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# Synthesis and structural characterization of diorganotin(IV) esters of salicylidene-amino acids

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**Abstract**

Eight diorganotin esters of salicylidene-L-tryptophan(Sal-T) and salicylidene-L-valine(Sal-V), [(*n*-Bu)$_2$Sn(Sal-T)] (**1**), [(*n*-Bu)$_2$Sn-(Sal-V)] (**2**), [Ph$_2$Sn(Sal-T)] (**3**), [Ph$_2$Sn(Sal-V)] (**4**), [(PhCH$_2$)$_2$Sn(Sal-T)] (**5**), [(PhCH$_2$)$_2$Sn(Sal-V)] (**6**), [(4-*Cl*C$_6$H$_4$CH$_2$)$_2$Sn(Sal-T)] (**7**) and [(4-*Cl*C$_6$H$_4$CH$_2$)$_2$Sn(Sal-V)] (**8**) have been synthesized and characterized by elemental analysis, IR and $^1$H NMR. The crystal structures of compounds **1** and **2** have been determined by X-ray single crystal diffraction. Their structures show the tin atoms of two compounds are rendered five-coordinated in distorted trigonal bipyramidal geometries.


*Keywords:* Salicylidene-amino acid; Diorganotin; Crystal structure

## 1. Introduction

Recently, organotin(IV) compounds with schiff bases have received increased attention owing to their anti-tumour activities [1–9], in particular the organotin(IV) esters of *N*-arylidene-amino acids have been observed to exhibit a great anti-tumour activity against human tumour cell lines [10]. As an extension of studies of organotin(IV) compounds with schiff bases, we synthesized eight new diorganotin esters of salicylidene-amino acids by the reaction of diorganotin oxide and salicylidene-amino acids in 1:1 stoichiometry. The details of the synthesis, structure and spectra characterizations of the compounds **1**–**8** are reported herein. Two of the compounds have been studied by X-ray diffraction, and show that both compound **1** and **2** are monomer and adopt the same structure to the literature [11] as shown in Scheme 1. The tin atoms are five-coordinated by the two *n*-butyl carbon atoms and two oxygen atoms one from carboxylate and one from the phenolic hydrogen and the imino nitrogen atom.

## 2. Experimental

### 2.1. Materials and methods

Dibutyltin oxide and diphenyltin oxide were commercially available and used without further purification. The melting points were obtained with Kolfer micro melting point apparatus and were uncorrected. IR spectra were recorded on a Nicolet-460 spectrophotometer using KBr discs and sodium chloride optics. $^1$H, $^{13}$C and $^{119}$Sn NMR spectra were obtained with Mercury Plus-400 NMR spectrometer and the chemical shifts are given in ppm relative to $Me_4Si$, $Me_4Sn$ in $CDCl_3$. Elemental analyses were performed in a PE-2400 II elemental analyzer.

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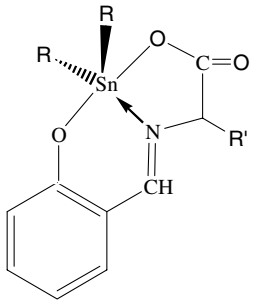


Scheme 1.

### 2.2. Preparation of schiff base

The schiff bases, Sal-T (**1**) and Sal-V (**2**) have been prepared by the refluxing of salicylidene with L-tryptophan and L-valine, respectively, in ethanol in 1:1 mole ratio for 5 h. The crude schiff bases were obtained after evaporation of solvent, washed with petroleum ether (40–60 °C) and was finally recrystallized from methanol before use. The molecular structures, melting points, abbreviation and yield of the two schiff bases are shown as follows (Table 1).

### 2.3. Synthesis of diorganotin compounds

To a benzene suspension of dialkyltin oxide (2.0 mmol) was added a benzene solution of Sal-T or Sal-V (2.0 mmol). The mixture was heated under reflux with strring for 6–7 h, and the clear solution thus obtained was evaporated under vacuum to leave a yellow solid, which was recrystallized from dichloromethane-hexane to give yellow crystals.

