′=Me), Ph_3Sn(MBZ) **6**, Ph_3Sn(MBT) **7** and Ph_3Sn(MMI) **8**, respectively. Characterisation has been carried out for all compounds by IR, Mössbauer, ^1H, ^{13}C and ^{119}Sn NMR spectroscopy as well as by X-ray crystallography for (**5**: R=Ph, R′=Me) and **6**. Both (**5**: R=Ph, R′=Me) and **6**, in the solid state, have *cis*-trigonal bipyramidal geometries due to intramolecular Sn–N(2) interactions. Mössbauer data for **7** was interpreted as indicating a similar *cis*-trigonal bipyramid geometry. The chelating ability of nitrogen-containing heteroarenethiolato groups, based on the strength of Sn–N inter-molecular bonds in Ph_3SnS-heteroarenes, decreases in the sequence: pyridine-2-thiolato>pyrimidine-2-thiolato>1-methylimidazole-2-thiolato>benzoxazole-2-thiolato>1-methyltetrazole-5-thiolato>1-phenyltetrazole-5-thiolato. On dissolution, the Sn–N interactions in **5**–**8** undergo at least partial breakage.

Keywords: X-ray crystallography; Triorganotin thiolates; Chelates; Mössbauer; Organotin compounds

1. Introduction

The coordination chemistry of tin is extensive with various geometries and coordination numbers known for both inorganic and organometallic compounds [1]. Higher coordination numbers can be generated either by inter- and/or intra-molecular interactions, especially in compounds where tin bonds to electronegative atoms, such as oxygen, nitrogen and sulfur. While tin is generally classified as a hard acid, many organotin–sulfur bonded compounds are known. Solid state structures of several triorganotin thiolates, R_3SnSR', have been reported and are listed in the Cambridge Crystallographic Data Base. Simple triorganotin thiolates, R_3SnSR', i.e. compounds in which the R′ groups contain no donor centres, are invariably 4-coordinate compounds, with essentially tetrahedral structures: examples of such compounds are Ph_3SnSPh [8] and Ph_3SnSMe [9]. However, if the R′ group does contain a donor centre [N or O], the coordination number at tin *can* increase, usually to five but also to six. As shown by triorganotin heteroarenethiolates, the higher coordination number can arise either via intramolecular coordination of the tin centre with the donor atom, e.g., as in **1** [10], **2** [11], **3** [12], **4** [13] and (**5**: R=R′=Ph) [14], or intermolecularly as in triphenyl(4-pyridinethiolato)stannane [15] or by both intra- and intermolecular interactions as in (**5**: R=Me or $PhCH_2$, R′=Ph) [16]. The geometry of the tin centre in the 5-coordinate triorganotin thiolates is usually distorted trigonal bipyramidal, as found in **1**, **3**, **4** and (**5**: R=Ph, R′=Ph): however,

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*Corresponding author. Tel.: +55-31-499-5734; fax: +55-31-499-5700.

E-mail address: rosalice@apob.qui.ufmg.br (R.M. Silva)

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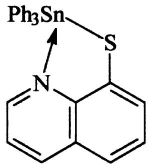
in one case, **2**, a square pyramidal geometry was reported [11]. Six-coordinate compounds, (**5**: R=Me or $PhCH_2$, R′=Ph), were described as having capped trigonal bipyramidal structures [16].



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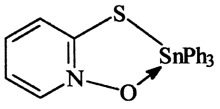

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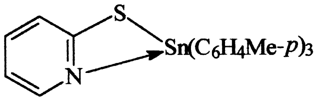

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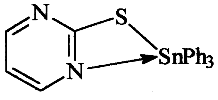

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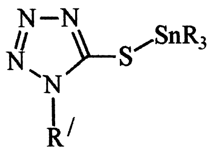

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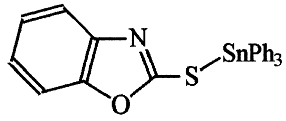

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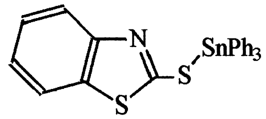

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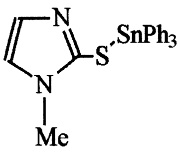

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The intramolecularly coordinated species **1** (as also does **2**) contains a 5-membered chelate ring, which has been shown by NMR spectroscopy to persist on dissolution [18]. Four-membered chelate rings, as in **3**, **4** and (**5**: R=R′=Ph), being more strained, are generally less stable than the 5-membered rings and may not persist in solution.

