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Synthesis and structural characterization of (2-oxazolinylthienyl)tetraorganotin(IV) compounds

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Abstract

The synthesis and spectroscopic characterization (^{119m}Sn Mössbauer and ^{13}C/^{119}Sn NMR) of a series of thienyl tetraorganotin compounds, L_nSnR_{4-n} (L = [2-(4,4-dimethyl-2-oxazolinyl)-3-thienyl]; R = CH_3, n-C_4H_9, c-C_6H_{11}, C_6H_5, p-$CH_3C_6H_4$ and p-ClC_6H_4; n = 1, 2) are described. The compounds are essentially four-coordinate structures in the solid state and in solution. An X-ray crystal structure analysis of [2-(4,4-dimethyl-2-oxazolinyl)-3-thienyl]tri(*p*-tolyl)tin confirms the tetrahedral geometry at tin. The oxazolinyl substituent on the thienyl ring is oriented in such a way that the oxygen atom rather than the nitrogen points towards tin at a non-bonded contact of 2.977(3) Å, thus inducing a slight distortion of the tetrahedral geometry. This finding contrasts with those for $LSnPh_2Cl$ and $LSnMe_2(S_2CNMe_2)$, in which the oxazolinyl nitrogen is intramolecularly coordinated to tin.

Key words: Tin; Nuclear magnetic resonance; Mössbauer spectroscopy; Thienyl; Crystal structure

1. Introduction

Tetraorganotin(IV) compounds have long been regarded as possessing negligible Lewis acceptor properties [1]. However, in recent years, a few examples of such compounds have been reported in which the tin atoms are penta- [2–4] or even hexa- [5] coordinated, as a result of intramolecular Sn–N or Sn–O coordination. Examples of crystallographically authenticated structures include [3-(2-pyridyl)-2-thienyl] tri(*p*-tolyl)tin [2], (2-carbomethoxy-1,4-cyclohexadien-1-yl)trimethyltin [4] and bis[3-(2-pyridyl)-2-thienyl]diphenyltin [5].

We previously reported studies on the synthesis and structure of thienyl triorganotin compounds containing the 3-(2-pyridyl) and 2-(4,4-dimethyl-2-oxazolinyl) substituent groups on the heteroaryl ring [6]. X-Ray crystal structure analysis revealed these to contain five-coordinate tin species containing intramolecular Sn–N bonds. In continuation of this work, we now report our results on thienyl tetraorganotins, L_nSnR_{4-n} (L = [2-(4,4-dimethyl-2-oxazolinyl)-3-thienyl]; R = CH_3, n-C_4H_9, c-C_6H_{11}, C_6H_5, p-$CH_3C_6H_4$ and p-ClC_6H_4; n = 1,2).

2. Experimental section

2.1. General

All lithiations were performed under dry, oxygen-free nitrogen. n-Butyllithium (15% solution in hexane), 2-thiophene carboxyl chloride and triphenyltin chloride were purchased from the Tokyo Kasei Company and tri(*n*-butyl)tin chloride and tri(cyclohexyl)tin chloride from the Aldrich Chemical Company. Diethyl ether and tetrahydrofuran were distilled from P_2O_5 and dried over sodium wire prior to use.

2.2. Physical measurements

Elemental analyses were carried out by the Microanalytical Service Laboratories at University College, London and University of Bath, UK. Melting points were determined on a MELT-TEMP apparatus and are uncorrected.

The tin-119*m* Mössbauer spectra (Table 2) were recorded at 80 K with a Cryophysics constant acceleration spectrometer with a 512 channel data store and a 15 mCi $Ca^{119}SnO_3$ source at room temperature. The velocity range was calibrated with $CaSnO_3$, and the spectra were fitted with a Lorentzian curve-fitting program. The isomer shifts, quadrupole splittings and line widths measured are accurate to ±0.05 mm s^{-1}.