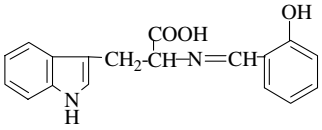
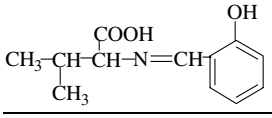
[($n$-Bu)$_2$Sn(Sal-T)] (**1**): Yield: 84%, m.p. 166–168 °C. Anal. Found: C, 57.83; H, 5.90; N, 5.23; Sn, 22.19%. Calc. for $C_{26}H_{32}N_2O_3Sn$: C, 57.91; H, 5.98; N, 5.19; Sn, 22.01. $^1$H NMR ($CDCl_3$): $\delta$ 8.10(1H, s, CH═N), 7.81(1H, s, N–H), 6.58–7.39(9H, m, aromatic-H), 4.24(1H, d, $J$ = 8.2 Hz, CHAr), 3.80(1H, dt, $J$ = 8.2 Hz, CHAr), 3.06(1H, dt, $J$ = 8.4 Hz, NCHCO), 1.21–1.70(12H, m, Sn–$(CH_2)_3$–), 0.79(3H, t, $J$ = 7.2 Hz, $CH_3$), 0.94(3H, t, $J$ = 7.2 Hz, $CH_3$). $^{13}$C NMR ($CDCl_3$): $\delta$ 173.85(CH═N), 172.03(COO), 68.61(═NCH), 32.40($CH_2$Ar), 169.21, 137.42, 136.48, 126.62, 124.32, 122.85, 120.33, 118.85, 116.83, 111.51(Ar–C), 27.08, 26.87, 26.71, 26.50, 21.87, 21.62, 13.61, 13.48-(Sn($CH_2CH_2CH_2CH_3$)$_2$). $^{119}$Sn NMR $\delta$ −305.55. IR (KBr, $cm^{-1}$): 3437(N–H), 1653, 1350($CO_2$), 1614-(C═N), 602, 541(Sn–O), 450(Sn–C), 428(Sn–N).

[($n$-Bu)$_2$Sn(Sal-V)] (**2**): Yield: 91%, m.p. 156–158 °C. Anal. Found: C, 53.25; H, 6.98; N, 3.37; Sn, 26.04%. Calc. for $C_{20}H_{31}NO_3Sn$: C, 53.13; H, 6.91; N, 3.10; Sn, 26.25. $^1$H NMR ($CDCl_3$): $\delta$ 8.24(1H, s, CH═N), 6.75–7.46(4H, m, aromatic-H), 3.84(1H, d, $J$ = 6.8 Hz, NCHCO), 2.33(1H, m, $CHMe_2$), 122–1.79(12H, m, Sn–$(CH_2)_3$–), 1.09(3H, d, $J$ = 6.8 Hz, $CH_3$), 1.06(3H, d, $J$ = 6.8 Hz, $CH_3$), 0.96(3H, t, $J$ = 7.2 Hz, $CH_3$), 0.80 (3H, t, $J$ = 7.2 Hz, $CH_3$). $^{13}$C NMR ($CDCl_3$): $\delta$ 173.14(CH═N), 172.37(COO), 74.64(═NCH), 169.63, 137.71, 135.47, 122.74, 117.38(Ar–C), 34.52, 19.08, 18.37(Pr-*i*), 26.97, 26.87, 26.95, 26.65, 22.55, 20.91, 13.58, 13.48 (Sn($CH_2CH_2CH_2CH_3$)$_2$). $^{119}$Sn NMR $\delta$−302.32. IR (KBr, $cm^{-1}$): 1670, 1334($CO_2$), 1608(C═N), 585, 541(Sn–O), 459(Sn–C), 414(Sn–N).

[$Ph_2$Sn(Sal-T)] (**3**): Yield: 86%, m.p. 216–218 °C. Anal. Found: C, 62.38; H, 4.25; N, 4.83; Sn, 20.33%. Calc. for $C_{30}H_{24}N_2O_3Sn$: C, 62.21; H, 4.18; N, 4.84; Sn, 20.49. $^1$H NMR ($CDCl_3$): $\delta$ 8.04(1H, s, CH═N), 7.94(1H, s, N–H), 6.52–7.82(19H, m, aromatic-H), 4.27(1H, d, $J$ = 11.0 Hz, CHAr), 3.70(1H, d, $J$ = 11.0 Hz, CHAr), 2.83(1H, q, $J$ = 10.2 Hz, NCHCO). $^{13}$C NMR ($CDCl_3$): $\delta$ 173.67(CH═N), 171.74(COO), 68.76(═NCH), 31.99($CH_2$Ar), 169.10, 138.01, 137.75, 136.61, 136.34, 135.34, 130.80, 129.05, 126.46, 124.68, 122.73 122.64, 120.25, 118.65, 117.54, 116.89, 111.54, 109.06(Ar–C). $^{119}$Sn NMR $\delta$ −352.37. IR (KBr, $cm^{-1}$): 3430(N–H), 1650, 1339($CO_2$), 1609(C═N), 586, 541(Sn–O), 446(Sn–C), 421(Sn–N).