We have investigated the structures of four triphenyltin heteroarenethiolate derivatives, (**5**: R=Ph, R′=Me), **6**–**8** in the solid state, as well as in solution, and have compared our data with those for similar triphenyltin thiolates in the literature. To obtain a good comparison of the chelating abilities of heteroarenethiolato groups (SAr_{HET}), which form 4-membered chelate rings in R_3SnSAr_{HET} compounds, really requires the R groups to be the same throughout the series being compared. The Mössbauer and NMR solution spectra of (**5**: R=Ph, R′=Me), **6**–**8** have been determined as have the crystal structures of (**5**: R=Ph, R′=Me) and **6**. The crystal structure of **8** was published during the course of our investigation [19]; unfortunately suitable crystals of **9** could not be obtained for an X-ray study.

2. Experimental

2.1. Materials and methods

All operations were carried out under nitrogen using Schlenk and vacuum techniques. Nitrogen was dried over molecular sieves. Hexane, tetrahydrofuran and toluene were distilled over sodium/benzophenone. Acetone was distilled and stored under nitrogen over molecule sieves.

Triphenyltin chloride and sodium 1-methyltetrazole-5-thiolate (MTS-Na), 2-mercaptobenzothiazole (MBT-H) from Aldrich, and 2-mercaptobenzoxazole (MBZ-H), from Merck, and 2-mercapto-1-methylimidazole (MMI-H), from Fluka, were used as supplied.

^{119}Sn Mössbauer spectra were recorded with the sample at liquid nitrogen temperature and a constant accelerated $CaSnO_3$ source, maintained at room temperature. All Mössbauer spectra were computer-fitted, assuming Lorentzian line-shapes. Infra-red spectra in the 4000–200 cm^{-1} region were recorded on a Perkin-Elmer 283 spectrometer in CsI plates. ^{1}H, ^{13}C and ^{119}Sn NMR spectra were recorded on Brucker AC-200 and AC-400 instruments and were referenced to $SiMe_4$ (for H and C) and $SnMe_4$ (for Sn). C, H, N analyses were performed using a Perkin-Elmer PE-2400 CHN Micro-analyser. Tin analyses were carried out using a Hitachi Z-8200 Polarized Zeeman Atomic Absorption Spectrophotometer.

2.2. Syntheses

2.2.1. Sodium benzoxazole-2-thiolate (MBZ-Na)

A mixture of 2-mercaptobenzoxazole (MBZ-H) (0.30 g, 2.00 mmol) and CH_3ONa (0.11 g, 2.00 mmol) in THF (40 ml) in a Schlenk flask was stirred at room temperature for 4 h. The white precipitate of MBZ-Na was collected, washed three times with THF and dried. The IR spectrum indicated the absence of the ν(S–H) absorption band at 2500 cm^{-1} [20]. Sodium benzothioxazole-2-thiolate (MBT-Na) and sodium 1-methylimidazole-2-thiolate (MMI-Na) were prepared similarly.

2.2.2. Triphenyltin benzoxazole-2-thiolate (Ph_3SnMBZ), **6**

A reaction mixture of MBZ-Na (0.45 g, 2.59 mmol) and Ph_3SnCl (1.00 g, 2.59 mmol) in THF (80 ml) in a Schlenk flask was refluxed for 4 h, cooled to room temperature and filtered through celite. The solvent from the filtrate was evaporated under vacuum. The yellow-oily residue was washed three times with hexane/acetone (1:1): the title compound was crystallised from CH_2Cl_2/hexane and was obtained as a pale yellow solid, yield 85%, m.p. 83.3–86.2°C. Found: C, 59.3; H, 3.7; N, 2.9; Sn, 24.6. $C_{25}H_{19}NOSSn$ requires: C, 60.0; H, 3.7; N, 2.7; Sn, 23.7%. ^{1}H NMR ($CDCl_3$): δ: 7.11–7.48 (m, C_6H_4), 7.60–7.89 (m, C_6H_5). ^{13}C NMR ($CDCl_3$): δ: 109.6–152.6 (aryl-

C), 165.0 (C=N). ^{119}Sn NMR ($CDCl_3$): δ: -78.9. Mössbauer spectrum (mm/s): $\delta=1.34\pm0.01$; $\Delta=2.03\pm0.02$. IR (CsI, cm^{-1}): ν(C=N) 1705, ν(Sn–S) 290.

2.2.3. Triphenyltin benzothioxazole-2-thiolate (Ph_3SnMBT), *7*

A reaction mixture of MBT-Na (0.47 g, 2.46 mmol) and Ph_3SnCl (0.94 g, 2.46 mmol) in THF (80 ml) in a Schlenk flask was refluxed for 2 h, cooled to room temperature and evaporated under vacuum. The yellow-oily solid residue was washed with hexane (6×20 ml) and was crystallised from CH_2Cl_2/hexane as a pale yellow solid, yield 83%, m.p. 88.8–90.4°C (lit. value 89–90° [21]). Found: C, 57.4; H, 3.7; N, 2.7; Sn, 22.8. $C_{25}H_{19}NS_2Sn$ requires: C, 58.2; H, 3.7; N, 2.7; Sn, 23.0%. ^{1}H NMR ($CDCl_3$): δ: 7.24–7.89 (m, C_6H_5). ^{13}C NMR ($CDCl_3$): δ: 122.2–137.6 (aryl-C), 139.9 (C=N). ^{119}Sn NMR ($CDCl_3$): δ: -91.4. Mössbauer spectrum (mm/s): $\delta=1.32\pm0.01$; $\Delta=1.79\pm0.01$. IR (CsI, cm^{-1}): ν(Sn–S) 290.

