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Synthesis and characterization of diorganotin(IV) complexes of tetradentate Schiff bases: crystal structure of *n*-Bu_2Sn(Vanophen)

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Abstract

Diorganotin(IV) complexes of the general formula R_2SnL (R=Ph, *n*-Bu and Me) have been prepared from diorganotin(IV) dichlorides (R_2SnCl_2) and tetradentate Schiff bases (H_2L) containing N_2O_2 donor atoms in the presence of triethylamine in benzene. The Schiff bases, H_2L, were derived from salicylaldehyde, 3-methoxysalicylaldehyde (*o*-vanillin), 1-phenyl-3-methyl-4-benzoyl-5-pyrazolone and diamines such as *o*-phenylenediamine and 1,3-propylenediamine. The complexes were characterized by IR, NMR (^1H, ^{13}C, ^{119}Sn) and elemental analysis. The structure of the complex, *n*-Bu_2Sn(Vanophen), was determined using single crystal X-ray diffraction. The tin atom has a distorted octahedral coordination, with the Vanophen ligand occupying the four equatorial positions and the *n*-butyl groups in the *trans* axial positions. Six-coordinated distorted octahedral structures have been proposed for all diorganotin(IV) complexes studied here, as they possess similar spectroscopic data.

Keywords: Diorganotin(IV) complexes; $^{13}C/^{119}Sn$ NMR spectra; Crystal structure; Tetradentate Schiff bases

1. Introduction

The coordination chemistry of mostly bidentate Schiff bases with inorganic tin(IV) and organotin(IV) compounds has recently received increased attention [1–12]. Organotin(IV) complexes of deprotonated Schiff bases are also known [13–16]. Our interest in the chemistry of organotin(IV) complexes of Schiff bases has stemmed from the reported biocidal [17–21] and antitumour [22–24] activities of organotin(IV) complexes, and the behaviour of Schiff bases as models for biological systems [25].

However, few studies have been conducted with the diorganotin(IV) chelated complexes containing dianionic tetradentate Schiff bases in comparison to their adducts. Hence, little information is available regarding the mode of interaction between diorganotin(IV) moieties and Schiff bases, and the behaviour of these complexes in the solid state and solution. Continuing our previous study [26], here we report the synthesis and characterization of some chelated diorganotin(IV) complexes of deprotonated tetradentate Schiff bases.

2. Experimental

2.1. General

All chemicals and reagents were of reagent-grade quality. Diphenyltin dichloride (Aldrich), di-*n*-butyltin dichloride (Alfa), dimethyltin dichloride (Fluka), *o*-phenylenediamine (Fluka), 1,3-propylenediamine (Fluka), salicylaldehyde (Merck) and 3-methoxysalicylaldehyde (*o*-vanillin) (Lancaster) were used as received. 1-Phenyl-3-methyl-4-benzoyl-5-pyrazolone (PMBP) was prepared as reported [27] from 1-phenyl-3-methyl-5-pyrazolone (Lancaster).

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Triethylamine (S.D. Fine Chemicals, India) was dried over KOH.

Benzene (AR, thiophene-free) and petroleum ether (40–60°C) were dried by refluxing over freshly cut sodium. All solvents were distilled prior to use. Other solvents were dried and purified by standard procedures.

2.2. 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. ^{1}H NMR spectra were recorded on a Bruker DPX-300 (300 MHz), a Jeol JNM FX-100 (100 MHz) or a Varian EM-360 (60 MHz) NMR spectrometer in $CDCl_3$ relative to internal tetramethylsilane (TMS). ^{13}C NMR spectra were recorded on a Bruker DPX-300 (at 75.47 MHz) NMR spectrometer in $CDCl_3$ with respect to TMS as the internal standard. ^{119}Sn NMR spectra were recorded on a Jeol JNM FX-90Q (at 33.35 MHz) in $CHCl_3$ as solvent (locking with D_2O) with reference to external tetramethyltin. Tin was estimated gravimetrically as SnO_2 after decomposition with conc. HNO_3. Analysis of carbon, hydrogen and nitrogen was carried out on a Perkin-Elmer 240C or 2400 II elemental analyser. Melting points (uncorrected) were recorded on an electrical heating-coil apparatus. All synthetic manipulations were carried out under a dry nitrogen atmosphere.

2.3. Crystallography: X-ray crystal structure determination of di-n-butyl[N,N′-bis(3-methoxysalicylaldehyde)-1,2-phenylenediiminato]tin(IV), $(n\text{-}Bu)_2Sn$(Vanophen) (**2a**)

Crystals of **2a** were grown by slow evaporation of a cyclohexane solution and were subsequently coated in nujol and vacuum grease and mounted on a glass fibre and cooled to 160 K using an Oxford Cryosystems Cryostream on a Siemens P4 diffractometer. Data collection as ω scans was performed with the program XSCANS [28]. No significant crystal decay was found. Data were corrected for absorption by psi scans and the structure was solved by direct and difference Fourier methods and refined by full-matrix least squares against F^2. All non-hydrogen atoms were refined anisotropically. All methylene, phenyl and methyl H atom positions were calculated and treated as riding models. Methylene, phenyl and methyl H-atom displacement parameters were treated as riding models, with U_{iso} being 1.2, 1.2 and 1.5 times the bound carbon atom U_{eq}, respectively. Crystallographic computing was performed using the SHELXTL [29,30] suite of programs on a Pentium 90 MHz PC. Further details are given in Table 1.