[$Ph_2$Sn(Sal-V)] (**4**): Yield: 87%, m.p. 191–193 °C. Anal. Found: C, 58.47; H, 4.75; N, 2.87; Sn, 24.21%. Calc. for $C_{24}H_{23}NO_3Sn$: C, 58.57; H, 4.71; N, 2.85; Sn, 24.12. $^1$H NMR ($CDCl_3$): 8.26(1H, s, CH═N), 6.80–8.04(19H, m, aromatic-H), 3.95(1H, d, $J$ = 4.8 Hz, NCHCO), 2.30(1H, m, $CHMe_2$), 0.97(3H, d, $J$ = 6.8 Hz, $CH_3$), 0.87(3H, d, $J$ = 6.8 Hz, $CH_3$). $^{13}$C NMR

Table 1
Structures, abbreviations and melting points of the schiff bases

| Structure | Abbreviation | Yield (%) | Melting point |
|---|---|---|---|
|  | Sal-T | 91 | decomposed (≧200 °C) |
|  | Sal-V | 92.5 | 182–183 °C |

($CDCl_3$): $\delta$ 172.95(CH═N), 172.71(COO), 74.34(═NCH), 169.68, 138.20, 137.65, 136.60, 135.79, 130.82, 130.67, 128.93, 123.05, 117.26(Ar–C), 34.87, 19.03, 18.49(Pr-*i*). $^{119}$Sn NMR $\delta$ −348.53. IR (KBr, $cm^{-1}$): 1671, 1331($CO_2$), 1613(C═N), 586, 541(Sn–O), 446(Sn–C), 419(Sn–N).

[$(PhCH_2)_2$Sn(Sal-T)] (**5**): Yield: 73%, m.p. 202–204 °C. Anal. Found: C, 63.50; H, 4.72; N, 4.77; Sn, 19.47%. Calc. for $C_{32}H_{28}N_2O_3Sn$: C, 63.29; H, 4.65; N, 4.61; Sn, 19.54. $^1$H NMR ($CDCl_3$): 8.18(1H, s, CH═N), 7.97(1H, s, N–H), 6.85–7.84(19H, m, aromatic-H), 4.25(1H, d, $J$ = 9.4 Hz, CHAr), 3.77(1H, d, $J$ = 9.4 Hz, CHAr), 3.11(1H, q, $J$ = 10.0 Hz, NCHCO), 3.01(4H, t, $J$ = 78.5 Hz, $CH_2Sn$). $^{13}$C NMR ($CDCl_3$): $\delta$ 173.91(CH═N), 172.06(COO), 68.59(═NCH), 32.04-($CH_2Ar$), 30.87($CH_2Sn$), 169.35, 138.27, 137.70, 136.81, 136.47, 135.50, 131.02, 130.10, 128.72, 126.52, 124.23, 122.58, 122.47, 118.74, 117.65, 116.72, 115.73, 109.57(Ar–C). $^{119}$Sn NMR $\delta$ −348.05. IR (KBr, $cm^{-1}$): 3425(N–H), 1653, 1333($CO_2$), 1605(C═N), 582, 547 (Sn–O), 448(Sn–C), 424(Sn–N).

[$(PhCH_2)_2$Sn(Sal-V)] (**6**): Yield: 77%, m.p. 178–179 °C. Anal. Found: C, 60.25; H, 5.18; N, 2.73; Sn, 22.69%. Calc. for $C_{26}H_{27}NO_3Sn$: C, 60.03; H, 5.23; N, 2.69; Sn, 22.82. $^1$H NMR ($CDCl_3$): 8.18(1H, s, CH═N), N), 7.03–7.92(14H, m, aromatic-H), 3.97(1H, d, $J$ = 5.0 Hz, NCHCO), 2.99(4H, t, $J$ = 80.2 Hz, $CH_2Sn$), 2.36(1H, m, $CHMe_2$), 0.96(3H, d, $J$ = 6.6 Hz, $CH_3$), 0.86(3H, d, $J$ = 6.6 Hz, $CH_3$). $^{13}$C NMR ($CDCl_3$): $\delta$ 173.46(CH═N), 172.88(COO), 74.85(═NCH), 30.18($CH_2Sn$), 169.65, 137.80, 135.62, 135.32, 134.23, 130.28, 129.15, 123.01, 117.42, 117.38(Ar–C), 34.92, 19.52, 18.63(Pr-*i*). $^{119}$Sn NMR $\delta$ −334.03. IR (KBr, $cm^{-1}$): 1663, 1341($CO_2$), 1610(C═N), 581, 547(Sn–O), 457(Sn–C), 417(Sn–N).

