

# Synthesis, spectra, and crystal structures of the triorganotin(IV) 5-[(*E*)-2-(4-methylphenyl)-1-diazenyl]-2-hydroxybenzoates ( $\text{Me}_3\text{Sn}\{\text{O}_2\text{CC}_6\text{H}_3\text{-}p\text{-OH}[\text{N}=\text{N}(\text{C}_6\text{H}_4\text{-4-CH}_3)]\})_n$ , $\text{Et}_3\text{Sn}\{\text{O}_2\text{CC}_6\text{H}_3\text{-}p\text{-OH}[\text{N}=\text{N}(\text{C}_6\text{H}_4\text{-4-CH}_3)]\}\text{OH}_2$ , and $\text{Bz}_3\text{Sn}\{\text{O}_2\text{CC}_6\text{H}_3\text{-}p\text{-OH}[\text{N}=\text{N}(\text{C}_6\text{H}_4\text{-4-CH}_3)]\}$

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## Abstract

The crystal structures of three triorganotin(IV) 5-[(*E*)-2-(4-methylphenyl)-1-diazenyl]-2-hydroxybenzoates, viz., ( $\text{Me}_3\text{Sn}\{\text{O}_2\text{CC}_6\text{H}_3\text{-}p\text{-OH}[\text{N}=\text{N}(\text{C}_6\text{H}_4\text{-4-CH}_3)]\})_n$  (**1**),  $\text{Et}_3\text{Sn}\{\text{O}_2\text{CC}_6\text{H}_3\text{-}p\text{-OH}[\text{N}=\text{N}(\text{C}_6\text{H}_4\text{-4-CH}_3)]\}\text{OH}_2$  (**2**), and  $\text{Bz}_3\text{Sn}\{\text{O}_2\text{CC}_6\text{H}_3\text{-}p\text{-OH}[\text{N}=\text{N}(\text{C}_6\text{H}_4\text{-4-CH}_3)]\}$  (**3**), have been determined. In the solid state, complex **1** exists as a one-dimensional polymer where a single benzoate ligand bridges adjacent Sn-centers. The Sn-atom is trigonal bipyramidal with the methyl ligands in the equatorial plane and the axial positions being occupied by the carboxyl O-atom from the carboxylate group of one benzoate ligand and the hydroxy O-atom of an adjacent ligand. Complex **2** exists as a monomeric molecule in which the Sn-atom has a slightly distorted trigonal bipyramidal coordination geometry with three ethyl ligands occupying equatorial positions, while the axial positions are occupied by an O-atom of a water molecule and a carboxylate O-atom. Complex **3** has a distorted tetrahedral geometry. The interpretations of the structures are augmented by IR, NMR (<sup>1</sup>H, <sup>13</sup>C, <sup>119</sup>Sn), and <sup>119m</sup>Sn Mössbauer experiments.

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## 1. Introduction

The chemistry of the 5-[(*E*)-2-(aryl)-1-diazenyl]-2-hydroxybenzoic acid (Fig. 1) ligating diorganotin(IV) centers was developed recently by our group and the mode of coordination is now known. The diorganotin(IV) com-

plexes of the types (i)  $\text{R}_2\text{Sn}(\text{LH})_2$  (R = <sup>n</sup>Bu, <sup>n</sup>Oct) [1–5], (ii)  $\text{R}_2\text{Sn}(\text{L}^a\text{H})(\text{L}^b\text{H})$  (R = Me, <sup>n</sup>Bu) [6], and (iii)  $\{\text{R}_2\text{Sn}(\text{LH})_2\text{O}\}_2$  [5,7] are of great interest because of their structural diversity in the crystalline state (Scheme 1) and their interesting biological activity.

A series of <sup>n</sup>Bu<sub>2</sub>Sn(LH)<sub>2</sub> complexes were prepared where the carboxylate residue is varied by virtue of changes to the aryl group and <sup>n</sup>Bu<sub>2</sub>Sn is held constant. The structures of <sup>n</sup>Bu<sub>2</sub>Sn(L<sup>1</sup>H)<sub>2</sub> · 0.5C<sub>6</sub>H<sub>6</sub> (**4**), <sup>n</sup>Bu<sub>2</sub>Sn(L<sup>2</sup>H)<sub>2</sub> (**5**), <sup>n</sup>Bu<sub>2</sub>Sn(L<sup>3</sup>H)<sub>2</sub> · 0.5C<sub>6</sub>H<sub>6</sub> (**6**), <sup>n</sup>Bu<sub>2</sub>Sn(L<sup>4-5</sup>H)<sub>2</sub> (**7–8**), and <sup>n</sup>Bu<sub>2</sub>Sn(L<sup>7-8</sup>H)<sub>2</sub> (**9–10**) adopt the same structural motif and reveal a monomeric molecule. The carboxylate groups on the

