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Synthesis, Spectroscopic Study, and X-ray Crystal Structure of Bis[3-(2-pyridyl)-2-thienyl-*C*,*N*]diphenyltin(IV): The First Example of a Six-Coordinate Tetraorganotin Compound

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Bis[3-(2-pyridyl)-2-thienyl-*C*,*N*]diphenyltin(IV) (1) has been synthesized and its structure examined by single-crystal X-ray analysis as well as by tin-119m Mössbauer spectroscopy, with evidence also from NMR spectroscopy in the ^{13}C and ^{119}Sn modes. Compound 1 crystallizes in space group $C2/c$ with a = 10.293 (5) Å, b = 16.846 (6) Å, c = 16.025 (6) Å, β = 109.32 (2)°, V = 2622 (1) Å^3, and Z = 4. The structure was determined from 3500 observed Mo Kα data and refined to R = 0.025. The crystal structure consists of discrete molecules, and there is no evidence of any intermolecular tin–sulfur interactions. Each tin atom is in a distorted octahedral environment with crystallographically imposed C_2 symmetry, in which the coordinating pyridyl nitrogens are cis to each other [Sn–N = 2.560 (2) Å; N–Sn–N = 77.1 (1)°] along with the phenyl groups [C–Sn–C = 101.9 (1)°], while the thienyl carbons are in an approximately trans relationship [C–Sn–C = 144.4 (1)°]. The Mössbauer parameters (IS = 1.03 and QS = 0.73 mm s^{-1}) are in accord with six-coordination for tin. The tin-119 chemical shift of 1 at ambient temperature in $CDCl_3$ (−245.5 ppm, relative to Me_4Sn) shows a pronounced shift to higher field compared to that of bis(2-thienyl)diphenyltin(IV) (2) (−140.8 ppm). Carbon-13 NMR examination of 1 in $CDCl_3$ reveals a value of 794.9 Hz for the one-bond tin–carbon (phenyl) coupling constant, [$^1J(^{119}\mathrm{Sn}-^{13}\mathrm{C}_{ipso})$]; by way of contrast, the corresponding value for 2 is 501.7 Hz. Integration of these spectral findings suggests a nontetrahedral environment at tin in the title complex even in solution.

Introduction

The tendency for tin to expand its covalency beyond four is widely observed[1–4] among mono-, di-, and triorganotin compounds, R_nSnX_{4-n} (n = 1–3), where X is an electronegative substituent, typically a halide or pseudohalide and, indeed, forms the basis of the extensive coordination chemistry of tin among main-group organometallics. A combination of modern physical techniques, notably NMR and Mössbauer spectroscopy, and X-ray crystallography has been used to study the tin coordination environment and structural characteristics in a range of neutral, cationic, and anionic complexes. When X is a carbon residue, the resulting tetraorganotin compound displays a negligible or weak acceptor property toward Lewis bases.[1,2] As far as we are aware, the literature contains only two references to isolable complexes of tetraorganotins, viz., the neutral adduct $Me_3SnCF_3 \cdot P(NMe_2)_3$[5] and the anionic salt lithium 1,1-bis(η^1-cyclopentadienyl)-1-halo-2,3,4,5-tetraphenylstannole,[6] the pentacoordinated structures of which have not been rigorously clarified. Spectroscopic studies in donor solvents of tetraorganotin compounds containing relatively electronegative carbon moieties such as perhaloaryl,[7,8] thienyl,[9,10] furyl,[9,10] or pyridyl[11,12] and in the solid state of compounds with an additional intramolecular donor site[13–15] attached to the α- or β-carbon atom have generally not provided unequivocal evidence for higher than four-coordination at the metal center. However, for one class of tetraorganotins, namely, the stannatranes represented by $Me_2Sn(CH_2CH_2CH_2)_2NMe$ and $MeSn(CH_2CH_2CH_2)_3N$, a multinuclear (^{1}H, ^{13}C, ^{119}Sn) NMR study has been reported[16] which strongly favors transannular N→Sn interactions in these compounds. The pentacoordinated structure of $MeSn(CH_2CH_2CH_2)_3N$ has since been confirmed.[16a]