[(4-*Cl*$C_6H_4CH_2)_2$Sn(Sal-T)] (**7**): Yield: 73%, m.p. 233–235 °C. Anal. Found: C, 556.98; H, 4.00; N, 4.09; Sn, 17.61%. Calc. for $C_{32}H_{26}N_2O_3Cl_2Sn$: C, 56.84; H, 3.88; N, 4.14; Sn, 17.55. $^1$H NMR ($CDCl_3$): 8.13(1H, s, CH═N), 7.94(1H, s, N–H), 6.55–7.90(17H, m, aromatic-H), 4.21(1H, d, $J$ = 11.4 Hz, CHAr), 3.82(1H, d, $J$ = 11.4 Hz, CHAr), 3.16(1H, q, $J$ = 9.6 Hz, NCHCO), 2.98(4H, t, $J$ = 76.2 Hz, $CH_2Sn$). $^{13}$C NMR ($CDCl_3$): $\delta$ 173.80(CH═N), 172.11(COO), 68.64(═NCH), 32.12($CH_2Ar$), 30.55($CH_2Sn$), 169.82, 168.43, 148.57, 137.63, 136.21, 134.30, 130.02, 126.49, 125.01, 124.37, 124.25, 123.02, 121.87, 120.47, 119.01, 117.13, 116.65, 111.30(Ar–C). $^{119}$Sn NMR $\delta$ −337.65. IR (KBr, $cm^{-1}$): 3436(N–H), 1653, 1336($CO_2$), 1607(C═N), 589, 546 (Sn–O), 441(Sn–C), 422(Sn–N).

[(4-*Cl*$C_6H_4CH_2)_2$Sn(Sal-V)] (**8**): Yield: 76%, m.p. 209–210 °C. Anal. Found: C, 53.24; H, 4.30; N, 2.34; Sn, 20.25%. Calc. for $C_{26}H_{25}NO_3Cl_2Sn$: C, 53.01; H, 4.28; N, 2.38; Sn, 20.15. $^1$H NMR ($CDCl_3$): 8.20(1H, s, CH═N), 6.84–7.92(12H, m, aromatic-H), 3.92(1H, d, $J$ = 5.0 Hz, NCHCO), 2.96(4H, t, $J$ = 77.8 Hz, $CH_2Sn$), 2.34(1H, m, $CHMe_2$), 0.94(3H, d, $J$ = 6.4 Hz, $CH_3$), 0.85(3H, d, $J$ = 6.4 Hz, $CH_3$). $^{13}$C NMR ($CDCl_3$): $\delta$ 173.32(CH═N), 172.24(COO), 74.57(═NCH), 30.24($CH_2Sn$), 169.72, 168.89, 146.42, 135.98, 135.64, 130.02, 122.69, 120.11, 117.51, 117.42(Ar–C), 34.72, 19.21, 18.63(Pr-*i*). $^{119}$Sn NMR $\delta$ −321.75. IR (KBr, $cm^{-1}$): 1661, 1330($CO_2$), 1613(C═N), 590, 551(Sn–O), 457(Sn–C), 423(Sn–N).