2.2.4. Triphenyltin 1-methyltetrazole-5-thiolate (Ph_3SnMTS), (*5*: R=Ph, R′=Me)

A reaction mixture of MTS-Na (0.36 g, 2.59 mmol) and Ph_3SnCl (1.00 g, 2.59 mmol) in THF (80 ml) in a Schlenk flask was refluxed for 4 h, cooled to room temperature and concentrated under vacuum. The yellow-oily solid residue was extracted with hexane (3×20 ml) and the combined hexane extracts were evaporated to leave an oily residue, which was crystallised from acetone/hexane as a white solid, yield 88%, m.p. 88.5–90.1°. Found: C, 52.2, H, 3.9, N, 11.7, Sn, 23.7. $C_{20}H_{18}N_4SSn$ requires C, 51.7, H, 3.9, N, 12.0, Sn, 24.6%. ^{1}H NMR ($CDCl_3$): δ: 3.82 (s, CH_3), 7.02–7.96 (m, C_6H_5). ^{13}C NMR ($CDCl_3$): δ: 33.8 (CH_3), 129.5–142.9 (aryl-C), 153.6 (C=N). ^{119}Sn NMR ($CDCl_3$): δ: -70.9. Mössbauer spectrum (mm/s): $\delta=1.36\pm0.01$; $\Delta=2.48\pm0.01$. IR (CsI, cm^{-1}): ν(Sn–S) 310.

2.2.5. Triphenyltin 1-methylimidazole-2-thiolate (Ph_3SnMMI), *8*

A reaction mixture of MMI-Na (0.36 g, 2.59 mmol) and Ph_3SnCl (1.00 g, 2.59 mmol) in THF (50 ml) in a Schlenk flask was refluxed for 16 h, cooled to room temperature and evaporated under vacuum. The yellow-oily solid residue was filtered through a Sephadex column and was eluted with methanol. Triphenyltin 1-methylimidazole-2-thiolate was obtained as a white solid, yield 83%, m.p. 73.9–76.7°C. Found: C, 56.62; H, 4.38; N, 6.32; Sn, 26.3. $C_{22}H_{20}N_2SSn$ requires: C, 57.1; H, 4.40; N, 6.00; Sn, 25.6%. ^{1}H NMR ($CDCl_3$): δ: 3.43 (s, CH_3), 6.77 (d, CH), 6.90 (d, CH), 7.31–7.75 (m, C_6H_5). ^{13}C NMR ($CDCl_3$): δ: 33.4 (CH=), 119.7 (CH), 128.3 (CH), 128.7–137.1 (aryl-C), 138.5 (C=N). ^{119}Sn NMR ($CDCl_3$): δ: -57.7 and -112.9 at ambient temperature; lit. value -112.2 [18]. Mössbauer spectrum (mm/s): $\delta=1.28\pm0.01$; $\Delta=2.98\pm0.01$. IR (CsI, cm^{-1}): ν(Sn–S) 290.

2.3. Crystal structure determination

Colorless crystals of (**5**: R=Ph, R′=Me) and **6** were mounted on a glass fiber and used for intensity data collection. The unit cell dimensions and the orientation matrix for the data collection for both compounds, resulted from a least square fit of 25 reflections. The automatic intensity search and indexing method indicated a cell belonging to an monoclinic crystal system with a *C* lattice (for **6**) and belonging to a monoclinic crystal system with a *P* lattice [for (**5**: R=Ph, R′=Me)]. X-ray intensity data were collected on an Enraf-Nonius CAD-4 diffractometer using Mo Kα radiation ($\lambda=0.71073$ Å) and a graphite monochromator [22], employing ω–2θ scans with a scan speed of 30 s/reflection. Every 60 min, the intensity and orientation of the standard reflections were measured; the observed intensity decay was less than 0.6% over the data collection. From the Bravais lattice and observed reflection conditions, the space group was chosen to be *Cc* for **6** and *P*2(1)/*c* for (**5**: R=Ph, R′=Me). Lorentz and polarization corrections were made on the intensity data. Despite the low linear absorption coefficients observed [(1.248 (**6**) and 1.394 mm^{-1} (**5**: R=Ph, R′=Me)], a semi-empirical absorption correction based on psi-scans were performed on intensity data [22].