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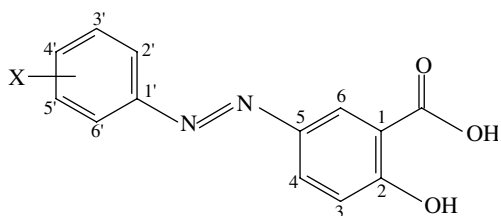
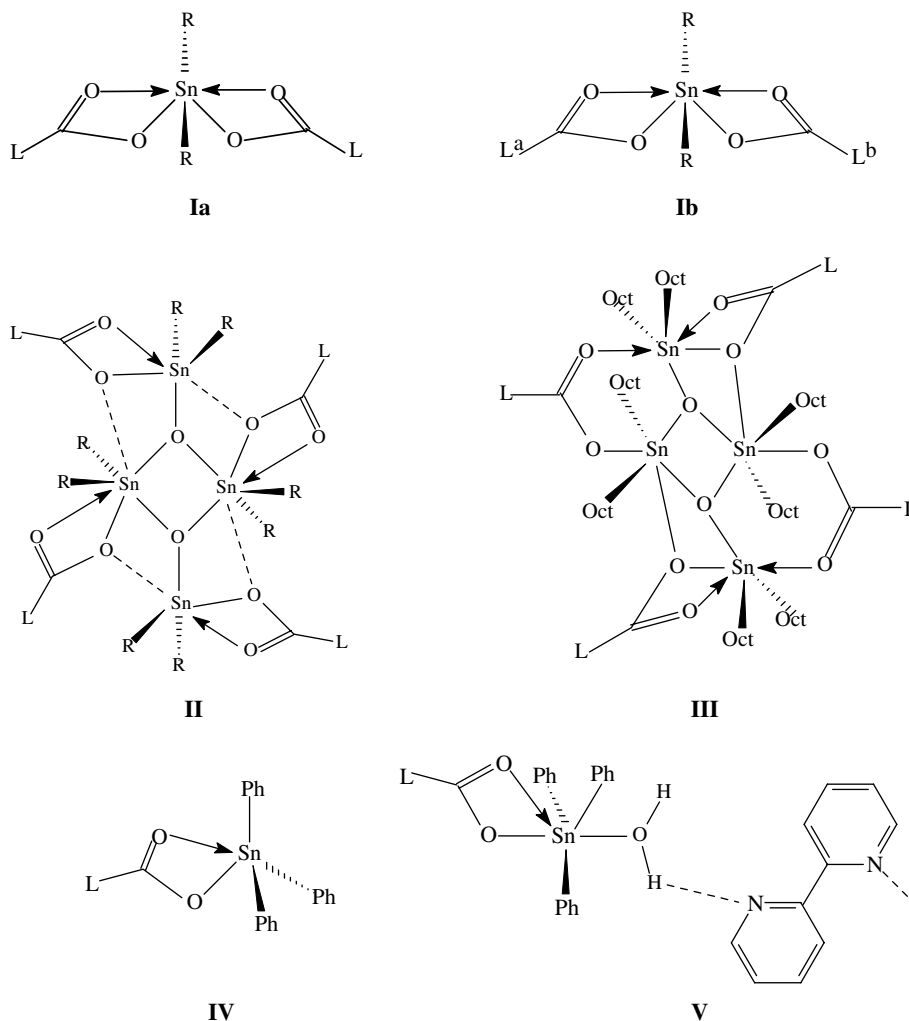


Fig. 1.  $L^1HH'$ : X = H;  $L^2HH'$ : 2-CH<sub>3</sub>;  $L^3HH'$ : 3-CH<sub>3</sub>;  $L^4HH'$ : 4-CH<sub>3</sub>;  $L^5HH'$ : 2-OCH<sub>3</sub>;  $L^6HH'$ : 4-OCH<sub>3</sub>;  $L^7HH'$ : 4-Cl;  $L^8HH'$ : 4-Br, where H and H' represent hydroxy and carboxylic acid H-atoms, respectively.

ligands act as bidentate chelating agents, giving an equatorial plane around the tin atom of four asymmetrically coordinated oxygen atoms. The butyl groups lie in axial positions, thereby completing six-coordination about the Sn-atom, but they are distorted from a true *trans* position, being pinned back somewhat over the open space left by the equatorial ligands to produce a skew-trapezoidal bipyramidal structure (Scheme 1, Ia). In the structures of **4**, **6**, and **8**, the open side of the Sn-atom actually allows one of the hydroxy oxygen atoms from the 2-hydroxybenzoate

moiety of one ligand of a neighboring molecule to form a bridge and coordinate very weakly with the Sn-atom, thereby completing a seventh coordination site in the extended Sn coordination sphere [3,4]. An  $^{10}O_2Sn(L^1H)_2$  (**11**) complex also revealed a monomeric six-coordinate structure [5], overall molecular geometry is quite akin to that of the  $^{10}Bu_2Sn(LH)_2$  complexes discussed above. In line with these developments, a few diorganotin(IV) complexes of the type,  $R_2Sn(L^aH)(L^bH)$ , for example,  $^{10}Bu_2Sn(L^7H)(L^4H)$  (**12**),  $^{10}Bu_2Sn(L^7H)(L^8H)$  (**13**), and  $Me_2Sn(L^7H)(L^4H)$  (**14**) have been reported, which furnished the first examples of diorganotin(IV) complexes containing mixed arylazobenzoates and having skew-trapezoidal bipyramidal geometry (Scheme 1, Ib) [6]. In complex **14**, only one of the two symmetry-independent molecules shows the additional seventh coordination site akin to that observed in **4**, **6**, and **8**, while the other molecule remains six-coordinate [6]. The structures of the type  $R_2Sn(LH)_2$  and  $R_2Sn(L^aH)(L^bH)$  described above conform to the predominant motifs found for compounds with the general formula  $[R_2Sn(O_2CR')_2]$  [8]. Further, the diorganotin(IV)



Scheme 1. Structural motifs in organotin(IV) 5-[(*E*)-2-(aryl)-1-diazenyl]-2-hydroxybenzoates.

complexes of formulation  $\{[R_2Sn(LH)_2O]_2\}$  ( $R = {}^nBu$  and  ${}^nOct$ ) were also investigated extensively [5,7], owing to useful applications in biology and catalysis. The crystal structures of four di-*n*-butyltin(IV) complexes, viz.,  $\{[{}^nBu_2Sn(L^1H)_2O]_2\}$  (**15**),  $\{[{}^nBu_2Sn(L^4H)_2O]_2\}$  (**16**),  $\{[{}^nBu_2Sn(L^7H)_2O]_2\}$  (**17**), and  $\{[{}^nBu_2Sn(L^8H)_2O]_2\}$  (**18**) were determined. The compounds **15–18** are centrosymmetric tetranuclear bis(dicarboxylatotetrabutyl-distannoxane) complexes containing a planar  $Sn_4O_2$  core in which two  $\mu_3$ -oxo O-atoms connect an  $Sn_2O_2$  ring to two exocyclic Sn-atoms (Scheme 1, II). The four carboxylate ligands display two different modes of coordination where both modes involve bridging of two structurally distinct Sn-atoms [7]. On the other hand, the crystal structures of  $\{[{}^nOct_2Sn(L^3H)_2O]_2\}$  (**19**) and  $\{[{}^nOct_2Sn(L^5H)_2O]_2\}$  (**20**) also confirmed the same bis(dicarboxylatotetraorganodistannoxane) formulation as observed for **15–18** but with a slight change in mode of coordination of the carboxylate ligands as shown in Scheme 1, III. In III, two carboxylate ligands each bridge one endocyclic to one exocyclic Sn-center *via* the two carboxylate O-atoms, with the Sn–O distances being quite similar. Two additional carboxylate ligands each have asymmetric bidentate coordination *via* the two carboxylate O-atoms to an exocyclic Sn-atom. The primary coordination sphere at each Sn-atom looks more like a slightly distorted trigonal bipyramid than an octahedron [5]. Also, the crystal structures of a series of triphenyltin(IV) complexes, viz.,  $Ph_3SnL^{1-4}H$  (**21–24**),  $Ph_3SnL^6H$  (**25**), and  $Ph_3SnL^7H \cdot 0.5C_6H_{14}$  (**26**) were determined where the carboxylate residue is varied [9–11]. In complexes **21–26**, the Sn-atom is four-coordinate, existing in a distorted tetrahedral geometry defined by a  $C_3O$  donor set (Scheme 1, IV). The observed structural motif resembles one of the four predominant motifs for structures of the general formula  $R_3Sn(O_2CR')$ , this being the monomeric distorted tetrahedral motif [8]. The reaction of a triphenyltin(IV) compound **22** with 2,2'-bipyridine (bipy) resulted in the formation of a cyclic tetrameric adduct of formula  $[Ph_3SnL^1H(H_2O)]_2 \cdot bipy_2$  (Scheme 1, V) [11]. Additionally, the organotin(IV) complexes of 5-[(*E*)-2-(aryl)-1-diazenyl]-2-hydroxybenzoate(s) have been studied in great detail for their biological properties, such as (i) larvicidal activity against the second larval instar of the *Aedes aegypti* mosquito [2], (ii) embryo toxicity toward two species of sea urchin, *Paracentrotus lividus* and *Sphaerechinus granularis* [12], and (iii) *in vitro* cytotoxicity against seven well characterized human tumor cell lines [4,7], and the initial results were found to be promising.