Our interest in biocidal organotin compounds has recently prompted us to embark on a study of heteroaryltin systems,[17] and in this paper we focus on the synthesis and structure of bis[3-(2-pyridyl)-2-thienyl]diphenyltin(IV) (1). Inasmuch as the preparation of this tetraorganotin compound entailed the initial directed lithiation[18] of 2-(3-

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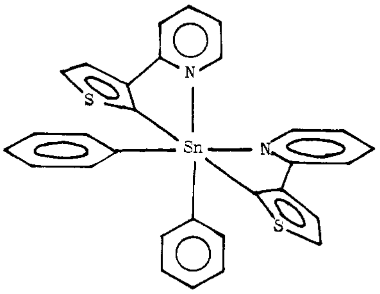
thienyl)pyridine followed by in situ transmetalation using diphenyltin(IV) dibromide, we hoped that one or both of the proximate pyridyl groups might also engage the new metal center in coordination, thereby providing an interesting case study for X-ray analysis.



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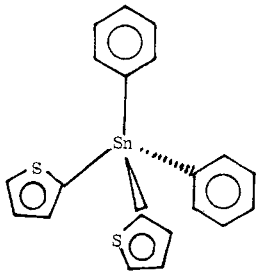

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Experimental Section

Preparation of Bis[3-(2-pyridyl)-2-thienyl-*C*,*N*]diphenyltin (1). To a solution of 2-(3-thienyl)pyridine (2 mL, 0.014 mol) in dry ether (30 mL) was added 1.5 mL of a 10.2 M *n*-BuLi solution in hexane dropwise at room temperature with stirring under nitrogen. The resulting brown solution was stirred for ca. 1 h, and to this was added dropwise a solution of Ph_2SnBr_2 (3.13 g, 0.007 mol) in dry ether (50 mL). The reaction mixture was then refluxed for 4 h, after which the LiBr formed was filtered and the filtrate concentrated. Addition of hexane dropwise to the concentrated filtrate caused immediate precipitation of **1** (3.4 g, 83% yield). Single crystals suitable for X-ray analysis were obtained upon recrystallization from toluene (mp 180–182 °C, with decomposition).

Mass spectrum: m/e (relative intensity) 517 ($M^{\bullet+}$ – Ph, 66.3), 440 ($M^{\bullet+}$ – 2Ph, 2.5), 434 ($M^{\bullet+}$ – L, 5.3), 357 ($M^{\bullet+}$ – L – Ph, 3.9), 280 ($M^{\bullet+}$ – L – 2Ph, 8.4), 274 ($M^{\bullet+}$ – 2L, 0.5), 197 ($M^{\bullet+}$ – 2L – Ph, 3.1), 161 (3-(C_5H_4N)C_4H_3S ($LH^{\bullet+}$), 100). ^1H NMR ($CDCl_3$, 28 °C): δ 7.78–6.80 (m). ^{119}Sn NMR (0.1 g/1.5 g of $CDCl_3$, 30 °C): δ –245.5 (relative to Me_4Sn). ^{13}C NMR [$CDCl_3$, saturated solution, 28 °C; δ_c (see Figure 1 for carbon labeling), $^nJ(^{119}Sn–^{13}C)$, except for values <100 Hz for which the ^{119}Sn and ^{117}Sn values were unresolved; couplings which could not be estimated are indicated by an asterisk]: phenyl, 135.5 [C_{10}(ipso), ^1J = 794.9 Hz], 136.3 [$C_{11,15}$(ortho), ^2J = 43.2 Hz], 127.6 ($C_{12,14}$(meta), ^3J = 56.6 Hz], 137.1 [C_{13}(para), ^4J < 10 Hz]; thienyl, 144.9 (C_1, $^1J^*$), 145.7 (C_4, $^2J^*$), 132.2 (C_3, ^3J = 32.2 Hz), 124.9 (C_2, ^4J = 50.8 Hz); pyridyl, 152.3 (C_5), 121.3 (C_6), 146.5 (C_7), 118.7 (C_8), 147.6 (C_9). Anal. Calcd for $C_{30}H_{22}N_2S_2Sn$: C, 60.81; H, 3.71; N, 4.73. Found: C, 61.13; H, 3.69; N, 4.85.

