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Synthesis, characterization and crystal structures of 2-[(E)-2-(4-hydroxy-3,5-dimethylphenyl)-1-diazenyl]benzoic acid and its polymeric and monomeric triorganotin(IV) complexes

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ABSTRACT

Three triorganotin(IV) complexes of composition R_3SnLH (R = Me, Bu and Ph and LH = 2-[(E)-2-(4-hydroxy-3,5-dimethylphenyl)-1-diazenyl]benzoate) have been synthesized and characterized by ^1H, ^{13}C, ^{119}Sn NMR, and IR spectroscopic techniques in combination with elemental analysis. The crystal structures of the carboxylate ligand $HO_2CC_6H_4\{N{=}N(C_6H_2\text{-}4\text{-}OH\text{-}3,5\text{-}(CH_3)_2)\}\text{-}o$ in its neutral form and three triorganotin(IV) complexes, *viz*., polymeric $(R_3Sn[O_2CC_6H_4\{N{-}N(H)(C_6H_2\text{-}4\text{-}O\text{-}3,5\text{-}(CH_3)_2)\}\text{-}o])_n$ (R = Me (**1**) and Bu (**2**)) and monomeric $Ph_3Sn[O_2CC_6H_4\{N{-}N(H)(C_6H_2\text{-}4\text{-}O\text{-}3,5\text{-}(CH_3)_2)\}\text{-}o]$ (**3**) complexes are reported. The polymeric complexes **1** and **2** exist as extended chains in which the LH-bridged Sn-atoms adopt a *trans*-R_3SnO_2 trigonal bipyramidal configuration with R groups in the equatorial positions and the axial sites occupied by an oxygen atom from the carboxylate ligand and the phenoxide O atom of the next carboxylate ligand. The Sn atom in complex **3** has a distorted tetrahedral geometry. In all three complexes, the carboxylate ligand is in the zwitterionic form with the phenolic proton moved to the nearby azo nitrogen atom, in contrast to the free carboxylic acid ligand which is in the azo form.

1. Introduction

Recently, we have investigated the crystal structures of 2-[(*E*)-(5-tert-butyl-2-hydroxyphenyl)diazenyl]benzoic acid [1] and 4-[(*E*)-(5-tert-butyl-2-hydroxyphenyl)diazenyl]benzoic acid [2], which featured essentially a planar diazo molecule with an *E* conformation about the N═N bond and centrosymmetrically related molecules associate into dimers via the eight-membered dicarboxylic acid $\{\cdots H{-}O{-}C{=}O\}_2$ synthon. Further, these ligands and their analogues have been explored for their coordination behaviour towards organotin(IV) in order to find possible candidates in this class of organotin(IV) complexes which might act as anticancer drugs owing to their remarkable cytotoxic activity that has been exhibited in some cases across a panel of cell lines [3–5]. As a result of promising cytotoxic activity [6,7], the mechanistic role of these organotin(IV) compounds was investigated, to ascertain the influence of the azo group nitrogen atoms, by docking studies with some of the key enzymes, such as ribonucleotide reductase, thymidylate synthase, thymidylate phosphorylase and topoisomerase II, that take part in the synthesis of raw materials for DNA and its replication [3–5]. The docking studies indicated that the azo group nitrogen atoms and formyl, carbonyl and ester oxygen atoms in the ligand moiety play an important role. They exhibit hydrogen bonding interactions with the active site of the amino acids of the aforementioned enzymes. The higher activity was attributed to the presence of the azo group nitrogen atoms in the triphenyltin(IV) complexes [4]. In addition, triorganotin(IV) carboxylates of the general formula $R_3Sn(O_2CR')$ are of great interest because of their structural diversity in the crystalline state [8]. Recently, the crystal structure of tributyltin(IV) 4-[(*E*)-(4-hydroxy-3-methylphenyl)diazenyl]benzoate revealed that the Sn atom has a distorted C_3O tetrahedral geometry involving one of the carboxylate O atoms and three C atoms from the butyl ligands [3]. On the other hand, its *ortho*-carboxy analogue i.e. tributyltin(IV) 2-[(*E*)-(4-hydroxy-3-methylphenyl)diazenyl]benzoate demonstrated an unprecedented structure where the tributyltin centre is coordinated by a carboxylate anion (in a quinoid form) as well as by its neutral form (coordinating as a ketone) [9]. The tin atom in this complex is five coordinate within a *trans*-C_3O_2 donor