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TABLE 1. Analytical data, melting points and yields

Compound [a]		m.p. (°C)	Yield (%)	Analyses (%) [b] C	H	N
LSn(p-MeC$_6$H$_4$)$_3$	**1**	181–184	75	62.68	5.25	2.36
				(62.97)	(5.42)	(2.45)
LSn(C$_6$H$_5$)$_3$	**2**	178–179	90	61.87	4.59	2.47
				(61.17)	(4.75)	(2.64)
LSn(p-ClC$_6$H$_4$)$_3$	**3**	168–170	65	50.88	3.44	2.19
				(51.18)	(3.49)	(2.21)
LSn(n-C$_4$H$_9$)$_3$	**4**	Oil	74	54.91	7.92	3.25
				(53.65)	(7.88)	(2.98)
LSn(c-C$_6$H$_{11}$)$_3$	**5**	82– 84	50	60.30	8.45	2.50
				(59.16)	(7.85)	(2.56)
L$_2$Sn(CH$_3$)$_2$	**6**	155–157	58	47.10	5.20	5.59
				(47.18)	(5.11)	(5.50)
L$_2$Sn(p-MeC$_6$H$_4$)$_2$	**7**	224–226	40	58.00	5.05	4.21
				(58.12)	(5.15)	(4.24)

[a] L = [2-(4,4-dimethyl-2-oxazolinyl)-3-thienyl]. [b] Found (calculated).

The ^{1}H and ^{13}C NMR spectra for the compounds were recorded in CDCl$_3$ on a JEOL JNM GX270 spectrometer, operating at 270.1 MHz and 67.8 MHz, respectively. A complete decoupling irradiation mode was used to record the ^{13}C spectra with the CDCl$_3$ functioning as internal lock. All the ^{119}Sn NMR spectra were obtained under Nuclear-Overhauser-suppressed conditions on the same instrument at 100.6 MHz. The NMR spectra were recorded at ambient temperature with concentrated CDCl$_3$ solutions for ^{13}C (Table 4) and ^{1}H NMR spectra and specific concentrations for ^{119}Sn NMR (Table 3). The ^{13}C chemical shifts (relative to Me$_4$Si) are accurate to ±0.05 ppm; the ^{119}Sn chemical shifts (relative to Me$_4$Sn) are accurate to ±0.1 ppm.

TABLE 2. Tin-119m Mössbauer data [a] (mm s^{-1}) for thienyl tetraorganotins and related compounds at 80 K

Compound [b]		IS [c]	QS	Γ_1	Γ_2
LSn(p-MeC$_6$H$_4$)$_3$	**1**	1.18	0.46	0.86	0.86
LSn(C$_6$H$_5$)$_3$	**2**	1.05	0.51	1.00	1.00
LSn(p-ClC$_6$H$_4$)$_3$	**3**	1.05	0.51	1.00	1.00
LSn(c-C$_6$H$_{11}$)$_3$	**5**	1.32	0.78	0.98	0.99
L$_2$Sn(CH$_3$)$_2$	**6**	1.16	1.06	0.94	0.94
L$_2$Sn(p-MeC$_6$H$_4$)$_2$	**7**	1.12	0.31	0.90	0.92
(3-C$_4$H$_3$S)$_2$Sn(p-MeC$_6$H$_4$)$_2$ [d]		1.15	0		
(2-C$_4$H$_3$S)Sn(C$_6$H$_5$)$_3$ [d]		1.16	0		
L'$_2$Sn(C$_6$H$_5$)$_2$ [e]		1.03	0.73	1.03	1.14
L'Sn(C$_6$H$_5$)$_3$ [f]		1.11	0.63	1.07	1.30
L'Sn(p-MeC$_6$H$_4$)$_3$ [f]		1.07	0.57	0.88	0.93
(C$_6$H$_5$)$_3$SnBox [g,h]		1.19	0.80	0.90	0.90
(C$_6$H$_5$)$_3$SnBtz [g,h]		1.25	0.81	1.02	1.08
(n-C$_4$H$_9$)$_3$SnBtz [g,h]		1.32	1.20	0.94	0.97

[a] Error ± 0.05 mm s^{-1}. [b] L = [2-(4,4-dimethyl-2-oxazolinyl)-3-thienyl], L' = [3-(2-pyridyl)-2-thienyl]. [c] Relative to CaSnO$_3$ or BaSnO$_3$. [d] Ref. 17. [e] Ref. 5. [f] Ref. 2. [g] Box = 2-benzoxazole; Btz, 2-benzothiazole. [h] Ref. 16.