Cognate Preparation. Bis(2-thienyl)diphenyltin(IV) (**2**) was prepared similarly from 2-lithiothiophene in 60% yield; mp 207–210 °C.

Table I. Crystal Data and Data Collection Parameters

formula	$C_{30}H_{22}S_2N_2Sn$
fw, amu	593.33
system	monoclinic
a, Å	10.293 (5)
b, Å	16.846 (6)
c, Å	16.025 (6)
β, deg	109.32 (2)
V, Å^3	2622 (1)
space group	$C2/c$
Z	4
d(calcd), g cm^{-3}	1.503
d(obsd), g cm^{-3} (KI/H_2O)	1.492
μ, cm^{-1} (Mo Kα)	11.50
cryst size, mm^3	0.44 × 0.40 × 0.32
mean μr	0.20
transmissn factors	0.612–0.772
collectn range	$0 \leqslant h \leqslant 14$; $0 \leqslant k \leqslant 22$; $-22 \leqslant 1 \leqslant 21$; $2\theta_{max} = 60°$
unique data measd	3656
obsd data with $\lvert F_o\rvert > 3\sigma(\lvert F_o\rvert)$, n	3500
no. of variables, p	159
$R_F = \sum\lvert\lvert F_o\rvert - \lvert F_c\rvert\rvert/\sum\lvert F_o\rvert$	0.025
weighting scheme, w	$[\sigma^2(F_o) + 0.0005\lvert F_o\rvert^2]^{-1}$
$R_G = [\sum w(\lvert F_o\rvert - \lvert F_c\rvert)^2/\sum w\lvert F_o\rvert^2]^{1/2}$	0.037
$S = [\sum w(\lvert F_o\rvert - \lvert F_c\rvert)^2/(n-p)]^{1/2}$	1.290
residual extrema in final diff map	+0.65 at 0.87 Å from the Sn atom to –0.38 e Å^{-3}

^{13}C NMR [$CDCl_3$, saturated solution, 28 °C; δ_c, $^nJ(^{117,119}Sn–^{13}C)$]: phenyl, 137.0 (C_{ipso}, ^1J = 501.7 Hz), 136.8 (C_o, ^2J = 44.0 Hz), 128.8 (C_m, ^3J = 56.2 Hz), 129.7 (C_p, ^4J = 13.4 Hz); thienyl, 131.8 (C_α, $^1J^*$) 137.5 (C_β, ^2J = 37.8 Hz), 128.3 (C_γ, ^3J = 57.3 Hz), 132.3 (C_δ, ^4J = 22.0 Hz). Anal. Calcd for $C_{20}H_{17}S_2Sn$: C, 54.80; H, 3.65; S, 14.6. Found: C, 54.62; H, 3.85; S, 14.9. The microanalyses were performed by the Microanalytical Service, University College, London, U.K. The tin-119 NMR spectrum was recorded at the International Tin Research Institute, Greenford, Middlesex, U.K., on a JEOL FX60Q instrument operating at 22.24 MHz under nuclear Overhauser suppressed conditions.[19] Proton and carbon-13 NMR spectra were recorded on a JEOL JNM-FX100 spectrometer operating at 99.55 MHz for ^1H and 25.00 MHz for ^{13}C. Complete proton decoupling irradiation mode was used to secure the ^{13}C spectrum in $CDCl_3$, with the solvent functioning also as an internal lock.

Mössbauer Data. The tin-119 Mössbauer spectrum of **1** was measured at 80 K by using a constant-acceleration microprocessor spectrometer (Cryophysics Model) with a 512-channel data store. The source was 15 mCi $Ca^{119m}SnO_3$ (Radiochemical Centre, Amersham), and $Ca^{119}SnO_3$ was the reference material for zero velocity at room temperature. The velocity calibration was based on $CaSnO_3$ and β-tin. A broad, partially resolved resonance line was obtained, which was fitted as Lorentzian doublet by a least-squares fitting program:[20] isomer shift (IS) = 1.03 mm s^{-1}; quadrupole splitting (QS) = 0.73 mm s^{-1}; Γ_+ = 1.03 mm s^{-1}; Γ_- = 1.14 mm s^{-1}.

