

Simple Synthesis, Characterization and Structure of Diorganotin(IV) Complexes Containing the *N*-(2-Salicylidene)-*N'*-benzoylhydrazone Ligand

Dilip Kumar Dey^{a,*}, Brajagopal Samanta^a, Antonin Lycka^b, and Lutz Dahlenburg^c

^a Department of Chemistry, Chandidas Mahavidyalaya, Khujutipara – 731 215, District – Birbhum, West Bengal, India

^b Research Institute for Organic Syntheses, 532 18 Pardubice-Rybitvi, Czech Republic

^c Department of Chemistry, Universität Erlangen-Nürnberg, D-91034 Erlangen, Germany

Reprint requests to Dr. D. K. Dey. E-mail: deydk@yahoo.com

Z. Naturforsch. **58b**, 336–344 (2003); received September 30, 2002

Two diorganotin(IV) complexes of general formula $R_2Sn[2-OC_6H_4CH=N-N=C(O)Ph]$ ($R = Ph$, **1**; $R = Me$, **2**) have been synthesized from the corresponding diorganotin(IV) dichloride and the Schiff base derived from salicylaldehyde and benzoyl hydrazide. The two compounds have been characterized by elemental analysis, IR and NMR (1H , ^{13}C , ^{15}N , ^{119}Sn) spectra, and their structures have been confirmed by single crystal X-ray structure analysis. Crystals of complex **1** are triclinic, space group $P\bar{1}$, $a = 11.1631(5)$, $b = 13.462(2)$, $c = 16.511(1)$ Å, $\alpha = 106.193(9)^\circ$, $\beta = 106.379(8)^\circ$, $\gamma = 94.932(8)^\circ$, $Z = 4$, $R_1 = 0.0461$, $wR_2 = 0.0939$ for 13194 unique reflections. Crystals of **2** are monoclinic, space group $P2_1$, $a = 10.2073(5)$, $b = 14.645(2)$, $c = 10.411(3)$ Å, $\beta = 92.572(9)^\circ$, $Z = 4$, $R_1 = 0.0395$, $wR_2 = 0.0835$ for 5050 unique reflections. The central tin atom of either complex adopts a distorted trigonal bipyramidal coordination with two ligand oxygen atoms in axial positions, the nitrogen atom of the ligand and two organic groups on tin occupying equatorial sites. The $\delta(^{119}Sn)$ values for the complexes **1** and **2** are -329.2 and -150.3 , respectively, thus indicating penta-coordinated tin centres.

Key words: Diorganotin(IV) Complexes, Hydrazone Ligand

Introduction

Studies on the coordination chemistry of tridentate ONO donor Schiff bases derived from amino acids ligating diorganotin(IV) centers have recently received some attention. The mode of coordination of *N*-arylidene- α -amino acids in diorganotin(IV) complexes is known [1–3]. The coordination chemistry of diorganotin(IV) complexes with some other ONO and NNO donor tridentate Schiff bases has also been described [4–7]. Moreover, several organotin(IV) complexes have shown antitumor activity and are effective antiviral and antineoplastic agents [8]. Also tridentate ligands having ONO donor atoms are pharmacologically active [6]. Recently, the coordination chemistry and mode of interaction of the tridentate ONO donor ligands *N*-(2-carboxyphenyl)salicylideneimine dianion and *N*-(2-carboxyphenyl)-5'-bromosalicylideneimine dianion towards diorganotin have been reported [9, 10]. However, very little study has been conducted on the diorganotin(IV) complexes derived from benzoic acid hydrazone [6]. The reported complexes [6] was prepared by a complicated method and under drastic

conditions. In order to facilitate the preparation of this type of diorganotin(IV) complexes and to compare the structure of the complexes in both solid and solution state, we undertook the present study.

In continuation of our previous studies [9, 10], we report here the simple synthesis, characterization, detailed NMR study and solid state X-ray structures of two diorganotin(IV) complexes derived from the tridentate ONO donor Schiff base, *N*-(2-salicylidene)-*N'*-benzoylhydrazone.

Experimental Section

Materials

All chemicals and reagents were of reagent grade quality. Diphenyltin dichloride (Aldrich), dimethyltin dichloride (Fluka), salicylaldehyde (Merck), 1-benzoylhydrazide (Aldrich), triethylamine (s. d. fine chemicals, India), methanol (Ranbaxy, India) were used as received. The Schiff base, *N*-(2-salicylidene)-*N'*-benzoylhydrazone, (H_2L) has been prepared by refluxing a 1:1 molar ratio mixture of salicylaldehyde and 1-benzoylhydrazide in methanol [6]. Its structure is given in Fig. 1.

Physical measurements

Infrared spectra were recorded on a Perkin-Elmer 883 infrared spectrophotometer from 4000–200 cm^{-1} as KBr discs and were calibrated with respect to the 1601 cm^{-1} band of polystyrene film. Tin was estimated gravimetrically as SnO_2 after decomposition with concentrated HNO_3 . Carbon, hydrogen and nitrogen analyses were carried out on a Perkin-Elmer 2400 II elemental analyser. Melting points (uncorrected) were recorded on an electrical heating-coil apparatus. ^1H (360.13 MHz), ^{13}C (90.566 MHz), ^{119}Sn (134.3 MHz) and ^{15}N (36.50 MHz) NMR spectra were recorded at 300 K on a Bruker AMX 360 spectrometer equipped with 5 mm broadband inverse probe and a Silicon Graphic Indy computer. The compounds studied were measured in deuteriochloroform and ^1H and ^{13}C chemical shifts were referred to the central signal of the solvent [$\delta = 7.25$ (^1H) and $\delta = 77.0$ (^{13}C)]. The ^{15}N and ^{119}Sn chemical shifts were referred to external nitromethane and tetramethylstannane, respectively, ($\delta = 0.0$) placed in a coaxial capillary. Positive values of the chemical shifts denote downfield shifts with respect to standards. Two dimensional H,H-COSY, gs (gradient selected)-HMQC and gs-HMBC techniques were measured using standard microprograms provided by Bruker.