Given the synthetic and structural importance and the potential biological activity of the organotin(IV) complexes of 5-[(*E*)-2-(aryl)-1-diazenyl]-2-hydroxybenzoate(s), it is of interest to explore further the chemistry of analogous complexes. We report here the synthesis, spectra, and crystal structures of three  $R_3Sn(IV)$  complexes where the R ligand has been varied such that  $R = Me, Et,$  and  $Bz$  while 5-[(*E*)-2-(4-methylphenyl)-1-diazenyl]-2-hydroxybenzoate is held constant.

## 2. Experimental

### 2.1. Materials

$Me_3SnCl$  and  $Et_3SnCl$  were obtained from Fluka and were used as received.  $Bz_3SnCl$  was prepared as described by Sisido et al. [13]. All of the solvents used in the reactions were AR grade and were dried using standard literature procedures. Toluene was distilled from sodium benzophenone ketyl.

### 2.2. Physical measurements

Carbon, hydrogen, and nitrogen analyses were performed with a Perkin Elmer 2400 series II instrument. IR spectra in the range  $4000\text{--}400\text{ cm}^{-1}$  were obtained on a BOMEM DA-8 FT-IR spectrophotometer as KBr discs. The  ${}^1H$ -,  ${}^{13}C$ -, and  ${}^{119}Sn$  NMR spectra were recorded on a Bruker ACF 300 spectrometer and measured at 300.13, 75.47, and 111.92 MHz, respectively, or on a Bruker AVANCE 500 spectrometer at 500.13, 125.57, and 186.53 MHz, respectively. The  ${}^1H$ ,  ${}^{13}C$ , and  ${}^{119}Sn$  chemical shifts were referenced to  $Me_4Si$  set at 0.00 ppm,  $CDCl_3$  set at 77.0 ppm, and  $Me_4Sn$  set at 0.00 ppm, respectively. The  ${}^{119}Sn$  Mössbauer spectra of the triorganotin(IV) complexes in the solid state were recorded using a Model MS-900 (Ranger Scientific Co., Burleson, TX) spectrometer in the acceleration mode with a moving source geometry. A 5 mCi  $Ca^{119m}SnO_3$  source was used, and counts of 30,000 or more were accumulated for each spectrum. The spectra were measured at 80 K using a liquid-nitrogen cryostat (CRYO Industries of America, Inc., Salem, NH). The velocity was calibrated at ambient temperature using a composition of  $BaSnO_3$  and tin foil (splitting  $2.52\text{ mm s}^{-1}$ ). The resultant spectra were analyzed using the Web Research software package (Web Research Co., Minneapolis, MN).

### 2.3. Synthesis of 5-[(*E*)-2-(4-methylphenyl)-1-diazenyl]-2-hydroxybenzoic acid

The 5-[(*E*)-2-(4-methylphenyl)-1-diazenyl]-2-hydroxybenzoic acid ( $L^4HH$ ) was prepared as described earlier [10].

### 2.4. Synthesis of triorganotin(IV) 5-[(*E*)-2-(4-methylphenyl)-1-diazenyl]-2-hydroxybenzoates

A typical method is described below.

#### 2.4.1. Synthesis of $Me_3Sn\{O_2CC_6H_3-p-OH[N=N(C_6H_4-4-CH_3)]\}$ (**I**)

$Me_3SnCl$  (0.43 g, 2.16 mmol) in anhydrous methanol (50 ml) was added drop-wise with continuous stirring to a hot methanol solution (50 ml) containing  $L^4HNa$  (0.60 g, 2.16 mmol). The reaction mixture was then refluxed for 6 h and filtered while hot. The orange colored filtrate was evaporated by stirring at room temperature almost to

dryness. The residue was washed with hexane, dried *in vacuo* and extracted into anhydrous benzene. The concentrated benzene solution was precipitated with hexane which yielded the crude product. The precipitate was separated by filtration, washed with hexane (2 × 5 ml) and finally dried *in vacuo*. The dried product was then recrystallized from hexane. Yield (0.36 g, 40%). M.p.: 80–82 °C. Anal. Calc. for C<sub>17</sub>H<sub>20</sub>N<sub>2</sub>O<sub>3</sub>Sn: C, 48.7; H, 4.8; N, 6.68. Found: C, 48.62; H, 4.9; N, 6.76%. IR (KBr): 1630 cm<sup>-1</sup> ν(OCO)<sub>asym</sub>. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300.13 MHz); δ<sub>H</sub>: Ligand skeleton: 2.42 [s, 3H, CH<sub>3</sub>], 7.03 [d, 1H, H-3], 7.28 [d, 2H, H-2' and H-6'], 7.77 [d, 2H, H-3' and H-5'], 8.0 [dd, 1H, H-4], 8.46 [d, 1H, H-6], 11.86 [s, 1H, OH]; Sn–Me skeleton: 0.71 [s, 9H, CH<sub>3</sub>], ppm. <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75.47 MHz); δ<sub>C</sub>: Ligand skeleton: 21.4 [CH<sub>3</sub>], 114.4 [C-1], 117.9 [C-3], 122.6 [C-2' and C-6'], 127.8 [C-6], 128.3 [C-4], 129.7 [C-3' and C-5'], 140.9 [C-4'], 145.3 [C-5], 150.8 [C-1'], 163.9 [C-2], 174.3 [CO<sub>2</sub>]; Sn–Me skeleton: -1.9 [CH<sub>3</sub>] [<sup>1</sup>J(<sup>13</sup>C–<sup>119/117</sup>Sn) 390/370 Hz], ppm. <sup>119</sup>Sn NMR (CDCl<sub>3</sub>); δ<sub>Sn</sub>: 160.4 ppm. <sup>119</sup>Sn Mössbauer spectrum: δ = 1.29, Δ = 3.69, Γ<sub>1</sub> = 1.94, Γ<sub>2</sub> = 1.36 mm s<sup>-1</sup>, ρ = 2.86.