2.4. Preparation of Schiff bases

The Schiff bases, H_2Salophen (**1**) and H_2Vanophen (**2**) have been prepared by refluxing *o*-phenylenediamine with

Table 1
Crystal data and data collection parameters of $(n\text{-}Bu)_2Sn$(Vanophen) (**2a**)

Empirical formula	$C_{30}H_{36}N_2O_4Sn$
Formula weight	607.30
Temperature (K)	160(2)
Crystal system	Triclinic
Space group	P-1
a (Å)	13.428(2)
b (Å)	14.013(2)
c (Å)	16.498(3)
α (°)	71.590(10)
β (°)	69.610(10)
γ (°)	88.130(10)
V (Å^3)	2750.5(8)
Z	4
ρ (calcd.), (mg/m^3)	1.467
u (mm^{-1})	0.967
F(000)	1248
Crystal habit, size (mm)	Rectangular block, 0.50×0.88×0.58
θ range (data collection) (°)	2.09 to 25.00
Reflections collected	10 814
Independent reflections	9499 [R(int)=0.0260]
Observed reflections ($I>2\sigma I$)	8827
Completeness $\theta=25.00°$	97.8%
Parameters	667
Goodness-of-fit on F^2	0.958
Final R indices [$I>2\sigma(I)$]	$R_1=0.0267$, w$R_2=0.0694$
R indices (all data)	$R_1=0.0291$, w$R_2=0.0713$
Largest diff. peak and hole (e/Å^{-3})	0.419 and −0.811

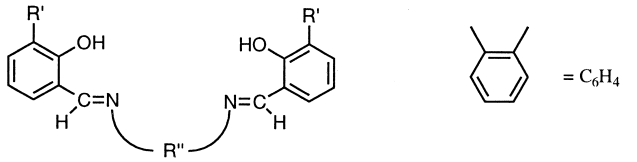


Fig. 1. Structure of ligands (**1–4**)

	R″	R′	Abbreviations	Melting point (°C)
1	C_6H_4	H	H_2Salophen	159–160
2	C_6H_4	OCH_3	H_2Vanophen	168–169
3	$(CH_2)_3$	H	H_2Salpn	50–51
4	$(CH_2)_3$	OCH_3	H_2Vanpn	94–95

salicylaldehyde and 3-methoxysalicylaldehyde (*o*-vanillin), respectively, in ethanol, while H_2Salpn (**3**) and H_2Vanpn (**4**) have been prepared by the same procedures using 1,3-propylenediamine with salicylaldehyde and 3-methoxysalicylaldehyde, respectively. H_2PMBP–*o*-phd (**5**) and H_2PMBP-pn (**6**) were obtained by reacting 1-phenyl-3-methyl-4-benzoyl-5-pyrazolone (PMBP) with *o*-phenylenediamine and 1,3-propylenediamine, respectively, in refluxing ethanol. The diamines are mixed with aldehydes or ketone in a 1:2 mole ratio. The crude Schiff bases were recrystallized from ethanol before use. The molecular structures of Schiff bases **1–6** used in the synthesis of diorganotin(IV) complexes are shown, with abbreviations and melting points, as follows (Figs. 1 and 2).

2.5. Synthesis of diorganotin(IV) complexes

All the complexes were similarly prepared from diorganotin(IV) dichlorides and the appropriate Schiff base ligands as follows. In a three-necked round-bottomed flask fitted with a reflux condenser and a dry nitrogen gas inlet, a solution of the appropriate Schiff base in dry benzene (50 ml) and triethylamine, in a 1:2 mole ratio (10% excess of the latter) was taken and stirred continuously. To this solution, a solution of the appropriate diorganotin(IV) dichlorides in benzene (20 ml) (in the same mole proportions to that of the Schiff base) was added slowly. When all of the diorganotin(IV) dichloride solution had been added, the mixture was refluxed for ca. 6 h. Then the reaction mixture was cooled to room temperature and the precipitated triethylamine hydrochloride was filtered off.

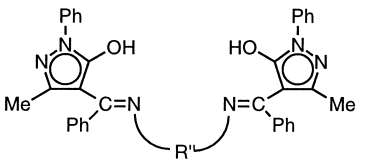


Fig. 2. Structure of ligands (**5** and **6**).

	R″	Abbreviations	Melting point (°C)
5	C_6H_4	H_2PMBP–*o*-phd	216–218
6	$(CH_2)_3$	H_2PMBP-pn	103–104

The crude product was obtained after evaporation of solvent washed with petroleum ether (40–60°C) and was finally crystallized from an appropriate solvent. The preparation of di-*n*-butyl[*N*,*N*′-bis(3-methoxysalicylaldehyde)-1,2-phenylenediiminato]tin(IV), (*n*-Bu)$_2$Sn(Vanophen) (**2a**) is described as an example.

Compound **2a** was prepared from 0.496 g (1.32 mmol) of ligand **2** (H_2Vanophen) and 0.40 g (1.32 mmol) of (*n*-Bu)$_2$SnCl$_2$. The crude product was crystallized from hot cyclohexane. Single crystals suitable for X-ray crystallography of **2a** were obtained by slow evaporation of cyclohexane at room temperature. Yield: 0.685 g (85.44%); m.p. 142–143°C. Found: C, 59.04; H, 6.00; N, 4.82; Sn, 19.88. Calcd. for $C_{30}H_{36}N_2O_4Sn$ (607.33): C, 59.33; H, 5.98; N, 4.61; Sn, 19.54.

Yields, melting points, solvent used for crystallisation and analytical data for other compounds are given below.

*2.5.1. Ph_2Sn(Salophen) (**1a**)*

Compound **1a** was recrystallized from toluene. Yield: 90.88%; m.p. 226–228°C. Found: C, 65.70; H, 4.30; N, 4.46; Sn, 20.45. Calcd. for $C_{32}H_{24}N_2O_2Sn$ (587.26): C, 65.45; H, 4.12; N, 4.77; Sn, 20.21.

*2.5.2. (n-Bu)$_2$Sn(Salophen) (**1b**)*

Compound **1b** was recrystallized from chloroform–petroleum ether. Yield: 91.25%; m.p. 101–103°C. Found: C, 61.75; H, 5.58; N, 4.84; Sn, 21.78. Calcd. for $C_{28}H_{32}N_2O_2Sn$ (547.28): C, 61.45; H, 5.89; N, 5.12; Sn, 21.69.

*2.5.3. Me_2Sn(Salophen) (**1c**)*

Compound **1c** was recrystallized from toluene. Yield: 85.86%; m.p.>244°C. Found: C, 57.45; H, 4.34; N, 5.84; Sn, 25.35. Calcd. for $C_{22}H_{20}N_2O_2Sn$ (463.12): C, 57.06, H, 4.35; N, 6.05; Sn, 25.63.