Synthesis and characteristics of diorganotin(IV) complexes

The following general procedure exemplified for the preparation of $\text{Ph}_2\text{Sn}[2\text{-OC}_6\text{H}_4\text{CH}=\text{N}-\text{N}=\text{C}(\text{O})\text{Ph}]$ (**1**) was used for the preparation of both the complexes.

To a solution of *N*-(2-salicylidene)-*N'*-benzoylhydrazone (1 g, 4.16 mmol) in 15 ml dry methanol, a few drops of triethylamine were added and the resulting yellow triethylammonium salt solution of the ligand was filtered to remove any insoluble impurities. To this solution, a solution of Ph_2SnCl_2 (1.43 g, 4.16 mmol) in 15 ml of dry methanol was added slowly at 20 °C. The resulting mixture was kept for 30 min when shiny yellow crystals of compound **1** appeared. These were filtered off, washed with petroleum ether (40–60 °C) and dried *in vacuo*. Single crystals suitable for X-ray crystallography were obtained from the same solution. Yield: 1.81 g (85%); m.p. 168–169 °C. – *Analysis for* $\text{C}_{26}\text{H}_{20}\text{N}_2\text{O}_2\text{Sn}$ (511.16): calcd. C 61.09, H 3.94, N 5.48, Sn 23.22; found C 61.25, H 3.85, N 5.62, Sn 22.97.

$\text{Me}_2\text{Sn}[2\text{-OC}_6\text{H}_4\text{CH}=\text{N}-\text{N}=\text{C}(\text{O})\text{Ph}]$ (**2**)

Yield: 1.32 g (82%); m.p. 154–155 °C (lit.[6] m.p. 152 °C). – *Analysis for* $\text{C}_{16}\text{H}_{16}\text{N}_2\text{O}_2\text{Sn}$ (387.02): calcd. C 49.65, H 4.16, N 7.24, Sn 30.67; found C 49.42, H 4.32, N 6.99, Sn 30.25.

X-ray structure analysis of **1** and **2**

Single crystals of $\text{Ph}_2\text{Sn}[2\text{-OC}_6\text{H}_4\text{CH}=\text{N}-\text{N}=\text{C}(\text{O})\text{Ph}]$ (**1**; $0.48 \times 0.43 \times 0.27$ mm) and $\text{Me}_2\text{Sn}[2\text{-OC}_6\text{H}_4\text{CH}=\text{N}-\text{N}=\text{C}(\text{O})\text{Ph}]$ (**2**; $0.49 \times 0.18 \times 0.11$ mm) were obtained from methanol. Diffraction measurements were made at 293(2) K on a Nonius MACH-3 diffractometer using graphite-monochromated Mo-K_α radiation ($\lambda = 0.71073$ Å). Orientation matrices and cell parameters were derived from the setting angles of 25 centered medium-angle reflections; diffraction intensities were collected by ω scans; data were corrected for absorptions by ψ scans. The structures were solved by direct methods employing the SIR-97 program system [11] and subsequently refined by full-matrix least-squares procedures on F^2 (SHELXL-97 [12]) with allowance for anisotropic thermal motion of all non-hydrogen atoms. Hydrogen atoms were included in the refinement assuming ideal geometry and using appropriate riding models. Crystal and refinement data are given in Table 1.

Crystallographic data have been deposited with the Cambridge Crystallographic Data Center as supplementary publications, CCDC-169098 (compound **1**) and CCDC-169099 (compound **2**). Copies of the data can be obtained on application to CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK [Fax: +44(0) 1223-336090, E-mail: deposit@ccdc.cam.uk].

Results and Discussion

Synthesis

The dimethyltin(IV) complexes of the Schiff bases derived from amino acids and salicylaldehydes were prepared previously by refluxing a mixture of dimethyltin oxide, Me_2SnO , and the corresponding Schiff bases in toluene with azeotropic removal of water [1, 2]. Similar compound types were likewise prepared by reaction between diorganotin dichlorides and the sodium/potassium salts of the respective Schiff bases [3]. Organotin(IV) complexes of tridentate ligands, such as *N*-(2-pyridinylmethylene)benzoylhydrazone and *N*-salicylidene derivatives of aroylhydrazones, were prepared by refluxing the sodium salt of the

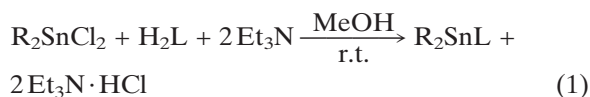
Table 1. Crystal data and structure refinement of $\text{Ph}_2\text{Sn}[2\text{-OC}_6\text{H}_4\text{CH=N-N=C(O)C}_6\text{H}_5]$ (**1**) and $\text{Me}_2\text{Sn}[2\text{-OC}_6\text{H}_4\text{CH=N-N=C(O)C}_6\text{H}_5]$ (**2**).

	1	2
Empirical formula	$\text{C}_{26}\text{H}_{20}\text{N}_2\text{O}_2\text{Sn}$	$\text{C}_{16}\text{H}_{16}\text{N}_2\text{O}_2\text{Sn}$
Formula weight	511.13	387.00
Crystal system	triclinic	monoclinic
Space group	$P\bar{1}$	$P2_1$
<i>a</i> (Å)	11.1631(5)	10.2073(5)
<i>b</i> (Å)	13.462(2)	14.645(2)
<i>c</i> (Å)	16.511(1)	10.411(3)
α (°)	106.193(9)	90
β (°)	106.379(8)	92.572(9)
γ (°)	94.932(8)	90
Volume (Å ³)	2249.3(4)	1554.7(5)
<i>Z</i> (Mg/m ³)	4	4
<i>D</i> _{calc.}	1.509	1.653
μ (mm ⁻¹)	1.160	1.649
<i>F</i> (000)	1024	768
θ Range for data collection (°)	2.28 to 30.07°	2.40 to 30.07°
Index ranges	$0 \leq h \leq 15, -18 \leq k \leq 18, -23 \leq l \leq 22$	$-1 \leq h \leq 14, -1 \leq k \leq 20, -14 \leq l \leq 14$
Reflections collected	13819	5819
Independent reflections	13194 [$R_{\text{int}} = 0.011$]	5054 [$R_{\text{int}} = 0.0289$]
Reflections with $I > 2\sigma(I)$	8751	3853
Max. and min. transmission	0.7446 and 0.6058	0.8394 and 0.4988
Data/restraints/parameters	13194/0/559	5054/1/383
Goodness-of-fit on F^2	1.048	1.042
Final <i>R</i> indices [$I > 2\sigma(I)$]	$R_1 = 0.0461, wR_2 = 0.0939$	$R_1 = 0.0395, wR_2 = 0.0835$
<i>R</i> Indices (all data)	$R_1 = 0.0840, wR_2 = 0.1078$	$R_1 = 0.0648, wR_2 = 0.0935$
Largest diff. peak and hole (e · Å ⁻³)	2.040 ^a and -0.649	0.511 and -0.754

