Journal of Organometallic Chemistry, 430 (1992) 149–166
Elsevier Sequoia S.A., Lausanne
JOM 22487

Synthesis and spectroscopic studies of thienyl triorganotin(IV) compounds. Crystal structures of [2-(4,4-dimethyl-2-oxazolinyl)-3-thienyl]dimethyltin *N*,*N*-dimethyldithiocarbamate and [2-(4,4-dimethyl-2-oxazolinyl)-3-thienyl]diphenyltin chloride

Kong Mun Lo [a], S. Selvaratnam [b], Seik Weng Ng [a], Chen Wei [b] and V.G. Kumar Das [b]

[a] *Institute of Advanced Studies and* [b] *Department of Chemistry, University of Malaya, 59100 Kuala Lumpur (Malaysia)*

(Received August 6, 1991)

Abstract

Two series of stannylated thiophenes of formula $(Z\text{-}C_4H_2S)SnR_2X$ (Z = 3-(2-pyridyl) and 2-(4,4-dimethyl-2-oxazolinyl); R = Me, ^{n}Bu, Ph, *p*-tolyl and ^{c}Hex; X = Cl, Br, I, OH, SC(S)NMe$_2$ and 8-quinolinolyl) have been prepared and their structures established by ^{119m}Sn Mössbauer and NMR (^{13}C and ^{119}Sn) spectral analyses. A pronounced *C*,*N*-chelate bonding mode is inferred for the 3-(2-pyridyl)-2-thienyl ligand in the first series, the tin atoms thus being essentially five-coordinate with *trans*-C_3SnNX trigonal bipyramidal geometries. Crystal structure determinations on two products in the second series, namely [2-(4,4-dimethyl-2-oxazolinyl)-3-thienyl]dimethyltin *N*,*N*-dimethyldithiocarbamate (**1**) and [2-(4,4-dimethyl-2-oxazolinyl)-3-thienyl]diphenyltin chloride (**2**), confirmed the spectroscopic indications of pentacoordinate trigonal bipyramidal tin environments and revealed that the oxazolinyl nitrogen is the intramolecularly coordinated donor atom in each case and is located in an apical position with respect to the C_3Sn trigonal girdle; the Sn–N bond length in **2** (2.580(8); 2.525(7) Å) is relatively shorter than in **1** (2.720(3) Å). The apical angle for **1** (162.12(7)°) shows the molecule to be more distorted than **2** (168.4(2) and 169.9(2)°).

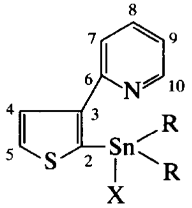
Introduction

C-Stannylated heterocyclic compounds have, in general, been little studied compared with their carbocyclic analogues [1,2], and there are only few examples of such triorganotin species; these include tris(quinolinyl)tin chloride (2- and 6-substituted), bis(2-thienyl)phenyltin chloride, bis(2-thienyl)vinyltin chloride [3], divinyl(2-thienyl)tin chloride [3,4], tris(thienyl)tin halides (2- and 3-substituted) [5,6], and tris(furyl)tin halides (2- and 3-substituted) [5].

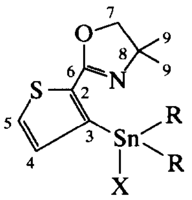
Correspondence to: Professor V.G. Kumar Das, University of Malaya, Department of Chemistry, 59100 Kuala Lumpur, Malaysia.

0022-328X/92/$05.00

Previously we used alkyl- and heteroaryl-substituted thienyl groups as *C*-bonded ligands in the preparation of some structurally novel thienyl tetraorganotin compounds [7–9]. These studies have now been extended to thienyl triorganotin species in which the heterocycle contains 3-pyridyl or 2-oxazolinyl substituents that can potentially coordinate to the tin atoms (I and II).



(I)



(II)

Experimental

The following commercial chemicals of reagent-grade quality were used in the syntheses: n-butyllithium (15% in hexane), thiophene, 2-(3-thienyl)pyridine, 8-hydroxyquinoline and sodium *N*,*N*-dimethyldithiocarbamate.

Synthesis

Published procedures were used to prepare 2-bromo-5-methylthiophene [10] (b.p.$_4$ 40–42°C), 4,4-dimethyl-2-(2-thienyl)-2-oxazoline [11] (b.p.$_{0.1}$ 71–73°C), di(*p*-tolyl)tin dibromide [12] (m.p. 72–73°C), chloro(*N*,*N*-dimethyldithiocarbamato)dimethyltin [13] (m.p. 138–140°C), diphenyltin dichloride [14] (m.p. 40–41°C), diphenyltin dibromide [15] (m.p. 39°C), chlorodi(n-butyl)tin acetate [16] (m.p. 61–62°C), tris(2-thienyl)phenyltin [7] (m.p. 168–170°C), and [3-(2-pyridyl)-2-thienyl]tricyclohexyltin [8] (m.p. 88–90°C).

*[3-(2-Pyridyl)-2-thienyl]di(*p*-tolyl)tin bromide*

To a solution of 2-(3-thienyl)pyridine (1 mL, 7.2 mmol) in diethyl ether (30 mL) was added dropwise at room temperature 5 mL of 15% n-butyllithium in hexane. The resulting yellow solution was stirred for 2 h and was then treated dropwise at 0°C with an ethereal solution of di(*p*-tolyl)tin dibromide (1.6 g, 3.5 mmol). The mixture was stirred at room temperature for 4 h and then filtered. The precipitate (LiBr) was washed with two portions of diethyl ether (20 mL) and the solvent removed from the combined filtrates in vacuo to give 1.5 g (79% yield) of a yellow solid, m.p. 218–220°C. This was recrystallised from toluene to give white crystals, m.p. 221–223°C. Anal. Found: C, 50.68; H, 3.67; N, 2.20. $C_{23}H_{20}BrNSSn$ calc.: C, 51.11; H, 3.70; N, 2.59%. ^{1}H NMR ($CDCl_3$), δ: 2.40 (s, 6H), 6.95–8.25 (m, 14H) ppm. IR (Nujol mull, 2000–400 cm^{-1}): 1600s, 1570m, 1495m, 1485m, 1430s, 1190m, 1150m, 1070m, 1060m, 1010m, 880m, 800s, 790m, 740s, 720s, 485s, 460s cm^{-1}.

*[3-(2-Pyridyl)-2-thienyl]di(*p*-tolyl)tin oxinate*

[3-(2-Pyridyl)-2-thienyl]di(*p*-tolyl)tin bromide (0.1 g, 0.18 mmol) and 8-hydroxyquinoline (0.025 g, 0.18 mmol) were dissolved separately in 15 mL of ethanol (95%)

and the solutions mixed to give a yellow solution. The solution was warmed for 5 min and cooled to give 0.08 g of yellow crystals, m.p. 220–221°C. Anal. Found: C, 63.67; H, 3.90; N, 4.93. $C_{32}H_{26}SN_2Sn$ calc.: C, 63.37; H, 4.29; N, 4.62%. λ_{max} (in $CHCl_3$): 387 nm (log $\epsilon = 3.711$).

*[3-(2-Pyridyl)-2-thienyl]di(*p*-tolyl)tin* N,N*-dimethyldithiocarbamate*

[3-(2-Pyridyl)-2-thienyl]di(*p*-tolyl)tin bromide (0.15 g, 0.22 mmol) and thallous *N*,*N*-dimethyldithiocarbamate (0.09 g, 0.27 mmol) were dissolved separately in 15 mL of ethanol (95%) and the solutions mixed to give an immediate precipitate of thallous bromide. After 1 h stirring the thallous bromide was filtered off and the filtrate concentrated to give 0.1 g of a white solid, m.p. 214–215°C. Anal. Found: C, 53.3; H, 4.96; N, 4.61. $C_{26}H_{26}N_2S_3Sn$ calc.: C, 53.6; H, 4.47; N, 4.81%. ^1H NMR ($CDCl_3$) δ: 2.23 (s, 6H), 3.38 (s, 6H, N-Me_2), 6.75–7.73 (m, 14H) ppm. IR (Nujol mull, 600–200 cm^{-1}): 575m, 483, 465m, 450w, 435w, 410w and 395m cm^{-1}.

[3-(2-Pyridyl)-2-thienyl]dimethyltin N,N*-dimethyldithiocarbamate*

To a solution of 2-(3-thienyl)pyridine (1 mL, 7.2 mmol) in diethyl ether (30 mL) was added dropwise with stirring at room temperature 5 mL of 15% n-butyllithium in hexane. The resulting brown solution was stirred for a further 2 h and then treated dropwise at −30°C with a benzene solution (30 mL) of chloro(*N*,*N*-dimethyldithiocarbamato)dimethyltin (1.8 g, 6 mmol). The mixture was stirred for 4 h while being allowed to warm to 0°C. The lithium chloride formed was filtered off and the filtrate concentrated. Addition of hexane to the concentrated filtrate afforded a white solid, which was recrystallised from a 1/1 (v/v) chloroform/hexane mixture. Yield 1.2 g, m.p. 148–150°C. Anal. Found: C, 38.45; H, 4.08; N, 6.11. $C_{14}H_{18}N_2S_3Sn$ calc.: C, 38.30; H, 4.20; N, 6.57%. ^1H NMR ($CDCl_3$) δ: 0.90 (s, 6H, Sn-Me), 3.45 (s, 6H, N-Me), 7.05–8.50 (m, 6H) ppm; $J(^{119}Sn-CH_3)$: 76 Hz. IR (Nujol mull, 2000–400 cm^{-1}): 1600s, 1570m, 1500s, 1440s, 1270m, 1250s, 1180m, 1160m, 1130m, 1050m, 1010m, 985s, 790s, 780s, 740s and 450s cm^{-1}.