The crystallographic analysis of [2-(4,4-dimethyl-2-oxazolinyl)-3-thienyl]tri(p-tolyl)tin (**1**) was performed on an automated Enraf-Nonius CAD4 diffractometer (graphite-monochromated Mo-Kα, $\lambda = 0.71073$ Å). Unit cell constants for the compound were calculated from 25 strong reflections in the $13 \leq \theta \leq 16°$ thin shell. Intensity data were collected to $2\theta_{max} = 50°$. Of the 5289 reflections measured, 5170 were unique; after rejection of systematically absent reflections, 4864 remained, of which 3550 obeyed the $I \geq 3\sigma(I)$ criterion. The structure was solved by the heavy atom method. Non-H atoms were refined anisotropically; H-atoms were assigned appropriate temperature factors and

TABLE 3. Tin-119 NMR data

Compound [a]		Conc. (w/v%) [b]	δ(^{119}Sn) (ppm) [c]
LSn(p-MeC$_6$H$_4$)$_3$	**1**	9.8	−147.5
LSn(C$_6$H$_5$)$_3$	**2**	11.5	−153.9
LSn(p-ClC$_6$H$_4$)$_3$	**3**	10.4	−153.4
LSn(n-C$_4$H$_9$)$_3$	**4**	7.4	−52.3
LSn(c-C$_6$H$_{11}$)$_3$	**5**	6.4	−104.0
L$_2$Sn(CH$_3$)$_2$	**6**	4.5	−101.3
L$_2$Sn(p-MeC$_6$H$_4$)$_2$	**7**	10.4	−171.6
(3-C$_4$H$_3$S)$_2$Sn(p-MeC$_6$H$_4$)$_2$ [e]		10.0	−146.3
(2-C$_4$H$_3$S)$_2$Sn(CH$_3$)$_2$ [f]		26.7 [d]	−62.7
(2-C$_4$H$_3$S)Sn(C$_6$H$_5$)$_3$ [e]		15.4 [d]	−135.5
(2-C$_4$H$_3$S)Sn(p-MeC$_6$H$_4$)$_3$ [e]		4.7 [d]	−134.6
(C$_6$H$_5$)$_4$Sn [g]		Satd. soln.	−128.1
L'Sn(p-MeC$_6$H$_4$)$_3$ [f]		8.0 [d]	−176.3
L''Sn(C$_6$H$_5$)$_3$ [h]		7.7	−155.1
L''Sn(p-MeC$_6$H$_4$)$_3$ [h]		7.1	−148.7

[a] L = [2-(4,4-dimethyl-2-oxazolinyl)-3-thienyl]; L' = [3-(2-pyridyl)-2-thienyl]; L'' = [2-(4,4-dimethyl-2-oxazolinyl)phenyl]. [b] Solvent: CDCl$_3$. [c] Relative to Me$_4$Sn. [d] Concentration in w/w%. [e] Ref. 17. [f] Ref. 2. [g] Ref. 18. [h] V.G. Kumar Das and Normawati Samsodin, unpublished results.

placed at calculated positions (C–H = 0.95 Å) in the structure factor calculations. Refinement on F for the 271 variables converged to $R = 0.034$, $R_w = 0.043$ ($w = [\sigma^2(F) + (0.02F)^2 + 1]^{-1}$) [7]. The final difference map had peaks no larger than 0.434 e Å^{-3} against a diffuse background. Computations were performed with the MOLEN structure determination program [8] on a DEC MicroVax II minicomputer. Atomic coordinates are given in Table 5, and selected bond parameters are listed in Fig. 1. Tables of structure factors, anisotropic temperature displacement parameters and hydrogen coordinates are available from the authors.

2.3. Crystal data

[2-(4,4-Dimethyl-2-oxazolinyl-3-thienyl]tri(*p*-tolyl) tin, $C_{30}H_{30}NSOSn$: fw = 571.33, monoclinic, $P\ 2_1/c$, $a = 10.551(2)$, $b = 10.1742(6)$, $c = 25.945(1)$ Å, $\beta = 97.369(9)°$, $V = 2762.3(6)$ Å^3, $F(000) = 1164$, $D_{\text{x-ray}} = 1.372$ g cm^{-3}, $\mu = 10.19$ cm^{-1} for $Z = 4$.