^a The highest peak in the final difference map (2.04 e · Å⁻³) was located at a distance of 0.93 Å from tin atom Sn2.

respective ligands and organotin(IV) chlorides in methanol in a rather complicated way [7, 8].

The compounds reported here have been synthesized in a very straightforward way and under mild condition from diorganotin(IV) dichlorides (Ph_2SnCl_2 or Me_2SnCl_2) and *N*-(2-salicylidene)-*N'*-benzoylhydrazone (H_2L) in methanol at room temperature in presence of triethylamine (eq. 1). The synthesized complexes separated out from the reaction mixture.



1: R = Ph; **2:** R = Me

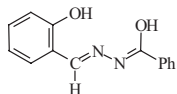


Fig. 1. Structure of ligand (H_2L) used in this study.

Although these two compounds have been prepared in methanol at room temperature, they could be prepared as well in other solvents such as benzene, toluene. The reaction time could be further reduced by carrying out the reaction at higher temperature and/or using more concentrated solutions. The resulting compounds are stable under atmospheric conditions.

The complexes have been characterized by elemental analysis, IR, NMR (¹H, ¹³C, ¹⁵N, ¹¹⁹Sn) spectra. Two-dimensional NMR spectra were used to assign proton and carbon chemical shifts unambiguously. H,H-COSY, gs(gradient selected)-HMQC and gs-HMBC techniques were applied [13, 14]. The ¹⁵N NMR spectra were measured using the gs-HMBC technique (the experiment being optimized for $^nJ(^{15}\text{N}, ^1\text{H}) = 6$ Hz). Both ¹⁵N signals in two-dimensional spectra correlate with C(7)-H only giving two signals of approximately the same intensities and hence, the differentiation between them was not possible. The structure of

pounds **1** and **2** has been confirmed by X-ray diffraction.

Spectroscopic Studies

Infrared spectra

The infrared spectra of the ligand is consistent with the formation of benzoyl hydrazone which also exist in ketamine form. The N–H stretching vibration appears as a strong sharp band at 3273 cm^{-1} , two strong bands at 1676 and 1623 cm^{-1} are assigned to amido carbonyl $\nu(\text{C}=\text{O})$ and azomethine $\nu(\text{C}=\text{N})$ stretching mode. The most significant difference which emerges from a comparison of the vibrational spectra of the ligand (H_2L) and its diorganotin(IV) complexes (**1** and **2**) is the disappearance of the $\nu(\text{N}–\text{H})$ band at 3273 cm^{-1} , and amido carbonyl $\nu(\text{C}=\text{O})$ at 1676 cm^{-1} . A weak broad band at 3180–2400 cm^{-1} , which has been assigned to the intramolecularly hydrogen bonded phenolic-OH in the spectra of the ligand is not observed in the IR spectra of these two complexes. Strong bands at 1609 cm^{-1} for **1** and at 1606 cm^{-1} for **2** are assigned to $\nu(\text{C}=\text{N}–\text{N}=\text{C})$ stretching. These findings suggest the coordination of imino nitrogen, deprotonated enolic and phenolic oxygen to the central tin(IV), and therefore the tridentate dibasic nature of the coordinated ligand.

NMR spectra

The NMR spectra (^1H , ^{13}C , ^{15}N , ^{119}Sn) for the compounds Ph_2SnL (**1**) and Me_2SnL (**2**) were measured and analyzed. The chemical shift data along with coupling constants for compounds **1** and **2** are collected in Table 2.

For compound **1** the detection of $^3J(\text{SnN}=\text{CH})$ coupling (52.5 Hz) confirms the presence of nitrogen-tin coordination. The $^1J(^{119}\text{Sn}, ^{13}\text{C})$ coupling constant value of 993.2 is somewhat larger than reported values for phenyltin compounds [15, 16]. The C–Sn–C angle for Ph_2SnL (**1**) was calculated from the equation [15] $\angle |^1J(^{119}\text{Sn}, ^{13}\text{C})| = (15.91 \pm 0.72) \theta - (1164 \pm 84)$ ($\theta = \text{C}–\text{Sn}–\text{C}$ angle) \angle and was found to be 135.6°. In the ^1H NMR spectrum of Me_2SnL (**2**), Sn–Me and N=CH proton signals appear at $\delta = 0.84$ and 8.76 ppm, respectively. Other proton signals appear at their usual positions and are well comparable with the reported values [6]. However, we have

Table 2. ^1H , ^{13}C , ^{119}Sn and ^{15}N chemical shifts and $^nJ(^{119}\text{Sn}, ^1\text{H})$ and $^nJ(^{119}\text{Sn}, ^{13}\text{C})$ coupling constants for compound $\text{R}_2\text{Sn}[2\text{-OC}_6\text{H}_4\text{CH}=\text{N}–\text{N}=\text{C}(\text{O})\text{C}_6\text{H}_5]$ (R = Ph: **1**, R = Me: **2**) in CDCl_3 . Coupling constants values (Hz) are given in parentheses. See Fig. 2 for atom numbering.