The structures were solved using the direct methods employing SHELXS-86 program [23] and all non-hydrogen atoms were located by subsequent Fourier difference synthesis. For structure refinement the SHELXL-97 program [24] was employed and the full-matrix least-squares method minimized on $\Sigma\ w(F_o^2-F_c^2)^2$ where w is a weighting scheme detailed below. All non-hydrogen atoms were refined using anisotropic thermal parameters. All the hydrogen atoms were obtained geometrically and their displacement parameters were refined isotropically on a groupwise basis. For the final refinement of the structure an isotropic extinction correction was included. Scattering factors for all atoms were as in the SHELXL-97 program [24]. The final refinements including 263 parameters gave $R_1=2.29\%$ and $wR_2=6.10\%$ with the weighting scheme, $w=1/[\sigma^2(F_o^2)+(0.0327P)^2+6.8036P]$ where $P=(F_o^2+2F_c^2)/3$ with a maximal shift/e.s.d.=1.684 for **6** and including 236 parameters gave $R_1=2.05\%$ and $wR_2=5.12\%$ with the weighting scheme, $w=1/[\sigma^2(F_o^2)+(0.0209P)^2+0.6416P]$ where $P=(F_o^2+2F_c^2)/3$ with a maximal shift/e.s.d.=0.311 for (**5**: R=Ph, R′=Me). Table 1 summarizes the crystal data and structure refinement parameters for **6** and (**5**: R=Ph, R′=Me). The ZORTEP package was used for the molecular drawings [25].

Table 1
Crystal data and structure refinement

Compound	**6**	(**5**: R=Ph, R′=Me)
Empirical formula	$C_{25}H_{19}NOSSn$	$C_{20}H_{18}N_4SSn$
Formula weight	500.16	465.13
Temperature (K)	293(2)	293(2)
Wavelength (λ)	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic
Space group	*Cc*	$P2_1/c$
Unit cell dimensions		
a (Å)	8.629(2)	9.584(2)
b (Å)	38.534(8)	21.854(4)
c (Å)	6.856(1)	9.603(3)
β (°)	100.62(3)	96.80(3)
Volume ($Å^3$)	2240.6(8)	1997.2(7)
Z	4	4
Density (calc.) (Mg/m^3)	1.483	1.547
Absorption coefficient (mm^{-1})	1.248	1.394
Max/min transmission factors	0.96289/0.91237	0.98848/0.91828
F(000)	1000	928
Crystal size (mm)	0.16×0.30×0.47	0.47×0.40×0.36
Theta range for data collection (°)	2.88 to 25.15	2.33 to 25.28
Index ranges	$-10 \leq h \leq 10$ $-46 \leq k \leq 0$ $0 \leq l \leq 8$	$-11 \leq h \leq 11$ $0 \leq k \leq 26$ $-11 \leq l \leq 0$
Reflections collected	2189	3860
Independent reflections	2181	3631
Observed reflections [$I>2\sigma(I)$]	2181	3631
R(int)	0.0181	0.0122
Refinement method	Full-matrix l.s. on F^2	Full-matrix l.s. on F^2
Number of parameters	263	236
Goodness-of-fit on F^2	1.043	1.097
Final *R* indices [$I>2\sigma(I)$]	$R1=0.0229$, $wR2=0.0610$	$R1=0.0205$, $wR2=0.0512$
R indices all data	$R1=0.0334$, $wR2=0.0734$	$R1=0.0309$, $wR2=0.0545$
Final weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0327P)^2+6.8036P]$ where $P=(F_o^2+2F_c^2)/3$	$w=1/[\sigma^2(F_o^2)+(0.0209P)+0.6416P]$ where $P=(F_o^2+2F_c^2)/3$
Absolute structure parameter	0.01(4)	
Residual diffraction max/min (e/A^3)	0.529/−0.836	0.322/−0.221

3. Results and discussion

3.1. Synthesis

Compounds were prepared by reaction of the sodium thiolate with Ph_3SnCl. All were crystalline solids. Compound **8** was particularly sensitive to hydrolysis to give Ph_3SnOH [δ $^{119}Sn=-89.8$ ppm] in solution, as found previously [19].

3.2. Crystal structures of (**5**: R=Ph, R′=Me) and **6**

Atom arrangements and numbering systems for (**5**: R=Ph, R′=Me) and **6** are shown in Figs. 1 and 2. Selected bond distances, bond angles and torsion angles are listed in Tables 2 and 3.