Adventitious preparation of [3-(2-pyridyl)-2-thienyl]diphenyltin hydroxide

To a solution of 2-(3-thienyl)pyridine (2 mL, 14 mmol) in diethyl ether (30 mL) at room temperature was added 1.5 mL of 10.2 *M* n-butyllithium in hexane. The resulting brown solution was stirred for 2 h, then added from a syringe to an ethereal solution of diphenyltin dibromide (3.13 g, 7 mmol) at −70°C. After 2 h stirring the lithium bromide was filtered off and the filtrate concentrated. Addition of hexane then afforded 0.2 g of a white solid, which was identified as bis[3-(2-pyridyl)-2-thienyl]diphenyltin(IV), m.p. 180–182°C. The mother liquor was filtered and concentrated to leave a viscous liquid, which was cooled to −30°C and triturated with ethanol (95%) to give a white solid, m.p. 338–340°C; this analysed for [3-(2-pyridyl)-2-thienyl]diphenyltin hydroxide rather than the expected bromide. Yield 1.2 g. Anal. Found: C, 56.05; H, 3.87; S, 3.81. $C_{21}H_{17}NOSSn$ calc.: C, 56.63; H, 3.55; S, 3.11%. ^1H NMR ($CDCl_3$), δ: 7.05–8.15 (m) ppm. IR (Nujol mull, 4000–400 cm^{-1}): 3045s, 3035m, 1590m, 1490m, 1435s, 1305m, 1207m, 1080s, 1035m, 1010m, 970m, 880m, 730s, 700s, 580s, 480s and 450s cm^{-1}.

2-Thienyl di-(n-butyl)tin chloride

To a solution of thiophene (3.2 mL, 42 mmol) in diethyl ether (20 mL) at room temperature was added 27 mL of n-butyllithium solution (15% in hexane). After

1 h stirring the resulting 2-lithiothiophene reagent was added from a syringe to a stirred suspension of cuprous iodide (7 g, 36 mmol) in diethyl ether (30 mL) at −70°C. During the addition the colour changed from grey to white and then to olive. The mixture was maintained at −70°C for 2 h then treated with chlorodi-(n-butyl)tin acetate (10 g, 30 mmol) in dry ether (20 mL). After 18 h stirring the cuprous acetate was filtered off and the filtrate was concentrated then vacuum distilled to give the pure product, b.p.$_{0.06}$ 110–115°C. Yield 5 g (47%). Anal. Found: C, 39.51; H, 5.99; S, 9.13. $C_{12}H_{21}ClSSn$ calc.: C, 40.35; H, 5.96; S, 9.08%. ^1H NMR ($CDCl_3$) δ: 0.61–2.12 (m, 18H), 6.72–7.60 (m, 3H).

5-Methyl-2-thienyl di(n-butyl)tin chloride

A two-necked round-bottomed flask fitted with a dropping funnel and a condenser carrying a nitrogen inlet tube was charged with magnesium turnings (0.36 g, 15 mmol) and dry ether (20 mL). A solution of 2-bromo-5-methylthiophene (2.65 g, 15 mmol) in dry ether (10 mL) was added dropwise from the dropping funnel with stirring. When reaction had subsided stirring was continued for 2 h. The Grignard solution was then transferred under nitrogen to a dropping funnel and slowly added dropwise to an ethereal solution (20 mL) of chlorodi(n-butyl)tin acetate (3 g, 9 mmol) at −70°C. The mixture was subsequently allowed to warm up to room temperature and stirred for 1 h. The magnesium salt formed was filtered off and the filtrate was concentrated and then distilled under reduced pressure to yield the product, b.p.$_{0.15}$ 135–142°C. Yield 1 g (30%). Anal. Found: C, 42.61; H, 6.21; S, 8.89. $C_{13}H_{23}SClSn$ calc.: C, 42.56; H, 6.27; S, 8.73%. ^1H NMR ($CDCl_3$) δ: 0.60–1.95 (m, 18H), 2.35 (s, 3H), 6.60–7.15 (m, 2H).

Bis(2-thienyl)phenyltin iodide

A solution of tris(2-thienyl)phenyltin (0.9 g, 2 mmol) and iodine (0.5 g, 2 mmol) in ether (200 mL) was stirred at room temperature for 15 min, during which the brown solution turned yellow, TLC analysis showed that almost all the tetraorganotin had been converted into the triorganotin compound along with a trace amount of the diorganotin derivative. The solvent was removed completely under aspirator pressure to give a brown solid, which was dissolved in 20 mL of petroleum ether (60–80°C). Filtration followed by concentration gave a viscous yellow liquid, which yielded colourless crystals upon cooling. Yield 0.6 g (60% yield), m.p. 72–74°C. Anal. Found: C, 35.95; H, 2.25. $C_{14}H_{11}S_2ISn$ calc.: C, 34.29; H, 2.24%.
[3-(2-pyridyl)-2-thienyl]di(cyclohexyl)tin iodide was prepared similarly from [3-(2-pyridyl)-2-thienyl]tricyclohexyltin. Yield 0.7 g (64%). Anal. Found: C, 44.14; H, 4.89; N, 2.21. $C_{21}H_{28}INSSn$ calc.: C, 43.98; H, 4.89; N, 2.44%. ^1H NMR ($CDCl_3$), δ: 1.20–2.15 (m, 22H), 7.10–8.00 (m, 5H), 8.60–8.90 (m, 1H).

$[(2\text{-}C_4H_3S)_2PhSn(Ph_3AsO)_2]^+[BPh_4]^-$

To a solution of 0.2 g (0.4 mmol) of $(2\text{-}C_4H_3S)_2PhSnI$ in ethanol (10 mL) was slowly added an ethanolic solution of $NaBPh_4$ (0.15 g, 0.44 mmol) and Ph_3AsO (0.3 g, 0.93 mmol). A white solid formed immediately, and was filtered off and dried under vacuum. Yield 0.4 g (69%), m.p. 205–208°C. Anal. Found: C, 66.19; H, 4.57. $C_{74}H_{61}As_2BO_2S_2Sn$ calc.: C, 67.05; H, 4.61%. IR (Nujol mull, 2000–400 cm^{-1}): 1590m, 1450s, 1320m, 1270m, 1220m, 1190m, 1150w, 1090s, 1075m, 1040m, 1030m, 1010s, 965m, 850s, 750s, 740s, 710s, 700s, 630m, 620s, 485s, 470s and 465 cm^{-1}.

[2-(4,4-Dimethyl-2-oxazolinyl)-3-thienyl]dimethyltin N,N-*dimethyldithiocarbamate (1)*

To a stirred ethereal solution (50 mL) of 4,4-dimethyl-2-(2-thienyl)-2-oxazoline (5 g, 28 mmol) cooled to −70°C under nitrogen was added during 15 min, 18.1 mL of 15% n-butyllithium in hexane. The resulting yellow solution was then stirred for a further 0.5 h at 0°C and then cooled to −70°C to yield the lithio derivative of the oxazolinylthiophene [17]. To this was added dropwise an ethereal solution (50 mL) of chloro(*N*,*N*-dimethyldithiocarbamato)dimethyltin (4.3 g, 14 mmol), and after 1 h stirring the solvent was completely removed under aspirator pressure. The residue was taken up in 30 mL of chloroform and the solution filtered. Concentration of the filtrate afforded 1.0 g of white solid, m.p. 200–203°C, which was identified as $\mathrm{Me_2Sn(S_2CNMe_2)_2}$. Subsequent addition of petroleum ether (60–80°C) to the filtrate gave the title product, yield, 0.67 g, m.p. 160–161°C. Single crystals suitable for an X-ray study were obtained by recrystallisation of the product from a 1/1 (v/v) chloroform/petroleum ether (60–80°C) mixture. Anal. Found: C, 37.10; H, 4.84; N, 6.13. $\mathrm{C_{14}H_{22}N_2OS_3Sn}$ calc.: C, 37.44; H, 4.90; N, 6.24%.

A second product was also obtained from the remaining filtrate and identified as *bis[2-(4,4-dimethyl-2-oxazolinyl)-3-thienyl]dimethyltin*. Yield 0.8 g, m.p. 154–157°C. Anal. Found: C, 47.10; H, 5.20; N, 5.59. $\mathrm{C_{20}H_{18}N_2O_2S_2Sn}$ calc.: C, 47.18; H, 5.11; N, 5.50%.

A similar procedure was used to give *[2-(4,4-dimethyl-2-oxazolinyl)-3-thienyl]diphenyltin chloride* (**2**) as the sole product from 2-(4,4-dimethyl-2-oxazolinyl)-3-thienyllithium and diphenyltin dichloride. Yield 2.1 g, m.p. 194–197°C. Anal. Found: C, 51.68; H, 4.06; N, 2.54. $\mathrm{C_{21}H_{20}NSOClSn}$ calc.: C, 51.62; H, 4.10; N, 2.53%.