H/C nr.	Compound 1 $\delta(^1\text{H})$	Compound 1 $\delta(^{13}\text{C})$	Compound 2 $\delta(^1\text{H})$	Compound 2 $\delta(^{13}\text{C})$
1	–	167.18 (31.9)	–	166.28 (32.6)
2	7.24	122.01	6.79	121.60 (8.3)
3	7.5	135.40	7.34	135.12
4	6.83	117.52	6.74	117.12
5	7.21	133.11	7.19	134.08
6	–	116.77	–	116.49
7	8.83 (52.5)	161.48 (23.6)	8.76 (46.3)	161.40 (22.2)
8	–	169.05 (3.5)	–	169.10 (9.0)
9	–	133.11	–	133.12
10	8.36	127.71	8.10	127.53
11	7.57	128.26	7.41	128.11
12	7.57	131.28	7.43	131.01
1'	–	139.05 (993.2)	0.84 (78.7)	1.37 (647.9)
2'	8.00 (79.9)	136.18 (55.5)	–	–
3'	7.46	128.83 (87.4)	–	–
4'	7.46	130.59 (17.3)	–	–
Sn	–	–329.2 ^a	–	–150.3 ^a
N _a	–	b ^c	–	d ^c
N _b	–	b ^c	–	d ^c

^a $\delta(^{119}\text{Sn})$; b = –115.6 or –122.6; ^c $\delta(^{15}\text{N})$; d = –127.1 or –131.8.

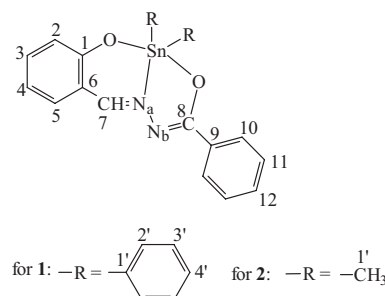


Fig. 2. Constitution of compounds **1** and **2** and numbering scheme for NMR assignments.

been able to detect all the proton and carbon signals separately. The $^3J(\text{SnN}=\text{CH})$ coupling detected for **2** indicates that the tin nucleus is located in a *trans* position to the azomethine proton in accordance with the literature [17] and thus confirms the presence of nitrogen-tin coordination in complex **2**. In addition, $^3J(\text{SnN}=\text{CH})$ (46.3 Hz) and $^2J(\text{SnCH}_3)$ (78.7 Hz) values are in good agreement with the values reported for the dimethyltin(IV) complexes derived from ONO donor tridentate ligands [9, 18, 19]. Using Lockhart's equation \angle

$[\text{Me-Sn-Me} = 0.0161 (|^2J(^{119}\text{Sn}, ^1\text{H})|)^2 - 1.32 (|^2J(^{119}\text{Sn}, ^1\text{H})|) + 133.4]$ [19]—the C–Sn–C angle for **2** is estimated to *ca.* 129.2°. ^{13}C NMR signals for each carbon atom appear at their usual positions and compare well with the reported values [6]. The C–Sn–C angle calculated from the $^1J(^{119}\text{Sn}, ^{13}\text{C})$ coupling constant (647.9 Hz) is found to be 133.4° using the equation $^1J(^{119}\text{Sn}, ^{13}\text{C}) = 10.7 \theta - 778$ [20].

The ^{119}Sn NMR spectra have been recorded in CDCl_3 . The $\delta(^{119}\text{Sn})$ values for **1** and **2** are –329.2 and –150.3 ppm, respectively. These ^{119}Sn chemical shifts are in the range reported for five-coordinated tin compounds [16, 21]. The $\delta(^{119}\text{Sn})$ value of **1** compare well with the value of $\text{Ph}_2\text{Sn}(2\text{-OC}_6\text{H}_4\text{C}(\text{CH}_3)=\text{NCH}_2\text{COO})$ [3]. It is well known that $\delta(^{119}\text{Sn})$ values depend on the coordination number of the tin centre and the ligand bite [16, 22]. Also the difference in the $\delta(^{119}\text{Sn})$ value (178.9 ppm) between Ph_2SnL (**1**) and Me_2SnL (**2**) is comparable with the difference found between Ph_2SnCl_2 and Me_2SnCl_2 [23], and other diorganotin(IV) complexes having a phenyl or methyl substituent on tin [24]. It is thus evident that the ligand bite is comparable in compounds **1** and **2**. From the ^{119}Sn NMR spectra it is also evident that the five-coordinated solid state structure (obtained from X-ray crystallography) is retained in solution.

Description of the X-ray structures of **1** and **2**

While chiral complex **1** crystallized as a racemate in the triclinic space group $P\bar{1}$, crystals of **2** have the non-centrosymmetric space group $P2_1$, indicating that spontaneous resolution of the racemic mixture had occurred during crystallization.

The molecular structure along with atom numbering scheme of one molecule (molecule 1) for complex **1** is given in Fig. 3. The molecular structure along with atom numbering scheme of one molecule (molecule 1) for complex **2** is given in Fig. 4. Selected bond lengths and angles for compounds **1** and **2** are listed in Tables 3 and 4, respectively. The X-ray structural investigations of $\text{Ph}_2\text{Sn}[(2\text{-OC}_6\text{H}_4\text{CH}=\text{N}-\text{N}=\text{C}(\text{O})\text{Ph})]$ (**1**) and $\text{Me}_2\text{Sn}[(2\text{-OC}_6\text{H}_4\text{CH}=\text{N}-\text{N}=\text{C}(\text{O})\text{Ph})]$ (**2**) show that the ligand, *N*-(2-salicylidene)-*N'*-benzoylhydrazone (H_2L) behaves as a tridentate dibasic coordinating agent via phenolic oxygen, imino nitro-

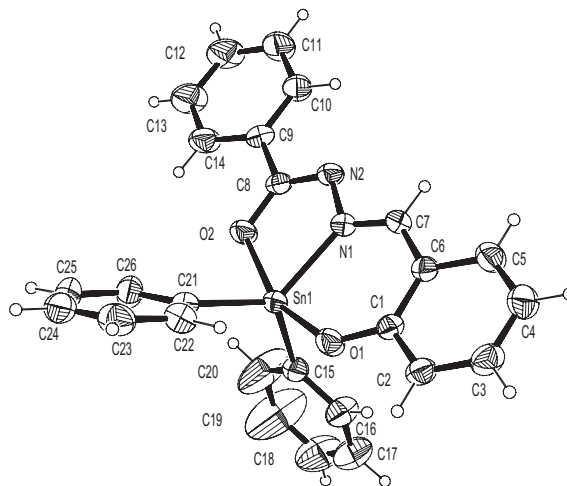


Fig. 3. Molecular structure and atom numbering scheme of compound **1** (molecule 1).

