

Simplified synthesis, ^1H , ^{13}C , ^{15}N , ^{119}Sn NMR spectra and X-ray structures of diorganotin(IV) complexes containing the 4-phenyl-2,4-butanedionebenzoylhydrazone(2–) ligand

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Abstract

Two diorganotin(IV) complexes of the general formula $\text{R}_2\text{Sn}[\text{Ph}(\text{O})\text{C}=\text{CH}-\text{C}(\text{Me})=\text{N}-\text{N}=\text{C}(\text{O})\text{Ph}]$ ($\text{R} = \text{Ph}$, **1**; $\text{R} = \text{Me}$, **2**) have been synthesised from the corresponding diorganotin(IV) dichloride and the ligand 4-phenyl-2,4-butanedionebenzoylhydrazone(2–) (H_2L), derived from benzoyl acetone and benzoyl hydrazide in methanol at room temperature in presence of triethylamine. The syntheses were performed under very mild conditions, at room temperature and without exclusion of air or moisture from the reaction vessel. Previously, rigorous conditions have been considered necessary for these species. The two compounds have been characterised by elemental analysis, IR and ^1H , ^{13}C , ^{15}N , ^{119}Sn NMR spectra, and their structures have been confirmed single crystal X-ray structure analysis. The central tin atom of both complexes 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. **2** has crystallised with two crystallographically independent molecules in the asymmetric unit. The $\delta(^{119}\text{Sn})$ values for the complexes **1** and **2** are -151.5 and -146.8 ppm, respectively, thus indicating penta-coordinated tin centres.

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1. Introduction

Studies on the coordination chemistry of tridentate amino acid derived Schiff bases [1–3] and other ONO and NNO donor tridentate Schiff bases [4–8] with diorganotin(IV) centres have been discussed widely. Most recently, Mössbauer and NMR studies on organotin complexed with dipeptides have been reported [9] as models for metal protein interactions for antitumour activity. Much interest in these species arises from their pharmacological activity [6]. Moreover, several organotin(IV) complexes have shown antitumour activity and are effective antiviral and antineoplastic

agents [8]. Recently the coordination modes of the ONO donor tridentate *N*-(2-carboxyphenyl)salicylideneimine dianion and *N*-(2-carboxyphenyl)-5'-bromosalicylideneimine dianion towards diorganotin have been reported [10,11]. However, hydrazone diorganotin(IV) complexes have been less widely studied [6,12]. Most of the above diorganotin(IV) complexes have synthesised using complex procedures under rigorously anhydrous conditions, e.g. (i) azeotropic removal of water from the reaction of dialkyl/diaryltin oxides and Schiff bases; (ii) reaction of dialkyl/diaryltin dichlorides with sodium/potassium salts of the respective ligands [4–7]. Our synthetic procedure described here confirms that air or moisture did not interfere with this type of complexation reaction thereby demonstrating a method by which diorganotin(IV) complexes can be prepared under mild conditions without having to exclude air and moisture.

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These complexes, derived from the more flexible hydrazone ligand [4-phenyl-2,4-butanedionebenzoylhydrazone(2-)], have been structurally characterised in both the solid and solution state by crystallography and NMR in continuation of our previous studies [10–12]. This structural comparison in both states will help to elucidate structure of new organotin(IV) complexes using NMR spectral results for which X-ray data are not available.

2. Experimental

2.1. Materials

All chemicals and reagents were of reagent grade quality. Diphenyltin dichloride (Aldrich), dimethyltin dichloride (Fluka), benzoyl acetone (Aldrich), 1-benzoyl hydrazide (Aldrich), trimethylamine (S.D. Fine Chemicals, India), methanol (Ranbaxy, India) were used as received.

2.2. Physical measurements

Infrared spectra were recorded on a Perkin–Elmer 883 infrared spectrophotometer from 4000 to 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 Graphics Indy computer. The compounds studied were measured in CDCl_3 and ^1H and ^{13}C chemical shifts were referred to the central signal of the solvent [$\delta = 7.25$ (^1H) and $\delta = 77.00$ (^{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 the standard software provided by Bruker.

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

Single crystals of $\text{Ph}_2\text{Sn}[\text{Ph}(\text{O})\text{C}=\text{CH}-\text{C}(\text{Me})=\text{N}-\text{N}=\text{C}(\text{O})\text{Ph}]$ (**1**) and $\text{Me}_2\text{Sn}[\text{Ph}(\text{O})\text{C}=\text{CH}-\text{C}(\text{Me})=\text{N}-\text{N}=\text{C}(\text{O})\text{Ph}]$ (**2**) were obtained from methanol. Diffraction measurements were made at 293(2) and 160(2) K for compounds **1** and **2**, respectively, on a Bruker AXS

P4 four circle diffractometer using graphite-monochromated Mo $\text{K}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) and were corrected for absorptions by ψ -scans. The structures were solved by direct methods (SIR-97) [13] and subsequently refined by full-matrix least-squares procedures on F^2 (SHELXL-97 [14]) with allowance for anisotropic motion of all non-hydrogen atoms. Hydrogen atom positions were calculated assuming ideal geometry and using appropriate riding models. The crystal structure of **2** consists of two molecules in the asymmetric unit, one of which is disordered in the orientation of one phenyl substituent on the tridentate ligand. In the crystal these two orientations must alternate to avoid unrealistic $\text{H}\cdots\text{H}$ contacts with neighbouring molecules.