*2.5.4. Ph_2Sn(Salpn) (**3a**)*

Compound **3a** was recrystallized from chloroform–petroleum ether. Yield: 83%; m.p. 92–95°C. Found: C, 62.78; H, 4.62; N, 4.97; Sn, 21.06. Calcd. for $C_{29}H_{26}N_2O_2Sn$ (553.24): C, 62.96; H, 4.74; N, 5.06; Sn, 21.45.

*2.5.5. Ph_2Sn(Vanpn) (**4a**)*

Compound **4a** was recrystallized from chloroform–petroleum ether. Yield: 84.10%; m.p. 118–120°C. Found: C, 60.46; H, 4.81; N, 4.93; Sn, 19.46. Calcd. for $C_{31}H_{30}N_2O_4Sn$ (613.30): C, 60.71; H, 4.93; N, 4.57; Sn, 19.35.

*2.5.6. Ph_2Sn(PMBP–o-phd) (**5a**)*

Compound **5a** was recrystallized from toluene. Yield: 79.65%; m.p.>244°C. Found: C, 69.98; H, 4.80; N, 9.65; Sn, 13.28. Calcd. for $C_{52}H_{40}N_6O_2Sn$ (899.63): C, 69.42; H, 4.48; N, 9.34; Sn, 13.20.

*2.5.7. Ph_2Sn(PMBP-pn) (**6a**)*

The crude product was extracted with benzene, evaporated, then dissolved in benzene and reprecipitated using *n*-pentane. Yield: 71.26%; m.p. 138–140°C. Found: C, 68.12; H, 5.03; N, 10.08; Sn, 13.89. Calcd. for $C_{49}H_{42}N_6O_2Sn$ (865.62): C, 67.99; H, 4.89; N, 9.71; Sn, 13.71.

3. Results and discussion

Many Schiff bases form complexes with organotin(IV), and inorganic tin(II) and tin(IV) in both neutral and deprotonated forms [1–16,26]. With the neutral forms of Schiff bases, adducts are formed by reactions in alcoholic media, while organotin(IV) complexes of deprotonated Schiff bases are formed in the presence of a base such as alkoxide ion or by the exchange reaction between a Tl Schiff base complex [e.g., Tl_2(Salen)] and an organotin(IV) halide [15]. However, the chelating complex, Ph_2Sn(NAPPDI), has been reported in which the reaction was carried out in ethanol without the presence of an auxiliary base [16].

Preliminary reports have dealt with the formation of H_2Acen adducts [H_2Acen=bis(acetylacetone)ethylenediamine] of organotin(IV) chlorides, $R_2SnCl_2(H_2Acen)$ [31], the adduct $SnCl_4(H_2Salen)$ and complexes of dianion, R_2Sn(Salen) (R=Me, Ph) [14]. Chelating complexes of the type R_2SnL (R=Me, Ph; H_2L=dibasic tetradentate Schiff bases) have been synthesized by the reaction of R_2SnCl_2 with Schiff bases, H_2L, in a 1:1 molar ratio in ethanol in the presence of an appropriate amount of triethylamine [13].

The reactions in this study were performed by stirring diorganotin(IV) dichloride, R_2SnCl_2 [R=Ph, *n*-Bu, Me] and appropriate Schiff bases (**1–6**) in the presence of triethylamine as a Lewis base in refluxing benzene. The HCl formed during the reaction was removed as triethylamine hydrochloride, which precipitated in benzene and served as the driving force for completion of the reaction. The diorganotin(IV) dichloride, (R_2SnCl_2), Schiff base (H_2L) and triethylamine were mixed in a 1:1:2 mole ratio (with a 10% excess of the latter) as shown below (Eq. (1)).

$$R_2SnCl_2 + H_2L + 2Et_3N \xrightarrow[\text{reflux}]{\text{Benzene}} R_2SnL + 2Et_3N.HCl$$

(H_2L = Tetradentate Schiff base) (1)

Analytical data and melting points of the synthesized compounds are given in the Experimental section. The compounds have been characterized by elemental analysis and IR, ^{1}H, ^{13}C, ^{119}Sn NMR spectra. Spectroscopically derived structures of the compounds have been confirmed by the X-ray crystal structure determination of one representative compound (n-Bu)$_2$Sn(Vanophen) (**2a**). The elemental analysis data for compounds **1a–6a** are consistent with those calculated from the formula shown in Eq. (1).

Although the reactions seem to be instantaneous when the reactants are mixed, refluxing for ca. 6 h was carried out to ensure complete reaction. The resulting compounds are stable under atmospheric conditions for a considerable length of time, and are thermally stable up to their melting points. They all have intense colour (red to yellow–green) and are soluble in most common organic solvents.

3.1. IR spectra

The infrared spectra of the Schiff bases and their diorganotin(IV) complexes have been recorded along with those of the starting diorganotin(IV) dichlorides. Some important assignments are shown in Table 2. A weak broad band in the region 3250–2350 cm^{-1}, which has been assigned to the intramolecularly hydrogen-bonded OH in the Schiff bases, is not observed in the infrared spectra of these complexes (**1a–6a**). This indicates that the reactions have taken place through the replacement of the phenolic hydrogen in the complexes, contrary to what was observed with adduct formation when the reactions were carried out solely in alcoholic medium [6–11]. This also confirms that organotin(IV) complexes are indeed those of the deprotonated forms of Schiff bases. The strong ν(CH=N) band occurring in the range 1630–1595 cm^{-1} is shifted considerably towards lower frequencies compared to that of the free Schiff bases (occurring at 1634–1612 cm^{-1}), indicating the coordination of an azomethine nitrogen to the diorganotin(IV) moiety. In contrast, when adduct formation takes place [32], the HC=N stretch shifts to higher frequencies.