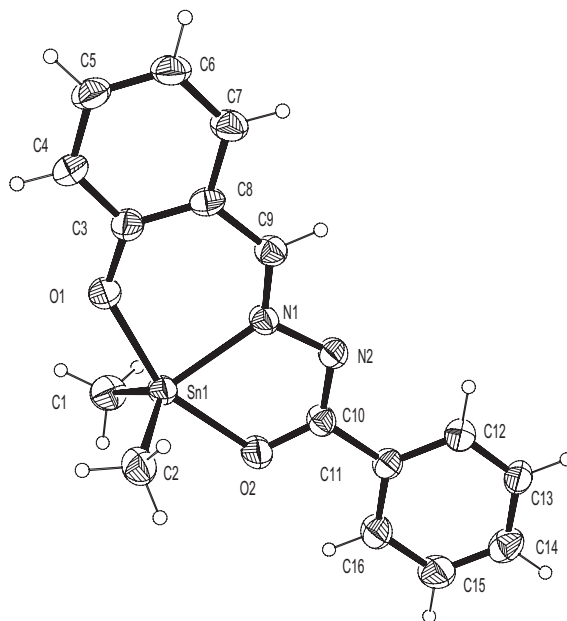


Fig. 4. Molecular structure and atom numbering scheme of compound **2** (molecule 1).

gen and enolic oxygen atoms. The two organic groups (phenyl for **1** and methyl for **2**) on tin and the imino nitrogen atom of the ligand occupy the equatorial positions, and phenolic and enolic oxygen atoms are in the axial positions. In both complexes, the ligand is not completely planar, and a distorted trigonal-bipyramidal geometry around

Molecule 1		Molecule 2	
Sn(1)–O(1)	2.059(3)	Sn(2)–O(3)	2.063(3)
Sn(1)–O(2)	2.132(3)	Sn(2)–O(4)	2.118(3)
Sn(1)–C(15)	2.114(4)	Sn(2)–C(41)	2.118(4)
Sn(1)–C(21)	2.122(4)	Sn(2)–C(47)	2.118(4)
Sn(1)–N(1)	2.153(3)	Sn(2)–N(3)	2.160(3)
O(1)–C(1)	1.326(4)	O(3)–C(27)	1.328(5)
O(2)–C(8)	1.302(4)	O(4)–C(34)	1.301(4)
N(1)–C(7)	1.291(4)	N(3)–C(33)	1.285(5)
N(1)–N(2)	1.397(4)	N(3)–N(4)	1.406(4)
N(2)–C(8)	1.298(5)	N(4)–C(34)	1.306(5)
O(1)–Sn(1)–C(15)	97.59(15)	O(3)–Sn(2)–C(41)	97.38(14)
O(1)–Sn(1)–C(21)	94.56(14)	O(3)–Sn(2)–C(47)	94.33(14)
C(15)–Sn(1)–C(21)	121.26(15)	C(41)–Sn(2)–C(47)	127.74(14)
O(1)–Sn(1)–O(2)	157.19(10)	O(3)–Sn(2)–O(4)	157.50(11)
C(15)–Sn(1)–O(2)	96.51(14)	C(41)–Sn(2)–O(4)	94.76(13)
C(21)–Sn(1)–O(2)	93.32(13)	C(47)–Sn(2)–O(4)	93.10(14)
O(1)–Sn(1)–N(1)	84.38(11)	O(3)–Sn(2)–N(3)	84.16(11)
C(15)–Sn(1)–N(1)	114.36(14)	C(41)–Sn(2)–N(3)	112.46(12)
C(21)–Sn(1)–N(1)	123.94(13)	C(47)–Sn(2)–N(3)	119.33(13)
O(2)–Sn(1)–N(1)	73.48(11)	O(4)–Sn(2)–N(3)	73.70(11)
C(1)–O(1)–Sn(1)	132.5(2)	C(27)–O(3)–Sn(2)	133.0(2)
C(8)–O(2)–Sn(1)	113.9(2)	C(34)–O(4)–Sn(2)	114.6(2)
C(7)–N(1)–Sn(1)	127.6(3)	C(33)–N(3)–Sn(2)	128.0(3)
N(2)–N(1)–Sn(1)	116.2(2)	N(4)–N(3)–Sn(2)	115.8(2)
Sn(1)–N(1)–N(2)–C(8)	1.2(4)	Sn(2)–N(3)–N(4)–C(34)	1.5(4)
Sn(1)–O(2)–C(8)–N(2)	1.1(5)	Sn(2)–O(4)–C(34)–N(4)	−0.9(5)
Sn(1)–O(1)–C(1)–C(6)	7.3(6)	Sn(2)–O(3)–C(27)–C(32)	−5.3(6)
Sn(1)–N(1)–C(7)–C(6)	−6.7(6)	Sn(2)–N(3)–C(33)–C(32)	4.9(6)

Table 3. Selected bond lengths (Å) and angles (°) for compound Ph₂Sn[2-OC₆H₄CH=N–N=C(O)C₆H₅] (**1**).

the tin centre is found. However, there are two crystallographically independent molecules (denoted 1 and 2) for each complex which differ most significantly in their C–Sn–C angles [C(15)–Sn(1)–C(21) 121.26(15)°, C(41)–Sn(2)–C(47) 127.74(14)° for **1** and C(1)–Sn(1)–C(2) 125.2(4)°, C(17)–Sn(2)–C(18) 122.73(3)° for **2**].

Crystals of compound **1** are built from discrete molecules, $\text{Ph}_2\text{Sn}[(2\text{-OC}_6\text{H}_4\text{CH=N-N=C(O)Ph})]$. The indices of trigonality, τ , within the continuum between tetragonal-pyramidal ($\tau = 0$) and trigonal-bipyramidal ($\tau = 1$), as defined by Addison and Reedijk [25] are $\tau = 0.6$ for molecule 1 and $\tau = 0.50$ for molecule 2. Thus in case of molecule 1, trigonal-bipyramidal geometry predominates over tetragonal-pyramidal geometry, whereas in case of molecule 2 contribution of both geometries is almost 1:1. Owing to the geometric requirements of the ligand the geometry around tin is not regular. The angles subtended at tin(IV) by two oxygen atoms are significantly compressed to 157.19(10)° (O(1)–Sn(1)–O(2)) and 157.50(11)° (O(3)–Sn(2)–O(4)) in molecule 1 and molecule 2, respectively.