The four primary bonds to Sn in **6** are to the three phenyl groups [Sn–C between 2.118(7) and 2.145(7) Å] and to S [Sn–S=2.458(2) Å], in addition there is a weak intramolecular Sn–N interaction [Sn–N(2)=3.070(6) Å], thus providing a 4-membered chelate ring with a bite

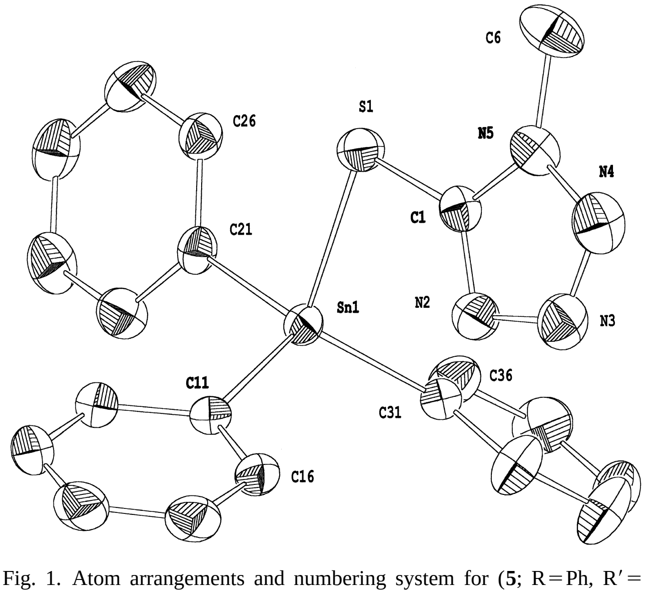


Fig. 1. Atom arrangements and numbering system for (**5**; R=Ph, R′=Me). Probability ellipsoids drawn at 30%.

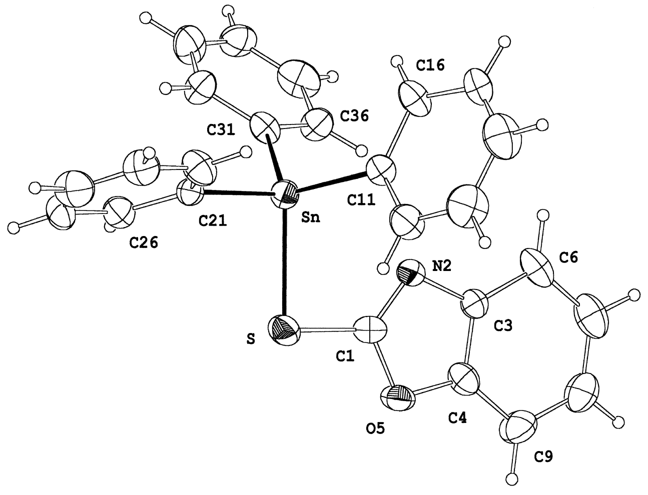


Fig. 2. Atom arrangements and numbering system for **6**. Probability ellipsoids drawn at 30%.

angle, N(2)–Sn–S(1), of 57.3(1)°. The Sn–S bond length in **6** is slightly outside the range [2.39–2.44 Å] found in 4-coordinate R_3SnSR' compounds [8]. The Sn–N(2) distance is midway between the sums of the van der Waals and covalent radii of Sn and N, 3.74 and 2.15 Å, respectively [27]. Including the tin–nitrogen interaction, the geometry at Sn becomes distorted *cis*-trigonal bipyramidal with C(21) and N(2) in axial sites [C(21)–Sn–N(2) = 154.7(2)°]. The Sn atom is displaced by 0.631(4) Å from the geometric centre of the equatorial plane of C(11), C(31) and S. The oxygen atom is not involved in coordination to any tin centre. The observed Flack parameter [28] 0.01(4), suggests that only one of the enantiomeric pair of **6** is present in the unit cell.

Crystalline (**5**: R = Ph, R′ = Me) has a similar distorted trigonal pyramidal geometry with a tin–nitrogen intramolecular interaction with Sn–C bond lengths of between 2.131(2) and 2.139(2) Å, Sn(1)–S(1) = 2.4708(8) and Sn(1)–(N2) = 3.161(3) Å. The axial–Sn–axial angle, [C(21)–Sn(1)–N(2)], is 153.5(8)° with a chelate bite angle of 56.61(6)°. The Sn(1) atom is displaced by 0.630(1) Å from the geometric centre of the equatorial plane of C(11), C(31) and 5(1). None of the other nitrogen atoms, N(1), N(3) and N(4) interact with tin centres. Molecule (**5**: R Ph, R′ = Me), thus, has a similar structure to compound (**5**: R = Ph, R′ = Ph) [14] in existing as discrete distorted trigonal bipyramidal molecules, in contrast to capped trigonal bipyramidal (**5**: R = Me or $PhCH_2$, R′ = Ph) [16]: additional inter-molecular Sn–N interactions result in (**5**: R = Me, R′ = Ph) existing as a cyclic trimer and (**5**: R = $PhCH_2$, R′ = Ph) as a linear polymer. The differences in these structures result more from differences in the steric demands of the R groups than from differences in their electronic effects.