Table 2
Crystallographic data of compounds **1** and **2**

| Compound | **1** | **2** |
|---|---|---|
| Empirical formula | $C_{26}H_{32}N_2O_3Sn$ | $C_{20}H_{31}NO_3Sn$ |
| Formula weight | 539.23 | 452.15 |
| Temperature (K) | 298(2) | 298(2) |
| Wavelength (Å) | 0.71073 | 0.71073 |
| Crystal system | Triclinic | Orthorhombic |
| Space group | $P\bar{1}$ | $P2_{(1)}2_{(1)}2_{(1)}$ |
| Unit cell dimensions | | |
| $a$ (Å) | 10.299(4) | 9.199(19) |
| $b$ (Å) | 11.332(4) | 10.01(2) |
| $c$ (Å) | 12.444(4) | 23.45(5) |
| $\beta$ (°) | 101.812(5) | 90 |
| Volume (Å$^3$) | 1236(8) | 2155(8) |
| $Z$ | 2 | 4 |
| Calculated density ($Mg/m^3$) | 1.449 | 1.394 |
| $F$(000) | 552 | 928 |
| Crystal size (mm) | 0.38×0.32×0.26 | 0.42×0.25×0.19 |
| Scan range $\theta$ (°) | 1.76–25.03 | 1.74–25.02 |
| Limiting indices | $-12 \leqslant h \leqslant 10$; $-13 \leqslant k \leqslant 12$; $-14 \leqslant l \leqslant 14$ | $-10 \leqslant h \leqslant 9$; $-11 \leqslant k \leqslant 11$; $-26 \leqslant l \leqslant 27$ |
| Total/unique/$R_{int}$ | 6530/4312/0.0211 | 10885/3737/0.0382 |
| Goodness-of-fit on $F^2$ | 0.989 | 0.959 |
| $R_1/wR_2$ | 0.0373/0.0847 | 0.0380/0.0806 |
| $\mu$ ($mm^{-1}$) | 1.062 | 1.202 |
| $\rho_{max}/\rho_{min}$ (e Å$^{-3}$) | 0.601/−0.592 | 0.981/−0.614 |

### 2.4. X-ray crystallography

Crystallographic data and refinement details are given in Table 2. All X-ray crystallographic data were collected on a Bruker SMART CCD 1000 diffractometer. A criterion of observability was used for the solution and refinement. The structure was solved by direct method and differential Fourier map using SHELXL-97 program, and refined by full-matrix least-squares on $F^2$. All non-hydrogen atoms were refined anisotropically. Position of hydrogen atoms were calculated and refined isotropically.

## 3. Results and discussion

### 3.1. IR data

The assignment of IR bands of diorganotin(IV) compounds **1**–**8** has been determined by comparison with

the IR spectra of related organotin compounds, schiff bases and dialkyltin oxides. A weak broad band in the region 3250–2350 $cm^{-1}$, which has been assigned to the intramolecular hydrogen-bond OH in the Schiff bases [12], is not observed in the infrared spectra of the eight title compounds. This indicates that the reactions have taken place through the replacement of the phenolic hydrogen in the compounds. This also confirms that organotin(IV) compounds are indeed those of the deprotonated forms of schiff base. The $\nu$(C═N) band, occurring between 1605 and 1614 $cm^{-1}$, is considerably shifted towards lower frequencies with respect to that of the free schiff bases (1638–1622 $cm^{-1}$), confirming the coordination of the azomethine nitrogen to diorganotin(IV) moiety. The stretching frequency is lowed owing to the displacement of electron density from N to Sn atom, this resulting in the weakening of the C═N bond as reported in the literature [13]. The $\Delta\nu(\nu_{as}(CO_2)-\nu_s(CO_2))$ value is used to determine the nature of bonding of carboxylate to tin(IV) atom [14]. It is generally believed that the difference in $\Delta\nu$ between asymmetric ($\nu_{as}(CO_2)$) and symmetric (($\nu_s(CO_2)$) absorption frequencies below 200 $cm^{-1}$ for the bidentate carboxylate moiety, but greater than 200 $cm^{-1}$ for the unidentate carboxylate moiety. All the values of $\Delta\nu$ of the eight compounds are between 303 and 340 $cm^{-1}$, and strongly indicate that all the eight title compounds adopt unidentate carboxylate structure.

### 3.2. $^{1}H$, $^{13}C$ and $^{119}Sn$ NMR spectra

The absence of the OH proton signal in the compounds suggests the binding of a tin atom to the ligand oxygen atoms through the replacement of phenolic protons (for **1**–**8**) according to the literature [15]. The chemical shift of the protons of azomethine (HC═N) proton resonances exhibit signals at 8.04–8.26 ppm as singlets for compounds **1**–**8**, they are similar to the literature [16–18], and it strongly suggests that the azomethine nitrogen atom coordinates to tin atom for all of the eight compounds. The $^{1}H$ NMR spectra of compounds **5**–**8** show that the chemical shifts of the protons of methylene on the benzyl group exhibit signals about 2.96–3.01 ppm as a triplet which is caused by the tin ($^{119}Sn$) hydrogen coupling. And the spin–spin coupling constant $Js_{n\text{-}H}$ is equal 76.2–80.2 Hz. In addition, the presence of the N–H proton signal (7.81–7.94 ppm) in the compounds **1, 3, 5** and **7** supports that the indolyl group N atom is in no coordination to Sn atom.