3.2. ^{1}H NMR spectra

The ^{1}H NMR data for the diorganotin(IV) complexes (**1a–6a**) are shown in Table 3. The absence of the OH proton signal in the complexes suggests the binding of a tin atom to the ligand oxygen atoms through the replacement of phenolic protons (for **1–4**) or enolic protons (for **5** and **6**). This observation supports the infrared data. The chemical shift values of the aromatic and aliphatic protons are as expected. A high field shift in the δ values of azomethine (HC=N) proton resonances, seen on complexation, supports the ligation of azomethine nitrogens to tin. The HC=N protons are observed as one sharp singlet in the Schiff base ligands (occurring at 8.61–8.99 ppm), as well as in the metal chelates (**1a–c** and **2a–4a**), which suggests that the two HC=N protons in Schiff bases (**1–4**) and in the metal chelates (**1a–c** and **2a–4a**) are equivalent. In the metal chelates of the planar tetradentate H_2Salen ligand, both the HC=N proton and $(CH_2)_2$ proton reso-

Table 2
Characteristic infrared bands (cm^{-1})[a] for diorganotin(IV) chelates

Compound no.	ν(C–H) (aryl)	ν(C–H) (alkyl)	ν(CH=N)[b]	ν(Sn–N)	ν(Sn–O)	ν(Sn–C)
1a	3065 m 3055 m		1605 s (1612)	459 m	592 m	364 m
1b	3057 mw 3013 w	2954 m 2927 m 2867 m 2861 m	1607 s (1612)	482 m	604 m	588 m
1c	3050 m 3014 m	2914 m 2900 w	1608 s (1612)	471 m	599 m	588 s
2a	3061 mw 3034 w	2993 w 2955 m 2923 m 2869 m 2832 w	1603 vs (1612)	498 s	547 m	534 m
3a	3062 m 3042 m	2922 m 2850 w	1630 s (1634)	455 s	600 m	400 w
4a	3064 w 3052 m 3000 m	2936 m 2854 w 2836 m	1624 vs (1634)	455 m	602 w	353 w
5a	3064 m 3050 m	2987 m 2968 w 2926 w	1625 s (1634)	456 s	590 m	327 m
6a	3060 m 3020 m,sh	2952 m 2922 m 2872 w 2862 m	1595 s (1616)	450 m	557 m	382 w

[a] s = strong, m = medium, w = weak, v = very, br = broad, sh = shoulder.
[b] Figures in parentheses indicate the corresponding ν(CH=N) stretching frequencies of the tetradentate Schiff bases.

nances each occur as singlets [33–35], suggesting the equivalence of two HC=N protons and $(CH_2)_2$ protons, respectively, and, hence, the planarity of the ligand moiety. In the dimethyltin(IV) chelate, $Me_2Sn(acac)_2$, the methyl resonances of the Me_2Sn moiety are observed as a sharp singlet [36–38], which is consistent with a *trans* configuration of the two methyl groups, as is also suggested on the basis of IR and Raman spectra [36]. In the dimethyltin(IV) chelate **1c**, there is only one sharp singlet at δ 0.79 ppm for the Me_2Sn moiety: this also indicates that the complex has a *trans* structure. Moreover, since the HC=N proton resonances appear as a singlet (only one for two HC=N protons) in all of the diorganotin(IV) chelates studied here (with the exception of **5a** and **6a**), it may be deduced that the ligand moieties lie in a plane and the two hydrocarbon groups on tin are *trans* to each other. For complexes **5a** and **6a**, there are no azomethine protons, but two methyl groups occupying 3-positions on the two pyrazolyl rings, which appear as one singlet (at δ 1.67 for **5a** and δ 1.36 ppm for **6a**), indicating that they equivalent, as one would expect from the planar arrangement of the ligand moiety (structure IV). For the complexes **2a** and **4a**, signals due to OCH_3 proton resonances appear at δ 3.83 and 3.86 ppm, respectively, as singlets, which further support the equivalence of the two OCH_3 groups.

There are single peaks for each of the following groups: two OCH_3 in **2a** and **4a**, two 3-CH_3 in **5a** and **6a**, two Sn–CH_3 groups in **1c**, and HC=N protons in all of the complexes (except **5a** and **6a**), which indicates that both of the respective groups are equivalent, which is only possible for a symmetrical arrangement of the chelate ligand moiety and *trans* arrangement of the two hydrocarbon groups on tin. Thus, the ^1H NMR data suggest an octahedral ligand environment around a central tin atom (Figs. 3 and 4). This interpretation, which is based on ^1H NMR results, is further supported by a ^{13}C NMR and X-ray structural study of one representative complex, **2a**.

3.3. ^{13}C NMR spectra

The ^{13}C NMR spectral data were recorded at room temperature in $CDCl_3$ and key signal assignments are shown in Table 4. For each compound, the number of signals observed is in good agreement with the numbering shown in Figs. 3 and 4. However, some general trends may be noted. The C=N carbon signal occurring as a sharp

Table 3
^{1}H and ^{119}Sn NMR spectral chemical shifts (δ in ppm) data of diorganotin(IV) chelates, R_2SnL[a]

Compound no.	Aromatic protons	Alkyl protons	CH=N protons	$\delta(^{119}Sn)$
1a[b]	6.49 t [2] 6.76 d [2] 6.96–7.68 m [18]		8.52 s [2]	−533.40
1b[c]	6.67–7.53 m [12]	0.61 t (Sn–$(CH_2)_3$–CH_3) [6] 0.80–1.56 m [Sn–$(CH_2)_3$–] [12]	8.43 s [2]	−414.50
1c[c]	6.73–7.61 m [12]	0.79 s (Sn–CH_3) [6]	8.48 s [2]	−390.70
2a[d]	6.48 t [2] 6.80–6.83 m [4] 7.38 s [4]	0.55 t [Sn–$(CH_2)_3$–CH_3] [6] 0.98–1.07 m [Sn–$(CH_2)_2$–CH_2–] [4] 1.28–1.38 m [Sn–$(CH_2)_2$–CH_2–] [8] 1.42–1.47 m 3.83 s (OCH_3) [6]	8.46 s [2]	−414.20
3a[c]	6.67–7.66 m [18]	2.03 q (N–CH_2–CH_2–CH_2–N) [2] 3.68 t (N–CH_2–CH_2–CH_2–N) [4]	8.37 s [2]	−219.56
4a[c]	6.49–7.33 m [16]	2.03 q (N–CH_2–CH_2–CH_2–N) [2] 3.66 t (N–CH_2–CH_2–CH_2–N) [4] 3.86 s (OCH_3) [6]	8.33 s [2]	−227.45
5a[c]	7.10–8.33 m [34]	1.67 s (3-CH_3 of pyrazolyl group) [6]		−626.20
6a[c]	7.06–7.80 m [26] 7.97 t 8.09 d [4]	1.72 q (N–CH_2–CH_2–CH_2–N) [2] 3.13 t (N–CH_2–CH_2–CH_2–N) [4] 1.36 s (3-CH_3 of pyrazolyl group) [6]		

[a] Measured as saturated solutions in $CDCl_3$ (99.8%) using TMS as the internal reference; s=singlet, d=doublet, t=triplet, q=quintet, m=multiplet. The italicised proton indicates the resonances due to that proton.
[b] Measured on a 100-MHz instrument.
[c] Measured on a 60-MHz instrument.
[d] Measured on a 300-MHz instrument.