The other triorganotin(IV) complexes were prepared by reacting L<sup>4</sup>HNa with the appropriate triorganotin(IV) halide by following analogous procedures. The characterization data of the complexes are given below.

#### 2.4.2. Synthesis of Et<sub>3</sub>Sn{O<sub>2</sub>CC<sub>6</sub>H<sub>3</sub>-p-OH[N=N(C<sub>6</sub>H<sub>4</sub>-4-CH<sub>3</sub>)]}OH<sub>2</sub> (2)

The orange crystals of **2** were isolated from benzene and dried *in vacuo*. Yield: 0.33 g, 26.5%. M.p.: 81–83 °C. Anal. Calc. for C<sub>20</sub>H<sub>28</sub>N<sub>2</sub>O<sub>4</sub>Sn: C, 50.14; H, 5.89; N, 5.85. Found: C, 50.89; H, 5.80; N, 5.95%. IR (KBr):

1635 cm<sup>-1</sup> ν(OCO)<sub>asym</sub>. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300.13 MHz); δ<sub>H</sub>: Ligand skeleton: 2.42 [s, 3H, CH<sub>3</sub>], 7.04 [d, 1H, H-3], 7.26 [d, 2H, H-2' and H-6'], 7.77 [d, 2H, H-3' and H-5'], 8.0 [dd, 1H, H-4], 8.48 [d, 1H, H-6], 11.96 [s, 1H, OH]; Sn–Et skeleton: 1.36 [s, 15H, C<sub>2</sub>H<sub>5</sub>], ppm. <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75.47 MHz); δ<sub>C</sub>: Ligand skeleton: 21.5 [CH<sub>3</sub>], 114.6 [C-1], 117.9 [C-3], 122.6 [C-2' and C-6'], 127.5 [C-6], 128.4 [C-4], 129.7 [C-3' and C-5'], 140.9 [C-4'], 145.4 [C-5], 150.9 [C-1'], 164.0 [C-2], 174.4 [CO<sub>2</sub>]; Sn–Et skeleton: 8.6 [CH<sub>2</sub>] [<sup>1</sup>J(<sup>13</sup>C–<sup>119/117</sup>Sn) 361/345 Hz], 9.8 [CH<sub>3</sub>] [<sup>2</sup>J(<sup>13</sup>C–<sup>119/117</sup>Sn) 28 Hz], ppm. <sup>119</sup>Sn NMR (CDCl<sub>3</sub>); δ<sub>Sn</sub>: 132.9 ppm. <sup>119</sup>Sn Mössbauer spectrum: δ = 1.42, Δ = 3.80, Γ<sub>1</sub> = 1.55, Γ<sub>2</sub> = 1.81 mm s<sup>-1</sup>, ρ = 2.67.

#### 2.4.3. Synthesis of Bz<sub>3</sub>Sn{O<sub>2</sub>CC<sub>6</sub>H<sub>3</sub>-p-OH[N=N(C<sub>6</sub>H<sub>4</sub>-4-CH<sub>3</sub>)]} (3)

The orange crystals of **3** were isolated from hexane and dried *in vacuo*. Yield: 0.34 g, 30.4%. M.p.: 94–96 °C. Anal. Calc. for C<sub>35</sub>H<sub>32</sub>N<sub>2</sub>O<sub>3</sub>Sn: C, 64.94; H, 4.98; N, 4.33. Found: C, 64.71; H, 4.76; N, 4.51%. IR (KBr): 1628 cm<sup>-1</sup> ν(OCO)<sub>asym</sub>. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300.13 MHz); δ<sub>H</sub>: Ligand skeleton: 2.44 [s, 3H, CH<sub>3</sub>], 6.85 [d, 1H, H-3], 7.18 [d, 2H, H-2' and H-6'], 7.83 [d, 2H, H-3' and H-5'], 8.07 [dd, 1H, H-4], 8.43 [d, 1H, H-6], 11.62 [s, 1H, OH]; Sn–Bz skeleton: 2.77 [s, 6H, H1\*], 6.8–7.06 [m, 9H, H4\* and H5\*], 7.32 [m, 6H, H3\*], ppm. <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75.47 MHz); δ<sub>C</sub>: Ligand skeleton: 21.7 [CH<sub>3</sub>], 113.3 [C-1], 117.9 [C-3], 123.0 [C-2' and C-6'], 127.9 [C-6], 128.3 [C-4], 128.6 [C-3' and C-5'], 140.1 [C-4'], 145.1 [C-5], 150.8 [C-1'], 164.3 [C-2], 174.9 [CO<sub>2</sub>]; Sn–Bz skeleton: 24.42 [C-1\*], 138.1 [C-2\*], 129.4 [C-4\*], 124.6 [C-5\*], 128.9 [C-3\*], ppm. <sup>119</sup>Sn NMR (CDCl<sub>3</sub>); δ<sub>Sn</sub>: 8.4 ppm. <sup>119</sup>Sn

Table 1

Crystallographic data and structure refinement parameters for the triorganotin(IV) complexes 1–3