Physical measurements

Melting points were determined in open capillaries. Elemental analyses were carried out by the Microanalytical Service, University College, London (UK) and Analytical Services, Polytechnic of North London, London (UK). The IR spectra were recorded as Nujol mulls on a Perkin–Elmer 1300 spectrometer calibrated with polystyrene.

The ^{119m}Sn Mössbauer spectra (Table 1) were obtained at 80 K using a Cryophysics constant acceleration spectrometer with a 512 channel data store and a 15 mCi $\mathrm{Ca^{119}SnO_3}$ source at room temperature. The velocity range was calibrated with $\mathrm{CaSnO_3}$ and the spectra were fitted with a Lorentzian curve-fitting program [18] supplied by the manufacturer.

The ^{119}Sn NMR spectra (Table 2) for the compounds were recorded in $\mathrm{CDCl_3}$ on the JEOL-FX60Q and JEOL JNM GX270 instruments operating at 22.24 and 100.55 MHz, respectively. ^{1}H and ^{13}C NMR spectra (Tables 3 and 4) of the compounds were recorded at 30°C on a JEOL JNM-FX 100 spectrometer operating at 99.55 MHz for ^{1}H and at 25.00 MHz, in the completely decoupled irradiation mode, for ^{13}C, with $\mathrm{CDCl_3}$ as solvent and internal lock.

Table 1

^{119m}Sn Mössbauer data for thienyl triorganotins [a] and related compounds at 80 K

Compound [b]	*IS* [c]	*QS*	Γ_1	Γ_2
$\mathrm{LSn}(p\text{-tolyl})_2\mathrm{Br}$	1.17	2.94	0.99	1.02
$\mathrm{LSn}(p\text{-tolyl})_2(\mathrm{S_2CNMe_2})$	1.16	2.47	0.90	1.00
$\mathrm{LSn}(p\text{-tolyl})_2(\mathrm{oxin})$	1.20	2.92	0.89	0.90
$\mathrm{LSnPh_2OH}$	1.28	2.82	0.85	0.84
$\mathrm{LSn(^cC_6H_{11})_2I}$	1.38	3.26	1.16	1.19
$\mathrm{LSnMe_2(S_2CNMe_2)}$	1.31	2.71	0.93	0.96
$\mathrm{L'SnMe_2(S_2CNMe_2)}$	1.27	2.59	0.87	0.87
$\mathrm{L'_2SnMe_2}$	1.16	1.06	0.94	0.94
$\mathrm{L'SnPh_2Cl}$	1.19	3.01	1.00	1.00
$\mathrm{L'SnPh_3}$ [d]	1.05	0.51	1.00	1.10
$\mathrm{(2\text{-}C_4H_3S)_2PhSnI}$	1.22	2.08	1.00	1.02
$\mathrm{[(2\text{-}C_4H_3S)_2PhSn(Ph_3AsO)_2]^+[BPh_4]^-}$	1.00	2.90	0.92	0.94
$\mathrm{Ph_3SnI}$ [e]	1.20	2.25	1.28	1.24

[a] Error ±0.03 $\mathrm{mms^{-1}}$. [b] L = 3-(2-pyridyl)-2-thienyl; L′ = 2-(4,4-dimethyl-2-oxazolinyl)-3-thienyl. [c] Relative to $\mathrm{CaSnO_3}$ or $\mathrm{BaSnO_3}$. [d] Unpublished results. [e] Ref. 25.

Crystallographic studies of the title compounds **1** and **2** were carried out on an automated Enraf–Nonius CAD4 diffractometer with graphite-monochromated Mo-K_α(λ = 0.71703 Å) radiation, and determination of crystal class, orientation matrix and accurate cell-parameters were performed by standard procedures [19]. Intensities were recorded at the laboratory temperature of 27°C up to a $2\theta_{\max}$ of 50°. Unit-cell constants for the triclinic lattice for **1** and **2** were derived from the angular settings of 25 strong random reflections. Crystal decay was monitored by using three reflections. The MULTAN [20] and SIMPEL [21] direct-methods programs

Table 2

^{119}Sn NMR data

Compound [a]	concentration (w/v%)	$\delta(^{119}\mathrm{Sn})$ (ppm) [b]
$\mathrm{LSn}(p\text{-tolyl})_2\mathrm{Br}$	4.6	−228.5
$\mathrm{LSn}(p\text{-tolyl})_2(\mathrm{S_2CNMe_2})$	4.5	−210.9
$\mathrm{LSn}(p\text{-tolyl})_2(\mathrm{oxin})$	4.1	−214.1
$\mathrm{LSnPh_2OH}$	6.0	−234.5
$\mathrm{L'SnPh_2Cl}$	10.9	−211.5
$\mathrm{LSnMe_2(S_2CNMe_2)}$	2.7	−173.9
$\mathrm{L'SnMe_2(S_2CNMe_2)}$	4.5	−138.9
$\mathrm{LSn}(p\text{-tolyl})_3$	8.0	−176.3
$\mathrm{LSnPh_3}$ [c]	6.2	−181.6
$\mathrm{L'SnPh_3}$ [d]	11.5	−153.9
$\mathrm{L'_2SnMe_2}$	4.5	−101.3
$\mathrm{(2\text{-}C_4H_3S)_2SnMe_2}$ [e]	26.7	−62.7
$\mathrm{(2\text{-}C_4H_3S)SnPh_3}$ [e]	15.4	−135.5
$\mathrm{(2\text{-}C_4H_3S)_4Sn}$ [e]	7.0	−147.0

[a] L = 3-(2-pyridyl)-2-thienyl; L′ = 2-(4,4-dimethyl-2-oxazolinyl)-3-thienyl. [b] Relative to $\mathrm{Me_4Sn}$. [c] Ref. 8. [d] Unpublished results. [e] Ref. 7.

Table 3

^{13}C NMR spectral data ^{a} for the heterocyclic moiety in thienyltriorganotin compounds

Compound ^{b,c}	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-9	C-10
LSn(*p*-tolyl)$_2$Br	145.5	140.3	131.0	124.5	151.9	122.7	136.0	119.7	147.1
	(– ^{j})	(– ^{j})	(34.9)	(64.1)					
LSn(*p*-tolyl)$_2$(S$_2$CNMe$_2$) ^{d}	145.7	141.2	129.4	123.6	151.9	121.9	134.7	118.9	147.1
	(– ^{j})	(– ^{j})	(32.4)	(86.6)					
LSn(*p*-tolyl)$_3$ ^{e}	147.4	141.3	133.9	125.5	152.4	121.7	138.6	118.9	148.0
	(– ^{j})	(– ^{j})	(29.0)	(45.5)					
LSnPh$_2$OH	141.4	140.3	131.3	124.5	152.1	122.7	137.5	119.7	147.2
	(– ^{j})	(– ^{j})	(33.3)	(74.1)					
LSnPh$_3$	147.4	142.3	134.2	125.5	152.1	121.7	137.3	118.8	147.1
	(– ^{j})	(– ^{j})	(32.2)	(45.4)					
LSnMe$_2$(S$_2$CNMe$_2$) ^{f}	145.1	138.9	– ^{g}	124.1	152.6	121.9	133.8	119.6	146.4
	(– ^{j})	(– ^{j})	(– ^{j})	(37.7)					
LSn(^{c}C$_6$H$_{11}$)$_2$I	145.3	138.6	131.3	126.2	154.1	122.2	136.6	120.2	149.2
	(– ^{j})	(– ^{j})	(12.9)	(25.6)					
LSn(^{c}C$_6$H$_{11}$)$_3$ ^{e}	147.5	139.2	131.7	126.5	154.6	120.9	136.5	119.8	148.2
	(– ^{j})	(– ^{j})	(13.4)	(31.7)					
L′SnMe$_2$(S$_2$CNMe$_2$) ^{h} (**1**)	132.7	153.6	130.0	135.3	161.2	66.9	81.2	28.3	
	(– ^{j})	(491.0)	(61.3)	(40.5)					
L′$_2$SnMe$_2$ ^{i}	130.9	147.3	128.2	134.7	158.4	67.5	79.2	27.9	
	(– ^{j})	(452.6)	(60.2)	(50.8)					
L′SnPh$_2$Cl (**2**)	141.7	149.4	132.2	133.2	163.2	67.1	82.6	27.7	
	(– ^{j})	(695.8)	(91.5)	(67.9)					
L′SnPh$_3$ ^{e}	140.0	141.9	129.3	135.6	158.0	67.8	79.2	27.8	
	(– ^{j})	(500.5)	(63.4)	(54.9)					
(2-C$_4$H$_3$S)$_2$PhSnI	130.5	137.9	133.2	128.4					
	(– ^{j})	(48.8)	(28.7)	(68.4)					
(2-C$_4$H$_3$S)$_3$SnPh ^{k}	131.4	137.6	132.5	128.3					
	(– ^{j})	(41.5)	(24.4)	(58.6)					