The structure had been solved and refined in the lower symmetry space group, Cc , where the phenyl group orientation did not appear disordered because the different orientations were modelled in separate molecules. However, high correlation coefficients exist between parameters for both tin and lighter atoms, related by an inversion centre. The standard uncertainties in the bond lengths and angles were also higher and the absolute structure (Flack x) parameter did not refine to a value close to zero. Therefore, the higher symmetry space group $C2/c$ was chosen. In the $C2/c$ model there are no significant correlation coefficients between atoms in the two independent molecules. As there were non-positive definite atomic displacement parameters in both models, the anisotropic refinement of these atoms was restrained to be closer to spherical (ISOR in Shelxl). The source of this problem is likely to be the space group ambiguity. Crystal and refinement data are given in Table 1.

2.4. Preparation of the ligand

The ligand, 4-phenyl-2,4-butanedionebenzoylhydrazone(2-) (H_2L) has been prepared by refluxing a 1:1 molar ratio mixture of benzoyl acetone and 1-benzoylhydrazide in methanol [15]. Its structure is given in Fig. 1.

2.5. Preparation and characteristics of the complexes **1** and **2**

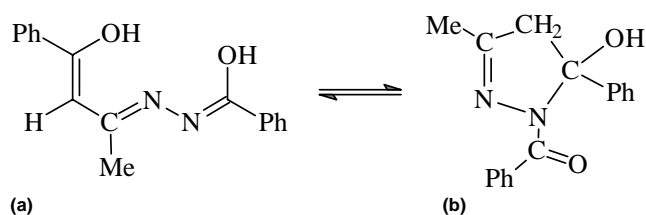
The following general procedure is exemplified for the preparation of $\text{Ph}_2\text{Sn}[\text{Ph}(\text{O})\text{C}=\text{CH}-\text{C}(\text{Me})=\text{N}-\text{N}=\text{C}(\text{O})\text{Ph}]$ (**1**) and was used for the preparation of both the complexes.

To a solution of 4-phenyl-2,4-butanedionebenzoylhydrazone(2-), $\text{Ph}(\text{HO})\text{C}=\text{CH}-\text{C}(\text{Me})=\text{N}-\text{N}=\text{C}(\text{OH})\text{Ph}$ (H_2L) (1.75 g, 6.25 mmol) in 25 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 (2.15 g, 6.25 mmol) in 20 ml of dry methanol was added slowly at room

Table 1

Crystal refinement data for $\text{Ph}_2\text{Sn}[\text{Ph}(\text{O})\text{C}=\text{CH}-\text{C}(\text{Me})=\text{N}-\text{N}=\text{C}(\text{O})\text{Ph}]$ (**1**) and $\text{Me}_2\text{Sn}[\text{Ph}(\text{O})\text{C}=\text{CH}-\text{C}(\text{Me})=\text{N}-\text{N}=\text{C}(\text{O})\text{Ph}]$ (**2**)

	1	2
Empirical formula	$\text{C}_{29}\text{H}_{24}\text{N}_2\text{O}_2\text{Sn}$	$\text{C}_{19}\text{H}_{21}\text{N}_2\text{O}_2\text{Sn}$
Formula weight	551.19	428.07
Temperature (K)	293(2)	160(2)
Space group	$P\bar{1}$	$C2/c$
a (Å)	9.1099(9)	55.258(8)
b (Å)	10.5304(17)	7.3890(12)
c (Å)	15.135(3)	17.771(3)
α (°)	108.091(13)	90
β (°)	94.941(15)	95.194(15)
γ (°)	110.553(10)	90
Volume (Å ³)	1260.9(4)	7226(2)
Z	2	16
$D_{\text{calc.}}$ (g cm ⁻³)	1.452	1.574
θ range for data collection (°)	2.16–25.00	2.30–25.00
Reflections collected	5143	6522
Independent reflections	4279 [$R_{\text{int}} = 0.0384$]	5552 [$R_{\text{int}} = 0.0261$]
Max. and min. transmission	0.8400 and 0.7036	0.8249 and 0.4782
Data/restraints/parameters	4279/0/307	5552/42/471
Goodness-of-fit on F^2	0.977	1.086
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0318$, $wR_2 = 0.0819$	$R_1 = 0.0620$, $wR_2 = 0.1545$
R indices (all data)	$R_1 = 0.0349$, $wR_2 = 0.0842$	$R_1 = 0.0786$, $wR_2 = 0.1641$
Largest diff. peak and hole (eÅ ⁻³)	0.521 and -0.726	0.589 and -3.446

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

temperature. After 30 min shiny yellow crystals of compound **1** appeared. This was filtered, 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: 2.79 g (81%); m.p. 191–192 °C. *Anal.* Calc. for $\text{C}_{29}\text{H}_{24}\text{N}_2\text{O}_2\text{Sn}$ (formula weight 551.19): C, 63.19; H, 4.39; N, 5.08; Sn, 21.74. Found: C, 63.41; H, 4.27; N, 5.17; Sn, 21.74%.