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set. In the crystal structure, two complex molecules self assemble via O−H···O hydrogen bonding leading to the formation of 48-membered macrocyclic rings [9]. Subsequently, the crystal structures of three triphenyltin(IV) 2-/4-[(*E*)-2-(aryl)-1-diazenyl]benzoates have been determined and all of them conform to the same motif, i.e. a distorted tetrahedral geometry [10]. In view of the synthetic and structural importance and the potential biological activity of the triorganotin(IV) complexes of the aforementioned ligands, it is of interest to explore the chemistry of the analogous ligands towards triorganotin(IV) where now the carboxylate ligand is 2-[(E)-2-(4-hydroxy-3,5-dimethylphenyl)-1-diazenyl]benzoate (LH) (Fig. 1). Three triorganotin(IV) complexes of composition R_3SnLH (R = Me, Bu and Ph) have been characterized by means of IR, ^{1}H, ^{13}C and ^{119}Sn NMR spectroscopic studies. The crystal and molecular structures of ligand **LHH′**, $[Me_3SnLH]_n$ (**1**), $[Bu_3SnLH]_n$ (**2**) and Ph_3SnLH (**3**) are also reported.

2. Experimental

2.1. Materials

Ph_3SnOH was prepared from Ph_3SnCl (Fluka) by following the literature method [11]. $(Bu_3Sn)_2O$ (Merck), Me_3SnCl (Merck), 2,6-dimethylphenol (Aldrich) and *o*-aminobenzoic acid (Aldrich) were used without further purification. The solvents used in the reactions were of AR grade and dried using standard 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 4000−400 cm^{-1} were obtained on a Perkin Elmer Spectrum BX series FT-IR spectrophotometer with samples investigated as KBr discs. The ^{1}H, ^{13}C and ^{119}Sn NMR spectra were recorded either on a Bruker AMX 400 or on a Varian Mercury 400 spectrometer and measured at 400.13, 100.62 and 149.32 MHz, respectively. The ^{1}H, ^{13}C and ^{119}Sn chemical shifts were referenced to Me_4Si and Me_4Sn set at 0.00, ppm, respectively.

2.3. Synthesis of the ligand and its triorganotin(IV) complexes

2.3.1. Synthesis of 2-[(E)-2-(4-hydroxy-3,5-dimethylphenyl)-1-diazenyl]benzoic acid (*LHH′*)

o-Aminobenzoic acid (5.0 g, 36.5 mmol) was mixed with HCl (5 ml) and water (16 ml) and digested on a water bath for 30 min. The hydrochloride was cooled to 5 °C and diazotized with ice-cold aqueous $NaNO_2$ solution (2.5 g, 20 ml). A cold solution of 2,6-dimethylphenol (4.45 g, 36.5 mmol), previously dissolved in 10% NaOH solution (50 ml), was then added to the cold diazonium salt solution with vigorous stirring. A red colour developed almost immediately and the stirring was continued for 1 h. The reaction mixture was kept overnight in a refrigerator, followed by 3 h at room temperature, and then acidified with dilute acetic acid, whereupon a yellow orange precipitate separated out. The precipitate was filtered, washed several times with water to remove excess acetic acid and water-soluble materials, and then dried in air. The crude product was washed with hexane to remove any tarry materials, dried in vacuo and recrystallized from methanol to yield yellow prismatic crystals of **LHH′** (2.25 g, 50%). M.p.: 212−214 °C. Anal. Found: C, 66.74; H, 5.30; N, 10.43%. Calcd. For $C_{15}H_{14}N_2O_3$: C, 66.66; H, 5.22; N, 10.36. IR (cm^{-1}): 1679 $(OCO)_{asym}$. ^{1}H NMR (DMSO-d$_6$); δ_H: 13.1 [CO_2H], 9.23 [OH], 7.73 [d, 7.5 Hz, 1H, H-3], 7.62 [t, 7.5 Hz, 1H, H-4], 7.52 [m, 4H, H-5, 6, 2′ and 6′], 2.25 [s, 6H, CH_3], ppm. ^{13}C NMR (DMSO-d$_6$); δ_C: 169.3 [CO_2], 158.0 [C-4′], 151.5 [C-1], 145.6 [C-1′], 132.1 [C-5], 130.0 [C-4], 129.7 [C-3], 125.6 [C-6, C-2′ and 6′], 124.3 [C-3′ and 5′], 118.8 [C-2], 17.4 [CH_3], ppm.