2.4. Synthesis

Published procedures were used to prepare tri(*p*-tolyl)tin chloride [9] (m.p. 96–98°C), tri(*p*-chloro-

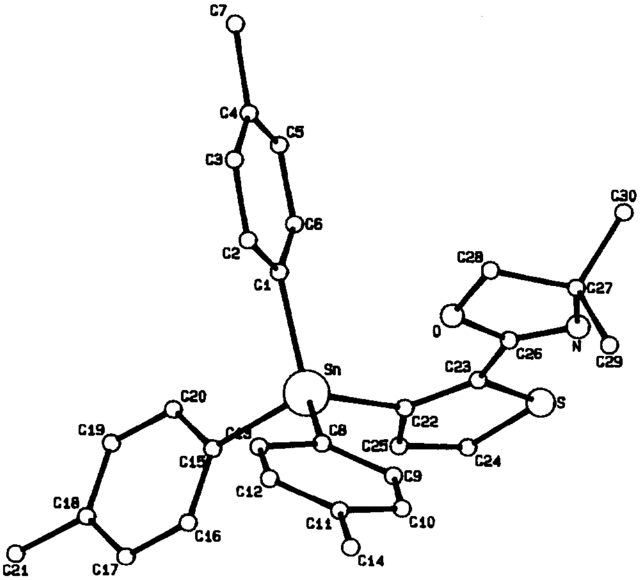
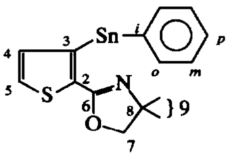


Fig. 1. [2-(4,4-Dimethyl-2-oxazolinyl)-3-thienyl]tri(*p*-tolyl)tin. Selected bond distances (Å) and angles (°): Sn–O 2.977(3), Sn–C(1) 2.134(4), Sn–C(8) 2.124(4), Sn–C(15) 2.144(4), Sn–C(22) 2.151(4); C(1)–Sn–C(8) 112.5(2), C(1)–Sn–C(15) 107.2(2), C(1)–Sn–C(22) 108.5(2), C(8)–Sn–C(15) 109.5(2), C(8)–Sn–C(22) 113.5(2), C(15)–Sn–C(22) 105.2(2).

TABLE 4. Carbon-13 NMR data [a–c]

Compound		C_i (α)	C_o (β)	C_m (γ)	C_p (δ)	C_2	C_3	C_4	C_5	C_6	C_7	C_8	C_9
LH						128.5	129.5	129.1	126.5	156.6	66.7	78.2	27.2
$LSn(p\text{-}MeC_6H_4)_3$ [e]	**1**	136.1	136.9	129.0	138.2	136.7	142.2	129.1	135.6	158.1	67.8	79.1	27.9
		(582.3)	(40.2)	(54.9)	(11.0)	(d)	(491.9)	(66.0)	(55.0)				
$LSn(C_6H_5)_3$	**2**	136.9	137.0	128.2	128.6	140.0	141.9	129.3	135.6	158.0	67.8	79.2	27.8
		(d)	(26.9)	(51.3)	(12.2)	(d)	(500.5)	(63.4)	(54.9)				
$LSn(p\text{-}ClC_6H_4)_3$	**3**	137.8	138.0	128.5	135.3	136.7	140.6	129.9	135.2	158.0	68.0	79.7	27.7
		(584.4)	(42.6)	(57.1)	(14.6)	(d)	(541.8)	(72.6)	(60.2)				
$LSn(n\text{-}C_4H_9)_3$	**4**	11.4	29.1	27.3	13.6	135.1	146.0	128.4	134.6	158.6	67.8	79.4	28.2
		(363.7)	(19.5)	(62.2)	(d)	(25.7)	(332.0)	(47.6)	(41.5)				
$LSn(c\text{-}C_6H_{11})_3$	**5**	29.2	27.3	29.5	32.2	135.5	144.8	128.4	135.2	158.7	67.9	79.4	28.5
		(361.3)	(6.2)	(59.2)	(15.6)	(d)	(265.8)	(41.5)	(34.3)				
$L_2Sn(CH_3)_2$ [f]	**6**					130.9	147.3	128.2	134.7	158.4	67.5	79.2	27.9
						(d)	(452.6)	(60.2)	(50.8)				
$L_2Sn(p\text{-}MeC_6H_4)_2$ [e]	**7**	136.6	136.8	128.8	137.9	137.6	144.8	135.7	135.5	158.2	67.8	79.0	27.9
		(600.0)	(41.5)	(59.9)	(12.2)	(d)	(538.7)	(d)	(57.3)				
$(3\text{-}C_4H_3S)_2Sn(p\text{-}MeC_6H_4)_2$ [g,h]		137.0	136.8	129.5	139.2	133.8	134.0	133.1	125.9				
		(417.6)	(41.0)	(56.4)	(9.2)	(59.8)	(d)	(57.6)	(63.2)				
$(3\text{-}C_4H_3S)_2Sn(C_6H_5)_2$ [h]		137.9	136.9	128.7	129.3	133.9	133.7	133.0	126.0				
		(499.5)	(39.0)	(54.2)	(12.4)	(58.0)	(546.4)	(58.6)	(60.8)				