2.5.1. $\text{Me}_2\text{Sn}[\text{Ph}(\text{O})\text{C}=\text{CH}-\text{C}(\text{Me})=\text{N}-\text{N}=\text{C}(\text{O})\text{Ph}]$ (**2**)

Yield: 1.36 g (79%); m.p. 163–164 °C. *Anal.* Calc. for $\text{C}_{19}\text{H}_{20}\text{N}_2\text{O}_2\text{Sn}$ (formula weight 427.07): C, 53.68; H, 4.72; N, 6.56; Sn, 27.79. Found: C, 53.43; H, 4.48; N, 6.48; Sn, 28.03%.

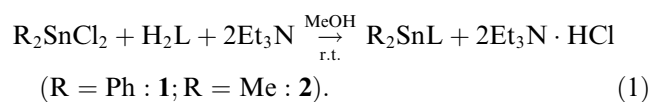
3. Results and discussion

3.1. 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 viz. *N*-(2-pyridinylmethylene)benzoylhydrazone and *N*-salicylidene derivatives of arylhydrazones were prepared by refluxing sodium salt of the respective ligands and organotin(IV) chlorides in methanol by more synthetically demanding methods [7,8].

The compounds reported here have been synthesised under mild conditions from diorganotin(IV) dichlorides (Ph_2SnCl_2 or Me_2SnCl_2) and H_2L in methanol at room temperature in presence of triethylamine (Eq. (1) below). The complexes separated out from the reaction mixture.



Although these two compounds have been prepared in methanol at room temperature, the compounds could be prepared as well in other solvents such as benzene, toluene. Carrying out the reaction at higher temperature and/or using more concentrated solutions could further reduce the reaction time. Both **1** and **2** are stable under atmospheric conditions.

The complexes have been characterised by elemental analysis, IR, ¹H, ¹³C, ¹⁵N, ¹¹⁹Sn NMR spectra. The structure of compounds **1** and **2** has been confirmed by X-ray diffraction.

3.2. Spectroscopic studies

The infrared spectra of the ligand, H₂L is consistent with the formation of benzoyl hydrazones. The ligand exists exclusively in the cyclic tautomeric form (Fig. 1(b)), assigned from comparison with the IR data of similar benzoylhydrazone [15]. The colourless solid ligand on dissolution in methanol in presence of triethylamine turns yellow. The ligand undergoes a ring opening reaction on complexation with diorganotin(IV) dichlorides, and behaves as dibasic tridentate ligand corresponding to the enol tautomer of the hydrazone form [Fig. 1(a)]. The O–H stretching vibration appears as a broad band at 3239 cm⁻¹. The two strong bands at 1663 and 1602 cm⁻¹ are assigned to an amido carbonyl $\nu(\text{C}=\text{O})$ and azomethyne $\nu(\text{C}=\text{N})$ stretching mode overlapping with other possible bands. The CH₂ stretching and bending vibrations are observed at 2936 and 1436 cm⁻¹, and O–H bending and C–O stretching vibrations are found around 1178 and 1317 cm⁻¹ [18]. The most significant difference in the vibrational spectra of the ligand (H₂L) when compared to its diorganotin(IV) complexes (**1** and **2**) is the disappearance of the $\nu(\text{O}-\text{H})$ band at 3239 cm⁻¹ and amido carbonyl $\nu(\text{C}=\text{O})$ at 1663 cm⁻¹. Strong bands at 1592 (**1**) and at 1593 cm⁻¹ (**2**) are assigned to $\nu(\text{C}=\text{N}-\text{N}=\text{C})$ stretching. The lowering of $\nu(\text{C}=\text{N})$ stretching of the complexes with respect to that of the ligand is expected on coordination of nitrogen and delocalisation in the chelate ring. The above assignments suggest the coordination of imino nitrogen and deprotonated enolic oxygens to the central

tin(IV) and therefore the tridentate dibasic nature of the coordinated ligand.

The NMR spectra (¹H, ¹³C, ¹⁵N, ¹¹⁹Sn) for the compounds Ph₂SnL (**1**) and Me₂SnL (**2**) were measured and analysed. 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 [16,17]. The ¹⁵N NMR spectra were measured using the gs-HMBC technique (the experiment being optimised for ⁿJ(¹⁵N, ¹H) = 6 Hz). Both ¹⁵N signals in two-dimensional spectra correlate with C(6)–H and CH₃ group protons, however, signals for N_a nitrogen are much more intensive because they are due to ³J(¹⁵N, ¹H) coupling constants while weak cross peaks for N_b nitrogen are due to ⁴J(¹⁵N, ¹H) coupling constants. The ¹⁵N chemical shifts are given in Table 2. For each compound the number of ¹H, ¹³C and ¹⁵N signals observed is in good agreement with the numbering shown in Fig. 2.