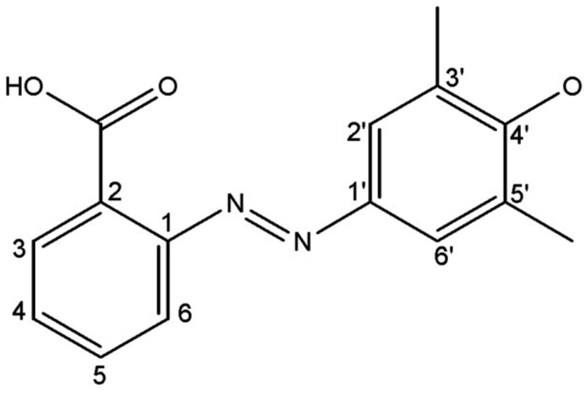

Fig. 1. Generic structure and numbering protocol of the ligand (**LHH′**) where H and H′ represent hydroxyl and carboxyl protons, respectively.

The sodium salt of the ligand (LHNa) was prepared by adding an aqueous solution of sodium hydrogen carbonate into pre-dissolved ligand in ethanol in an equimolar ratio. The solution was stirred for 2 h under mild heating conditions and was evaporated under reduced pressure to give a red solid which was dried in vacuo. The dried sodium salt was extracted in anhydrous methanol and filtered while hot, which upon concentration afforded LHNa in 50% yield. This product was used for the subsequent reactions. IR (cm^{-1}): 1629 $(OCO)_{asym}$.

2.3.2. Synthesis of Me_3SnLH (**1**)

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 LHNa (0.60 g, 2.16 mmol). The reaction mixture was then refluxed for 5 h and filtered while hot. The filtrate was kept for crystallisation. Red crystals were obtained the following day. M.p.: 246−248 °C. Yield 0.05 g, (30%). Anal. Found: C, 50.61; H, 5.11; N, 6.36%. Calcd. For $C_{18}H_{22}N_2O_3Sn$: C, 49.92; H, 5.12; N, 6.47%. IR (cm^{-1}): 1626 $(OCO)_{asym}$. ^{1}H NMR (CDCl$_3$); δ_H: 12.8 [s, 1H, OH], 8.05 [d, 7.5 Hz, 1H, H-3], 7.84 [d, 8.8 Hz, 1H, H-6], 7.51 [t, 7.2 Hz, 1H, H-4], 7.31 [s, 1H, H-2′], 7.18 [s, 1H, H-6′], 7.00 [t, 8 Hz, 1H, H-5], 2.16 and 2.07 [s, 6H, CH_3]; Sn-Me: 0.70 [s, 9H, Sn-CH_3] [^2J(^{1}H−$^{119/117}$Sn) 60 Hz], ppm. ^{13}C NMR (DMSO-*d*$_6$); δ_C: 169.5 [CO_2], 154.3 [C-4′], 147.7 [C-1], 134.3 [C-1′], 126.8 [C-4 and 5], 125.7 [C-3], 122.5 [C-6], 121.4 [C-2′, 6′, 3′ and 5′], 114.0 [C-2], 14.8 [CH_3]; Sn-Me: −1.76 [Sn−CH_3] [^1J(^{13}C−$^{119/117}$Sn) 513 Hz], ppm. ^{119}Sn NMR (CDCl$_3$): 149.6 ppm.