Consequently, the bite angles N(1)–Sn(1)–O(1) (84.38(11)°), O(2)–Sn(1)–N(1) (73.48(11)°) (for molecule 1) and O(3)–Sn(2)–N(3) (84.16(11)°), O(4)–Sn(2)–N(3) (73.70(11)°) (for molecule 2) are compressed from 90°. These distortion is due to the rigidity of chelate rings, together with the large covalent radius of tin(IV). These bite angles are comparable to those reported for other diorganotin(IV) complexes containing both five- and six-membered chelate rings with oxygen and nitrogen donor atoms [1–5, 9, 10, 24, 26–29]. Displacement of Sn1 from the plane defined by N1, C15, C21 is 0.082 Å towards O1 and Sn2 from the plane defined by N3, C41, C47 is 0.084 Å towards O3. The C(15)–Sn(1)–C(16) angle of 121.26(15)° (for molecule 1) is close to 120° but a higher deviation of the C–Sn–C angle from 120° [C(41)–Sn(2)–C(47), 127.74(14)°] is observed in case of molecule 2. The two phenyl groups on tin are mirror images to each other. However, the C–Sn–C angles for both molecules are less than those calculated from $^1J(^{119}\text{Sn}, ^{13}\text{C})$ coupling constant values (*vide supra*). The five-membered chelate rings of

Molecule 1		Molecule 2	
Sn(1)–O(1)	2.073(4)	Sn(2)–O(3)	2.080(5)
Sn(1)–O(2)	2.143(5)	Sn(2)–O(4)	2.137(4)
Sn(1)–C(1)	2.102(9)	Sn(2)–C(17)	2.089(9)
Sn(1)–C(2)	2.106(8)	Sn(2)–C(18)	2.103(8)
Sn(1)–N(1)	2.166(5)	Sn(2)–N(3)	2.180(5)
O(1)–C(3)	1.312(8)	O(3)–C(19)	1.330(8)
O(2)–C(10)	1.286(9)	O(4)–C(26)	1.293(9)
N(1)–C(9)	1.293(8)	N(3)–C(25)	1.297(8)
N(1)–N(2)	1.403(7)	N(3)–N(4)	1.400(7)
N(2)–C(10)	1.306(8)	N(4)–C(26)	1.296(8)
O(1)–Sn(1)–C(1)	95.9(3)	O(3)–Sn(2)–C(18)	4.6(4)
O(1)–Sn(1)–C(2)	97.4(3)	O(3)–Sn(2)–C(17)	99.2(3)
C(1)–Sn(1)–C(2)	125.2(4)	(17)–Sn(2)–C(18)	122.7(3)
O(1)–Sn(1)–O(2)	155.83(19)	O(3)–Sn(2)–O(4)	155.89(19)
C(1)–Sn(1)–O(2)	92.7(3)	C(18)–Sn(2)–O(4)	93.3(3)
C(2)–Sn(1)–O(2)	6.0(3)	C(17)–Sn(2)–O(4)	95.7(3)
O(1)–Sn(1)–N(1)	83.7(2)	O(3)–Sn(2)–N(3)	83.8(2)
C(1)–Sn(1)–N(1)	121.0(3)	C(18)–Sn(2)–N(3)	121.5(3)
C(2)–Sn(1)–N(1)	113.2(3)	C(17)–Sn(2)–N(3)	115.1(3)
O(2)–Sn(1)–N(1)	72.55(19)	O(4)–Sn(2)–N(3)	72.66(19)
C(3)–O(1)–Sn(1)	133.7(5)	C(19)–O(3)–Sn(2)	132.7(5)
C(10)–O(2)–Sn(1)	115.0(4)	C(26)–O(4)–Sn(2)	114.5(4)
C(9)–N(1)–Sn(1)	129.0(5)	C(25)–N(3)–Sn(2)	127.8(4)
N(2)–N(1)–Sn(1)	116.4(8)	N(4)–N(3)–Sn(2)	116.4(4)
Sn(1)–N(1)–N(2)–C(10)	2.9(8)	Sn(2)–N(3)–N(4)–C(26)	–2.5(8)
Sn(1)–O(2)–C(10)–N(2)	3.9(11)	Sn(2)–O(4)–C(26)–N(4)	–0.9(11)
Sn(1)–O(1)–C(3)–C(8)	6.0(14)	Sn(2)–O(3)–C(19)–C(24)	–6.6(14)
Sn(1)–N(1)–C(9)–C(8)	–3.5(11)	Sn(2)–N(3)–C(25)–C(24)	3.4(12)

Table 4. Selected bond lengths (Å) and angles (°) for compound $\text{Me}_2\text{Sn}[2\text{-OC}_6\text{H}_4\text{CH=N-N=C(O)C}_6\text{H}_5]$ (**2**).

both molecules of compound **1** are nearly planar but the six-membered chelate rings are non-planar as shown by their respective torsion angles in Table 3.