We have been able to detect all proton and carbon signals separately for both compounds. For the diphenyltin(IV) compound, diphenyl[4-phenyl-2,4-butanedi-onebenzoylhydrazone(2-)]tin(IV) (**1**) detection of ²J(¹¹⁹Sn, ¹³C) coupling (29.1 and 28.4 Hz) with C(5) and C(7) carbons, and ³J(¹¹⁹Sn, ¹³C) coupling (27.7 Hz) with C(6) carbon indicate the coordination of oxygen and nitrogen atoms of the ligand with tin. The corresponding ²J(¹¹⁹Sn, ¹³C) coupling with C(7) for **2** 27.7 Hz, indicates the coordination of nitrogen to tin.

The ¹J(¹¹⁹Sn, ¹³C) coupling constant 982.8 Hz for **1** is comparable with reported values for phenyltin com-

Table 2
¹H, ¹³C, ¹¹⁹Sn and ¹⁵N chemical shifts and ⁿJ(¹¹⁹Sn, ¹H) and ⁿJ(¹¹⁹Sn, ¹³C) coupling constants for **1** and **2** in CDCl₃

H/C No.	Compound 1		Compound 2	
	$\delta(^1\text{H})$	$\delta(^{13}\text{C})$	$\delta(^1\text{H})$	$\delta(^{13}\text{C})$
1	–	138.35	–	138.78
2	8.07	126.63	7.79	126.50
3	7.5	a	7.4	d
4	7.5	130.45	7.4	e
5	–	173.87 (29.1)	–	173.93 (28.4)
6	5.86	94.86 (27.7)	5.65	94.29 (27.7)
7	–	169.99 (28.4)	–	169.91 (27.7)
8	2.61	23.66 (9.0)	2.57	23.59 (7.6)
9	–	164.14	–	164.15 (4.2)
10	–	134.18	–	134.33
11	8.32	127.38	8.09	127.23
12	7.5	a	7.4	d
13	7.5	130.33	7.4	e
1'	–	139.82 (982.8)	0.80 (78.5)	1.14 (647.1)
2'	7.96	136.05 (54.1)	–	–
3'	7.4	128.74 (85.3)	–	–
4'	7.4	130.33 (16.6)	–	–
Sn	–	–151.5 ^b	–	–146.8 ^b
N _a	–	–77.9 ^c	–	f ^c
N _b	–	–49.9 ^c	–	f ^c

Coupling constants values (Hz) are given in parentheses.

a = 128.08 or 128.44, ^b $\delta(^{119}\text{Sn})$, ^c $\delta(^{15}\text{N})$, d = 128.00 or 128.20, e = 130.11 or 130.16, f = not measured because of very low solubility.

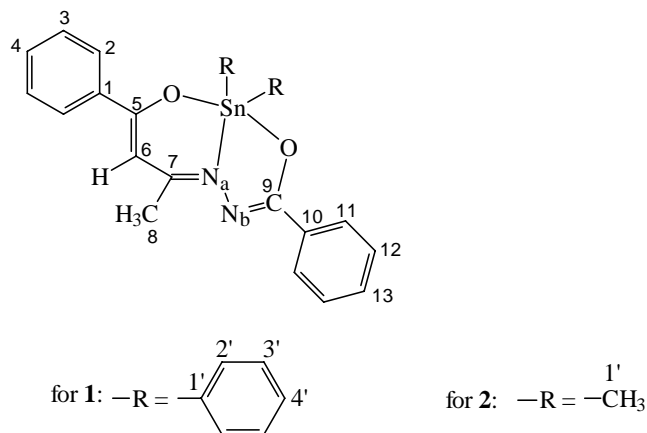


Fig. 2. Constitution of compounds **1** and **2** and numbering scheme for NMR assignments.

pounds [19a,19b,20] but lower than the value (993.2 Hz) seen in the hydrazone $\text{Ph}_2\text{Sn}[2\text{-OC}_6\text{H}_4\text{CH}=\text{N}-\text{N}=\text{C}(\text{O})\text{C}_6\text{H}_5]$ [11]. The $^1J(^{119}\text{Sn}, ^{13}\text{C})$ coupling constant, 647.9 Hz, of **2** is comparable with the value $\text{Me}_2\text{Sn}[2\text{-OC}_6\text{H}_4\text{CH}=\text{N}-\text{N}=\text{C}(\text{O})\text{C}_6\text{H}_5]$ [12].