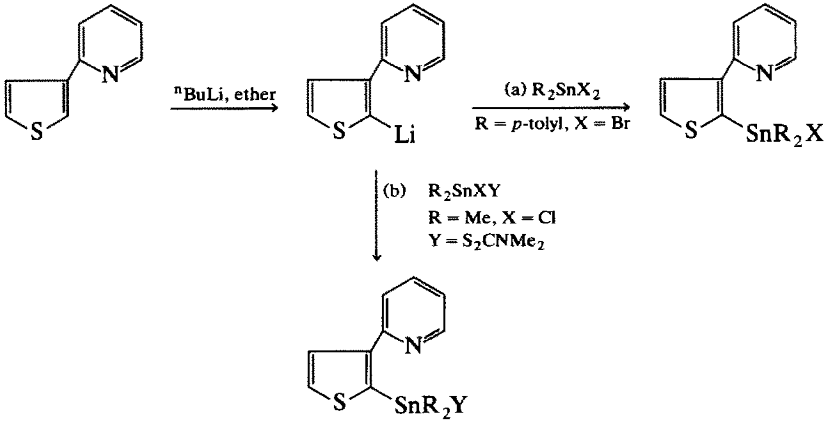
[a] In ppm (CDCl$_3$ solution). Values given in parentheses refer to $^{n}J(^{119}Sn-^{13}C)$ values (Hz). [b] L = 3-(2-pyridyl)-2-thienyl; L′ = 2-(4,4-dimethyl-2-oxazolinyl)-3-thienyl. [c] C-2–C-10 refer to ring carbon atoms of the substituted thienyl ligands as per numbering scheme illustrated in I and II (see Introduction). [d] δ(N-Me) 44.9 ppm. [e] Ref. 8. [f] δ(N-Me) 44.7, δ(Sn-Me) 4.7 ppm. [g] Chemical shift not discernable from spectrum. [h] δ(N-Me) 44.7 ppm; δ(C=S) 200.7 ppm; δ(Sn-Me) 4.3 ppm, $^{1}J(^{119}Sn-^{13}C_{Me})$ 576.1 Hz. [i] δ(Sn-Me) −4.7 ppm, $^{1}J(^{119}Sn-^{13}C_{Me})$ 459.5 Hz. [j] Coupling constant cannot be estimated from data. [k] Ref. 7.

were used to solve the structures. The non-H atoms were refined anisotropically, and the weighting scheme $w = [\sigma(F)^2 + (\mathrm{PWT}F)^2 + \mathrm{QWT}]^{-1}$ [22] with PWT = 0.02, QWT = 1.0, was used. Refinement was discontinued when the shift/error ratio was less than 0.01. The H atoms were included in calculated positions (C–H 0.95 Å) in the structure factor calculations. Refinement based on F converged to values listed in Table 5. Computations were performed with the MOLEN structure determination programs [23] on a DEC MicroVax II minicomputer. The structure of **1** is shown in Fig. 1. Figure 2 is a PLUTO drawing of one of the two symmetry-independent molecules of **2**. Atomic coordinates are listed in Tables 6 and 7. Structure factor tables, anisotropic temperature displacement parameters, hydrogen coordinates and complete tables of bond distances and angles are available from the authors on request.

Results and discussion

Synthesis

The unsymmetrical triorganotin compounds containing the 3-(2-pyridyl)-2-thienyl ligand are stable, crystalline solids which can be obtained in reasonable yields by a one-step synthesis involving the reaction of the lithiated heterocycle with a diorganotin dihalide, R_2SnX_2 (eq. 1a). Monodehalogenation is also achieved if R_2SnXY is used, where Y is an anionic residue such as dithiocarbamate (eq. 1b).



(1)

Table 4

^{13}C NMR spectral data [a] for the non-heteroaryl ligand fragments

Compound [b,c]	C_i/C_1	C_o/C_2	C_m/C_3	C_p/C_4	other
LSn(*p*-tolyl)$_2$Br	137.7	135.6	128.9	139.3	21.39 [d]
	(894.8)	(56.2)	(80.4)	(13.9)	
LSn(*p*-tolyl)$_2$(S_2CNMe_2)	138.1	135.6	129.0	138.8	21.50 [d]
	(1052.8)	(51.3)	(77.5)	(< 10)	
LSn(*p*-tolyl)$_3$ [e]	137.2	136.9	128.9	137.8	21.50 [d]
	(647.5)	(41.7)	(56.4)	(11.7)	
LSnPh$_2$OH	135.9	135.7	128.7	129.5	
	(– [f])	(53.1)	(75.7)	(< 7)	
LSnPh$_3$ [e]	137.3	136.8	128.0	128.2	
	(726.6)	(39.6)	(43.2)	(11.7)	
LSn($^cC_6H_{11}$)$_2$I	32.3	26.7	28.8	32.1	
	(296.7)	(7.9)	(65.9)	(16.5)	
LSn($^cC_6H_{11}$)$_3$ [e]	30.3	27.2	29.5	32.2	
	(374.8)	(< 7)	(62.3)	(15.9)	
L′SnPh$_2$Cl (**2**)	135.4	135.6	128.6	129.5	
	(– [f])	(50.1)	(73.3)	(14.7)	
L′SnPh$_3$	136.9	137.0	128.2	128.6	
	(– [f])	(26.9)	(51.3)	(12.2)	
(2-C_4H_3S)$_2$PhSnI	136.0	135.7	129.2	130.9	
	(715.3)	(54.9)	(74.5)	(18.3)	
(2-C_4H_3S)$_3$SnPh [g]	136.0	136.5	128.9	129.9	
	(615.5)	(46.4)	(61.0)	(12.1)	

[a] In ppm ($CDCl_3$ solution). Values given in parentheses refer to $^nJ(^{119}Sn-^{13}C)$ values (Hz). [b] L = 3-(2-pyridyl)-2-thienyl; L′ = 2-(4,4-dimethyl-2-oxazolinyl)-3-thienyl. [c] *i*(*ipso*), *o*(*ortho*), *m*(*meta*), *p*(*para*) refer to phenyl ring carbons, while 1–4 designate the corresponding carbons of the cycloalkyl ring. [d] Ar-CH_3. [e] Ref. 8. [f] Coupling constant could not be estimated from data. [g] Ref. 7.

Table 5

Crystal data and refinement details for compounds **1** and **2**

Crystal	**1**	**2**
Formula	$C_{14}H_{22}N_2OS_3Sn$	$C_{21}H_{20}ClNOSSn$
Molecular weight	449.23	488.61
Crystal system	triclinic	triclinic
Space group	$P\bar{1}$	$P\bar{1}$
a, Å	8.8817(7)	9.093(2)
b, Å	9.2359(8)	9.395(2)
c, Å	11.9582(7)	24.296(8)
α, °	96.060(5)	92.83(2)
β, °	101.066(7)	92.64(3)
γ, °	89.913(7)	92.23(2)
V, Å^3	957.1(1)	2069(1)
Z	2	4
$D_{\text{X-ray}}$, g cm^{-3}	1.559	1.568
μ, cm^{-1}	16.5	14.7
No. of unique reflections	3351	5390
No. of $I \geq 3\sigma(I)$ reflections	3001	3583
R, R_W	0.026, 0.033	0.038, 0.043
Esd of an observation of unit weight	0.715	0.479
No. of variables	190	469
Residual extreme, e Å^{-3}	0.44(3)	0.61(6)

The above strategy was employed with limited success in preparing [2-(4,4-dimethyl-2-oxazolinyl)-3-thienyl]dimethyltin *N*,*N*-dimethyldithiocarbamate from the lithio derivative of 2-oxazolinylthiophene and $Me_2SnCl(S_2CNMe_2)$ (eq. 2); use of

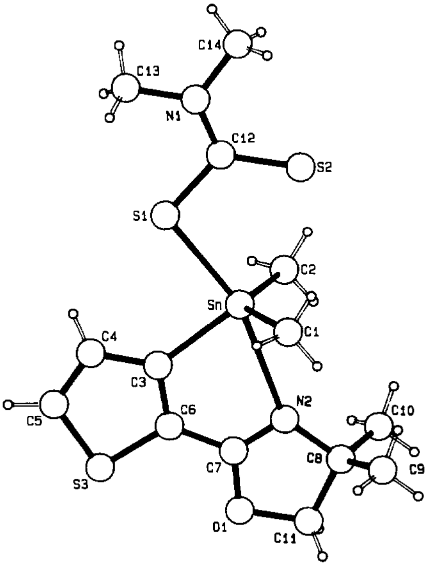


Fig. 1. Asymmetric unit of [2-(4,4-dimethyl-2-oxazolinyl)-3-thienyl]dimethyltin *N*,*N*-dimethyldithiocarbamate with atomic labelling.

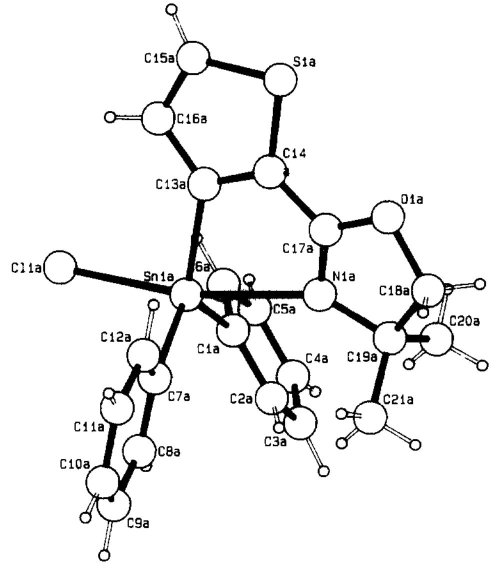


Fig. 2. Molecular geometry and atom numbering of molecule a of [2-(4,4-dimethyl-2-oxazolinyl)-3-thienyl]diphenyltin chloride.