The crystals of compound **2** are also built from discrete molecules, $\text{Me}_2\text{Sn}[(2\text{-OC}_6\text{H}_4\text{CH=N-N=C(O)Ph})]$. The geometry around central tin atom may also be described as a compromise between trigonal-bipyramidal structure ($\tau = 0.51$ for molecule 1 and $\tau = 0.55$ for molecule 2) and tetragonal-pyramidal structure. This type of geometry of compound **1** (obtained from X-ray crystallography) is contrary to the slightly distorted trigonal-bipyramidal structure as proposed by Iskander *et al.* [6] on the basis of IR and NMR data. The angles subtended at tin(IV) by two oxygen atoms are compressed to $155.83(19)^\circ$ (O(1)–Sn(1)–O(2)) and $155.89(19)^\circ$ (O(3)–Sn(2)–O(4)) in molecule 1 and molecule 2, respectively. These compressions of O–Sn–O angles are greater than those found in case of compound **1**. The bite angles N(1)–Sn(1)–O(1) ($83.7(2)^\circ$), O(2)–Sn(1)–N(1) ($72.55(19)^\circ$) (for molecule 1) and O(3)–Sn(2)–N(3) ($83.8(2)^\circ$),

O(4)–Sn(2)–N(3) ($72.66(19)^\circ$) (for molecule 2) are also compressed from 90° . Displacement of Sn1 from the plane defined by N1, C1, C2 is 0.095 Å towards O1 and Sn2 from the plane defined by N3, C17, C18 is 0.097 Å towards O3. The C(1)–Sn(1)–C(2) angle of $125.2(4)^\circ$ (for molecule 1) and the C(17)–Sn(2)–C(18) angle of $122.7(3)^\circ$ (for molecule 2) also deviate from the exact trigonal angle of 120° . In case of compound **2**, the C–Sn–C angles for both molecules are also less than those calculated on the basis of $^1J(^{119}\text{Sn},^{13}\text{C})$ and $^2J(^{119}\text{Sn},^1\text{H})$ coupling constant values (*vide supra*). Both the five- and six-membered chelate rings of compound **2** are non-planar as shown by their torsion angles in Table 4, with a higher deviation from planarity being observed for the six-membered rings.

The Sn–O bond lengths [$2.059(3)$, $2.063(3) \text{ Å}$ for Sn–O(phenolic) and $2.132(3)$, $2.118(3) \text{ Å}$ for Sn–O(enolic) in molecules 1 and 2 respectively] of compound **1** and [$2.073(4) \text{ Å}$, $2.080(5) \text{ Å}$ for Sn–O(phenolic) and $2.143(5) \text{ Å}$, $2.137(4) \text{ Å}$ for Sn–O(enolic) in molecule 1 and 2, respectively] of

compound **2** compare well with the reported values for diorganotin(IV) complexes derived from ONO donor tridentate Schiff bases [1–5, 9, 10] but are shorter than diorganotin(IV) complexes derived from ONNO donor tetradentate Schiff bases [24, 26–29]. The Sn–O(phenolic) bond lengths are shorter than Sn–O(enolic) bond lengths. Such differences in bond lengths are found in other similar compounds [1–3, 9, 10]. The Sn–O(phenolic) (Sn(1)–O(1) and Sn(2)–O(3)) bond lengths of the complex **1** are among the shortest (see Table 5) so far observed in this type of five-coordinated diorganotin(IV) complexes [1–5, 9, 10] and very much shorter than those found in six-coordinated diorganotin(IV) complexes [24, 26–29]. The Sn–N bond lengths of compound **1** (2.153(3), 2.168(3)) Å for molecule 1 and 2, respectively) and compound **2** (2.166(5) Å for molecule 1 and 2.180(5) Å for molecule 2)

are very close to Bu₂Sn(2-OC₆H₄CH=NCH(*i*-pr)COO) [1] and shorter than in Ph₂Sn(2-OC₆H₄CH=NC₆H₄O) [4], Me₂Sn(2-OC₆H₄CH=NC₆H₄O) [5], Me₂Sn(2-OC₆H₄CH=NC₆H₄COO) [9] and much shorter than those found in six-coordinated diorganotin(IV) complexes [24, 26–29].

The Sn–C(phenyl) bond lengths [2.114(4), 2.122(4) and 2.118(4) Å] of compound **1** are very close to the Sn–C bond lengths in five-coordinated diorganotin(IV) complexes derived from ONO donor tridentate Schiff bases [1–5] and shorter than six-coordinated diorganotin(IV) complexes derived from ONNO donor tetradentate Schiff bases [26–29]. As expected, there is a slight increase in Sn–C(phenyl) bond lengths with increase in coordination number from four (in Ph₂SnCl₂) [29] to five in Ph₂Sn[(2-OC₆H₄CH=N–N=C(O)Ph] (**1**). The Sn–C(methyl) bond lengths [2.102(9), 2.106(8), 2.089(9) and 2.103(8) Å] of

Table 5. Comparison of Sn–N, Sn–O and Sn–C bond lengths (Å) of Ph₂Sn[2-OC₆H₄CH=N–N=C(O)C₆H₅] (**1**) and Me₂Sn[2-OC₆H₄CH=N–N=C(O)C₆H₅] (**2**) with those in some other organotin(IV) complexes derived from ONO donor tridentate Schiff bases.

Sn-N	Sn-O	Sn-C	Reference
Ph ₂ Sn[2-OC ₆ H ₄ CH=N–N=C(O)C ₆ H ₅] 2.153(3) 2.160(3)	2.059(3) 2.063(3) 2.132(3) 2.118(3)	2.114(4) 2.122(4) 2.118(4)	This work
Ph ₂ Sn[2-OC ₆ H ₄ CH=NC ₆ H ₄ O] 2.241(13)	2.085(8) 2.103(8)	2.125(11) 2.124(10)	[4]
Me ₂ Sn[2-OC ₆ H ₄ CH=NC ₆ H ₄ O] 2.229(11)	2.105(8) 2.118(9)	2.091(14) 2.142(14)	[5]
Bu ₂ Sn[2-OC ₆ H ₄ CH=NCH(<i>i</i> -pr)COO] 2.158(8)	2.078(10) 2.151(8)	2.100(12) 2.138(14)	[1]
Me ₂ Sn[2-OC ₆ H ₄ CH=NC ₆ H ₄ COO] 2.230(5)	2.135(4) 2.187(4)	2.102(7) 2.103(6)	[9]
Ph ₂ Sn[2-OC ₁₀ H ₆ CH=NCH ₂ COO] 2.136(5)	2.068(4) 2.188(3)	2.108(8) 2.127(8)	[2]
Ph ₂ Sn[2-OC ₆ H ₄ C(CH ₃)=NCH ₂ COO] 2.190(5) 2.178(5)	2.064(4) 2.059(4) 2.127(4) 2.131(4)	2.120(6) 2.138(6) 2.102(7) 2.111(6)	[3]
Me ₂ Sn[2-OC ₆ H ₄ CH=N–N=C(O)C ₆ H ₅] 2.166(5) 2.180(5)	2.073(4) 2.080(5) 2.143(5) 2.137(4)	2.102(9) 2.106(8) 2.089(9) 2.103(8)	This work

compound **2** are comparable with other reported diorganotin(IV) complexes [1–5, 24, 26–29]. These Sn–C(methyl) bond lengths are much shorter than the Sn–C(methyl) bond lengths in Me₂SnCl₂ as expected [30].