The C–Sn–C angle for **1** was calculated from the $^1J(^{119}\text{Sn}, ^{13}\text{C})$ value [19b] and was found to be 134.9° (cf. $120.81(12)^\circ$ in the X-ray study). For compound **2**, the C–Sn–C angle was calculated using the equation $^1J(^{119}\text{Sn}, ^{13}\text{C}) = 10.7\theta - 778$ [23] with the $^1J(^{119}\text{Sn}, ^{13}\text{C})$ value of 649.9 Hz and the angle was determined as 133° . The $^2J(\text{Sn}-\text{CH}_3)$ (78.5 Hz) is in agreement with values reported (77–81 Hz) for the dimethyltin(IV) complexes also derived from ONO donor tridentate ligands [10,12,21,22]. Using Lockhart's equation $[\text{Me}-\text{Sn}-\text{Me} = 0.0161(^2J(^{119}\text{Sn}, ^1\text{H}))^2 - 1.32(^2J(^{119}\text{Sn}, ^1\text{H})) + 133.4]$ [22], the C–Sn–C angle for **2** is estimated to ca. 129° , closer to the values seen in the X-ray structure [$125.8(3)^\circ$ and $126.9(3)^\circ$] than the angle estimated from $^1J(^{119}\text{Sn}, ^{13}\text{C})$.

In the ^1H NMR spectrum of **2**, Sn–Me and CH_3 proton signals appear at δ 0.80 and 2.57 ppm, respectively. Ethylenic ligand protons appear at 5.65 ppm, comparable with reported values [15]. The ^{15}N NMR spectra of compound **1** showed signals for N_a and N_b nitrogen at δ -77.9 and -49.9 ppm, respectively.

The $\delta(^{119}\text{Sn})$ values for **1** and **2** are -151.5 and -146.8 ppm, respectively. These ^{119}Sn chemical shifts are in the range reported (90–300 Hz) for five-coordinate tin compounds [19,23]. From ^{119}Sn NMR spectra it is also evident that the five-coordinate solid state structure (obtained from X-ray crystallography) is retained in solution.

4. Crystal structures of $\text{Ph}_2\text{Sn}[\text{Ph}(\text{O})\text{C}=\text{CH}-\text{C}(\text{Me})=\text{N}-\text{N}=\text{C}(\text{O})\text{Ph}]$ (**1**) and $\text{Me}_2\text{Sn}[\text{Ph}(\text{O})\text{C}=\text{CH}-\text{C}(\text{Me})=\text{N}-\text{N}=\text{C}(\text{O})\text{Ph}]$ (**2**)

The molecular structures along with atom numbering schemes for **1** and **2** are given in Figs. 3 and 4, respec-

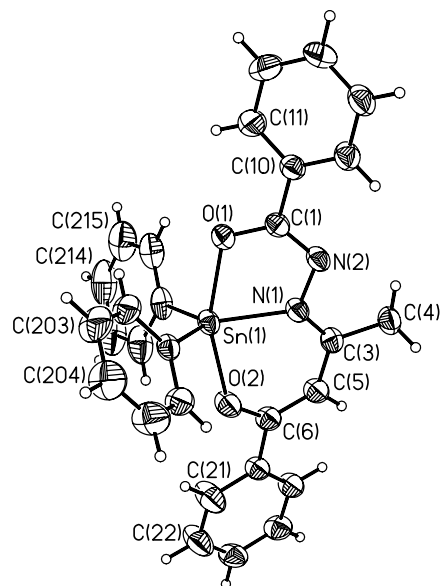


Fig. 3. Molecular structure and atom numbering scheme of compound **1**.

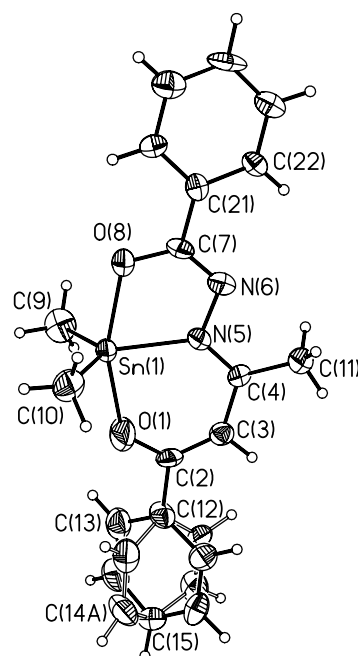


Fig. 4. Molecular structure and atom numbering scheme of compound **2** (molecule A).

tively. Selected bond lengths and angles for **1** and **2** are listed in Tables 3 and 4, respectively.

The X-ray structural investigations of $\text{Ph}_2\text{Sn}[\text{Ph}(\text{O})\text{C}=\text{CH}-\text{C}(\text{Me})=\text{N}-\text{N}=\text{C}(\text{O})\text{Ph}]$ (**1**) and $\text{Me}_2\text{Sn}[\text{Ph}(\text{O})\text{C}=\text{CH}-\text{C}(\text{Me})=\text{N}-\text{N}=\text{C}(\text{O})\text{Ph}]$ (**2**) confirm that the ligand, H_2L behaves as a tridentate dibasic coordinating agent via imino nitrogen and two enolic oxygen atoms. The two organic groups (phenyl for **1** and methyl for **2**) and imino nitrogen atom of ligand take the equatorial