3.3. Comparison of the solid state structures of triphenyltin heteroarenethiolates

The solid state structures of several triorganotin heteroarenethiolates have now been determined by X-ray crystallography. Table 4 provides structural details of triphenylstannylthiolato derivatives of nitrogen-containing heteroarenes, in which the thiolate group is *ortho* to a ring nitrogen, as well as of **1**. Although a structure determination of triphenyltin pyridine-2-thiolate (**9**, Ar = Ph) has been attempted, disorder prevented an adequate solution being obtained [12]: however structural details of the close analogue, tri(*p*-tolyl)tin pyridine-2-thiolate, **3**, are available [12]. As the influence of the R group on the structure of a R_3SnSR' compound appears to be due more to steric than electronic effects, the bond length data for tri(*p*-tolyl)tin pyridine-2-thiolate is assumed to be similar to

Table 2
Selected bond lengths (Å) and angles (°) for (**5**: R = Ph, R′ = Me) with e.s.d.'s in parenthesis

S(1)–C(1)	1.730(3)	S(1)–Sn(1)	2.4708(8)
Sn(1)–C(31)	2.131(2)	Sn(1)–C(11)	2.134(2)
Sn(1)–C(21)	2. 139(2)	Sn(1)–N(2)	3. 161(3)
N(2)–C(1)	1.322(3)	N(2)–N(3)	1.355(3)
N(3)–N(4)	1.288(4)	N(4)–N(5)	1.340(3)
N(5)–C(1)	1.336(3)	N(5)–C(6)	1.448(4)
C(1)–S(1)–Sn(1)	96.55(9)	C(31)–Sn(1)–C(11)	120.73(9)
C(31)–Sn(1)–C(21)	110.24(9)	C(11)–Sn(1)–C(21)	110.32(9)
C(31)–Sn(1)–S(1)	109.53(7)	C(11)–Sn(1)–S(1)	106.33(7)
C(21)–Sn(1)–S(1)	96.99(7)	C(1)–N(2)–N(3)	105.6(2)
N(2)–Sn(1)–S(1)	56.61(6)	N(2)–Sn(1)–C(11)	82.34(9)
N(2)–Sn(1)–C(2 1)	153.5(1)	N(2)–Sn(1)–C(31)	80.09(9)
N(4)–N(3)–N(2)	110.6(2)	N(3)–N(4)–N(5)	107.2(2)
C(1)–N(5)–N(4)	107.9(2)	C(1)–N(5)–C(6)	129.2(3)
N(4)–N(5)–C(6)	122.8(3)	N(2)–C(1)–N(S)	108.7(2)
N(2)–C(1)–S(1)	127.1(2)	N(5)–C(1)–S(1)	124.2(2)
C(26)–C(21)–Sn(1)–S(1)	164.8(2)	C(12)–C(11)–Sn(1)–S(1)	95.6(2)
C(32)–C(31)–Sn(1)–S(1)	82.5(3)		

Table 3
Selected bond lengths (Å) and angles (°) for **6** with e.s.d.'s in parenthesis

Sn–C(11)	2.118(7)	Sn–C(21)	2.131(7)
Sn–C(31)	2. 145(7)	Sn–S	2.458(2)
Sn–N(2)	3.070(8)	S–C(1)	1.724(8)
N(2)–C(1)	1.286(9)	N(2)–C(3)	1.422(9)
O(5)–C(1)	1.368(9)	O(5)–C(4)	1.379(9)
C(3)–C(4)	1.361(10)	C(3)–C(6)	1.380(11)
C(11)–Sn–C(21)	108.3(3)	C(11)–Sn–C(31)	118.2(3)
C(21)–Sn–C(31)	110.3(3)	C(11)–Sn–S	108.8(2)
C(21)–Sn–S	98.4(2)	C(31)–Sn–S	111.0(2)
N(2)–Sn–S(1)	57.3(1)	N(2)–Sn–C(11)	76.8(2)
N(2)–Sn–C(21)	154.8(3)	N(2)–Sn–C(31)	87.1(2)
C(1)–S–Sn	95.0(2)	C(1)–N(2)–C(3)	103.8(6)
C(1)–O(5)–C(4)	103.3(5)	N(2)–C(1)–O(5)	115.9(7)
N(2)–C(1)–S	127.2(6)	O(5)–C(1)–S	116.9(5)
C(4)–C(3)–C(6)	121.7(7)	C(4)–C(3)–N(2)	108.2(6)
C(6)–C(3)–N(2)	130.1(7)	C(26)–C(21)–Sn–S	59.7(7)
C(12)–C(11)–Sn–S	35.6(7)		
C(36)–C(31)–Sn–S	67.8(7)		

those for triphenyltin pyridine-2-thiolate and hence are included in Table 4.