X-ray Analysis. Crystallographic measurements were carried out by using a Nicolet R3m automated four-circle diffractometer and graphite-monochromatized Mo Kα radiation (λ = 0.710 69 Å) at an ambient laboratory temperature of 22 °C. The ω–2θ scan technique was used with scan range 1° below Kα_1 to 1° above Kα_2 and scan speeds between 2.02 and 8.37 deg min^{-1}. Backgrounds were measured at each end of the scan range for one-half of the scan time. Standard centering and auto-indexing procedures[21] indicated a C-centered monoclinic cell. Crystal data and data collection parameters are listed in Table I. Two standard reflections were used to monitor every 125 reflections. Empirical absorption corrections were applied by a pseudoellipsoidal treatment of intensities of selected strong reflections measured at different azimuthal (ψ) angles.[22-24] Redundant and equivalent

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Table II. Atomic Coordinates ($\times 10^5$ for Sn and S; $\times 10^4$ for Other Atoms) with Estimated Standard Deviations in Parentheses

atom	*x*	*y*	*z*
Sn	0	16326 (1)	25000
S	−13449 (7)	16190 (4)	42374 (4)
N	1566 (2)	2822 (1)	3133 (1)
C(1)	−293 (2)	2025 (1)	3711 (1)
C(2)	−756 (3)	2254 (2)	5123 (2)
C(3)	198 (3)	2754 (2)	5016 (1)
C(4)	475 (2)	2622 (1)	4210 (1)
C(5)	1448 (2)	3066 (1)	3906 (1)
C(6)	2206 (3)	3717 (1)	4352 (2)
C(7)	3053 (3)	4109 (2)	3996 (2)
C(8)	3163 (3)	3867 (2)	3197 (2)
C(9)	2396 (3)	3213 (2)	2793 (2)
C(10)	1707 (2)	818 (1)	3072 (1)
C(11)	1513 (2)	197 (1)	3594 (1)
C(12)	2560 (3)	−326 (1)	4014 (2)
C(13)	3832 (3)	−239 (2)	3914 (2)
C(14)	4057 (3)	364 (2)	3411 (2)
C(15)	2999 (2)	892 (1)	2987 (2)

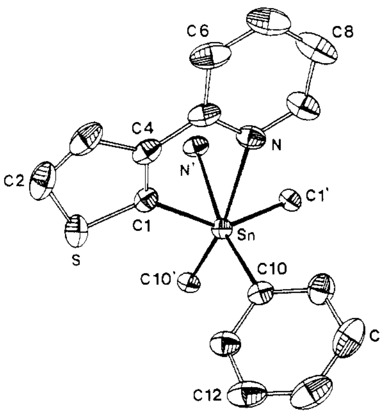

Figure 1. Perspective view of the molecular structure of bis[3-(2-pyridyl)-2-thienyl]diphenyltin(IV) with the atom numbering scheme. The thermal ellipsoids are drawn at the 35% probability level, and the C_2 axis runs vertically through the tin atom.

reflections were averaged and converted into unscaled $|F_o|$ values after corrections for Lorentz and polarization effects. Intensity statistics strongly favored the centrosymmetric space group *C*2/*c*. A sharpened Patterson function revealed the position of the Sn atom; the remaining non-hydrogen atoms were located from subsequent difference Fourier maps. All non-hydrogen atoms were refined anisotropically. The 11 ring hydrogen atoms were generated geometrically [d(C–H) = 0.96 Å] and allowed to ride on their respective parent C atoms with individual fixed isotropic temperature factors. All computations were performed on a Data General Corporation Nova 3/12 minicomputer with the SHELXTL program package.[22] Analytic expressions[25] of neutral atom scattering factors[26] were employed, and anomalous dispersion corrections[27] were applied. Blocked-cascade least-squares refinement[22,28] of 159 parameters converged to the *R* indices listed in Table I. Final positional parameters of non-hydrogen atoms are given in Table II, bond distances and angles in Table III, and least-squares planes and dihedral angles in Table IV (supplementary material). The labeling scheme adopted is shown in Figure 1. Lists of structure factors, anisotropic thermal parameters, hydrogen coordinates, and deviations from least-squares planes are available along with Table IV as supplementary material.