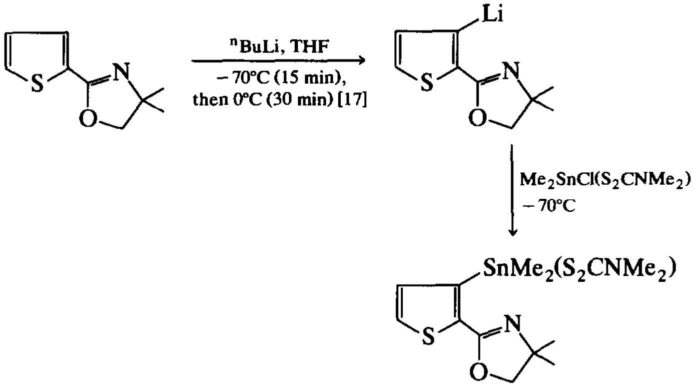
Table 6

Positional and thermal parameters for [2-(4,4-dimethyl-2-oxazolinyl)-3-thienyl]dimethyltin *N*,*N*-dimethyldithiocarbamate (**1**)

Atom	*x*	*y*	*z*	B_{iso} (Å^2) [a]
Sn	0.74215(3)	0.09074(3)	0.23332(2)	3.271(5)
S(1)	0.6766(1)	0.2940(1)	0.3737(1)	4.84(2)
S(2)	0.9260(1)	0.4044(1)	0.2668(1)	4.81(2)
S(3)	0.4022(1)	−0.2836(1)	0.25356(9)	4.43(2)
O(1)	0.6065(3)	−0.3810(3)	0.0826(2)	4.27(6)
N(1)	0.7981(4)	0.5577(4)	0.4229(3)	4.38(8)
N(2)	0.7399(3)	−0.1701(3)	0.1034(3)	3.43(6)
C(1)	0.9675(5)	0.0316(5)	0.3093(4)	5.1(1)
C(2)	0.6731(5)	0.1664(5)	0.0709(4)	4.39(9)
C(3)	0.5670(4)	−0.0489(4)	0.2718(3)	3.30(7)
C(4)	0.4603(5)	−0.0234(5)	0.3453(3)	4.28(9)
C(5)	0.3660(5)	−0.1383(5)	0.3438(4)	4.9(1)
C(6)	0.5471(4)	−0.1871(4)	0.2167(3)	3.17(7)
C(7)	0.6368(4)	−0.2442(4)	0.1331(3)	3.18(7)
C(8)	0.8035(4)	−0.2622(4)	0.0146(3)	4.02(8)
C(9)	0.9722(5)	−0.2855(6)	0.0584(5)	5.9(1)
C(10)	0.7764(7)	−0.1900(6)	−0.0948(4)	6.8(1)
C(11)	0.7097(5)	−0.4044(5)	0.0026(4)	5.4(1)
C(12)	0.8039(5)	0.4326(4)	0.3580(3)	3.83(8)
C(13)	0.6985(6)	0.5829(6)	0.5066(4)	6.1(1)
C(14)	0.8959(6)	0.6839(5)	0.4131(5)	5.8(1)

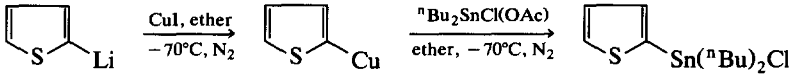
[a] Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: $(4/3)[a^2B_{1,1} + b^2B_{2,2} + c^2B_{3,3} + ab(\cos\gamma)B_{1,2} + ac(\cos\beta)B_{1,3} + bc(\cos\alpha)B_{2,3}]$.

the more reactive Me_2SnCl_2 yielded essentially the unsymmetrical tetraorganotin product, while with $Me_2Sn(S_2CNMe_2)$, no perceptible reaction occurred under the same conditions.

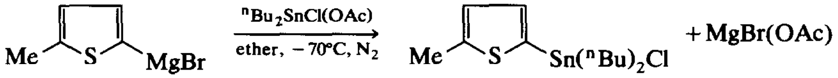


(2)

Reaction 2 is accompanied by the formation of an almost equal amount of the tetraorganotin product, bis[2-(4,4-dimethyl-2-oxazolinyl)-3-thienyl]dimethyltin, along with dimethyltin bis(*N*,*N*-dimethyldithiocarbamate). Formation of these products is explicable in terms of the partial disproportionation of $Me_2SnCl(S_2CNMe_2)$ to Me_2SnCl_2 and $Me_2Sn(S_2CNMe_2)_2$ during the reaction, and subsequent reaction of the dichloride to yield the tetraorganotin. In the case of 2-thienyllithium and 5-methyl-2-thienyllithium the attempted monodehalogenation reactions with R_2SnX_2 or R_2SnXY proved especially difficult to control, and yielded exclusively the unsymmetrical tetraorganotins, $(Het)_2SnR_2$. However, use of the less reactive 2-thienylcopper (eq. 3) and 5-methyl-2-thienylmagnesium bromide (eq. 4) as the transmetallating agents allowed the synthesis of the triorganotin products in low to moderate yields.



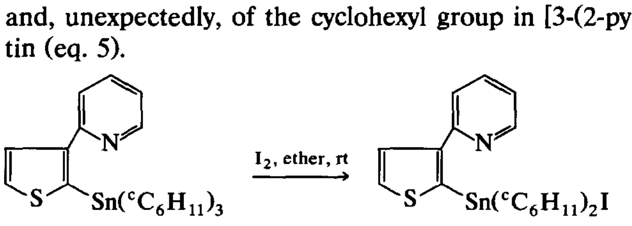
(3)



(4)

With $^nBu_2SnCl(OAc)$ these reagents preferentially cleaved the acetato group. The resulting triorganotin chlorides were yellow liquids which decomposed when kept for a week, giving a mixture of di-, tri- and tetra-organotin products.

An attempt was also made to synthesize the unsymmetrical triorganotin halides from the corresponding tetraorganotin compounds by controlled cleavage of the tin–carbon bond with iodine. In general, such reactions are seldom achieved satisfactorily when the tin atom carries relatively labile hydrocarbon groups, but we did observe a selective removal of the heteroaryl group in tris(2-thienyl)phenyltin and, unexpectedly, of the cyclohexyl group in [3-(2-pyridyl)-2-thienyl]tricyclohexyltin (eq. 5).



(5)

Table 7

Positional and thermal parameters for [2-(4,4-dimethyl-2-oxazolinyl)-3-thienyl]diphenyltin chloride (**2**)