Table 3
Selected bond lengths (Å) and angles (°) for **1**

Sn(1)–O(1)	2.118(3)	O(1)–C(1)	1.311(4)
Sn(1)–O(2)	2.098(2)	O(2)–C(6)	1.309(4)
Sn(1)–C(211)	2.113(3)	N(1)–C(3)	1.310(4)
Sn(1)–C(201)	2.118(3)	N(1)–N(2)	1.401(4)
Sn(1)–N(1)	2.145(3)	C(1)–N(2)	1.302(4)
C(211)–Sn(1)–C(201)	120.81(12)	O(2)–Sn(1)–C(211)	97.14(14)
O(2)–Sn(1)–C(201)	93.63(11)	O(2)–Sn(1)–O(1)	157.77(10)
C(211)–Sn(1)–O(1)	95.93(13)	C(201)–Sn(1)–O(1)	94.97(11)
O(2)–Sn(1)–N(1)	83.84(10)	C(211)–Sn(1)–N(1)	117.79(12)
C(201)–Sn(1)–N(1)	121.17(11)	O(1)–Sn(1)–N(1)	74.16(10)
O(2)–Sn(1)–O(1)–C(1)	–1.5(4)	N(1)–Sn(1)–O(1)–C(1)	–10.0(2)
O(1)–C(1)–N(2)–N(1)	–2.7(4)	Sn(1)–N(1)–N(2)–C(1)	–6.8(3)
Sn(1)–N(1)–C(3)–C(5)	–8.9(5)	N(1)–C(3)–C(5)–C(6)	–6.5(6)
Sn(1)–O(2)–C(6)–C(5)	29.2(5)	C(3)–C(5)–C(6)–O(2)	–4.0(6)

Table 4
Selected bond lengths (Å) and angles (°) for **2**

Sn(1)–O(1)	2.117(8)	Sn(1')–O(1')	2.112(5)
Sn(1)–O(8)	2.137(6)	Sn(1')–O(8')	2.124(5)
Sn(1)–N(5)	2.140(6)	Sn(1')–N(5')	2.134(6)
Sn(1)–C(9)	2.106(10)	Sn(1')–C(9')	2.135(7)
Sn(1)–C(10)	2.122(9)	Sn(1')–C(10')	2.103(7)
O(1)–C(2)	1.267(10)	O(1')–C(2')	1.314(9)
C(4)–N(5)	1.331(10)	C(4')–N(5')	1.329(11)
N(5)–N(6)	1.403(9)	N(5')–N(6')	1.395(9)
C(7)–O(8)	1.324(10)	C(7')–O(8')	1.314(9)
C(9)–Sn(1)–C(10)	125.8(3)	C(10')–Sn(1')–C(9')	126.9(3)
C(10)–Sn(1)–O(8)	96.0(3)	C(10')–Sn(1')–O(8')	93.6(3)
C(9)–Sn(1)–O(1)	93.2(4)	O(1')–Sn(1')–C(9')	97.0(3)
O(1)–Sn(1)–C(10)	92.5(4)	C(10')–Sn(1')–O(1')	91.9(3)
O(1)–Sn(1)–O(8)	159.5(2)	O(1')–Sn(1')–O(8')	158.7(2)
C(9)–Sn(1)–O(8)	96.9(3)	O(8')–Sn(1')–C(9')	96.1(3)
C(10)–Sn(1)–N(5)	117.0(3)	C(10')–Sn(1')–N(5')	123.6(3)
O(1)–Sn(1)–N(5)	85.7(3)	O(1')–Sn(1')–N(5')	85.6(2)
C(9)–Sn(1)–N(5)	117.2(3)	N(5')–Sn(1')–C(9')	109.2(3)
O(8)–Sn(1)–N(5)	73.8(2)	O(8')–Sn(1')–N(5')	74.2(2)
Sn(1)–O(1)–C(2)–C(3)	–1.2(16)	Sn(1')–O(1')–C(2')–C(3')	8.7(10)
Sn(1)–O(1)–C(2)–C(12)	–178.6(7)	Sn(1')–O(1')–C(2')–C(12')	–172.6(4)
C(3)–C(4)–N(5)–Sn(1)	–1.1(9)	C(3')–C(4')–N(5')–Sn(1')	–9.2(13)
O(8)–Sn(1)–N(5)–C(4)	179.1(7)	O(8')–Sn(1')–N(5')–C(4')	–171.4(8)
O(1)–Sn(1)–N(5)–N(6)	178.7(6)	O(1')–Sn(1')–N(5')–N(6')	–172.4(5)
O(8)–Sn(1)–N(5)–N(6)	–2.2(5)	O(8')–Sn(1')–N(5')–N(6')	0.7(5)
Sn(1)–N(5)–N(6)–C(7)	1.1(8)	Sn(1')–N(5')–N(6')–C(7')	–2.2(7)
N(6)–C(7)–O(8)–Sn(1)	–3.6(11)	N(6')–C(7')–O(8')–Sn(1')	–2.6(8)

positions, and the enolic oxygen atoms are in the axial positions [O(2)–Sn(1)–O(1) 157.77(10); O(1)–Sn(1)–O(8) 159.5(2); O(1')–Sn(1')–O(8'), 158.7(2)°]. The ligand forms six- and five-membered chelate rings. The electron density difference map indicates that no hydrogen is bonded to the nitrogen atoms and that extensive delocalisation has taken place. The ligand, H₂L is not completely planar in either **1** or **2** and a distorted trigonal-bipyramidal geometry around the tin centre is found. However, there are two crystallographically independent molecules (denoted by A and B, referring to molecules with undashed and dashed atom labels, re-

spectively) for **2** which differ most significantly in the following distances and angles: O(1)–C(2) [1.264(10) in A and 1.312(9) Å in B], C(3)–C(4) [1.482(11) in A and 1.385(12) Å in B] distances and C–Sn–N angles [C(10)–Sn(1)–N(5), 117.0(3); C(9)–Sn(1)–N(5), 117.2(3)° in A and C(10')–Sn(1')–N(5), 123.6(3); C(9')–Sn(1')–N(5'), 109.2(3)° in B].