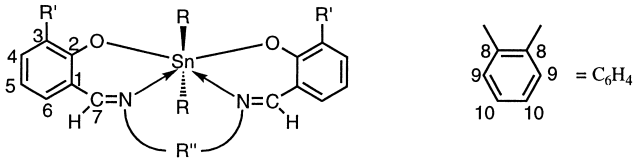


Fig. 3. Structure of compounds **1a–c** and **2a–4a**

$R''=C_6H_4$	$R'=H$	R=Ph	(**1a**)
$R''=C_6H_4$	$R'=H$	R=*n*-Bu	(**1b**)
$R''=C_6H_4$	$R'=H$	R=Me	(**1c**)
$R''=C_6H_4$	$R'=OCH_3$	R=Ph	(**2a**)
$R''=(CH_2)_3$	$R'=H$	R=Ph	(**3a**)
$R''=(CH_2)_3$	$R'=OCH_3$	R=Ph	(**4a**)

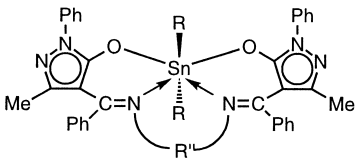


Fig. 4. Structure of compounds **5a** and **6a**

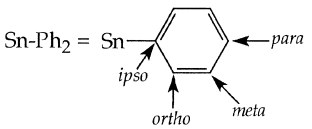
$R''=C_6H_4$	R=Ph	(**5a**)
$R''=(CH_2)_3$	R=Ph	(**6a**)

singlet at δ 165.50–161.68 ppm in the ligands moves downfield, to δ 171.98–163.39 ppm, upon complexation, indicating the coordination of azomethine nitrogens to tin. Also, the occurrence of C=N carbon as one sharp singlet indicates the equivalence of the two C=N carbon atoms both in the Schiff bases and their organotin(IV) complexes. The signal for carbon atoms of OCH_3 groups occurs at the usual position. In the complexes **2a** and **4a**, the resonances appear as singlets at δ 55.76 and 56.00 ppm, respectively. The two 3-CH_3 groups of the pyrazolyl rings in complex **6a** appear as a singlet at δ 15.25 ppm, indicating that they are equivalent. For the propylenediamine fragment (N–CH_2–CH_2–CH_2–N) in complexes **3a**, **4a** and **6a**, two signals are observed for three carbon atoms, indicating the equivalence of the two carbons attached to nitrogen atoms. For the butyl groups of Sn–butyl, and phenyl groups of Sn–phenyl, four signals appear for each of two organic groups and they are assigned tentatively [39,40] (Table 4). Thus, the ^{13}C NMR data also support the arrangement of donor atoms around tin in which the ligand system lies symmetrically in the equatorial plane, with the two organic groups on tin being *trans* to each other. For a *cis* configuration, more signals would be expected in the ^{13}C NMR spectra.

Table 4
^{13}C chemical shift data (δ in ppm) of diorganotin(IV) chelates, R_2SnL[a]

Compound no.	C=N carbon	Ph_2Sn[b]/Bu_2Sn[c]/ Me_2Sn carbons	Aromatic carbons	Other carbons (OCH_3, CH_3, N–$(CH_2)_3$–N[d])
1a	170.41	*ipso*-C:139.20 *ortho*-C:127.44 *meta*-C:137.05 *para*-C:127.78	163.22, 146.53, 136.07 135.09, 128.29, 124.53 119.66, 117.65, 115.52	
1b	171.98	α-C: 28.64 β-C: 26.88 γ-C: 26.79 δ-C: 14.09	164.23, 141.38, 137.85 136.73, 128.93, 124.78 120.29, 118.50, 115.62	
2a	163.39	α-C: 27.97 β-C: 26.98 γ-C: 25.95 δ-C: 13.21	162.49, 152.77, 140.79, 127.92, 126.91, 119.08 117.69, 115.32, 113.50	55.76 (OCH_3)
3a	165.46	*ipso*-C:136.46 *ortho*-C:129.01 *meta*-C:135.82 *para*-C: 130.24	161.35, 132.38, 131.31 118.59, 118.55, 117.06	56.55 (^1C) 31.57 (^2C)
4a	165.53	*ipso*-C:134.46 *ortho*-C:127.42 *meta*-C:128.36 *para*-C:128.26	151.83, 148.36, 122.84 118.37, 117.88, 113.82	56.88 (^1C) 31.54 (^2C) 56.00 (OCH_3)
6a	165.61	*ipso*-C:139.01 *ortho*-C:128.65 *meta*-C:136.12 *para*-C:130.48	130.77, 130.28, 129.13, 129.01, 127.13, 124.23, 119.22, 119.05	41.02 (^1C) 30.74 (^2C) 15.25,147.67, 99.98 (3-CH_3, C-3 and C-4 of pyrazolyl ring)

[a] Measured in $CDCl_3$ (99.8%) using TMS as the internal reference.
[b]



[c] Sn–Bu_2 = Sn–$^{\alpha}CH_2$–$^{\beta}CH_2$–$^{\gamma}CH_2$–$^{\delta}CH_3$.
[d] N–$(CH_2)_3$–N = N–$^{1}CH_2$–$^{2}CH_2$–$^{1}CH_2$–N.