[a] L = [2-(4,4-dimethyl-2-oxazolinyl-3-thienyl]. [b] In ppm ($CDCl_3$ solution); values in parentheses refer to ^nJ ($^{119}Sn-^{13}C$) values in Hz. [c] The carbon numbering scheme is as illustrated below:



[d] Coupling constants could not be estimated from spectra. [e] δ(Ar–Me) = 21.4 ppm. [f] δ(Sn–Me) = −4.7 ppm (459.5 Hz). [g] δ(Ar–Me) = 21.5 ppm. [h] Ref. 17.

TABLE 5. Positional and equivalent temperature factors for [2-(4,4-dimethyl-2-oxazolinyl)-3-thienyl]tri(*p*-tolyl)tin

Atom	x	y	z	B_{eq} (Å^2) [a]
Sn	0.18223(3)	0.15199(3)	0.57343(1)	3.513(6)
S	0.1579(1)	−0.2817(1)	0.63135(5)	4.46(3)
O	0.1121(4)	0.0818(3)	0.6775(1)	4.66(8)
N	0.0488(4)	−0.1043(4)	0.7134(2)	4.04(9)
C1	0.3241(5)	0.2412(5)	0.6284(2)	3.9(1)
C2	0.3131(5)	0.3672(6)	0.6464(2)	5.6(1)
C3	0.4036(6)	0.4217(7)	0.6837(3)	7.0(2)
C4	0.5085(5)	0.3524(7)	0.7041(2)	5.9(1)
C5	0.5214(6)	0.2281(8)	0.6856(3)	7.4(2)
C6	0.4316(6)	0.1716(6)	0.6486(3)	6.3(2)
C7	0.6078(7)	0.407(1)	0.7459(3)	9.8(2)
C8	0.0010(5)	0.2439(5)	0.5714(2)	3.5(1)
C9	−0.1051(5)	0.1767(5)	0.5847(2)	4.1(1)
C10	−0.2228(5)	0.2376(6)	0.5830(2)	4.7(1)
C11	−0.2394(5)	0.3677(6)	0.5685(2)	4.7(1)
C12	−0.1347(5)	0.4337(5)	0.5556(2)	4.6(1)
C13	−0.0180(5)	0.3736(5)	0.5565(2)	4.1(1)
C14	−0.3679(6)	0.4344(8)	0.5664(3)	7.7(2)
C15	0.2468(4)	0.1677(5)	0.4987(2)	3.7(1)
C16	0.1649(4)	0.1858(5)	0.4527(2)	3.8(1)
C17	0.2094(5)	0.1968(6)	0.4055(2)	4.6(1)
C18	0.3384(5)	0.1899(6)	0.4013(2)	4.8(1)
C19	0.4204(5)	0.1688(8)	0.4463(3)	6.7(2)
C20	0.3766(5)	0.1583(8)	0.4944(2)	6.0(1)
C21	0.3897(7)	0.2068(9)	0.3502(3)	7.9(2)
C22	0.1786(4)	−0.0553(5)	0.5893(2)	3.4(1)
C23	0.1452(4)	−0.1124(4)	0.6329(2)	3.14(9)
C24	0.2120(5)	−0.2745(5)	0.5717(2)	4.2(1)
C25	0.2184(4)	−0.1510(6)	0.5540(2)	4.0(1)
C26	0.0988(4)	−0.0505(5)	0.6771(2)	3.28(9)
C27	0.0105(5)	0.0048(5)	0.7469(2)	4.4(1)
C28	0.0678(7)	0.1248(5)	0.7246(2)	5.8(1)
C29	−0.1331(6)	0.0143(7)	0.7391(3)	6.9(2)
C30	0.0607(6)	−0.0187(7)	0.8032(2)	6.1(2)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as:

$$B_{eq} = (4/3)\left[a^2B_{1,1} + b^2B_{2,2} + c^2B_{3,3} + ab(\cos\gamma)B_{1,2} + ac(\cos\beta)B_{1,3} + bc(\cos\alpha)B_{2,3}\right].$$

phenyl)tin chloride [10] (m.p. 111–113°C), di(*p*-tolyl)tin dichloride [11] (m.p. 48–49°C) and 4,4-dimethyl-2-(2-thienyl)-2-oxazoline [12] (b.p.$_{0.1}$ 71–73°C).

2.4.1. *[2-(4,4-Dimethyl-2-oxazolinyl)-3-thienyl]tri(p-tolyl)tin (1)*

A solution of 15% n-butyllithium in hexane (7 ml, 10.00 mmol) was added to a stirred ethereal solution of 4,4-dimethyl-2-(2-thienyl)-2-oxazoline (2.0 g, 10.00 mmol) cooled to −70°C (acetone-dry ice bath) under nitrogen. The mixture was held at this temperature for 15 min and the temperature then quickly raised to 0°C, kept there for 0.5 h, then lowered again to −70°C before treatment with an ethereal solution of tri(*p*-tolyl)tin chloride (3.4 g, 8.00 mmol). After additional stirring for 1 h at −70°C, the mixture was brought to room temperature and the solvent evaporated off under reduced pressure. The resulting residue was taken up in chloroform (50 ml) and the solution filtered. Concentration of the filtrate afforded 3.5 g of the product as a white solid. Single crystals suitable for X-ray study were obtained by recrystallization from toluene.

A similar procedure was used to obtain oxazolinyltriphenyltin (**2**), -tri(*p*-chlorophenyl)tin (3), -tri(n-butyl)tin (**4**) and -tri(cyclohexyl)tin (**5**), whose melting points and analytical data are listed in Table 1.

2.4.2. *Bis[2-(4,4-dimethyl-2-oxazolinyl)-3-thienyl]dimethyltin (6)*

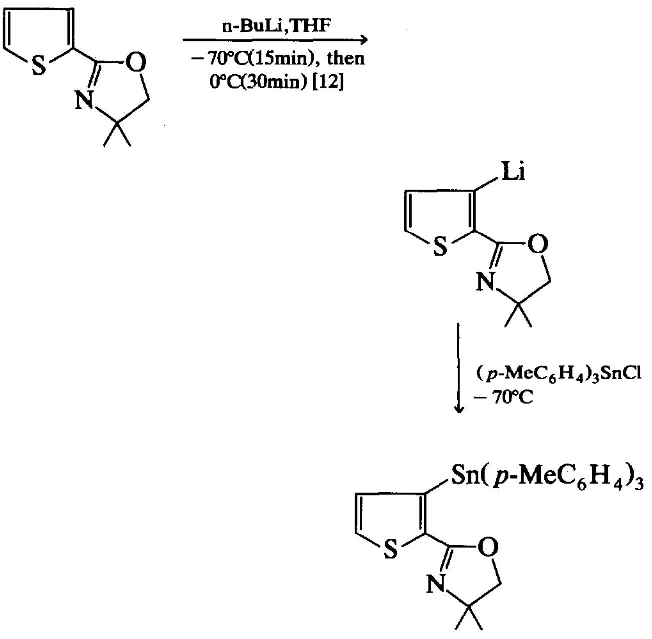
To the 3-lithio oxazolinylthiophene intermediate (8.30 mmol), prepared as described for **1**, was added an ethereal solution of dimethyltin dichloride (1.8 g, 8.30 mmol) at −70°C. The mixture was stirred for 1 h and the solvent then completely removed under reduced pressure. The residue was taken up in chloroform and the solution filtered. The filtrate was concentrated to give 1.5 g of the product as a white solid.

A similar procedure with di(*p*-tolyl)tin dichloride (2.8 g, 7.48 mmol) yielded 3.0 g of bis[2-(4,4-dimethyl-2-oxazolinyl)-3-thienyl] di(*p*-tolyl)tin (**7**) upon work-up.