2.3.3. Synthesis of Bu_3SnLH (**2**)

Compound **2** was synthesized by refluxing a 2:1 M ratio of **LHH′** (0.50 g, 1.95 mmol) and $(Bu_3Sn)_2O$ (0.58 g, 0.97 mmol) in 50 ml of anhydrous toluene in a 100 ml flask equipped with a Dean−Stark moisture trap and a water-cooled condenser. The reaction mixture was refluxed for 5 h. The solvent was distilled off to half of the initial solvent volume. The remaining solvent was removed using a rotary evaporator. The dark-red residue was then dissolved in 20 ml of hexane and filtered to give, upon refrigeration, the crude product. Dark red crystals were isolated by recrystallisation from toluene/hexane. M.p: 120−122 °C. Yield (0.57 g) 35%. Anal. Found: C, 58.10; H, 7.37; N, 4.98%. Calcd. For $C_{27}H_{40}N_2O_3Sn$: C, 57.98; H, 7.21; N, 5.01%. IR (KBr): 1633 cm^{-1} $(OCO)_{asym}$. ^{1}H NMR (CDCl$_3$); δ_H: 12.9 [s, 1H, OH], 8.04 [d, 7.5 Hz, 1H, H-3], 7.82 [d, 8.8 Hz, 1H, H-6], 7.50 [t, 7.2 Hz, 1H, H-4], 7.34 [s, 1H, H-2′], 7.18 [s, 1H, H-6′], 7.00 [t, 8 Hz, 1H, H-5], 2.16 and 2.07 [s, 6H, CH_3]; Sn-Bu: 1.71 [m, 6H, $H_{(\alpha)}$], 1.38 [m, 12H, $H_{(\beta)}$ and $H_{(\gamma)}$], 0.93 [t, 7.5 Hz, 9H, $H_{(\delta)}$], ppm. ^{13}C NMR

(CDCl$_3$); δ_C: 187.3 [CO$_2$], 173.1 [C-4′], 144.8 [C-1], 138.9 [C-1′], 137.8 [C-5], 136.9 [C-4], 134.7 [C-3], 134.1 [C-6], 132.4 [C-2′], 121.2 [C-6′], 119.1 [C-3′], 114.7 [C-5′], 113.8 [C-2], 17.5 and 16.1 [CH$_3$]; Sn–Bu: 27.8 [C$_{(\beta)}$][$^2J(^{13}C-^{119/117}Sn)$ 21 Hz], 27.0 [C$_{(\gamma)}$][$^3J(^{13}C-^{119/117}Sn)$ 65 Hz], 17.0 [C$_{(\alpha)}$][$^1J(^{13}C-^{119/117}Sn)$ 354 Hz], 13.7 [C$_{(\delta)}$], ppm. ^{119}Sn NMR (CDCl$_3$): 126.2 ppm.

2.3.4. Ph_3SnLH (**3**)

Compound **3** was synthesized by reacting **LHH′** (0.73 g, 2.04 mmol) and Ph$_3$SnOH (0.75 g, 2.04 mmol) in 50 ml of anhydrous toluene by following the method described for compound **2**. The filtrate was collected and the volatiles were removed using a rotary evaporator. The residue was dried in vacuo, washed with hexane (3 × 5 ml), extracted into chloroform and filtered. The filtrate upon concentration afforded the crude product. The crude product was dried in vacuo and recrystallized from toluene to yield orange crystals of the desired product. M.p.: 190–192 °C. Yield (0.07 g, 30%). Anal. Found: C, 64.71; H, 4.65; N, 4.51%. Calcd. For $C_{33}H_{28}N_2O_3Sn$: C, 64.00; H, 4.56; N, 4.52%. IR (KBr): 1638 cm^{-1} (OCO)$_{asym}$. ^{1}H NMR (CDCl$_3$): 12.7 [s, 1H, OH], 8.15 [d, 7.5 Hz, 1H, H-3], 7.30 [s, 1H, H-2′], 7.14 [s, 1H, H-6′], 7.00 [t, 8 Hz, 1H, H-5], 2.15 and 2.06 [s, 6H, CH$_3$]; Sn–Ph: 7.81[m, 7H, Sn–*Ph*$_{(o)}$ and H-6], 7.50 [m, 10H, Sn–Ph$_{(m+p)}$ and H-4], ppm. ^{13}C NMR (CDCl$_3$); δ_C: 187.3 [CO$_2$], 174.2 [C-4′], 145.0 [C-1], 139.1 [C-1′], 138.1 [C-5], 134.9 [C-4], 134.8 [C-3], 132.7 [C-6], 121.3 [C-2′ and 6′], 119.1 [C-3′ and 5′], 113.9 [C-2], 17.7 and 16.1 [CH$_3$]; Sn–Ph: 138.0 [C$_{(i)}$][$^1J(^{13}C-^{119/117}Sn)$ 630 Hz], 136.8 [C$_{(o)}$][$^2J(^{13}C-^{119/117}Sn)$ 50 Hz], 130.3 [C$_{(p)}$][$^4J(^{13}C-^{119/117}Sn)$ 13 Hz], 129.1 [C$_{(m)}$][$^3J(^{13}C-^{119/117}Sn)$ 65 Hz], ppm. ^{119}Sn NMR (CDCl$_3$): −104.0 ppm.