	1	2	3
Empirical formula	C <sub>17</sub> H <sub>20</sub> N <sub>2</sub> O <sub>3</sub> Sn	C <sub>20</sub> H <sub>28</sub> N <sub>2</sub> O <sub>4</sub> Sn	C <sub>35</sub> H <sub>32</sub> N <sub>2</sub> O <sub>3</sub> Sn
Formula weight	418.96	479.05	647.25
Crystal size (mm)	0.20 × 0.25 × 0.25	0.17 × 0.35 × 0.35	0.07 × 0.20 × 0.25
Crystal color, habit	Orange, prism	Orange, prism	Orange, prism
Temperature (K)	160(1)	160(1)	160(1)
Crystal system	Monoclinic	Orthorhombic	Monoclinic
Space group	<i>P</i> 2 <sub>1</sub> / <i>n</i>	<i>Pbca</i>	<i>P</i> 2 <sub>1</sub> / <i>c</i>
<i>a</i> (Å)	9.9807(2)	14.5583(2)	10.0110(1)
<i>b</i> (Å)	15.2712(3)	12.3530(2)	24.7277(4)
<i>c</i> (Å)	12.1171(2)	24.1212(4)	24.5907(4)
β (°)	91.119(1)	90	91.314(1)
<i>V</i> (Å <sup>3</sup> )	1846.50(6)	4337.9(1)	6085.8(2)
<i>Z</i>	4	8	8
<i>D</i> <sub>x</sub> (g cm <sup>-3</sup> )	1.507	1.467	1.413
μ (mm <sup>-1</sup> )	1.397	1.202	0.876
Transmission factors (min, max)	0.593, 0.764	0.658, 0.814	0.801, 0.944
2θ <sub>max</sub> (°)	60	60	52
Reflections measured	45939	52729	110851
Independent reflections ( <i>R</i> <sub>int</sub> )	5387 (0.067)	6333 (0.066)	11996 (0.065)
Reflections with <i>I</i> > 2σ( <i>I</i> )	4460	4367	9671
Number of parameters	217	260	750
<i>R</i> ( <i>F</i> ) ( <i>I</i> > 2σ( <i>I</i> ) reflns)	0.033	0.044	0.041
<i>wR</i> ( <i>F</i> <sup>2</sup> ) (all data)	0.082	0.120	0.080
GOF( <i>F</i> <sup>2</sup> )	1.11	1.04	1.14
Max, min Δρ (e/Å <sup>3</sup> )	1.38, -0.66	1.65, -1.20	0.65, -0.56

Mössbauer spectrum:  $\delta = 1.26$ ,  $\Delta = 2.48$ ,  $\Gamma_1 = 1.77$ ,  $\Gamma_2 = 2.10 \text{ mm s}^{-1}$ ,  $\rho = 1.96$ .

### 2.5. X-ray crystallography

Crystals of the triorganotin(IV) complexes suitable for an X-ray crystal-structure determination were obtained from hexane (**1** and **3**) and benzene/hexane (v/v 2:1) (**2**) by slow evaporation of the solvent at room temperature. All measurements were made at low temperature on a Nonius Kappa CCD diffractometer [14] with graphite-

monochromated Mo K $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) and an Oxford Cryosystems Cryostream 700 cooler. Data reduction was performed with HKL Denzo and Scalepack [15]. The intensities were corrected for Lorentz and polarization effects, and an empirical absorption based on the multi-scan method [16] was applied. Equivalent reflections were merged. The data collection and refinement parameters are given in Table 1, and views of the molecules are shown in Figs. 2–5. The structures were solved by direct methods using SIR92 [17]. In each structure, the non-hydrogen atoms were refined anisotropically.

Compound **1** is a one-dimensional polymer and the asymmetric unit contains one of the chemical repeat units. In **3**, there are two symmetry-independent molecules in the asymmetric unit. The atomic coordinates of the two molecules were tested carefully for a relationship from a higher symmetry space group using the program PLATON [18], but none could be found.

The hydroxy H-atom in each structure and the water ligand H-atoms in **2**, were placed in the positions indicated by difference electron density maps and their positions were allowed to refine together with individual isotropic displacement parameters. All remaining H-atoms were placed in geometrically calculated positions and refined by using a riding model where each H-atom was assigned a fixed iso-

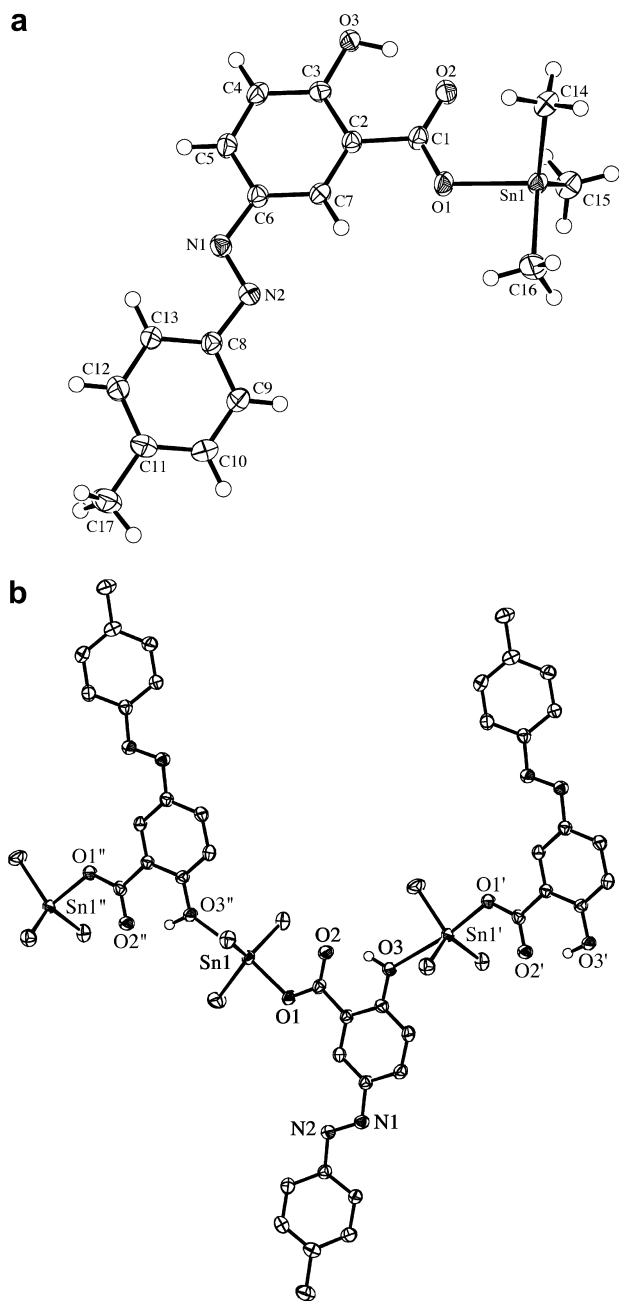


Fig. 2. (a) The asymmetric unit of  $(\text{Me}_3\text{Sn}\{\text{O}_2\text{CC}_6\text{H}_3\text{-}p\text{-OH}[\text{N}=\text{N}(\text{C}_6\text{H}_4\text{-}4\text{-CH}_3)]\})_n$  (**1**) showing the atom-labeling scheme (50% probability ellipsoids); (b) a three-unit segment of the polymeric chain in **1** (50% probability ellipsoids).