Atom	x	y	z	B (Å^2) [a]
Sn(1a)	0.21692(8)	0.25481(7)	0.39622(3)	3.31(1)
Cl(1a)	−0.0138(3)	0.3716(3)	0.4141(1)	5.42(7)
S(1a)	0.5260(4)	0.3199(4)	0.5501(1)	6.14(8)
O(1a)	0.6579(8)	0.1236(9)	0.4601(3)	5.1(2)
N(1a)	0.4766(9)	0.1534(8)	0.3971(3)	3.5(2)
C(1a)	0.2666(9)	0.369(1)	0.3254(4)	3.1(2)
C(2a)	0.302(1)	0.295(1)	0.2773(4)	4.4(2)
C(3a)	0.330(1)	0.371(1)	0.2300(5)	5.3(3)
C(4a)	0.330(1)	0.519(1)	0.2338(5)	5.9(3)
C(5a)	0.295(1)	0.593(1)	0.2811(6)	5.9(3)
C(6a)	0.262(1)	0.518(1)	0.3285(5)	4.4(2)
C(7a)	0.127(1)	0.043(1)	0.3844(4)	3.4(2)
C(8a)	0.055(1)	−0.005(1)	0.3352(5)	4.7(3)
C(9a)	−0.012(1)	−0.143(1)	0.3293(5)	5.7(3)
C(10a)	−0.007(1)	−0.229(1)	0.3738(6)	6.1(3)
C(11a)	0.062(1)	−0.181(1)	0.4236(6)	6.1(3)
C(12a)	0.131(1)	−0.042(1)	0.4289(5)	4.8(3)
C(13a)	0.317(1)	0.311(1)	0.4756(4)	3.7(2)
C(14a)	0.453(1)	0.263(1)	0.4863(4)	3.6(2)
C(15a)	0.368(2)	0.411(1)	0.5627(5)	6.4(3)
C(16a)	0.264(1)	0.397(1)	0.5195(4)	4.8(3)
C(17a)	0.528(1)	0.178(1)	0.4467(4)	3.4(2)
C(18a)	0.695(1)	0.033(1)	0.4114(5)	5.0(3)
C(19a)	0.587(1)	0.073(1)	0.3659(4)	4.1(2)
C(20a)	0.661(1)	0.178(1)	0.3283(5)	5.4(3)
C(21a)	0.513(1)	−0.056(1)	0.3337(5)	5.7(3)
Sn(1b)	0.27020(8)	0.23132(7)	0.89189(3)	3.22(1)
Cl(1b)	0.5233(3)	0.3351(3)	0.9073(1)	4.62(6)
S(1b)	0.0023(4)	0.3321(4)	1.0426(1)	5.29(7)
O(1b)	−0.1652(8)	0.1155(9)	0.9558(3)	5.2(2)
N(1b)	0.0055(8)	0.1403(8)	0.8934(3)	3.4(2)
C(1b)	0.332(1)	0.015(1)	0.8871(4)	3.6(2)
C(2b)	0.359(1)	−0.051(1)	0.9362(5)	4.9(3)
C(3b)	0.395(1)	−0.195(1)	0.9349(6)	6.1(3)
C(4b)	0.400(1)	−0.270(1)	0.8849(6)	6.3(3)
C(5b)	0.372(1)	−0.204(1)	0.8353(6)	6.9(4)
C(6b)	0.338(1)	−0.060(1)	0.8366(5)	5.0(3)
C(7b)	0.221(1)	0.346(1)	0.8215(4)	3.3(2)
C(8b)	0.095(1)	0.430(1)	0.8197(5)	5.1(3)
C(9b)	0.068(1)	0.511(1)	0.7735(6)	6.1(3)
C(10b)	0.159(1)	0.510(1)	0.7310(5)	5.8(3)
C(11b)	0.282(1)	0.427(1)	0.7326(5)	6.1(3)
C(12b)	0.313(1)	0.342(1)	0.7765(4)	4.8(3)
C(13b)	0.196(1)	0.307(1)	0.9691(4)	3.5(2)
C(14b)	0.055(1)	0.264(1)	0.9802(4)	3.7(2)
C(15b)	0.172(1)	0.418(1)	1.0546(5)	5.2(3)
C(16b)	0.265(1)	0.398(1)	1.0124(4)	4.2(2)
C(17b)	−0.036(1)	0.172(1)	0.9411(4)	3.5(2)
C(18b)	−0.219(1)	0.016(1)	0.9109(5)	5.4(3)
C(19b)	−0.114(1)	0.049(1)	0.8643(4)	4.0(2)
C(20b)	−0.049(1)	−0.087(1)	0.8377(5)	5.4(3)
C(21b)	−0.190(1)	0.135(1)	0.8190(5)	5.8(3)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: $(4/3)[a^2B_{1,1} + b^2B_{2,2} + c^2B_{3,3} + ab(\cos\gamma)B_{1,2} + ac(\cos\beta)B_{1,3} + bc(\cos\alpha)B_{2,3}]$.

We attribute the cleavage of the tin–cyclohexyl bond in the last case to the strong coordinative interaction at tin of the pyridyl substituent and the relief of steric strain in the molecule accompanying the loss of a bulky cyclohexyl group.

The products of the iodination are solids stable at room temperature in the dark. Although attempts to prepare adducts of these with neutral oxygen-donor ligands were not successful, the acceptor property of the bis(2-thienyl)phenyltin system was clearly demonstrated by the isolation of its cationic complex, $[(2\text{-}C_4H_3S)_2SnPh(Ph_3AsO)_2]^+[BPh_4]^-$ (eq. 6), which is formally five-coordinate at tin.

$$(2\text{-}C_4H_3S)_2PhSnI + 2Ph_3AsO + Na[BPh_4] \xrightarrow{\text{ethanol}}$$
$$[(2\text{-}C_4H_3S)_2PhSn(Ph_3AsO)_2]^+[BPh_4]^- + NaI \qquad (6)$$

Spectroscopic studies

The ^{119m}Sn Mössbauer data of the thienyl triorganotin derivatives, together with those of some related complexes are listed in Table 1. The Mössbauer spectra are well-resolved quadrupole split doublets with the isomer shift (*IS*) values lying in the range of 1.17–1.31 mm s^{-1}. The *IS* values for the series, $LSn(p\text{-tolyl})_2X$, where L = 3-(2-pyridyl)-2-thienyl and X = Br, S_2CNMe_2 and 8-quinolinolyl are invariant at 1.17 ± 0.03 mm s^{-1}, suggesting a negligible influence of the anionic ligands on the *s*-electron density at the tin atom. In contrast, $LSnMe_2(S_2CNMe_2)$, $LSn(^cC_6H_{11})_2I$ and $L'SnMe_2(S_2CNMe_2)$ [L′ = 2-(4,4-dimethyl-2-oxazolinyl)-3-thienyl] have higher *IS* values (1.31, 1.38 and 1.27 mm s^{-1}) than $LSn(p\text{-tolyl})_2(S_2CNMe_2)$ (1.16 mm s^{-1}), and this is attributable to the electronegativity difference between aryl and alkyl/cycloalkyl groups.

The large quadrupole splitting (*QS*) values (2.47–3.26 mm s^{-1}) for the triorganotin compounds containing the 3-(2-pyridyl)-2-thienyl and 2-(4,4-dimethyl-2-oxazolinyl)-3-thienyl ligands are specifically diagnostic of higher-than-four coordination at tin. This conclusion is well supported by the large ρ values defined by the ratio *QS*/*IS*. A ρ value of > 2.1 is often associated with higher-than-four coordination at tin [24]. In contrast, bis(2-thienyl)phenyltin iodide, which has a *QS* value of 2.08 mm s^{-1} and a ρ value of 1.70, is assigned a tetrahedral structure, similar to that of Ph_3SnI ($QS = 2.25$ mm s^{-1}; $\rho = 1.88$ [25]). Not unexpectedly, the cationic complex, $[(2\text{-}C_4H_3S)_2SnPh(Ph_3AsO)_2]^+$ $[BPh_4]^-$, derived from bis(2-thienyl)phenyltin iodide, shows Mössbauer parameters consistent with five-fold coordination at tin. It is noteworthy that the tetraorganotin derivatives L'_2SnMe_2 (isolated as a side-product in the preparation of $L'SnMe_2(S_2CNMe_2)$) and $L'SnPh_3$ (prepared for purposes of comparison) gave resolvable doublet spectra with *QS* values of 1.06 and 0.51 mm s^{-1}, respectively. Such splittings are unusual for R_4Sn compounds, for which variations in the Sn–C bond polarities are usually too small to generate an electric field gradient at the Mössbauer nucleus, and the quadrupole splitting in the above two tetraorganotin compounds is probably the result of an additional coordinative interaction at tin.

Information on the solution state structures of the title compounds was next sought for selected cases from ^{119}Sn chemical shift data (Table 2), and for a wider range of compounds from measurements of the time-averaged one-bond coupling constants $^1J(^{119}Sn-^{13}C)$, from ^{13}C NMR spectra (Tables 3 and 4). The ^{119}Sn NMR spectra of LSn(*p*-tolyl)$_2$Br, LSnPh$_2$OH, LSn(*p*-tolyl)$_2$(S$_2$CNMe$_2$), LSn(*p*-tolyl)$_2$(oxin) (L = 3-(2-pyridyl)-2-thienyl) and L'SnPh$_2$Cl (L' = 2-(4,4-dimethyl-2-oxazolinyl)-3-thienyl) at ambient temperatures in CDCl$_3$ show in each case a single sharp resonance at -228.5, -234.5, -210.9, -214.1 and -211.0 ppm, respectively, relative to Me$_4$Sn. These resonances are located at significantly higher fields than those for tetrakis(2-thienyl)tin and the mixed thienyl tetraorganotins listed in Table 2. A similar upfield shift was also observed for LSnMe$_2$(S$_2$CNMe$_2$) and L'SnMe$_2$(S$_2$CNMe$_2$) [$\delta(^{119}$Sn) -173.9 and -138.9 ppm, respectively] relative to that of (2-C$_4$H$_3$S)$_3$SnCl [$\delta(^{119}$Sn) -64.4 ppm] or (3-C$_4$H$_3$S)$_3$SnCl [$\delta(^{119}$Sn) -70.3 ppm] [5]. It is also noteworthy that L'$_2$SnMe$_2$ and L'SnPh$_3$ gave $\delta(^{119}$Sn) values of -101.3 and -153.9 ppm, respectively, which are at significantly higher fields relative to that of (2-C$_4$H$_3$S)$_2$SnMe$_2$ [$\delta(^{119}$Sn) -62.7 ppm] and (2-C$_4$H$_3$S)SnPh$_3$ [$\delta(^{119}$Sn) -135.5 ppm] [7]. In view of the strong dependence of $\delta(^{119}$Sn) on coordination number [26–28], these results suggest that the compounds containing the 3-(2-pyridyl)-2-thienyl and 2-(4,4-dimethyl-2-oxazolinyl)-3-thienyl ligands effectively retain a pentacoordinate or pseudo-pentacoordinate environment at tin in solution.