Table III. Selected Bond Distances and Angles with Estimated Standard Deviations in Parentheses

	(a) Bond Distances (Å)		
Sn–N	2.560 (2)	C(5)–C(6)	1.398 (3)
Sn–C(1)	2.163 (2)	C(6)–C(7)	1.361 (4)
Sn–C(10)	2.179 (2)	C(7)–C(8)	1.383 (5)
S–C(1)	1.719 (2)	C(8)–C(9)	1.384 (4)
S–C(2)	1.720 (3)	C(10)–C(11)	1.395 (3)
N–C(5)	1.348 (3)	C(10)–C(15)	1.387 (3)
N–C(9)	1.330 (4)	C(11)–C(12)	1.383 (3)
C(1)–C(4)	1.364 (2)	C(12)–C(13)	1.379 (5)
C(2)–C(3)	1.348 (4)	C(13)–C(14)	1.364 (4)
C(3)–C(4)	1.429 (3)	C(14)–C(15)	1.396 (3)
C(4)–C(5)	1.457 (3)		
	(b) Bond Angles (deg)		
N–Sn–C(1)	70.3 (1)	C(2)–C(3)–C(4)	112.9 (2)
N–Sn–C(10)	90.7 (1)	C(1)–C(4)–C(3)	113.3 (2)
N–Sn–N	77.1 (1)	C(1)–C(4)–C(5)	120.7 (2)
N–Sn–C(1′)	82.0 (1)	C(3)–C(4)–C(5)	126.0 (2)
N–Sn–C(10′)	166.9 (1)	N–C(5)–C(4)	115.6 (2)
C(1)–Sn–C(10)	98.5 (1)	N–C(5)–C(6)	120.3 (2)
C(1)–Sn–N′	82.0 (1)	C(4)–C(5)–C(6)	124.0 (2)
C(1)–Sn–C(1′)	144.4 (1)	C(5)–C(6)–C(7)	119.5 (3)
C(1)–Sn–C(10′)	103.7 (1)	C(6)–C(7)–C(8)	120.3 (2)
C(10)–Sn–C(10′)	101.9 (1)	C(7)–C(8)–C(9)	117.3 (3)
C(1)–S–C(2)	92.9 (1)	N–C(9)–C(8)	123.2 (3)
Sn–N–C(5)	111.5 (1)	Sn–C(10)–C(11)	118.0 (2)
Sn–N–C(9)	129.1 (1)	Sn–C(10)–C(15)	124.6 (1)
C(5)–N–C(9)	119.3 (2)	C(11)–C(10)–C(15)	117.3 (2)
Sn–C(1)–S	128.0 (1)	C(10)–C(11)–C(12)	121.8 (2)
Sn–C(1)–C(4)	121.7 (2)	C(11)–C(12)–C(13)	119.6 (3)
S–C(1)–C(4)	110.0 (2)	C(12)–C(13)–C(14)	120.1 (2)
S–C(2)–C(3)	110.9 (2)	C(13)–C(14)–C(15)	120.3 (3)
C(10)–C(15)–C(14)	120.9 (2)		

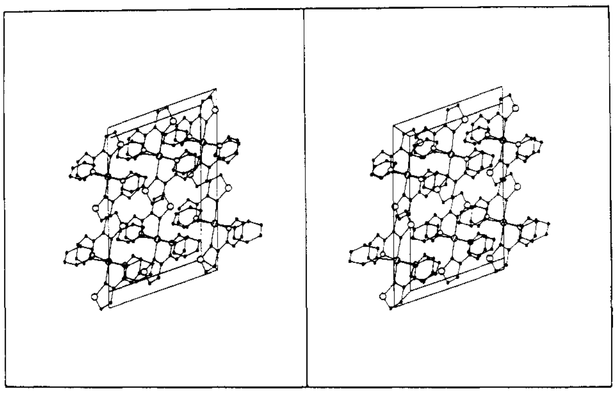

Figure 2. Stereoscopic view of the molecular packing. The origin of the unit cell lies at the upper left corner, with *a* pointing from left to right at a slant, *b* toward the reader, and *c* downward.