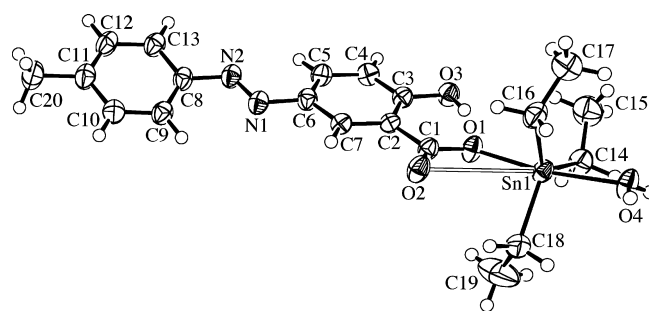


Fig. 3. The molecular structure of  $\text{Et}_3\text{Sn}\{\text{O}_2\text{CC}_6\text{H}_3\text{-}p\text{-OH}[\text{N}=\text{N}(\text{C}_6\text{H}_4\text{-}4\text{-CH}_3)]\}\text{OH}_2$  (**2**) showing the atom-labeling scheme (50% probability ellipsoids).

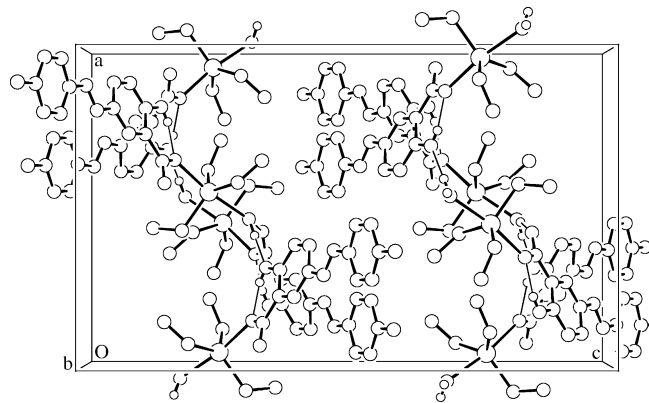


Fig. 4. The molecular packing of  $\text{Et}_3\text{Sn}\{\text{O}_2\text{CC}_6\text{H}_3\text{-}p\text{-OH}[\text{N}=\text{N}(\text{C}_6\text{H}_4\text{-}4\text{-CH}_3)]\}\text{OH}_2$  (**2**) showing the intra- and intermolecular hydrogen bonding (thin lines).



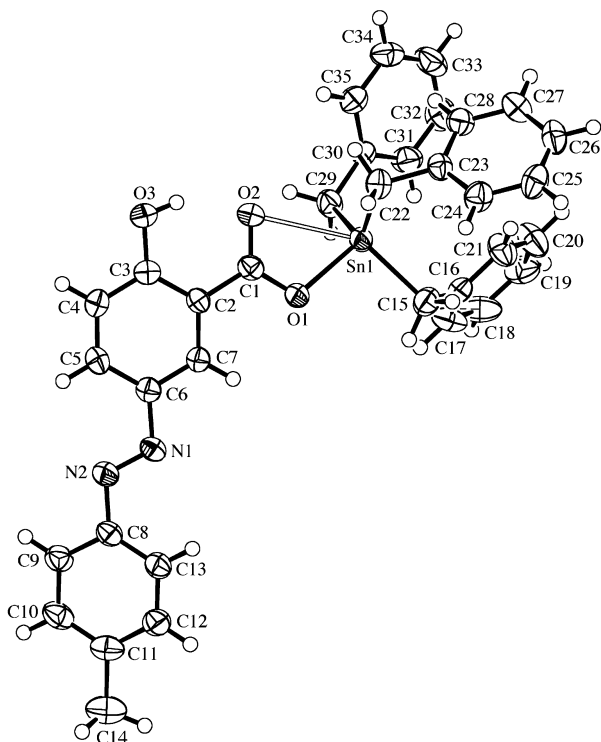


Fig. 5. The molecular structure of one of the two symmetry-independent molecules of  $\text{Bz}_3\text{Sn}\{\text{O}_2\text{CC}_6\text{H}_3\text{-}p\text{-OH}[\text{N}=\text{N}(\text{C}_6\text{H}_4\text{-}4\text{-CH}_3)]\}$  (**3**) showing the atom-labeling scheme (50% probability ellipsoids).

tropic displacement parameter with a value equal to  $1.2U_{\text{eq}}$  of its parent C-atom ( $1.5U_{\text{eq}}$  for the methyl groups). The refinement of each structure was carried out on  $F^2$  by using full-matrix least-squares procedures, which minimized the function  $\sum w(F_o^2 - F_c^2)^2$ . Corrections for secondary extinction were applied for **1** and **3**. Five reflections (in **1**) and one reflection (in **3**), whose intensities were considered to be extreme outliers, were omitted from the final refinement. All calculations were performed using the SHELXL97 [19] program.

### 3. Results and discussion

#### 3.1. Spectroscopic studies

The triorganotin(IV) 5-[(*E*)-2-(4-methylphenyl)-1-diazenyl]-2-hydroxybenzoates (**1–3**) were characterized by means of IR, NMR ( $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{119}\text{Sn}$ ), and  $^{119}\text{Sn}$  Mössbauer spectroscopic techniques. The infrared absorption band associated with the antisymmetric [ $\nu_{\text{asym}}(\text{OCO})$ ] stretching vibration in complexes **1–3** was detected at around  $1630\text{ cm}^{-1}$  compared with that of the uncomplexed  $\text{L}^4\text{HH}'$  at  $1653\text{ cm}^{-1}$ . The shift of this band to lower wave-number is ascribed to carboxylate coordination in accordance with earlier reports [9,10].