The ^{13}C NMR spectral data obtained for selected thienyl triorganotin compounds are given in Tables 3 and 4. For comparison the chemical shift data of a few related thienyl tetraorganotin compounds are also shown. In the 3-(2-pyridyl)-2-thienyltin series there are no systematic variations in the chemical shift values of the aryl or heteroaryl ring carbons when the relevant cycloalkyl or aryl group in the parent tetraorganotin is replaced by the more electronegative Br, I or S$_2$CNMe$_2$ ligands, except for a slight upfield shift in the thienyl *ipso*-carbon (C-2). On the other hand, upfield shifts are observed for all the thienyl ring carbons in [3-(2-py)-2-C$_4$H$_2$S]SnPh$_2$OH, but most conspicuously for C-2 ($\Delta\delta$ 6 ppm) relative to [3-(2-py)-2-C$_4$H$_2$S]SnPh$_3$ [8]. A similar trend is observed for the 2-oxazolinylthienyltin compounds, **1** and **2**, relative to their parent tetraorganotins. Thus, the replacement of a heteroaryl group by the S$_2$CNMe$_2$ moiety in L'$_2$SnMe$_2$ results in an upfield shift of all the thienyl carbons, with the *ipso*-carbon (C-3) shifted the most ($\Delta\delta$ 6.3 ppm). The tin-bound methyl carbons also suffer an upfield shift ($\Delta\delta$ 9 ppm), with a concomitant increase in the one-bond coupling constant $^1J(^{119}\text{Sn}-^{13}\text{C}_{\text{Me}})$ from 459.5 to 576.1 Hz. The one-bond coupling associated with the thienyl *ipso*-carbon is similarly increased from 452.6 to 491.0 Hz. The signals from thienyl ring carbons C-2 to C-4 of **2** also show a similar shift to higher field relative to those from corresponding carbons in L'SnPh$_3$, but the C-5 signal curiously undergoes a downfield shift. It is instructive that the one-bond coupling associated with the thienyl *ipso*-carbon is substantially higher in **2** (695.8 Hz) than that in L'SnPh$_3$ (500.5 Hz) or **1** (491.0 Hz). It is generally accepted that the Fermi contact term is dominant for organometallics [29], and that the value of the one-bond coupling constant $^1J(^{119}\text{Sn}-^{13}\text{C})$ may reflect the amount of *s*-character in the Sn–C bond [29,30]. While caution must be exercised in the use of coupling constants [31], they are strongly indicative of the coordination state of the tin atom, and indeed such a classification has been made for a number of alkyl- and aryl-tin compounds [32,33].

As indicated in Table 4, [3-(2-py)-2-C$_4$H$_2$S]Sn(*p*-tolyl)$_2$Br and the corresponding dithiocarbamato derivative have $^1J(^{119}\text{Sn}-^{13}\text{C}_{\text{aryl}})$ values of 894.8 and 1052.8 Hz, respectively, relative to 647.5 Hz for [3-(2-py)-2-C$_4$H$_2$S]Sn(*p*-tolyl)$_3$ [8] and 536.9 Hz for (2-C$_4$H$_3$S)Sn(*p*-tolyl)$_3$ [7]. These results indicate that in contrast to the last-mentioned compound, which is unequivocally four-coordinate at tin, the solution structures of pyridyl-substituted thienyltins show varying extents of pyridyl coordination to tin, the tendency being especially pronounced for both of the thienyl trioganotins. For $(2\text{-}C_4H_3S)_2SnPhI$, the $^1J(^{119}Sn-^{13}C_{phenyl})$ value is 715.3 Hz. Although this is about 100 Hz higher than that for $(2\text{-}C_4H_3S)_3SnPh$, assumption of a higher coordination state for tin in the iodide, which might conceivably arise through autocomplexation, appears to be unjustified since from the Mössbauer spectrum there is no evidence for this feature even in the solid state. By contrast, $(3\text{-py-}2\text{-}C_4H_2S)Sn(^cC_6H_{11})_2I$, which is clearly five-coordinate from Mössbauer evidence, appears to be four-coordinate in solution, with a ^1J value of 296.7 Hz, which is less than that for the parent tetraorganotin, $(3\text{-py-}2\text{-}C_4H_2S)Sn(^cC_6H_{11})_3$ (374.8 Hz), for which a distorted 5-coordinate tin structure has been proposed [8].

For the compounds L'_2SnMe_2 and $L'SnMe_2(S_2CNMe_2)$ (**1**), the combined spectral observations for the solid (Mössbauer) and solution (^{119}Sn and ^{13}C NMR) states support the presence of intramolecular bonding, which is more pronounced in **1** than in L'_2SnMe_2. The spectral data contrast markedly with those for $(2\text{-}C_4H_3S)_2SnMe_2$, which is unequivocally four-coordinate at tin [7]. A similar conclusion may be drawn in respect of the pair of compounds, $L'SnPh_3$ [$\delta(^{119}Sn)$ -153.9 ppm; $^1J(^{119}Sn-^{13}C_{thienyl})$ 500.5 Hz] and $L'SnPh_2Cl$ [$\delta(^{119}Sn)$ -211.5 ppm; $^1J(^{119}Sn-^{13}C_{thienyl})$ 695.8 Hz], whose spectroscopic data in the solution state are different from those for $(2\text{-}C_4H_3S)SnPh_3$ [$\delta(^{119}Sn)$ -135.5 ppm] [7].

Whereas the spectroscopic studies described above on the substituted thienyltins strongly indicate the presence of pentacoordination at tin, these studies, however, do not reveal which of the heteroatoms (N or O) is involved in intramolecular coordination in the case of the oxazolinylthienyltin compounds. This prompted the X-ray diffraction study of compounds **1** and **2**, discussed below.

Crystallography

The structure of [2-(4,4-dimethyl-2-oxazolinyl)-3-thienyl]dimethyltin *N*,*N*-dimethyldithiocarbamate, **1** is shown in Fig. 1, in which the atomic numbering scheme differs from that depicted in structure II (see Introduction). The tin atom has a trigonal bipyramidal coordination geometry as a result of *C*,*N*-chelate bonding by the 2-(4,4-dimethyl-2-oxazolinyl)-3-thienyl group. The carbon ligands are in equatorial sites and the more electronegative nitrogen and sulphur atoms in the axial positions. The tin–nitrogen distance of 2.720(3) Å is appreciably longer than that in, for example, [2-(4,4-dimethyl-2-oxazolinyl)phenyl]dimethyltin bromide (Sn–N 2.414(4) Å) [34] and bis[3-(2-pyridyl)-2-thienyl]diphenyltin (Sn–N 2.580(8) Å) [9]. The Sn–S(1) bond distance of 2.526(1) Å is only slightly longer than that in $^nBuPh_2SnS_2CNMe_2$ [35] (2.466 Å) and $Me_3SnS_2CNMe_2$ [36] (2.47 Å). The Sn–S(2) distance of 3.276(1) Å is, however, appreciably longer than that in the above and other triorganotin dithiocarbamato compounds having essentially tetrahedral geometries [37,38]. The title compound thus constitutes an unusual example of a five-coordinate triorganotin dithiocarbamate. The distortion from the ideal trigonal bipyramidal geometry in **1** is evident from the magnitude of S(1)–Sn–N(2) apical angle (162.12(7)°) and the sum of the C–Sn–C angles in the trigonal girdle (350.4°). The largest carbon–tin–carbon angle is the Me–Sn–Me angle, which is opened to 126.5(2)° in order to minimize steric interactions with the dimethyldithiocarbamato group. For similar reasons, the S(1)–Sn–C(1) and S(1)–Sn–C(2)

Table 8

Selected bond lengths (Å) and bond angles (°) in compounds **1** and **2**

Compound **1**

Sn–S(1)	2.526(1)	Sn–C(1)	2.135(4)	Sn–C(2)	2.127(4)
Sn–C(3)	2.163(4)	Sn–S(2)	3.2767(1)	Sn–N(2)	2.720(3)

S(1)–Sn–C(1)	104.0(1)	S(1)–Sn–N(2)	162.12(7)
S(1)–Sn–C(2)	104.6(1)	N(2)–Sn–C(1)	83.9(2)
S(1)–Sn–C(3)	90.7(1)	N(2)–Sn–C(2)	82.3(2)
C(1)–Sn–C(2)	126.5(2)	N(2)–Sn–C(3)	71.5(1)
C(1)–Sn–C(3)	112.5(2)	C(7)–N(2)–C(8)	107.8(3)
C(2)–Sn–C(3)	111.4(1)	Sn–N(2)–C(8)	148.2(2)
Sn–N(2)–C(7)	104.0(2)		

Compound **2** (molecule a)

Sn(1a)–C(11a)	2.451(3)	Sn(1a)–N(1a)	2.580(8)	Sn(1a)–C(1a)	2.13(1)
Sn(1a)–C(7a)	2.12(9)	Sn(1a)–C(13a)	2.13(1)		

Cl(1a)–Sn(1a)–N(1a)	168.4(2)	Cl(1a)–Sn(1a)–C(1a)	96.1(2)
Cl(1a)–Sn(1a)–C(7a)	97.4(3)	Cl(1a)–Sn(1a)–C(13a)	94.9(3)
N(1a)–Sn(1a)–C(1a)	89.7(3)	N(1a)–Sn(1a)–C(7a)	88.7(3)
N(1a)–Sn(1a)–C(13a)	73.5(3)	C(1a)–Sn(1a)–C(13a)	122.2(4)
C(1a)–Sn(1a)–C(7a)	118.4(4)	C(7a)–Sn(1a)–C(13a)	116.0(4)