The discrepancy between the C–Sn–C angles from X-ray data and estimation in solution may be due to relieve of some strain of the molecule in solution. However, ¹¹⁹Sn chemical shift values indicate that the five-coordinated structure is retained in solution.

Acknowledgements

Financial assistance from UGC (New Delhi) and DST (Government of India) is gratefully acknowledged. We thank Professor S. Mitra, Department of Chemistry, Jadavpur University, Kolkata – 700 032, India for help. A. L. thanks the Grant Agency of the Czech Republic for financial support (Grant No. 203/00/0920). This work is also supported by the Deutsche Forschungsgemeinschaft (Bonn, Germany) and the Fonds der Chemischen Industrie (Frankfurt am Main, Germany).

- [1] F. E. Smith, R. C. Hynes, T. T. Ang, L. E. Khoo, and G. Eng, *Can. J. Chem.* **70**, 1114 (1992).
- [2] L. E. Khoo, Y. Xu, N. K. Goh, L. S. Chia, and L. L. Koh, *Polyhedron* **16**, 573 (1997) and references therein.
- [3] D. Dakternieks, T. S. Basu Baul, S. Dutta, and E. R. T. Tiekink, *Organometallics* **17**, 3058 (1998).
- [4] H. Preut, F. Huber, R. Barbieri, and N. Bertazzi, *Z. Anorg. Allg. Chem.* **423**, 75 (1976).
- [5] H. Preut, F. Huber, H. J. Haupt, R. Cefalu, and R. Barbieri, *Z. Anorg. Allg. Chem.* **410**, 88 (1974).
- [6] M. F. Iskander, L. Labib, M. M. Z. Nour El-Din, and M. Tawfik, *Polyhedron* **8**, 2755 (1989) and references therein.
- [7] T. E. Khalil, L. Labib, M. F. Iskander, and L. S. Refaat, *Polyhedron* **13**, 2569 (1994).
- [8] A. J. Crowe, in M. Gielen (ed.), *Metal Based Antitumor Drugs*, Vol. 1, p. 103, Freund, London (1989).
- [9] D. K. Dey, M. K. Saha, M. Gielen, M. Kemmer, M. Biesemans, R. Willem, V. Gramlich, and S. Mitra, *J. Organomet. Chem.* **590**, 88 (1999).
- [10] G. M. Rosair, D. K. Dey, B. Samanta, S. Mitra, *Acta Crystallogr.* **C58**, m266 (2002).
- [11] A. Altomare, G. Cascarano, C. Giacovazzo, A. Guagliardi, A. G. G. Moliterni, M. C. Burla, G. Polidori, M. Camalli, and R. Spagna, SIR-97, A package for crystal structure solution by direct methods and refinement; Bari, Perugia, and Rome (Italy) (1997).
- [12] G. M. Sheldrick, SHELXL-97, Program for the refinement of crystal structures from diffraction data, Göttingen, Germany (1997).
- [13] W. Hull, in W. R. Croasmun and R. M. K. Carlson (eds): *Two-Dimensional NMR Spectroscopy. Application for Chemists and Biochemists*, 2nd ed., Chapter 2. VCH Publishers, New York (1994).
- [14] S. Braun, H.-O. Kalinowski, and S. Berger, 150 and More Basic NMR Experiments, 2nd ed., Wiley-VCH, Weinheim (1998).
- [15] J. Holeček, K. Handlír, M. Nádvorník, and A. Lyčka, *Z. Chem.* **30**, 265 (1990).
- [16] J. Holeček, M. Nádvorník, K. Handlír, and A. Lyčka, *J. Organomet. Chem.* **241**, 177 (1983).
- [17] G. Matsubayashi, T. Tanaka, S. Nisbigaki, and N. Nakatsu, *J. Chem. Soc. Dalton Trans.* 501 (1979).
- [18] K. Kawakami and T. Tanaka, *J. Organomet. Chem.* **49**, 409 (1973).
- [19] T. P. Lockhart and W. F. Manders, *Inorg. Chem.* **25**, 892 (1986).
- [20] T. P. Lockhart and F. Davidson, *Organometallics* **6**, 2471 (1987).
- [21] J. Otera, *J. Organomet. Chem.* **221**, 57 (1981).
- [22] V. K. Jain, *Coord. Chem. Rev.* **135/136**, 809 (1994) and references therein.
- [23] P. J. Smith and A. P. Tupciaukas, *Ann. Rep. NMR Spectrosc.* **8**, 291 (1978).
- [24] D. K. Dey, M. K. Das, and H. Nöth, *Z. Naturforsch.* **54b**, 145 (1999) references therein.
- [25] A. W. Addison, T. N. Rao, J. Reedijk, J. Van Rijn, and G. C. Verschoor, *J. Chem. Soc. Dalton Trans.* 1349 (1984).
- [26] D. K. Dey, M. K. Saha, N. Bhartiya, R. K. Bansal, G. Rosair, and S. Mitra, *Polyhedron* **18**, 2687 (1999) and references therein.
- [27] D. K. Dey, M. K. Saha, S. Mitra, R. K. Bansal, and L. Dahlenburg, *Chem. Lett.* **10**, 1190 (2000).
- [28] S. G. Teoh, G. Y. Yeap, C. C. Loh, L. W. Foong, S. B. Teo, and H. K. Fun, *Polyhedron* **16**, 2213 (1997).
- [29] M. Calligaris, G. Nardin, and L. Randaccio, *J. Chem. Soc. Dalton Trans.* 2003 (1972).
- [30] W. W. Issacs and H. L. Kennard, *J. Chem. Soc. A* 257 (1970).