Results and Discussion

The title tetraorganotin compound exists as monomers with crystallographically imposed C_2 molecular symmetry (Figure 1). There are no unusual intermolecular contacts, and the molecular packing is illustrated in Figure 2. Inspection of the measured dimensions (Table III) shows that the angle subtended at tin by the thienyl groups is significantly enlarged to 144.4° from the ideal tetrahedral value, while the other R–Sn–R angles lie in the range 98.5–103.7°. These contrast with the valence angle of 112.6° observed for the distorted tetrahedral tetrakis(2-thienyl)tin(IV) molecule.[29] If the pyridyl nitrogens are included in the primary coordination sphere of tin, then the angle subtended at tin by one nitrogen atom and each ipso-carbon of the two phenyl groups is, respectively, 166.9 (1)° and 90.7 (1)°. Reflecting the distorted octahedral

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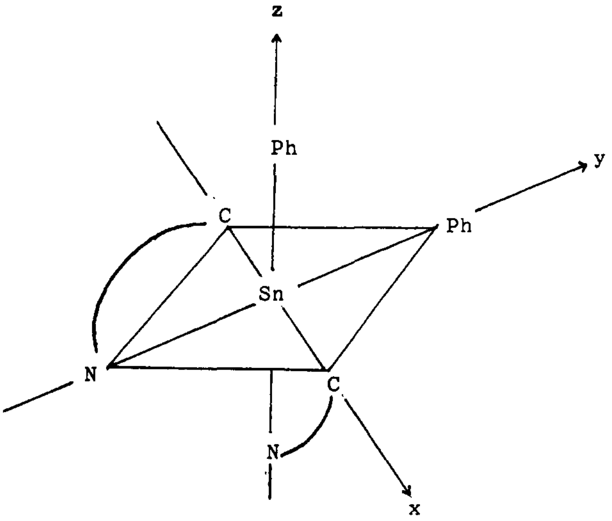
Table V. Comparison of Tin-Nitrogen Ligand Bond Lengths in Bis[3-(2-pyridyl)-2-thienyl-*C*,*N*]diphenyltin(IV) with Those in Selected Organotin(IV) Compounds

no.	compd	Sn–N, Å	ref
1	$Me_3SnCl{\cdot}py$	2.26	56
2	$(p\text{-}ClC_6H_4)_2SnCl_2{\cdot}(4,4'\text{-}Me_2bpy)$		36
	cis isomer	2.294 (6), 2.322 (6)	
	trans isomer	2.406 (8)	
3	$(p\text{-tolyl})_2SnCl_2{\cdot}bpy$	2.306 (3), 2.374 (6)	35
4	$Me_2SnCl_2{\cdot}2(NMiz)^a$	2.329 (5)	32
5	$Ph_2Sn(NCS)_2{\cdot}bpy$	2.333 (5)^b	34
6	$Ph_2SnCl_2{\cdot}bpy$	2.344 (6), 2.375 (6)	33
7	$ClSn(CH_2CH_2CH_2)_3N$	2.372 (29)	16
8	$Me_2SnCl_2{\cdot}2py$	2.39	57
9	$[2,6\text{-}(Me_2NCH_2)_2C_6H_3SnMe_2]Br$	2.39, 2.60^c	54
10	$Me_2Sn(Cl)SCH_2CH(NH_2)\text{-}CO_2Et$	2.434 (12)	52
11	$Cl_2Sn(CH_2CH_2CH_2)_2NMe$	2.44	16a
12	$Ph_2Sn(Br)(o\text{-}Me_2NCH_2C_6H_4)$	2.511 (2)	53
13	$[Me_3SnO_2CCH_2NH_2]_2$	2.53 (3)^b	55
14	$n\text{-}Pr(Et)Sn(quin)_2{}^d$	2.542 (5), 2.597 (6)	58
15	$Ph_2SnCl_2{\cdot}SC_7H_5N$	2.548 (2)	51
16	1	2.560 (2)	this work
17	$Ph_3SnCl{\cdot}SC_5H_4N$	2.62 (2)^e	60
18	$MeSn(CH_2CH_2CH_2)_3N$	2.62	16a
19	$Me_2Sn(CN)_2$	2.68 (11)^e	59
20	$(Ph_2SnCl_2{\cdot}pyz)_n{}^f$	2.965 (11), 2.782 (11)	30