The comparison of $^{13}C$ NMR spectra of the ligand with the corresponding organotin compounds (**1**–**8**) shows a downfield shifts in the position of $C_{CH=N}$ and $C_{C-O}$ signals and an upfield shifts in the position of $C_{COO}$ signal. These shifts indicate the tridentate behaviour of the carboxylate moieties in the compounds.

The $^{119}Sn$ chemical shift values in compounds (**1**–**8**) are found to be in the range of −305.55 to −348.53 ppm. The appearance of chemical shift values in this region indicates five-coordination environment [11] around the central tin atoms in these compounds.

### 3.3. X-ray studies

The crystal structure and unit cell of compound **1** are shown in Fig. 1, and those of compound **2** in Figs. 2 and 3, respectively. All hydrogen atoms have been omitted for the purpose of clarity. Tables 3 and 4, respectively, list selected bond lengths and angles for compounds **1** and **2**.

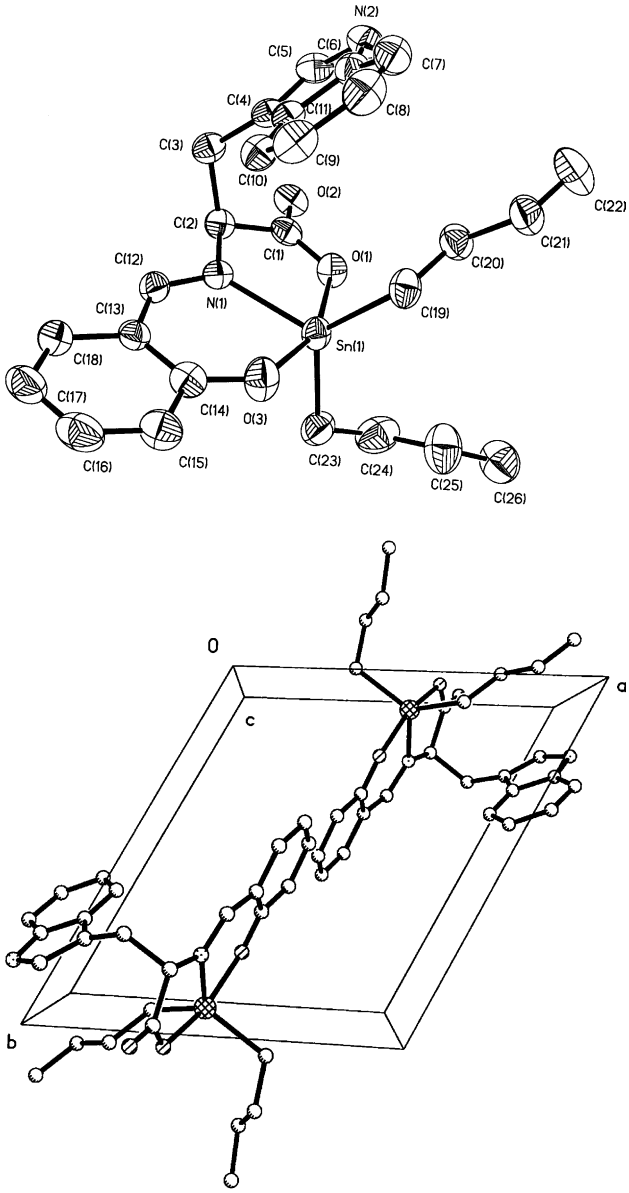



Fig. 1. Molecular structure and projection of compound **1**.