Compound **1** was reported to have a 5-membered chelate ring, with Sn–S and Sn–N bond lengths of 2.441(3) and 2.427(3) Å and 2.592(9) and 2.611(8) Å, respectively, in two independent molecules [10], see Table 4. Crystal structure determinations of all the other 5-coordinate triphenyltin heteroararenethiolates listed in Table 4 revealed intramolecular Sn–N interactions and strained 4-membered chelate rings [12]. A comparison of the donor abilities (chelating abilities) of the heteroaryl units is readily available from the Sn–N intramolecular bond lengths: the shorter the Sn–N separation, the stronger the interaction. The Sn–N bond in **1**, with the 5-membered chelate ring, is shorter than in any of the 4-membered chelates. The chelating ability sequence, based on the Sn–N bond lengths, is: quinoline-8-thiolato > pyridine-2-thiolato > pyrimidine-2-thiolato > 1-methylimidazole-2-thiolato > benzoxazole-2-thiolato > 1-methyltetrazole-5-thiolato > 1-phenyltetrazole-5-thiolato. Two conclusions from this comparison are (i) the 6-membered heteroaryl species [pyridinyl and pyrimidinyl] provide stronger chelates than do the 5-membered species and (ii) weaker donors are obtained on increasing substitution of carbon by nitrogen atoms. The Sn–S bond in the 5-coordinate triphenyltin heteroarenethiolates are all slightly longer than Sn–S bonds in 4-coordinate R_3SnSR': however, there is no obvious relationship between Sn–S and Sn–N bond lengths in these 5-coordinate species.

3.4. Mössbauer spectra

Mössbauer spectra were obtained in this study for (**5**: R = Ph, R′ = Me) and **6**–**8**; details are included in Table 4 along with literature values for other compounds [13]. The Mössbauer data for **7** are particularly valuable since suitable crystals of **7** could not be grown for X-ray crystallographic study.

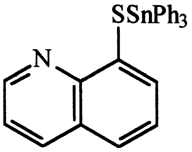
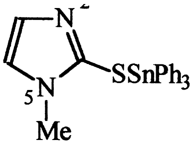
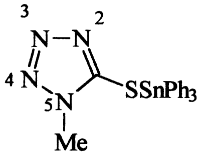
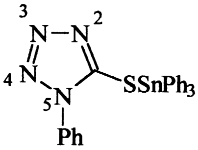
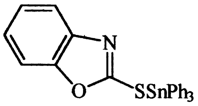
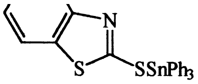
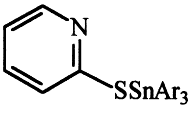
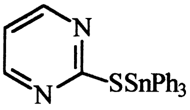
The isomer shift value for **1**, with the stronger Sn–N interaction, was reported to be 1.20 mm/s [31], compared to the range of 1.26 to 1.36 mm/s for the other heteroarenethiolates, **4**–**9**, with the weaker Sn–N interactions, as well as for 4-coordinate $Ph_3SnSC_6H_4X$-*p* [32]. The quadrupole splitting for **1** was reported to be 1.37 mm/s [31]: values for **4**–**9** are in the range from 1.60 (for **4**) to 2.98 mm/s (for **8**) and for $Ph_3SnSSC_6H_4X$-*p*, which are ca. 1.3–1.4 mm/s. An approximate range of quadrupole splitting values for *cis*-trigonal bipyramidal, [*fac*-R_3], R_3SnX compounds is quoted as being 1.70–2.55 mm/s and overlaps both the ranges for tetrahedral [1.2–3.3 mm/s] and (*eq*-R_3)-trigonal bipyramidal [2.4–4.2 mm/s] R_3SnX species [33]. However, there is no doubt from the X-ray work that the solid triphenyltin heteroarenethiolates are all *cis*-trigonal bipyramidal R_3SnX compounds, albeit with weak Sn–N interactions. There is no correlation between the intramolecular Sn–N bond length and the quadrupole splitting value.

From the Mössbauer data, it is assumed that **7** also has a *cis*-trigonal bipyramidal structure in the solid state.