[a] NMiz = N-methylimidazole. [b] Mean value. [c] Structure determination is of low accuracy ($R > 20\%$). [d] Hquin = 2-methylquinolin-8-ol. [e] Intermolecular Sn–N distance. [f] pyz = pyrazine.

geometry of 1 are the N–Sn–C "bite" angle of 70.3 (1)° of the 3-pyridyl-2-thienyl unit and the intramolecular Sn–N bond distance of 2.560 (2) Å, of which the latter is comparable to the values reported in the literature for a range of di- and triorganotin compounds. A selection of these cases is given in Table V, including the compound $[Ph_2SnCl_2{\cdot}Pyz]_n$,[30] where two types of bridging pyrazines [d(Sn–N) = 2.782, 2.965 Å] have been encountered in the polymeric chain, with the 2.965 Å bond being the largest ascribed to Sn←N coordinative interaction. It is seen that in all cases the Sn–N bond distances exceed the sum of atomic radii of Sn and N (2.10 Å),[31] supporting the suggestion[32] that the Sn–N bond has intrinsically a low degree of covalent character. As seen in the perspective view of the pseudooctahedral molecule (Figure 1), the thienyl and pyridyl rings are virtually coplanar with little torsional twist between them [torsional angle C(1)–C(4)–C(5)–N = −2.6 (3)°], unlike the case with, for example, bipyridyl chelation.[33-36] This conformational preference, we suggest, has its origin in the coordinative interaction at tin. The dihedral angle between the mean planes of the two thienyl units is 78.2°, while that between the cis phenyl rings is 73.1° (Table IV). Atoms N, N′, and C(10′) are within ±0.09 Å of their mean plane, and the Sn atom lies exactly on it; atoms N′, C(1), C(1′), C(10) lie within ±0.11 Å of their mean plane, the Sn atom being displaced from it by 0.36 Å toward the C(10′) atom. The Sn–C bond involving the phenyl group is somewhat longer than that involving the heterocyclic moiety [2.179 (2) Å vs. 2.163 (2) Å]. The latter bond is, however, longer than that involving the 3-thienyl group (2.122 Å) in five-coordinate $(C_4H_3S)_3SnBr{\cdot}Ph_3PO$[37] and that reported in tetrahedral tetrakis(2-thienyl)tin[29] (2.136 and 2.157 Å), a trend which is not inconsistent with the higher coordination state of tin in 1. Coordinative 'anchoring' of the thienyl groups in the title complex also appears to be responsible for the absence of orientational disorder of these groups in 1 relative to the other two cases.[29,37]



$$V_{xx} = V_{yy} = V_{zz} = [Ph] + [N] - 2[C]$$

$$QS = [Ph] + [N] - 2[C], \text{ where } [N] = \text{p.q.s.pyridine;}$$

$$[Ph] = \text{p.q.s.phenyl; } [C] = \text{p.q.s.thienyl}$$

Figure 3. Electric field gradient components and quadrupole splitting for 1. Partial EFG's are expressed in quadrupole splitting units (mm s^{-1}). The choice of axes respects $|V_{zz}| \geq |V_{yy}| \geq |V_{xx}|$, $0 \leq n \leq 1$.[40]

In the light of the X-ray structural study, it was of interest to examine the Mössbauer spectrum of 1. A broad, partially resolved resonance line was obtained at 80 K which was fitted as a Lorentzian doublet with quadrupole splitting (QS) of 0.73 mm s^{-1}. On the other hand, an unresolved spectrum was obtained for the unsubstituted thienyl derivative bis(2-thienyl)diphenyltin(IV) (2) even with extended spectral accumulation (isomer shift = 1.12 mm s^{-1}). It is, however, pertinent to note here that the Mössbauer literature on tetraorganotin compounds contains several anomalies of resolvable and nonresolvable splittings (for a lucid discussion of this, see ref 13), including a case of two quadrupole splittings (2.70 and 0.76 mm s^{-1} at 80 K) for $Sn(ad)_4$ (ad = adamant-1-yl).[38] Thus while the presence of a resolvable QS for 1 in contrast to 2 may not necessarily indicate a difference in the coordination environment at tin in the two cases, it is instructive that the application of the point-charge treatment[39,40] (Figure 3) to 1 [assuming identity of partial quadrupole splitting values for the thienyl and phenyl