Crystals of compound **1**, Ph₂Sn[Ph(O)C=CH–C(Me)=N–N=C(O)Ph] are composed of discrete molecules. The index of trigonality, τ , for describing the continuum between tetragonal-pyramidal ($\tau = 0$) and trigonal-bipyramidal ($\tau = 1$), defined by Addison and

Reedijk [24] is $\tau = 0.62$. Thus for compound **1**, trigonal-bipyramidal geometry predominates over tetragonal-pyramidal geometry. 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 O(1)–Sn(1)–O(2), $157.77(10)^\circ$ as are the bite angles N(1)–Sn(1)–O(1), $74.16(10)$, O(2)–Sn(1)–N(1), $83.84(10)^\circ$ compressed from 90° . These distortions arise from the rigidity of chelate rings, compounded by the large tin(IV) covalent radius. 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 [1–5,10–12,25–29]. Displacement of Sn(1) from the plane defined by N(1), C(201), C(211) is 0.059 \AA towards O(2). However the trigonal angles do not differ significantly from 120° [C(201)–Sn(1)–C(211), $120.81(12)$; C(201)–Sn(1)–N(1), $121.17(11)$, C(211)–Sn(1)–C(1), $117.79(12)^\circ$]. The C–Sn–C angle is much less than that calculated from $^1J(^{119}\text{Sn},^{13}\text{C})$ coupling constant values (vide supra). The five-membered chelate ring of compound **1** is nearly planar but the six-membered chelate ring is slightly boat shaped in appearance.

The crystals of $\text{Me}_2\text{Sn}[\text{Ph}(\text{O})\text{C}=\text{CH}-\text{C}(\text{Me})=\text{N}-\text{N}=\text{C}(\text{O})\text{Ph}]$ (**2**) are also composed from discrete molecules, but contains two crystallographically independent molecules denoted by A and B (primed and unprimed labels, respectively). Here trigonal-bipyramidal geometry also just predominates over tetragonal-pyramidal geometry ($\tau = 0.56$ for molecule A and $\tau = 0.53$ for molecule B). The angles subtended at tin(IV) by two oxygen atoms are compressed to $159.5(2)^\circ$ [O(1)–Sn(1)–O(8)] and $158.7(2)^\circ$ [O(1')–Sn(1')–O(8')]. These compressions of O–Sn–O angles are comparable with those found in compound **1** and other similar compounds [2–5,10–12]. The bite angles N(5)–Sn(1)–O(1) [$85.7(3)^\circ$], O(8)–Sn(1)–N(5) [$73.9(2)^\circ$] (A) and N(5')–Sn(1')–O(1')

[$85.6(2)^\circ$], O(8')–Sn(1')–N(5') [$74.3(2)^\circ$] (B) are also compressed from 90° . Displacement of Sn(1) from the plane defined by N(5), C(9), C(10) is 0.026 \AA towards O1 whilst Sn(1') is displaced further, 0.061 \AA , towards O(1') from the plane defined by N(5'), C(9'), and C(10'). In the case of compound **2**, the C–Sn–C angles for both molecules [$125.8(3)^\circ$, $126.9(3)^\circ$] are 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) but have closer agreement with the latter. For compound **2** the six-membered chelate ring of molecule A is almost planar [Sn(1)–O(1)–C(2)–C(3), $-1.2(16)^\circ$] while that of molecule B is more buckled [Sn(1')–O(1')–C(2')–C(3'), $8.7(10)^\circ$] as shown by their torsion angles in Table 4.