3.5. Solution NMR data

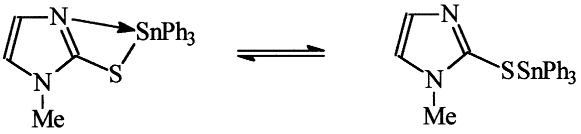
The Sn–N intramolecular interaction in **1** remains intact on dissolution in $CHCl_3$ solution as shown by the similar ^{119}Sn NMR chemical shift values in the solid state [δ ^{119}Sn: −147.0 and −159.0 ppm] and in solution [δ ^{119}Sn: −147.0 ppm] [18]. In contrast, the Sn–N interactions in (**5**: R = Ph, R′ = Me or Ph), and **6**–**8** are, at least, partially broken in chlorocarbon solution. Sordo et al. reported a single δ ^{119}Sn NMR value of −112.2 ppm for **8** in $CDCl_3$ solution [19]. We observed, in this study, two δ ^{119}Sn values at ambient temperature, −57.1 and −112.9

Table 4
Selected structural and spectral data for triphenyltin heteroarenethiolates

Compound	Solution	Solid state				
	NMR	Mössbauer		X-ray		
	δ^{119}Sn	IS (mm/s)	QS (mm/s)	d(Sn–S) Å	d(Sn–N) Å	Geometry at tin
 **(1)**	−150.5 (solution) −147.0 & −159.0 (solid state) [15]	1.20 [28]	1.37 [28]	2.441(3) & 2.427(3) [8]	2.592(9) & 2.611(8) [8]	Distorted *cis*-trigonal bipyramidal
 **(8)**	−57.1[a] −112.9[a] −112.2 [16]	1.28[a]	2.98[a]	2.437 [16]	2.920(3) Sn–N(2) [16]	Distorted *cis*-trigonal bipyramidal
 **(5:R=Ph, R′=Me)**	−70.9[a]	1.36[a]	2.48[a]	2.4708(8)[a]	3.161(3)[a] Sn–N(2)	Distorted *cis*-trigonal bipyramidal
 **(5:R=R′=Ph)**	−69.4 [26]	1.33 [26]	2.38 [26]	2.482(1) [12]	3.275(3) Sn–N(2) [12]	Distorted *cis*-trigonal bipyramidal
 **(6)**	−78.9[a]	1.34[a]	2.03[a]	2.458(2)[a]	3.070(6)[a]	Distorted *cis*-trigonal bipyramidal
 **(7)**	−91.4[a]	1.32[a]	1.79[a]			
 **(9)**	−116.3 Ar = Ph [27]	1.26 Ar = Ph [27]	1.62 Ar = Ph [27]	2.455(7) 2.444(7) Ar = C_6H_4Me-*p* [10]	2.73(3) 2.74(3) Ar = C_6H_4Me-*p* [10]	Distorted *cis*-trigonal bipyramidal
 **(4)**		1.31 [11]	1.65 [11]	2.442(3) [11]	2.88(5) [11]	Distorted *cis*-trigonal bipyramidal
Ph_3SnSPh	−65.2(CH_2Cl_2) [31]	1.33 [29]	1.41 [29]	2.421(1) [6]	–	Distorted tetrahedral
$Ph_3SnSC_6H_4Bu^t$-*p*	−65.8 [31]	1.31 [29]	1.34 [29]	2.413 [23]	–	Distorted tetrahedral

[a] This study.

ppm. The relative intensities of the two peaks varied with temperature: lowering the temperature led to a reduction in the relative intensity of the lower field value and at 240 K, only the higher field peak (now at −124.0 ppm) was present. As the temperature effects are reversible, an equilibrium between 4- and 5-coordinate species is assumed, Eq. (1), which is slow on the NMR timescale. The lower field peak (from −57.1 to −60 ppm) is associated with a 4-coordinate species, by comparison with the values [≈ -65 ppm] for 4-coordinate $Ph_3SnSC_6H_4X$-*p* in chlorocarbon solvents [34]. The higher field value of between −112.9 and −124.0 ppm is assigned to the 5-coordinate, chelated species and is close to the δ^{119}Sn value of −116.3 ppm reported for triphenyltin pyridine-2-thiolate (**9**: R=Ph) in chlorocarbon solution [29]. The difference [ca. 30 ppm] in the solution δ^{119}Sn NMR values for 5-coordinate **1**, on one hand, and for 5-coordinate **8** and **9**, on the other, is considered to arise from the different chelate ring sizes and the consequent differences in Sn–N bond lengths.



8 (1)

Only single ^{119}Sn chemical shifts were observed for each of the compounds, (**5**: R=Ph, R′=Me) [−70.9 ppm], **6** [−78.9 ppm] and **7** [−91.4 ppm] at room temperature in $CDCl_3$ solution. The δ^{119}Sn NMR value for (**5**; R=Ph, R′=Me) is close to the value anticipated for a 4-coordinate triphenyltin thiolate [−60±5 ppm] [34]; the single values for each of **6** and **7**, both of which are between values expected for 4- and 5-coordinate triphenyltin thiolates, are accounted for by assuming the presence of 4- and 5-coordinate species, undergoing sufficiently fast exchanges on the NMR timescale to result in average values only being observed.

Supplementary data

Supplementary data are available from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK on request, quoting the deposition numbers 114156 and 114157 for compounds **6** and **5**, respectively.

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