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Table VI. Comparison of Tin-119 NMR Data (in $CDCl_3$) for Some Thienyltin Complexes and Related Compounds

compd	$\delta(^{119}Sn)^a$	ref
1	−245.5	this work
$(2\text{-}C_4H_3S)_4Sn$	−147.0	9
Ph_4Sn	−137.0	44
$(2\text{-}C_4H_3S)_2SnPh_2$ (2)	−140.8	*b*
$(3\text{-}C_4H_3S)_2Sn(p\text{-tolyl})_2$	−157.8	*b*
$(3\text{-}C_4H_3S)_4Sn$	−168.7	9
$(3\text{-}C_4H_3S)_3SnBr\cdot Ph_3PO$	−183.8	9

[a] Relative to Me_4Sn. [b] Kumar Das, V. G.; Lo, K. M.; Blunden, S. J., unpublished work.

groups (−0.95 mm s^{-1})[41,42] and regarding the pyridyl substituent as a distinct ligand (pqs = −0.10 mm s^{-1})] yields a calculated value of 0.85 mm s^{-1} for the QS, in reasonable agreement with the observed value. Suggestive also of the coordinative involvement of the pyridyl nitrogens at tin is the failure of 1 to react with methyl iodide. The nonmetalated ligand 2-(3-thienyl)pyridine, on the other hand, reacted smoothly with methyl iodide upon reflux to yield 1-methyl-2-(3-thienyl)pyridinium iodide (mp 135–137 °C). However, the absence of reaction of 1 with methyl iodide could also be ascribed to steric reasons. A better assessment of N→Sn coordination in 1, particularly in the solution state, was therefore sought from NMR spectral studies.

The tin-119 NMR spectrum of 1 at ambient temperature in $CDCl_3$ shows a single sharp resonance at −245.5 ppm (relative to Me_4Sn), shifted significantly to higher field compared to tetrakis(2-thienyl)tin and the mixed thienylaryltins listed in Table VI. On the basis of the known strong dependence of $\delta(^{119}Sn)$ on coordination number,[43–45] this result suggests a solution structure for 1 which is minimally five-coordinate, but which may, in all probability, have the same stereochemical configuration as in solid state. This view is supported also by the ^{13}C NMR data for 1 (see Experimental Section). Recent studies on *n*-butyl-[46,47] and aryltin[48] compounds have demonstrated that the time-averaged one-bond $^{119}Sn-^{13}C_{ipso}$ or α coupling constants provide a sensitive measure of the state of hybridization at the tin atom and increase with coordination number in these compounds. In the present context, it is instructive that $^1J(^{119}Sn-^{13}C_{ipso})$, where C_{ipso} refers to the ipso-carbon of the phenyl group bonded to tin, has a value of 794.9 Hz for the title compound relative to 501.7 Hz for bis(2-thienyl)diphenyltin (**2**). A further and more secure evidence for higher than four-coordination at the metal center in 1 could conceivably be obtained, in the absence of dynamic behavior in solution, from ^{15}N NMR spectroscopy,[49,50] detections of $^1J(^{119}Sn-^{15}N)$, but such investigations are beyond the scope of the present work.

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Registry No. **1**, 105102-78-1; **2**, 54663-75-1; Ph_2SnBr_2, 4713-59-1; 2-lithiothiophene, 2786-07-4; 2-(3-thienyl)pyridine, 21298-55-5.

Supplementary Material Available: Listings of anisotropic thermal parameters, hydrogen coordinates, and least-squares plane data (4 pages); a listing of structure factors (21 pages). Ordering information is given on any current masthead page.

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