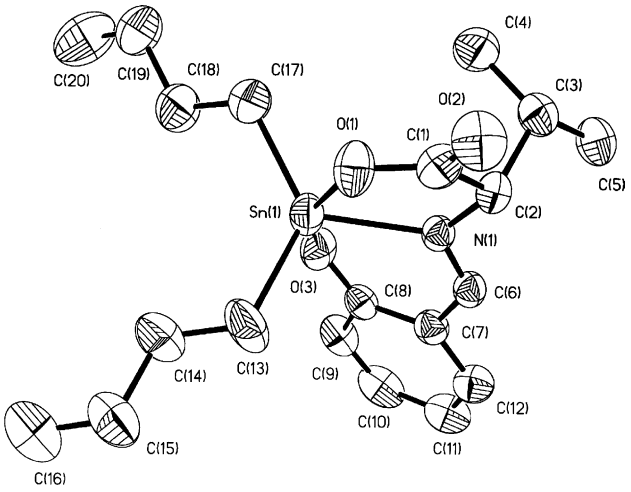



Fig. 2. Molecular structure of compound **2**.

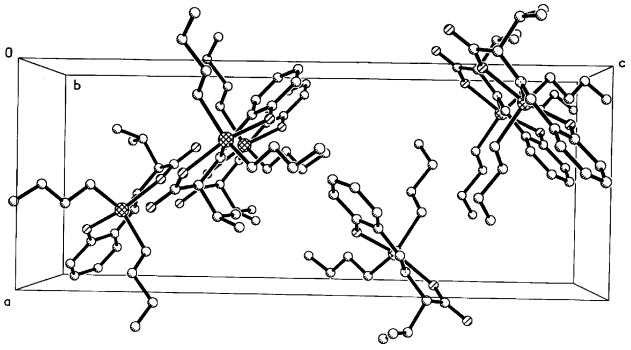



Fig. 3. Projection of compound **2**.

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

| | | | |
|---|---|---|---|
| Sn(1)–O(3) | 2.093(3) | N(1)–C(12) | 1.298(4) |
| Sn(1)–C(19) | 2.112(4) | N(1)–C(2) | 1.479(4) |
| Sn(1)–C(23) | 2.127(4) | O(1)–C(1) | 1.267(5) |
| Sn(1)–N(1) | 2.161(3) | O(2)–C(1) | 1.218(4) |
| Sn(1)–O(1) | 2.162(3) | O(3)–C(14) | 1.315(5) |
| O(3)–Sn(1)–C(19) | 92.98(15) | C(23)–Sn(1)–N(1) | 113.12(15) |
| O(3)–Sn(1)–C(23) | 95.50(16) | O(3)–Sn(1)–O(1) | 158.75(11) |
| C(19)–Sn(1)–C(23) | 126.55(17) | C(19)–Sn(1)–O(1) | 96.50(14) |
| O(3)–Sn(1)–N(1) | 83.72(11) | C(23)–Sn(1)–O(1) | 94.04(15) |
| C(19)–Sn(1)–N(1) | 120.24(14) | N(1)–Sn(1)–O(1) | 75.07(11) |

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

| | | | |
|---|---|---|---|
| Sn(1)–C(17) | 2.104(7) | N(1)–C(6) | 1.300(7) |
| Sn(1)–O(3) | 2.108(5) | N(1)–C(2) | 1.461(7) |
| Sn(1)–C(13) | 2.109(7) | O(1)–C(1) | 1.288(8) |
| Sn(1)–N(1) | 2.146(6) | O(2)–C(1) | 1.208(7) |
| Sn(1)–O(1) | 2.152(5) | O(3)–C(8) | 1.301(7) |
| C(17)–Sn(1)-O(3) | 95.3(3) | C(13)–Sn(1)–N(1) | 109.1(2) |
| C(17)–Sn(1)-C(13) | 126.3(3) | C(17)–Sn(1)–O(1) | 93.0(3) |
| O(3)–Sn(1)–C(13) | 98.5(3) | O(3)–Sn(1)–O(1) | 155.07(18) |
| C(17)–Sn(1)–N(1) | 123.9(3) | C(13)–Sn(1)–O(1) | 95.4(3) |
| O(3)–Sn(1)–N(1) | 81.62(19) | N(1)–Sn(1)–O(1) | 74.28(19) |