3.4. ^{119}Sn NMR spectra

The ^{119}Sn NMR spectra have been recorded in $CHCl_3$ (locking with D_2O) and data are shown in Table 3. A δ value in the range -219.56 to -626.20 ppm is obtained for the complexes, in agreement with the range of ca. -125 to -525 ppm reported for six-coordinated tin compounds [41,42]. It is well known that an increase in the coordination number of tin should give rise to a high field shift of $\delta(^{119}Sn)$ [43]. The $\delta(^{119}Sn)$ values also depend on the ligand [44,45] and show an upfield shift with increasing distance between the two coordinating atoms [46]. The $\delta(^{119}Sn)$ values also depend on the groupings attached to tin. For complexes **1a** and **5a**, which have phenyl substituents on tin, $\delta(^{119}Sn)$ values appear at -533.40 and -626.20 ppm, respectively, but for the complexes **1b**, **1c** and **2a**, which have *n*-butyl and methyl substituents on tin, $\delta(^{119}Sn)$ values appear at -414.50, -390.70 and -414.20 ppm, respectively. These differences in the δ values are comparable with the differences found in starting diorganotin(IV) dichlorides [47]. These $\delta(^{119}Sn)$ values compare well with the six-coordinated tin compounds of the type R_2Sn(Vanophen) [R=Ph (-542.95); R=Me (-398.15 ppm)] [26]. Thus, OCH_3 groups have no significant effect on the shielding or deshielding of tin nucleus. From ^{119}Sn NMR spectra, it is also evident that the solid state structure (confirmed for **2a**) is retained in solution. The relatively low δ values of **3a** and **4a** may be due to weaker ligand bonding with tin, as **3** and **4,** derived from 1,3-propylenediamine, will not be stabilised by resonance effects, compared with ligands **1**, **2** and **5**, derived from *o*-phenylenediamine. Alternatively, there could be some dissociation of complexes **3a** and **4a** in solution, at least on the NMR time scale.

3.5. Description of X-ray crystal structure

The X-ray structural investigation of (n-Bu)$_2$S-

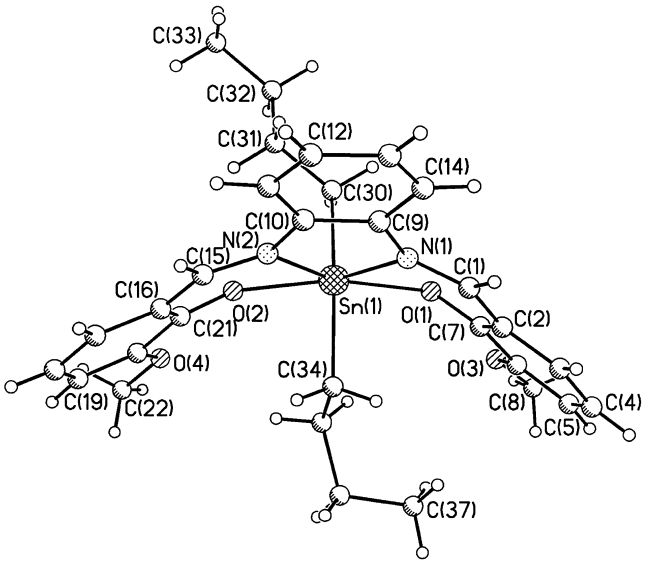


Fig. 5. Molecular structure and atom numbering scheme of the diorganotin(IV) complex (**2a**), molecule **A**.

n(Vanophen) (**2a**) shows that the ligand behaves as a tetradentate agent via two phenolic oxygen and two imino nitrogen atoms. As predicted, the two organic groups (*n*-butyl) on tin take the *axial* positions and four donor atoms from ligand are in the equatorial positions. The vanophen ligand is not completely planar, but is slightly bow shaped. The molecular structure of one molecule (**A**) is shown in Fig. 5 and selected bond lengths and angles are given in Table 5. However, there are two crystallographically independent molecules [denoted **A** and **B** (primed labels)], which differ most significantly in the C_{butyl}–Sn–C_{butyl} bond angles [C(30)–Sn(1)–C(34), 156.76(9); C(30′)–Sn(1′)–C(34)′, 166.87(10)°]. In both molecules, the *n*-butyl groups are of a *gauche* conformation within the fold of the bow-shaped Vanophen ligand, and *trans* on the opposing side, yet the *n*-butyl groups are not superimposable, as shown by their respective torsion angles in Table 5.

The greatest distortion from regular octahedral geometry results from the constraints of the tetradentate Vanophen