3. Results and discussion

3.1. *Synthesis*

The inherent preference for 2-metallation of thiophene can be overcome by placing an *ortho*-directing oxazolinyl group in 2-position. The directing effect of the oxazolinyl group, however, is only effective if the metallating agent and solvent are carefully chosen [12–14]. Lithiation of 4,4-dimethyl-2-(2-thienyl)-2-oxazoline (LH) in ether (−70°C for 0.25 h, then 0°C for 0.5 h) with *n*-butyllithium proceeds predominantly at the *ortho*-position to the oxazoline group [12]. Similar directed lithiation has been reported for thienyl compounds containing the 2-pyridyl ligand [15]. The directed lithiation of 4,4-dimethyl-2-(2-thienyl)-2-oxazoline and subsequent treatment with a triorganotin halide results in the formation of a tetraorganotin compound in which there is potentially a coordination of more than four at tin as a result of intramolecular coordination by the N or O atom of the oxazolinyl group (Scheme 1).



Scheme 1.

Except for of n-Bu_3SnL (compound **4**), which is a colourless oil, all the tetraorganotin compounds thus synthesized were white solids. They were purified by recrystallization from a 9:1 (v/v) chloroform/petroleum ether (60–80°C) mixture. Compound **4** was purified by passage through a silica gel chromatographic column using a mixture of chloroform and *n*-hexane (1:9 v/v) as the eluting solvent; it was found to be somewhat unstable, decomposing to di-and triorganotin derivatives upon prolonged standing.

Compound **6** was isolated as the sole product from the reaction between the lithiated 2-oxazolinyl thiophene and an equimolar amount of dimethyltin dichloride. Compound **7** was prepared analogously from di(*p*-tolyl)tin dichloride.

3.2. Spectral characterization

3.2.1. ^{119}mSn Mössbauer spectra

The tin-119*m* Mössbauer data for the tetraorganotin compounds are listed in Table 2. The compounds (**1–3**, **5–7**) yielded partially resolved spectra at 80 K that were fitted as Lorentzian doublets with quadrupole splitting (QS) values ranging from 0.31 to 1.06 mm s^{-1}. Such splittings are unusual for R_4Sn compounds for which differences in the Sn–C bond polarities are often too small to generate an electric field gradient at the Mössbauer nucleus, as is the case, for example, even in the mixed tetraalkyltins, $(3\text{-}C_4H_3S)_2Sn(p\text{-tolyl})_2$ and $(2\text{-}C_4H_3S)SnPh_3$ (Table 2). On the other hand, differences in the tin–carbon bond polarities have been proposed [16] to account for the small splittings (0.80–1.20 mm s^{-1}) observed for Ph_3SnBox, Ph_3SnBtz and Bu_3SnBtz (Box = 2-benzoxazole; Btz = 2-benzothiazole); the essentially tetrahedral geometry at tin in Ph_3SnBtz was confirmed by an X-ray study [16]. The quadrupole splittings in the present 2-oxazolinylthienyltins could similarly be the result of slight differences in Sn–C bond polarities, although it is also conceivable that they could arise from an intramolecular coordinative interaction of the oxazolinyl substituent with tin. Such coordinative interactions were previously advanced to account for the partially resolved Mössbauer spectra (QS = 0.57–0.96 mm s^{-1}) in 3-pyridyl-substituted thienyl tetraorganotin compounds [2,5]. Whereas in the latter case, the pyridyl nitrogen is unambiguously the donor atom (as confirmed by X-ray analysis [5]), in compounds **1–7** either the N or O could serve as the donor atom.