Note: α, β, γ and δ denote the proton and carbon numbers of tin-butyl while *i*-, *o*-, *m*- and *p*- refer to the proton and carbon numbers of tin-phenyl groups.

2.4. X-ray crystallography

Crystals of the compounds suitable for an X-ray crystal-structure determination were obtained from methanol (**LHH′**), toluene/chloroform/hexane (**1**), hexane (**2**) and toluene (**3**) by slow evaporation of the solvent at room temperature. The measurements for **1**–**3** were made at low temperature on a Nonius KappaCCD diffractometer [12] with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) and an Oxford Cryosystems Cryostream 700 cooler. The data for **LHH′** were recorded on an Agilent Technologies SuperNova area-detector diffractometer [13] using Cu *K*α radiation (λ = 1.54184 Å) from a micro-focus X-ray source and an *Oxford Instruments Cryojet XL* cooler. Data reduction on **1**–**3** was performed with HKL Denzo and Scalepack [14] while CrysAlisPro [13] was used for **LHH′**. The intensities were corrected for *Lorentz* and polarization effects. An empirical absorption correction based on the multi-scan method was applied for **1**–**3** [15], and **LHH′** [13]. Equivalent reflections were merged. The data collection and refinement parameters are given in Table 1, and views of the structures of **LHH′** and **1**–**3** (segments of the polymeric structures in the case of **1** and **2**) are shown in Figs. 2–5.

The structures of **1**–**3** were solved by heavy-atom Patterson methods [16], followed by the Fourier expansion routine of DIRDIF94 [17] while the structure of **LHH′** was solved by direct methods by using SHELXS97 [18].

Complex **1** crystallises as a 1:1 solvate with CHCl$_3$. The asymmetric unit of compound **2** contains four independent repeats of the chemically unique fragment, which generate three symmetry-independent polymeric chains. The terminal methyl group of one butyl ligand in one residue is disordered over two conformations. Two positions were defined for this methyl group and the site occupation factor of the major conformation of this group refined to 0.600(9). Similarity restraints were applied to the chemically equivalent bond lengths involving the disordered C-atoms. The non-hydrogen atoms in each structure were refined anisotropically. The amine H-atoms in **1**–**3** and the hydroxy H-atoms in **LHH′** were placed in the positions indicated by difference electron density maps and their positions were allowed to refine together with isotropic displacement parameters. All remaining H-atoms were placed in geometrically calculated positions and refined using a riding model where each H-atom was assigned a fixed isotropic displacement parameter with a value equal to 1.2 U_{eq} of its parent

Table 1
Crystallographic data and structure refinement parameters for the ligand **LHH′** and the triorganotin(IV) complexes **1**–**3**.