Table 5
Selected bond lengths (Å) and angles (°) for compound **2a**

A		**B**	
Sn(1)–C(30)	2.139(2)	Sn(1′)–C(30′)	2.138(2)
Sn(1)–C(34)	2.140(2)	Sn(1′)–C(34′)	2.131(3)
Sn(1)–O(1)	2.2347(16)	Sn(1′)–O(1′)	2.2190(17)
Sn(1)–O(2)	2.2374(16)	Sn(1′)–O(2′)	2.2370(17)
Sn(1)–N(1)	2.266(2)	Sn(1′)–N(1′)	2.277(2)
Sn(1)–N(2)	2.2797(19)	Sn(1′)–N(2′)	2.280(2)
O(1)–C(7)	1.308(3)	O(1′)–C(7′)	1.303(3)
O(2)–C(21)	1.296(3)	O(2′)–C(21′)	1.301(3)
N(1)–C(1)	1.305(3)	N(1′)–C(1′)	1.297(3)
N(1)–C(9)	1.422(3)	N(1′)–C(9′)	1.423(3)
N(2)–C(15)	1.304(3)	N(2′)–C(15′)	1.304(3)
N(2)–C(10)	1.422(3)	N(2′)–C(10′)	1.423(3)
C(30)–Sn(1)–C(34)	156.76(9)	C(34′)–Sn(1′)–C(30′)	166.87(10)
C(30)–Sn(1)–O(1)	83.30(8)	C(30′)–Sn(1′)–O(1′)	90.09(8)
C(34)–Sn(1)–O(1)	87.57(8)	C(34′)–Sn(1′)–O(1′)	87.87(9)
C(30)–Sn(1)–O(2)	82.62(8)	C(30′)–Sn(1′)–O(2′)	84.46(8)
C(34)–Sn(1)–O(2)	86.61(8)	C(34′)–Sn(1′)–O(2′)	86.73(8)
O(1)–Sn(1)–O(2)	128.81(6)	O(1′)–Sn(1′)–O(2′)	128.80(6)
C(30)–Sn(1)–N(1)	103.26(8)	C(30′)–Sn(1′)–N(1′)	97.32(9)
C(34)–Sn(1)–N(1)	95.86(8)	C(34′)–Sn(1′)–N(1′)	95.06(9)
O(1)–Sn(1)–N(1)	78.98(7)	O(1′)–Sn(1′)–N(1′)	79.54(7)
O(2)–Sn(1)–N(1)	152.21(7)	O(2′)–Sn(1′)–N(1′)	151.66(7)
C(30)–Sn(1)–N(2)	101.24(8)	C(30′)–Sn(1′)–N(2′)	94.87(8)
C(34)–Sn(1)–N(2)	97.10(8)	C(34′)–Sn(1′)–N(2′)	93.18(9)
O(1)–Sn(1)–N(2)	150.95(6)	O(1′)–Sn(1′)–N(2′)	151.04(7)
O(2)–Sn(1)–N(2)	80.19(6)	O(2′)–Sn(1′)–N(2′)	80.13(7)
N(1)–Sn(1)–N(2)	72.04(7)	N(1′)–Sn(1′)–N(2′)	71.53(7)
C(7)–O(1)–Sn(1)	122.40(15)	C(7′)–O(1′)–Sn(1′)	124.90(15)
C(21)–O(2)–Sn(1)	126.32(14)	C(21′)–O(2′)–Sn(1′)	124.56(15)
C(1)–N(1)–Sn(1)	123.78(16)	C(1′)–N(1′)–Sn(1′)	125.03(17)
C(9)–N(1)–Sn(1)	116.21(14)	C(9′)–N(1′)–Sn(1′)	115.77(15)
C(15)–N(2)–Sn(1)	124.43(16)	C(15′)–N(2′)–Sn(1′)	124.14(16)
C(10)–N(2)–Sn(1)	115.53(14)	C(10′)–N(2′)–Sn(1′)	115.58(15)
C(31)–C(30)–Sn(1)	116.83(16)	C(31′)–C(30′)–Sn(1′)	119.64(17)
C(35)–C(34)–Sn(1)	115.24(16)	C(35′)–C(34′)–Sn(1′)	117.63(17)
C(30)–C(31)–C(32)–C(33)	179.83(23)	C(30′)–C(31′)–C(32′)–C(33′)	172.62(23)
C(34)–C(35)–C(36)–C(37)	−80.6(3)	C(34′)–C(35′)–C(36′)–C(37′)	71.4(3)

ligand where the N–Sn–N angles are compressed, [N(1)–Sn(1)–N(2), 72.04(7) and N(1′)–Sn(1′)–N(2′), 71.53(7)° in **A** and **B**, respectively]. Correspondingly, the O–Sn–O angles are opened to 128.81(6) and 128.80(6)°. In similar uranium [48] and tin [16,26,49] complexes, the O–M–O (M = U or Sn) angle was open enough to allow coordination of another ligand into the equatorial plane.

The Sn–O bond lengths differ more within molecule **B**, which has a greater C_{butyl}–Sn–C_{butyl} bond angle than between **A** and **B** [Sn(1)–O(1), 2.2347(16), Sn(1)–O(2) 2.2374(16) cf. Sn(1′)–O(1′), 2.2190(17), Sn(1′)–O(2′), 2.2370(17) Å]. This range is similar to that seen in the dimethyl [2.236(2), 2.197(1) Å] tin Vanophen complex [26]. In the diphenyl tin Vanophen species [26], the Sn–O bond lengths are slightly shorter [2.188(7), 2.202(8) Å].

The Sn–N bond lengths are also very similar between these tin Vanophen species. The Sn–N bond distances [2.266(2) and 2.2797(19) Å in **A**; 2.277(2) and 2.280(2) Å in **B**] are similar to those in Me_2Sn(Salen) derived from Me_2SnCl_2 and *N*,*N*′-bis(salicylaldehyde)ethylenediimine [49] and R_2Sn(Vanophen) (R = Ph, Me) [26]. The Sn–N distances are longer than the average Sn–N bond distance, 2.235 Å, found in Ph_2(NAPPDI) [NAPPDI = *N*,*N*′-bis(2-hydroxy-1-naphthaldehyde)-1,2-phenylenediimine] [16]. The Sn–N bond distances are all very similar between the R_2Sn(vanophen) species, (R = Ph, Me [26]) with no obvious trends.

The average Sn–C bond length (2.137 Å) in **2a** is midway between those of the diphenyl and dimethyl Sn(Vanophen) analogues [26] [2.168(2), 2.172(12) and 2.100(3), 2.115(3) Å, respectively]. In this case, the Sn–C bond lengths appear to be influenced by steric bulk on the hydrocarbon ligands rather than by donor ability. Moreover, the Sn–C bonds [both 2.138(3) Å] in a six-coordinated tin Schiff base adduct species [50], are closer to those in **2a** than the diphenyl and dimethyl Vanophen analogues. Similar seven-coordinated dibutyl tin compounds [51,52] tend to have shorter Sn–C bonds, in the range 2.086(5)–2.114(8) Å.

4. Conclusion

The similarities in the spectra of all of the compounds studied here and the X-ray crystal structure of one representative compound (**2a**) indicate that a six-coordinated distorted octahedral structure should be proposed for all of these diorganotin(IV) compounds.

Supplementary data

Crystallographic data have been deposited with the CCDC (12 Union Road, Cambridge, CB2 1EZ, UK, and are available on request, quoting the deposition number CCDC 115795).