3.2.2. ^{119}Sn NMR spectra

The tin-119 NMR spectra at ambient temperatures of compounds **1–3** in $CDCl_3$ (Table 3) gave single sharp resonances at −153.9, −147.5 and −153.4 ppm, respectively. These appear at slightly higher fields than for $(2\text{-}C_4H_3S)SnPh_3$ [$\delta(^{119}Sn) = -135.5$ ppm] and $(2\text{-}C_4H_3S)Sn(p\text{-tolyl})_3$ [$\delta(^{119}Sn) = -134.6$ ppm], but at a lower field compared to that in [3-(2-pyridyl)-2-thienyl]tri(p-tolyl)tin [$\delta(^{119}Sn) = -176.3$ ppm], whose structure in solution, as in the solid state, has been shown to be as a pseudo-trigonal bipyramid, involving a weak intramolecular Sn–N bond [2]. A higher-than-four coordination at tin does not appear to be indicated for compounds **1–3** on the basis of such comparisons. Compounds **4** and **5** gave $\delta(^{119}Sn)$ values of −52.3 and −104.0 ppm, respectively, the smaller shifts being in accord with the reduced electronegativities of the butyl and cyclohexyl groups relative to those of the aryl group. Tin resonances at higher field were noted for the compounds containing two 2-oxazolinylthiophene groups; thus values of $\delta(^{119}Sn)$ for **6** and **7** were −101.3 and −171.6 ppm, respectively, compared with values of −62.7 and −146.3 ppm, respectively, for the unsubstituted thienyl compounds, $(2\text{-}C_4H_3S)_2SnMe_2$ [2] and $(3\text{-}C_4H_3S)_2Sn(p\text{-tolyl})_2$ [17]. The upfield shifts of **6** and **7** are suggestive of an enhanced coordination environment at tin in these compounds.

3.2.3. ^{13}C NMR spectra

The ^{13}C NMR spectral data for the thienyl tetraorganotin compounds are given in Table 4, along with those for a few related thienyltins. The data reveal that the ^{13}C signals of the thienyl carbons, C2, C3 and C5 of compounds **1–5** are shifted to higher field relative to those for the unsubstituted thienyltin compounds, with the *ipso*-carbon (C3) shifted the most. Carbon C4, on the other hand, experiences a shielding effect and its resonance is thus shifted upfield by approximately 3 ppm. In contrast to compounds **1–5**, compound **7**, $L_2Sn(p\text{-tolyl})_2$, shows a downfield shift for C4 as well as also for all the other thienyl ring carbons, the shifts being particularly marked for C3 and C5 ($\Delta\delta \approx 10$ ppm). For the series, $LSn(p\text{-}ZC_6H_4)_3$ (where Z = H, Me, Cl), it is noted that the shift to higher field of the thienyl *ipso*-carbon (C3) follows the sequence *p*-Me < H < *p*-Cl; no particular trend is, however, apparent for the aryl ^{13}C chemical shifts.

The one-bond coupling constants, $^1J(^{119}Sn-^{13}C)$, whose magnitudes are generally a strong indicator of the coordination status at tin [18,19], were also derived from the ^{13}C NMR spectra of the compounds and are listed in parentheses in Table 4. The $^1J(^{119}Sn-^{13}C)$ values involving both C_{aryl} and $C_{thienyl}$ for the arylthienyltin compounds lie in the range 492–600 Hz, well within the range reported by Holecek *et al.* [18] as indicative of tetrahedral geometry at tin.

3.2.4. Crystallographic studies

The molecular structure of [2-(4,4-dimethyl-2-oxazolinyl)-3-thienyl]tri(*p*-tolyl)tin (**1**) is shown in Fig. 1; it should be noted that the atomic numbering scheme used there differs from that used in the discussion of the NMR spectra. The tin atom is bonded to four carbon atoms with Sn–C (tolyl) distances of 2.134(4), 2.124(4) and 2.144(4) Å and a Sn–C (thienyl) distance of 2.151(4) Å. In contrast to the previously reported crystal structures of $LSnMe_2(S_2CNMe_2)$ [6], $LSnPh_2Cl$ [6] [L = {2-(4,4-dimethyl-2-oxazolinyl)-3-thienyl}] and [2-(4,4-dimethyl-2-oxazolinyl)-5-methylphenyl]methylphenyltin bromide [20], in which the oxazolinyl nitrogen intramolecularly coordinates to the tin atom, the oxazoline ring in the title compound, **1**, is oriented in such a way that the nitrogen and the adjacent carbon-bound methyl groups lie away from tin to avoid steric interactions. In this arrangement the oxygen atom is at a non-bonded distance of 2.977(3) Å from tin, a value significantly below the sum of the Van der Waals radii of Sn and O (3.7 Å). The oxazolinyl ring is nearly planar, with a maximum deviation from least squares planes of 0.055(7) Å, and makes a dihedral angle of 13.0(5)° with the flat thienyl ring. The three tolyl groups form angles of 109.5(2), 107.2(2) and 108.5(2)° at the tin atom, in keeping with the tetrahedral description of the geometry.

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