	LHH′	**1**	**2**	**3**
Empirical formula	$C_{15}H_{14}N_2O_3$	$C_{19}H_{23}Cl_3N_2O_3Sn$	$C_{27}H_{40}N_2O_3Sn$	$C_{33}H_{28}N_2O_3Sn$
Formula weight	270.29	552.36	559.22	619.19
Crystal size (mm)	0.10 × 0.15 × 0.20	0.10 × 0.18 × 0.23	0.10 × 0.25 × 0.25	0.10 × 0.20 × 0.30
Crystal shape	Prism	Tablet	Tablet	Plate
Temperature (K)	103(1)	160(1)	160(1)	160(1)
Crystal system	Monoclinic	Monoclinic	Monoclinic	Triclinic
Space group	$C2/c$	$P2_1/c$	$P2_1/c$	$P\bar{1}$
a (Å)	11.95231(11)	14.5151(2)	31.8017(3)	9.9441(2)
b (Å)	16.77432(14)	18.2399(2)	19.8331(2)	12.0176(2)
c (Å)	13.53109(12)	8.9687(1)	18.1605(2)	13.4453(2)
α (°)	90	90	90	111.9873(9)
β (°)	104.5241 (9)	103.6542(8)	104.3134(5)	90.268(1)
γ (°)	90	90	90	108.8208(7)
V (Å^3)	2626.18(4)	2307.39(5)	11098.7(2)	1395.76(4)
Z	8	4	16	2
D_x (g cm^{-3})	1.367	1.590	1.339	1.473
μ (mm^{-1})	0.798	1.474	0.948	0.952
Transmission factors (min, max)	0.604; 1.000	0.815, 0.898	0.832, 0.911	0.849, 0.911
$2\theta_{max}$ (°)	153.1	58	55	60
Reflections measured	11,028	65,265	191,552	37,409
Independent reflections (R_{int})	2736 (0.013)	6195 (0.063)	25378 (0.075)	8041 (0.045)
Reflections with $I > 2\sigma(I)$	2552	4732	17219	7189
Number of parameters	191	263	1236	359
$R(F)$ ($I > 2\sigma(I)$ reflns)	0.033	0.039	0.047	0.028
$wR(F^2)$ (all data)	0.095	0.102	0.123	0.068
GOF(F^2)	1.05	1.04	1.04	1.05
max, min $\Delta\rho$ (e/Å^3)	0.36, −0.20	1.05, −1.10	2.72, −1.02	1.17, −1.02

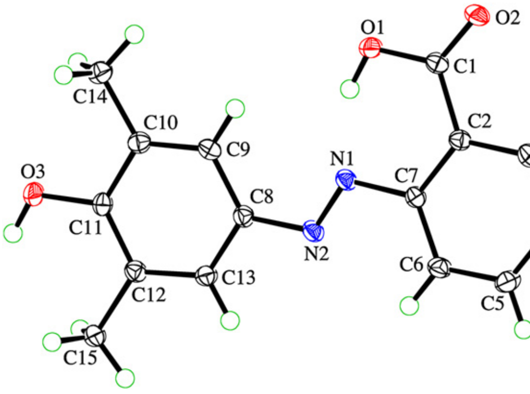

Fig. 2. View of the molecule of **LHH′** showing the atom-labelling scheme (50% probability ellipsoids).

C-atom (1.5 U_{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 $\Sigma w(F_o^2 - F_c^2)^2$. Corrections for secondary extinction were applied for **1** and **3**. Seven reflections for **2** and one reflection for **3** whose intensities were considered to be extreme outliers, were omitted from the final refinement. All calculations were performed using the SHELXL97 program [18]. The crystallographic diagrams were drawn using ORTEPII [19].

3. Results and discussion

3.1. Spectroscopy

Diagnostically important infrared absorption frequencies for the carboxylate antisymmetric [ν_{asym}(OCO)] stretching vibration of the triorganotin complexes (**1**–**3**) are given in Section 2.3. The assignment of the symmetric [ν_{sym}(OCO)] stretching vibration band could not be made owing to the complex pattern of the spectra. The antisymmetric [ν_{asym}(OCO)] stretching vibration band of the uncomplexed ligand (**LHH′**) appears at ~1680 cm^{-1}. For the triorganotin complexes, the corresponding carbonyl stretching frequency appears at ~1630 cm^{-1}. The shift of the band in **1**–**3** relative to its position for the free ligand is ascribed to carboxylate coordination to the tin atom in accordance with earlier reports [3–5,20–22].