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References

[1] K. Kawakami, M. Miya-Uchi, T. Tanaka, J. Inorg. Nucl. Chem. 33 (1971) 3773.
[2] K. Kawakami, T. Tanaka, J. Organomet. Chem. 49 (1973) 409.
[3] J.N.R. Ruddick, J.R. Sams, J. Organomet. Chem. 60 (1973) 233.
[4] T.N. Srivastava, A.K.S. Chauhan, J. Inorg. Nucl. Chem. 39 (1977) 371.
[5] B.S. Saraswat, G. Srivastava, R.C. Mehrotra, Inorg. Chim. Acta 36 (1979) 289.
[6] L.E. Khoo, J.P. Charland, E.J. Gabe, F.E. Smith, Inorg. Chim. Acta 128 (1987) 139.
[7] L.E. Khoo, F.E. Smith, Polyhedron 1 (1982) 213.
[8] B.S. Saraswat, G. Srivastava, R.C. Mehrotra, J. Organomet. Chem. 164 (1979) 153.
[9] J.P. Charland, F.L. Lee, E.J. Gabe, L.E. Khoo, F.E. Smith, Inorg. Chim. Acta 130 (1987) 55.
[10] H.K. Fun, S.B. Teo, S.G. Teoh, G.Y. Yeap, T.S. Yeoh, Acta Crystallogr., Sect. C 47 (1991) 1602.
[11] M.E. Kamwaya, L.E. Khoo, Acta Crystallogr., Sect. C 41 (1985) 1027.
[12] L.E. Khoo, Y. Xu, N.K. Goh, L.S. Chia, L.L. Koh, Polyhedron 16 (1997) 573, and references cited therein.
[13] B.N. Ghose, Synth. React. Inorg. Met.-Org. Chem. 12 (1982) 835.
[14] A. van-den Bergen, R.J. Cozens, K.S. Murray, J. Chem. Soc. (A) (1970) 3060, and references cited therein.
[15] F. Maggio, R. Bosco, N. Cefalu, R. Barbieri, Inorg. Nucl. Chem. Lett. 4 (1968) 389.
[16] S.G. Teoh, G.Y. Yeap, C.C. Loh, L.W. Foong, S.B. Teo, H.K. Fun, Polyhedron 16 (1997) 2213.
[17] A.K. Saxena, F. Huber, Coord. Chem. Rev. 95 (1989) 109, and references cited therein.
[18] M. Gielen, Tin-Based Antitumour Drugs, Coord. Chem. Rev. 151 (1996) 41.
[19] A.J. Crowe, P.J. Smith, C.J. Cardin, H.E. Parge, F.E. Smith, Cancer Lett. 24 (1984) 45.
[20] A.J. Crowe, P.J. Smith, J. Organomet. Chem. 244 (1982) 223.
[21] F. Huber, G. Roge, L. Carl, G. Atassi, F. Spreafico, S. Filippeschi, R. Barbieri, A. Silvestri, E. Rivarola, G. Ruisi, F. Di Bianca, G. Alonzo, J. Chem. Soc., Dalton Trans. (1985) 523.
[22] M. Gielen, Metal-Based Drugs 1 (1994) 213.
[23] A.J. Crowe, Drugs Future 12 (1987) 40.
[24] A.J. Crowe, P.J. Smith, G. Attasi, Chem.–Biol. Interact. 32 (1980) 171.
[25] S.R. Collinson, D.E. Fenton, Coord. Chem. Rev. 148 (1996) 19.
[26] D.K. Dey, M.K. Das, H. Nöth, Z. Naturforsch. 54b (1999) 145.
[27] H.C. Arora, G.N. Rao, Ind. J. Chem. 20A (1981) 539.
[28] XSCANS, Data Collection and Reduction Program, Version 2.2, Siemens Analytical X-ray Instruments Inc, Madison, WI, 1994.
[29] G.M. Sheldrick, Structure Determination and Refinement Programs. Version 5.03, Siemens Analytical X-ray Instruments Inc, Madison, WI, 1994.

[30] G.M. Sheldrick, SHELXL-97, Structure Determination and Refinement Program, University of Göttingen, Germany, 1997.
[31] G. Faraglia, F. Maggio, R. Cefalu, R. Bosco, R. Barbieri, Inorg. Nucl. Chem. Lett. 5 (1969) 177.
[32] A.D. Garnovskii, A.L. Nivorozhkin, V.I. Minkin, Coord. Chem. Rev. 126 (1993) 1.
[33] H.A.O. Hill, K.G. Morallee, G. Pellizer, G. Mestroni, G. Costa, J. Organomet. Chem. 11 (1968) 167.
[34] C. Floriani, M. Puppis, F. Calderazzo, J. Organomet. Chem. 12 (1968) 209.
[35] R.J. Cozens, G.B. Deacon, P.W. Felder, K.S. Murray, B.O. West, Aust. J. Chem. 23 (1970) 481.
[36] M.M. McGrady, R.S. Tobias, J. Am. Chem. Soc. 1965 (1909) 87.
[37] K. Kawakami, R. Okawara, J. Organomet. Chem. 6 (1966) 249.
[38] W. Kitching, J. Organomet. Chem. 6 (1966) 586.
[39] W. Plass, J. Pinkas, J.G. Verkade, Inorg. Chem. 1997 (1973) 36.
[40] V.K. Jain, J. Mason, B.S. Saraswat, R.C. Mehrotra, Polyhedron 4 (1985) 2089.
[41] J. Otera, J. Organomet. Chem. 221 (1981) 57.
[42] D.K. Dey, M.K. Das, R.K. Bansal, J. Organomet. Chem. 535 (1997) 7.
[43] J. Holecek, M. Nadvornik, K. Handlir, A. Lycka, J. Organomet. Chem. 241 (1983) 177.
[44] J.S. Casas, A. Castineiras, E. Garcia Martinez, A. Sanchez Gonzalez, J. Sordo, E.M. Vazquez Lopez, U. Russo, Polyhedron 15 (1996) 891, and references cited therein.
[45] V.K. Jain, Coord. Chem. Rev. 135–136 (1994) 809, and references cited therein.
[46] W.F. Howard Jr., R.W. Crecely, W.H. Nelson, Inorg. Chem. 24 (1985) 2204.
[47] P.J. Smith, A.P. Tupciauskas, Ann. Rep. NMR Spectrosc. 8 (1978) 291.
[48] G. Bandoli, D.A. Clemente, U. Croatto, M. Vidali, P.A. Vigato, J. Chem. Soc., Chem. Commun. (1971) 1330.
[49] M. Calligaris, G. Nardin, L. Randaccio, J. Chem. Soc., Dalton Trans. (1972) 2003.
[50] G.Y. Yeap, N. Ishizawa, Acta Crystallogr., Sect. C 54 (1998) 720.
[51] F. Huber, H. Preut, E. Hoffmann, M. Gielen, Acta Crystallogr., Sect. C 45 (1989) 51.
[52] S.W. Ng, Acta Crystallogr., Sect. C 54 (1998) 914.