Compound **2** (molecule b)

Sn(1b)–Cl(1b)	2.469(3)	Sn(1b)–N(1b)	2.525(7)	Sn(1b)–C(1b)	2.128(9)
Sn(1b)–C(7b)	2.10(1)	Sn(1b)–C(13b)	2.12(1)		

Cl(1b)–Sn(1b)–N(1b)	169.9(2)	Cl(1b)–Sn(1b)–C(1b)	95.8(3)
Cl(1b)–Sn(1b)–C(7b)	95.1(3)	Cl(1b)–Sn(1b)–C(13b)	95.3(3)
N(1b)–Sn(1b)–C(1b)	87.9(3)	N(1b)–Sn(1b)–C(7b)	90.7(3)
N(1b)–Sn(1b)–C(13b)	74.6(3)	C(1b)–Sn(1b)–C(7b)	122.7(4)
C(1b)–Sn(1b)–C(13b)	115.8(4)	C(7b)–Sn(1b)–C(13b)	118.9(4)

angles of 104.0(1) and 104.6(1)°, respectively, are widened relative to the S(1)–Sn–C(3) angle of 90.7°. The thienyl and oxazolinyl rings are virtually coplanar, with little torsional twist between them (torsional angle C(3)–C(6)–C(7)–N(2) −0.8°), unlike the situation in, for example, bis[3-(2-pyridyl)-2-thienyl]diphenyltin (torsional angle, −2.6°) [9] and [3-(2-pyridyl)-2-thienyl]tri(*p*-tolyl)tin (torsional angle, −6.2°) [8]. The tin atom is seen to lie in the plane of the oxazolinyl ring (sum of angles subtended at N(2) by C(7), C(8) and Sn equals to 360.0°); the bisector of the C(7)–Sn–C(8) angle, however, makes an appreciable angle of 22.3° with the Sn–N bond.

The crystal of [2-(4,4-dimethyl-2-oxazolinyl)-3-thienyl]diphenyltin chloride, **2**, has two symmetry independent molecules, a (see Fig. 2) and b, in the unit cell. Both tin atoms are five-coordinate in a distorted *trans*-C_3SnClN trigonal bipyramidal environment as a result of intramolecular bonding to tin by the oxazolinyl nitrogen. The axial angle (Cl–Sn–N) is 168.4(2)° in molecule a and 169.9(2)° in molecule b, the deviation from ideality being on account of the small bite angle of the 2-oxazolinylthienyl ligand (73.5(5)° in molecule a and 74.6(3)° in molecule b) spanning the axial-equatorial positions of the trigonal bipyramid. The corresponding bite angle in **1** is 71.5(1)°. In both molecules a and b the tin atoms lie out of the equatorial plane defined by the *ipso*-carbon atoms of the aromatic rings in the direction of the axial chlorine occupant, as indicated by the sum of C–Sn–C bond angles of 356.6 and 357.4°, respectively. The tin–nitrogen distances in **2** (Sn(1a)–N(1a) 2.580(8) Å, Sn(1b)–N(1b) 2.525(7) Å) are shorter than in **1**, and comparable with those in the six-coordinate bis[3-(2-pyridyl)-2-thienyl]diphenyltin (Sn–N 2.560(2) Å) and the five-coordinate triphenyltin 3-quinolinylthiolate (Sn–N 2.592(9), 2.611(8) Å [39].

Acknowledgements

This work was supported by a grant from the National Science Council for Research and Development, Malaysia (Grant No. 2-07-04-06), One of us (S.S.) is grateful to the University of Malaya for a tutorship grant.

References

1 V.G. Kumar Das, K.M. Lo and S.W. Ng, Main Group Met. Chem., 11 (1988) 251.
2 A.G. Davies and P.J. Smith, in G. Wilkinson, F.G.A. Stone and E.W. Abel (Eds.), Comprehensive Organometallic Chemistry, Vol. 2, Pergamon Press, Oxford, 1982, p. 519, and references therein.
3 H.E. Ramsden, British Patent, 825039 (1959); Chem. Abstr., 54 (1960) 18438b.
4 H.E. Ramsden, British Patent 829243 (1960); Chem. Abstr., 54 (1960) 21139d.
5 D.W. Allen, D.J. Derbyshire, J.S. Brooks and P.J. Smith, J. Chem. Soc., Dalton Trans., (1984) 1889.
6 D.W. Allen, D.J. Derbyshire, J.S. Brooks and P.J. Smith, J. Organomet. Chem., 251 (1983) 45.
7 V.G. Kumar Das, K.M. Lo and S.J. Blunden, J. Organomet. Chem., 334 (1987) 307.
8 V.G. Kumar Das, K.M. Lo, Chen Wei, S.J. Blunden and T.C.W. Mak, J. Organomet. Chem., 322 (1987) 163.
9 V.G. Kumar Das, K.M. Lo, Chen Wei and T.C.W. Mak, Organometallics, 6 (1987) 10.
10 K. Dittmer, R.P. Martin, W. Herz and S.J. Cristol, J. Am. Chem. Soc., 71 (1949) 1201.
11 A.J. Carpenter and D.J. Chadwick, J. Chem. Soc., Perkin Trans. I, (1985) 173.
12 O.A. Ptitsyna, O.A. Reutov and M.F. Turchinskii, Dokl. Akad. Nauk SSSR, 114 (1957) 110; Chem. Abstr., 52 (1957) 1090.
13 M. Honda, M. Komura, Y. Kawasaki, T. Tanaka and R. Okawara, J. Inorg. Nucl. Chem., 30 (1968) 3231.
14 H. Gilman and L.A. Gist, Jr., J. Org. Chem., 22 (1957) 250.
15 H.G. Kuivila and E.R. Jakusik, J. Org. Chem., 26 (1961) 1430.
16 A.K. Sawyer and H.G. Kuivila, Chem. Ind. (London), (1961) 260.
17 L.D. Vecchia and I. Vlattas, J. Org. Chem., 42 (1977) 2649.
18 F.W.D. Woodhams, Software Microsyst., 1 (1982) 108.
19 J.D. Schagen, L. Straver, F. van Meurs and G. Williams, Enraf–Nonius CAD4 user's manual, version 5.0, update Dec. 1989, Enraf–Nonius Delft, Netherlands.
20 P. Main, S.J. Fiske, S.E. Hull, L. Lessinger, G. Germain, J.-P. DeClercq and M.M. Woolfson, MULTAN80, A system of computer programs for the automatic solution of crystal structures from X-ray diffraction data, 1982, University of York, England.
21 R. Peshar and H. Schenk, Acta Crystallogr., Sect. A, 43 (1987) 751.
22 R.C.G. Killean and J.L. Lawrence, Acta Crystallogr., Sect. B, 25 (1969) 1750.
23 C.K. Fair, MoLEN Structure Determination System, (1990) Delft Instruments, Delft, Netherlands.
24 R.H. Herber, H.A. Stöckler and W.T. Reichle, J. Chem. Phys., 42 (1965) 2447.
25 R.V. Parish and R.H. Platt, J. Chem. Soc., Chem. Commun., (1968) 1118.
26 C.R. Lassigne and E.J. Wells, Can. J. Chem., 55 (1977) 927.
27 P.J. Smith and A.P. Tupciauskas, Ann. Rep. NMR Spectrosc., 8 (1978) 291.
28 R.K. Harris, J.D. Kennedy and W. McFarlane, in R.K. Harris and B.E. Mann (Eds.), NMR and the Periodic Table, Academic Press, London, 1978, p. 342 and references therein.
29 V.S. Petrosyan, Prog. NMR Spectrosc., 11 (1977) 115.

30 R. Barbieri, R. Benassi and F. Taddei, J. Organomet. Chem., 129 (1977) 27.
31 Bertha de Porter and M. Gielen, J. Organomet. Chem., 124 (1977) 161.
32 P.G. Domazetis, R.J. Magee and R.D. James, J. Organomet. Chem., 148 (1976) 339.
33 J. Holeček, M. Nadvornik, K. Handlir and A. Lyčka, J. Organomet. Chem., 275 (1984) 43, 241 (1983) 177, and 258 (1983) 147.
34 J.T.B.H. Jastrzebski, Ph.D. Thesis, Rijksuniversiteit Utrecht, Utrecht, Netherlands, 1991.
35 V.G. Kumar Das, Chen Wei and E. Sinn, J. Organomet. Chem., 290 (1985) 291.
36 G.M. Sheldrick and W.S. Sheldrick, J. Chem. Soc. (A), (1970) 490; G.M. Sheldrick, W.S. Sheldrick, F.F. Dalton and K. Jones, J. Chem. Soc. (A), (1970) 493.
37 E.M. Holt, F.A.K. Nasser, A. Wilson Jr. and J.J. Zuckerman, Organometallics, 4 (1985) 2073.
38 O.-S. Jung, M.J. Kim, J.W. Jeong and Y.S. Sohn, Bull. Korean Chem. Soc., 11 (1990) 164.
39 N.G. Furmanova, Yu.T. Struchkov, E.M. Rokhlina and D.N. Kravtsov, J. Struct. Chem. (Engl. Transl.), 21 (1980) 766.