### 3.3.1. Structure of [(n-Bu)$_2$Sn(Sal-T)] (1)

For compound **1**, as shown in Fig. 1, the tin atom forms four primary bonds: two to the *n*-butyl groups, and two to oxygen atoms. In addition, there exists a coordination interaction between tin and the imino nitrogen atom. The Sn–N, 2.161(3) Å bond of the compound **1** is a little longer than that of the compound {[$Ph_2Sn(2\text{-}OC_{10}H_6CH{=}NCH_2COO)$]$SnPh_2Cl_2$} 2.136 Å [19], but shorter than that of [$SnMe_2$(Salop)] 2.221(3) Å [16] and [$Ph_2Sn(2\text{-}OC_6H_4C(CH_3){=}NCH_2COO)$] 2.190(5) Å [11], and it is considerably less than the sum of the van der Waals radii of tin and nitrogen, 3.74 Å [20]. The Sn(1)–O(1), 2.162(3) Å bond of the compound is longer than that of [$Ph_2Sn(2\text{-}OC_6H_4C(CH_3){=}NCH_2COO)$], 2.127(4) Å [11], but shorter than that of [$2\text{-}OHC_{10}H_6CH{=}N(CH_2)_2COOCOOSnBu_3$], 2.383(5) Å [21]. The Sn(1)–O(3), 2.093(3) Å bond is longer than that of the compound [$Ph_2Sn(2\text{-}OC_6H_4C(CH_3){=}NCH_2COO)$], 2.064 Å but a little shorter than that of the compound [$Vin_2Sn(2\text{-}OC_6H_4C(CH_3){=}NCH_2COO)OH_2$], 2.105 Å [11].

The tin atom lies in the ligand plane and forms a five-membered and a six-membered chelate ring with the ligand. Thus, two *n*-butyl groups and the imino nitrogen take up the equatorial position, while the oxygen atoms, O(1) and O(3), take up the axial sites around the Sn(1) atom. The trigonal bipyramidal geometry of the central tin atom is distorted as indicated by bonding angles of 158.75(11)°, 113.12(15)°, 122.4(12)° and 126.55(17)° for O(3)–Sn(1)–O(1), C(23)–Sn(1)–N(1), C(19)–Sn(1)–N(1) and C(19)–Sn(1)–C(23), respectively. The sum of the angles O(1)–Sn(1)–N(1), 75.07(11)°, and O(3)–Sn(1)–N(1), 83.72(11)° is 158.79°, and it is the same with the angle O(3)–Sn(1)–O(1), 158.75(11)°, so that the atoms Sn(1), N(1), O(1) and O(3) are co-planer. The sum of the angles C(23)–Sn(1)–N(1), C(19)–Sn(1)–N(1) and C(19)–Sn(1)–C(23) is 362.07°, thus the atoms Sn(1), N(1), C(19) and C(23) are almost in the same plane.

### 3.3.2. Structure of [(n-Bu)$_2$Sn(Sal-V)] (2)

The structure of compound **2** is similar to compound **1** as shown in Fig. 2. The tin atom coordinates to two *n*-butyl groups (Sn(1)–C(17) 2.104(7), Sn(1)–C(13) 2.109(7) Å) and to two oxygen atoms (Sn(1)–O(1) 2.152(5), Sn(1)–O(3) 2.108(5) Å), and the imino nitrogen atom also coordinates to the tin atom (Sn(1)–N(1) 2.146(6) Å), thus providing an five-membered and an six-membered chelate ring. The sum of the angles N(1)–Sn(1)–O(1), 74.28(19)° and O(3)–Sn(1)–N(1), 81.62(19)° is 155.9°, and it is consistent with the angle O(3)–Sn(1)–O(1), 155.07(18)°, so the atoms Sn(1), N(1), O(1) and O(2) are in the same plane. Including the tin-nitrogen interaction the geometry at tin becomes distorted trigonal bipyramidal with two oxygen atoms in axial sites (O(3)–Sn(1)–O(1), 155.07(18)°) and one nitrogen and two *n*-butyl carbon

atoms occupying the equatorial plane (C(17)–Sn(1)–C(13), 126.6(3)°; C(13)–Sn(1)–N(1), 109.1(2) and C(17)–Sn(1)–N(13), 123.9(3)°). The sum of the angles subtended at the tin atom in trigonal plane is 359.6°, so that the atoms Sn(1), N(1), C(13) and C(17) are in the same plane (see Fig. 3).

The Sn–C bond lengths (2.104(7) and 2.109(7) Å) of the compound **2** is longer than those of compound **1** (2.112(4) and 2.127(4) Å). The Sn–N bond length (2.146(6) Å) is quite close to compound **1** and other compounds described in literature [11,19].

## 4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Center, CCDC No. 234625 for compound **1** and CCDC No. 234626 for compound **2**. Copies of this information may be obtained from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1233-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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