The Sn–O bond lengths [$2.118(3)$ and $2.098(2) \text{ \AA}$] of **1** and **2** [$2.118(8)$, $2.138(6) \text{ \AA}$ in molecule A and $2.113(5)$, $2.124(5) \text{ \AA}$ in molecule B] compare well with the reported values for diorganotin(IV) complexes derived from ONO donor tridentate Schiff bases [1–5,10–12] (Table 5) but are shorter than diorganotin(IV) complexes derived from ONNO donor tetradentate Schiff bases 2.163 – 2.228 \AA [28]. The Sn–N bond lengths of compound **1** [$2.145(3) \text{ \AA}$] and compound **2** [$2.141(6) \text{ \AA}$ (A) and $2.135(6) \text{ \AA}$ (B)] are very close to $\text{Ph}_2\text{Sn}(2\text{-OC}_{10}\text{H}_6\text{CH}=\text{NCH}_2\text{COO})$ [2] and shorter than in $\text{Ph}_2\text{Sn}(2\text{-OC}_6\text{H}_4\text{CH}=\text{NC}_6\text{H}_4\text{O})$ [4], $\text{Me}_2\text{Sn}(2\text{-OC}_6\text{H}_4\text{CH}=\text{NC}_6\text{H}_4\text{O})$ [5], $\text{Me}_2\text{Sn}(2\text{-OC}_6\text{H}_4\text{CH}=\text{NC}_6\text{H}_4\text{COO})$ [10], $\text{R}_2\text{Sn}[2\text{-OC}_6\text{H}_4\text{CH}=\text{N}-\text{N}=\text{C}(\text{O})\text{C}_6\text{H}_5]$ (R = Ph, Me) [12] (Table 5) and much shorter than those found in six-coordinated diorganotin(IV) complexes [25–29], e.g. $2.236(6) \text{ \AA}$ [28].

The Sn–C(phenyl) bond lengths [$2.113(3)$, and $2.118(3) \text{ \AA}$] of **1** are very close to the Sn–C bond lengths in five-coordinated diorganotin(IV) complexes derived from ONO donor tridentate Schiff bases [1–5,10–12] (Table 5) and shorter than six-coordinated diorganotin(IV) complexes derived from ONNO donor tetradentate Schiff bases, e.g. $2.126(8)$ – $2.154(9) \text{ \AA}$ [28]. The

Table 5

Comparison of Sn–N, Sn–O and Sn–C bond lengths (\AA) **1** and **2** with those in some other organotin(IV) complexes derived from ONO donor tridentate Schiff bases

	Reference	Sn–N (\AA)	Sn–O (\AA)	Sn–C (\AA)
$\text{Ph}_2\text{Sn}[\text{Ph}(\text{O})\text{C}=\text{CH}-\text{C}(\text{Me})=\text{N}-\text{N}=\text{C}(\text{O})\text{Ph}]$ (1)	This work	2.145(3)	2.098(2), 2.118(2)	2.113(3), 2.118(3)
$\text{Ph}_2\text{Sn}[2\text{-OC}_6\text{H}_4\text{CH}=\text{N}-\text{N}=\text{C}(\text{O})\text{C}_6\text{H}_5]$	[11]	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)
$\text{Ph}_2\text{Sn}[2\text{-OC}_6\text{H}_4\text{CH}=\text{NC}_6\text{H}_4\text{O}]$	[4]	2.241(13)	2.085(8), 2.103(8)	2.125(11), 2.124(10)
$\text{Me}_2\text{Sn}[2\text{-OC}_6\text{H}_4\text{CH}=\text{NC}_6\text{H}_4\text{O}]$	[5]	2.229(11)	2.105(8), 2.118(9)	2.091(14), 2.142(14)
$\text{Bu}_2\text{Sn}[2\text{-OC}_6\text{H}_4\text{CH}=\text{NCH}(i\text{-pr})\text{COO}]$	[1]	2.158(8)	2.078(10), 2.151(8)	2.100(12), 2.138(14)
$\text{Me}_2\text{Sn}[2\text{-OC}_6\text{H}_4\text{CH}=\text{NC}_6\text{H}_4\text{COO}]$	[9]	2.230(5)	2.135(4), 2.187(4)	2.102(7), 2.103(6)
$\text{Ph}_2\text{Sn}[2\text{-OC}_{10}\text{H}_6\text{CH}=\text{NCH}_2\text{COO}]$	[2]	2.136(5)	2.068(4), 2.188(3)	2.108(8), 2.127(8)
$\text{Ph}_2\text{Sn}[2\text{-OC}_6\text{H}_4\text{C}(\text{CH}_3)=\text{NCH}_2\text{COO}]$	[3]	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)
$\text{Me}_2\text{Sn}[2\text{-OC}_6\text{H}_4\text{CH}=\text{N}-\text{N}=\text{C}(\text{O})\text{C}_6\text{H}_5]$	[11]	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)
$\text{Me}_2\text{Sn}[\text{Ph}(\text{O})\text{C}=\text{CH}-\text{C}(\text{Me})=\text{N}-\text{N}=\text{C}(\text{O})\text{Ph}]$ (2)	This work	2.140(6), 2.134(6)	2.117(8), 2.137(6), 2.112(5), 2.124(5)	2.122(9), 2.106(10), 2.103(7), 2.135(7)

Sn–C(methyl) bond lengths [2.106(10)–2.135(7) Å] in **2** are comparable with other reported diorganotin(IV) complexes (Table 5) [1–5,10–12,25–29].

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, ^{119}Sn chemical shift values indicate that the five-coordinate structure is retained in solution.

5. Supplementary material

Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre, CCDC-213984 (**1**) and CCDC-213985 (**2**). Copies of the data can be obtained on application to The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK [fax: +44(0) 1223-336090, E-mail: deposit@ccdc.cam.ac.uk or <http://www.ccdc.cam.ac.uk/>].

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