The  $^1\text{H}$  and  $^{13}\text{C}$  NMR data of  $\text{L}^4\text{HH}'$  has been reported earlier [10] and the signals were assigned by the use of correlated spectroscopy (COSY), heteronuclear single-quantum correlation (HMQC), and heteronuclear multi-

ple-bond connectivities (HMBC) experiments. The conclusions drawn from the ligand assignments were subsequently extrapolated to the spectra of complexes **1–3**, owing to the similarity of the spectra. The  $^1\text{H}$  and  $^{13}\text{C}$  chemical shift assignment of the triorganotin(IV) moiety is straightforward from the multiplicity patterns, resonance intensities and also by examining the  $^nJ(^{13}\text{C}\text{--}^{119/117}\text{Sn})$  coupling constants [20]. The  $^1\text{H}$  NMR integration values were completely consistent with the formulation of the products. The  $^{119}\text{Sn}$  NMR chemical shifts of triorganotin(IV) complexes **1–3** in  $\text{CDCl}_3$  solution are listed in Section 2.4. The chemical shift data, as well as the  $^nJ(^{13}\text{C}\text{--}^{119/117}\text{Sn})$  coupling constants, are unambiguously characteristic for four-coordinate Sn-atoms [9,10,20]. Undoubtedly, the five-coordinate structure of compounds **1** and **2** in the solid state (see Section 3.2) is lost upon dissolution, giving rise to a four-coordinate structure in solution. This behavior has been observed previously for triorganotin(IV) carboxylates [21–23].

The  $^{119}\text{Sn}$  Mössbauer spectra of complexes **1–3** were recorded in order to obtain the structure of the complexes in the solid state. The ratio of the quadrupole splitting value to isomer shift value ( $\rho = \Delta/\delta$ ) can be used to distinguish between the different coordination states of the central tin atom [24]. Tin compounds which are four-coordinate have  $\rho$  values less than 1.8 while  $\rho$  values larger than 2.1 would indicate compounds with greater than four coordination. As can be seen in Section 2.4, complexes **1** and **2** have  $\rho$  values greater than 2.1 suggesting that the complexes have a coordination number greater than four, while complex **3** shows  $\rho$  value of around 2.00 which is indicative of a four-coordinated structure. The values found for the quadrupole splitting ( $\Delta$ ) may be divided into two sets. Compounds **1** and **2**, with  $\Delta$  values of  $3.69$  and  $3.80\text{ mm s}^{-1}$ , respectively, matches perfectly well with a trigonal bipyramidal geometry [22,25–28]. Compound **3**, exhibits a  $\Delta$  value of  $2.48\text{ mm s}^{-1}$ , which is well within the range of  $2.3\text{--}3.0\text{ mm s}^{-1}$  characteristic for a tetrahedral geometry [20,22,25–28]. The isomer shift ( $\delta$ ) value of  $1.24\text{ mm s}^{-1}$  is indicative of typical quadrivalent organotin derivatives [10,20]. Thus, the  $\Delta$  values are in excellent agreement with the crystal structures described below.

#### 3.2. X-ray crystallography

Compound **1** is a  $(\text{Me}_3\text{Sn}\{\text{O}_2\text{CC}_6\text{H}_3\text{-}p\text{-OH}[\text{N}=\text{N}(\text{C}_6\text{H}_4\text{-}4\text{-CH}_3)]\})_n$  polymer consisting of extended chains where a single benzoate ligand bridges adjacent Sn-centers *via* its carboxylate and hydroxy O-atoms. The asymmetric unit contains one of the chemical repeat units. The primary coordination sphere of the Sn-atom is trigonal bipyramidal with the methyl ligands in the equatorial plane and the axial positions being occupied by the carboxyl O-atom and the hydroxy O-atom of a second ligand (Fig. 2a and b; Table 2). The carbonyl O-atom of the carboxylate group of the carboxylate ligand in **1** also coordinates very weakly

Table 2  
Selected bond lengths (Å) and angles (°) for complexes **1** and **2**

<b>1</b> <sup>a</sup>		<b>2</b>	
Sn(1)–O(1)	2.112(2)	Sn(1)–O(1)	2.228(2)
Sn(1)–O(3) <sup>i</sup>	2.709(2)	Sn(1)–O(4)	2.366(3)
Sn(1)–O(2)	3.136(2)	Sn(1)–O(2)	3.305(2)
Sn(1)–C(14)	2.119(3)	Sn(1)–C(14)	2.141(3)
Sn(1)–C(15)	2.114(3)	Sn(1)–C(16)	2.132(4)
Sn(1)–C(16)	2.117(2)	Sn(1)–C(18)	2.140(4)
O(1)–C(1)	1.291(3)	O(1)–C(1)	1.304(4)
O(2)–C(1)	1.247(3)	O(2)–C(1)	1.228(4)
O(1)–Sn(1)–O(3) <sup>i</sup>	171.91(6)	O(1)–Sn(1)–O(4)	171.1(1)
O(1)–Sn(1)–C(14)	101.01(8)	O(1)–Sn(1)–C(14)	88.3(1)
O(1)–Sn(1)–C(15)	98.81(9)	O(1)–Sn(1)–C(16)	92.5(1)
O(1)–Sn(1)–C(16)	91.76(9)	O(1)–Sn(1)–C(18)	96.9(1)
O(3) <sup>i</sup> –Sn(1)–C(14)	83.81(8)	O(2)–Sn(1)–C(14)	129.6(1)
O(3) <sup>i</sup> –Sn(1)–C(15)	84.04(9)	O(2)–Sn(1)–C(16)	74.4(1)
O(3) <sup>i</sup> –Sn(1)–C(16)	80.22(9)	O(2)–Sn(1)–C(18)	72.9(1)
C(14)–Sn(1)–C(15)	120.7(1)	O(4)–Sn(1)–C(14)	86.2(1)
C(14)–Sn(1)–C(16)	117.8(1)	O(4)–Sn(1)–C(16)	85.3(1)
C(15)–Sn(1)–C(16)	116.9(1)	O(4)–Sn(1)–C(18)	91.8(1)
C(1)–O(1)–Sn(1)	120.1(2)	C(14)–Sn(1)–C(16)	126.9(2)
C(1)–O(2)–Sn(1)	71.1(1)	C(14)–Sn(1)–C(18)	115.1(2)
		C(16)–Sn(1)–C(18)	117.5(2)
		C(1)–O(1)–Sn(1)	122.8(2)
		C(1)–O(2)–Sn(1)	71.2(2)

<sup>a</sup> Symmetry operations for primed atoms “i” refer to the atom at the position  $\frac{1}{2} + x, \frac{1}{2} - y, z - \frac{1}{2}$ .

to the Sn-atom *via* long Sn···O(2) bonds of 3.136(2) Å. This O-atom is also the acceptor of an intraligand hydrogen bond from the adjacent hydroxy group. Although these long Sn···O(2) distances are well inside the sum of the van der Waals radii of the Sn- and O-atoms (*ca.* 3.6 Å), there does not appear to be any major distortion of the trigonal bipyramidal Sn-coordination geometry as a result of this contact. Polymeric structures with a similar mode of coordination and geometry about the Sn-atom have been observed for Ph<sub>3</sub>Sn(2-OHC<sub>6</sub>H<sub>4</sub>C(H)=NCH<sub>2</sub>COO)<sub>n</sub> [29] and (Ph<sub>3</sub>Sn[O<sub>2</sub>CC<sub>6</sub>H<sub>4</sub>{N=N(C<sub>6</sub>H<sub>3</sub>-4-OH(C(H)=NC<sub>6</sub>H<sub>4</sub>Br-4))}-2])<sub>n</sub> [30].

Although the same slightly distorted trigonal bipyramidal *trans*-R<sub>3</sub>SnO<sub>2</sub> structural motif is found in the structure of Et<sub>3</sub>Sn{O<sub>2</sub>CC<sub>6</sub>H<sub>3</sub>-*p*-OH[N=N(C<sub>6</sub>H<sub>4</sub>-4-CH<sub>3</sub>)]}OH<sub>2</sub> (**2**), the structure consists of discrete monomeric molecule (Fig. 3). The three ethyl ligands occupy equatorial positions about the Sn-atom, while the axial positions are occupied by a water molecule and the carboxyl O-atom from the carboxylate ligand (Table 2). The carbonyl O-atom of the carboxylate group has a very weak interaction with the Sn-atom [Sn(1)···O(2) = 3.305(2) Å].

In **2**, the hydroxy H-atom forms an intramolecular hydrogen bond with the carboxyl O-atom, thereby creating a loop with a graph set motif [31] of S(6). This contrasts with the involvement of the carboxylate carbonyl O-atom in this hydrogen bond in the structure of **1**. The H-atoms of the water ligand form intermolecular hydrogen bonds with the hydroxy O-atom of one neighboring molecule and with the carboxylate carbonyl O-atom of a different neighboring molecule. The former interaction links the

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

Molecule A		Molecule B	
Sn(1)–O(1)	2.077(2)	Sn(41)–O(41)	2.080(2)
Sn(1)–O(2)	2.817(2)	Sn(41)–O(42)	2.950(2)
Sn(1)–C(15)	2.154(3)	Sn(41)–C(55)	2.141(3)
Sn(1)–C(22)	2.133(4)	Sn(41)–C(62)	2.137(3)
Sn(1)–C(29)	2.149(3)	Sn(41)–C(69)	2.139(3)
O(1)–C(1)	1.308(4)	O(41)–C(41)	1.300(4)
O(2)–C(1)	1.251(4)	O(42)–C(41)	1.241(4)
O(1)–Sn(1)–C(15)	97.4(1)	O(41)–Sn(41)–C(55)	95.3(1)
O(1)–Sn(1)–C(22)	109.6(1)	O(41)–Sn(41)–C(62)	102.1(1)
O(1)–Sn(1)–C(29)	102.7(1)	O(41)–Sn(41)–C(69)	112.9(1)
O(2)–Sn(1)–C(15)	148.4(1)	O(42)–Sn(41)–C(55)	142.6(1)
O(2)–Sn(1)–C(22)	78.8(1)	O(42)–Sn(41)–C(62)	85.7(1)
O(2)–Sn(1)–C(29)	82.9(1)	O(42)–Sn(41)–C(69)	80.7(1)
C(15)–Sn(1)–C(22)	112.8(1)	C(55)–Sn(41)–C(62)	116.9(2)
C(15)–Sn(1)–C(29)	113.2(2)	C(55)–Sn(41)–C(69)	110.4(2)
C(22)–Sn(1)–C(29)	118.4(2)	C(62)–Sn(41)–C(69)	116.9(2)
C(1)–O(1)–Sn(1)	110.4(2)	C(41)–O(41)–Sn(41)	114.4(2)
C(1)–O(2)–Sn(1)	77.0(2)	C(41)–O(42)–Sn(41)	74.2(2)

molecules into extended chains which run parallel to the [100] direction and can be described by a graph set motif of C(8). The latter interaction links the molecules into extended chains which run parallel to the [010] direction and can be described by a graph set motif of C(4). Together, the intermolecular interactions link the molecules into a two-dimensional network which lies parallel to the (001) plane (Fig. 4).

In contrast to the polymeric and monomeric structures of **1** and **2**, which contain the trigonal bipyramidal *trans*-R<sub>3</sub>SnO<sub>2</sub> structural motif, the structure of Bz<sub>3</sub>Sn{O<sub>2</sub>CC<sub>6</sub>H<sub>3</sub>-*p*-OH[N=N(C<sub>6</sub>H<sub>4</sub>-4-CH<sub>3</sub>)]} (**3**), is built from monomeric molecules which have a distorted tetrahedral coordination geometry (Fig. 5). There are two symmetry-independent molecules in the asymmetric unit, but there are no significant differences between the geometries or conformations of these molecules (Table 3). The primary coordination sphere involves the three benzyl ligands and the carboxyl O-atom of the benzoate ligand. The C–Sn–C angles are slightly larger than the ideal tetrahedral value, presumably as a result of steric effects arising between the benzyl ligands. The carbonyl O-atom of the carboxylate group has a weak interaction with the Sn-atom [Sn(1)–O(2) = 2.817(2); Sn(41)–O(42) = 2.950(2) Å]. In this case the Sn–O distance is short enough that the interaction influences the coordination geometry with the small O(1)–Sn(1)–C(15) and O(41)–Sn(41)–C(55) angles of *ca.* 96° being a direct consequence. The crystal structure of complex **3** resembles that of the type IV motif exemplified by the structure of the triphenyltin(IV) analogue, Ph<sub>3</sub>Sn{O<sub>2</sub>CC<sub>6</sub>H<sub>3</sub>-*p*-OH[N=N(C<sub>6</sub>H<sub>4</sub>-4-CH<sub>3</sub>)]} [11], and the principal geometric parameters of these two structures do not differ significantly. As observed for complex **1**, the hydroxy group in each symmetry-independent molecule forms an intraligand hydrogen bond with the carboxylate carbonyl O-atom.

#### 4. Supplementary material

CCDC 637046, 637047 and 637048 contain the supplementary crystallographic data for for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

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