The ^{1}H and ^{13}C NMR data of **LHH′** and triorganotin(IV) complexes **1**–**3** are reported in Section 2.3. The NMR signals of **LHH′** were assigned from the multiplicity patterns, resonance intensities and also by comparing the NMR spectrum with those of the cognate ligands [1,3–5]. The conclusions drawn from the ligand assignments were then subsequently extrapolated to the complexes owing to the data similarity. The ^{1}H- and ^{13}C-chemical shift assignments of the triorganotin moiety are straightforward from the multiplicity patterns, resonance intensities and also by examining the $^nJ(^{13}C-^{119/117}Sn)$ coupling constants [21–23]. The ^{1}H NMR integration values were completely consistent with the formulation of the products. The ^{119}Sn NMR chemical shifts of the complexes (**1**–**3**) in $CDCl_3$ solution are listed in Section 2.3. Complexes **1**–**3** exhibit a single sharp resonance at *ca.* 150, 126 and −104 ppm, respectively, suggesting that the tin atom is four-coordinate [3,4,20–23]. In contrast, the solid-state polymeric structures found for complexes **1** and **2**, reveal five-coordinate tin atoms (vide infra). It is anticipated that the multinuclear structures break down in solution to generate monomeric four-coordinate tetrahedral complexes [23].

3.2. X-ray crystallography

The crystal structure of **LHH′** is shown in Fig. 2, while selected geometric parameters are collected in Table 2. The molecule is approximately planar with just small twists about the central C–N bonds linking the two phenyl rings, as indicated by the torsion angles N(2)–N(1)–C(7)–C(6) = −12.14(12)° and N(1)–N(2)–C(8)–C(9) = 3.63(13)°. The carboxylic acid group is coplanar with its parent phenyl ring [O(1)–C(1)–C(2)–C(3) = −177.17(8)°]. The carboxylic acid H-atom forms an intramolecular hydrogen bond with the azo N-atom closest to the carboxylic acid group. The hydroxy group forms an intermolecular hydrogen bond with the carboxylic acid carbonyl O-atom of a neighbouring molecule and thereby links the molecules into extended chains which run parallel to the [201] direction (Table 3). The intra- and

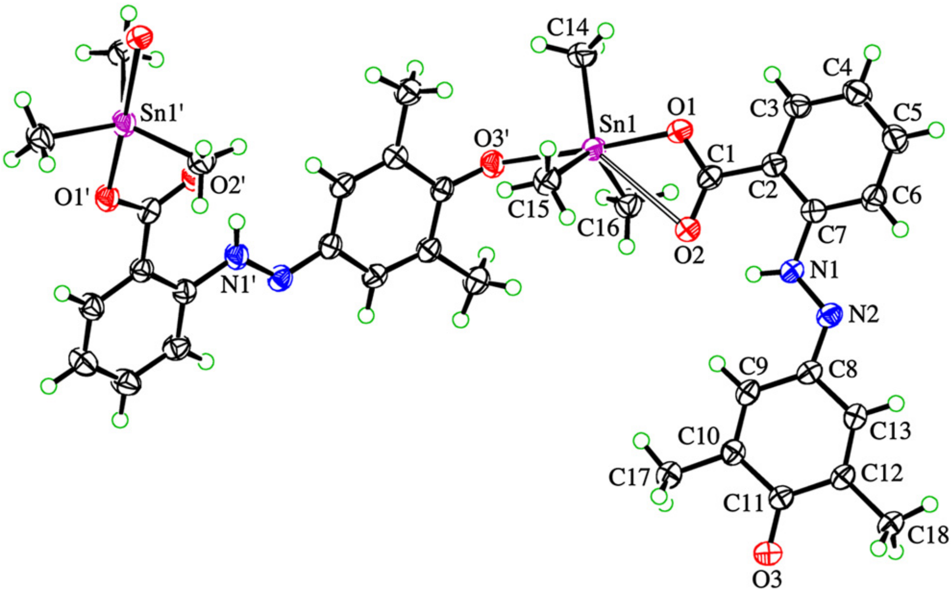

Fig. 3. Three repeats of the crystallographically and chemically unique unit in the polymeric $[Me_3SnLH]_n$ chain structure of **1** (50% probability ellipsoids).

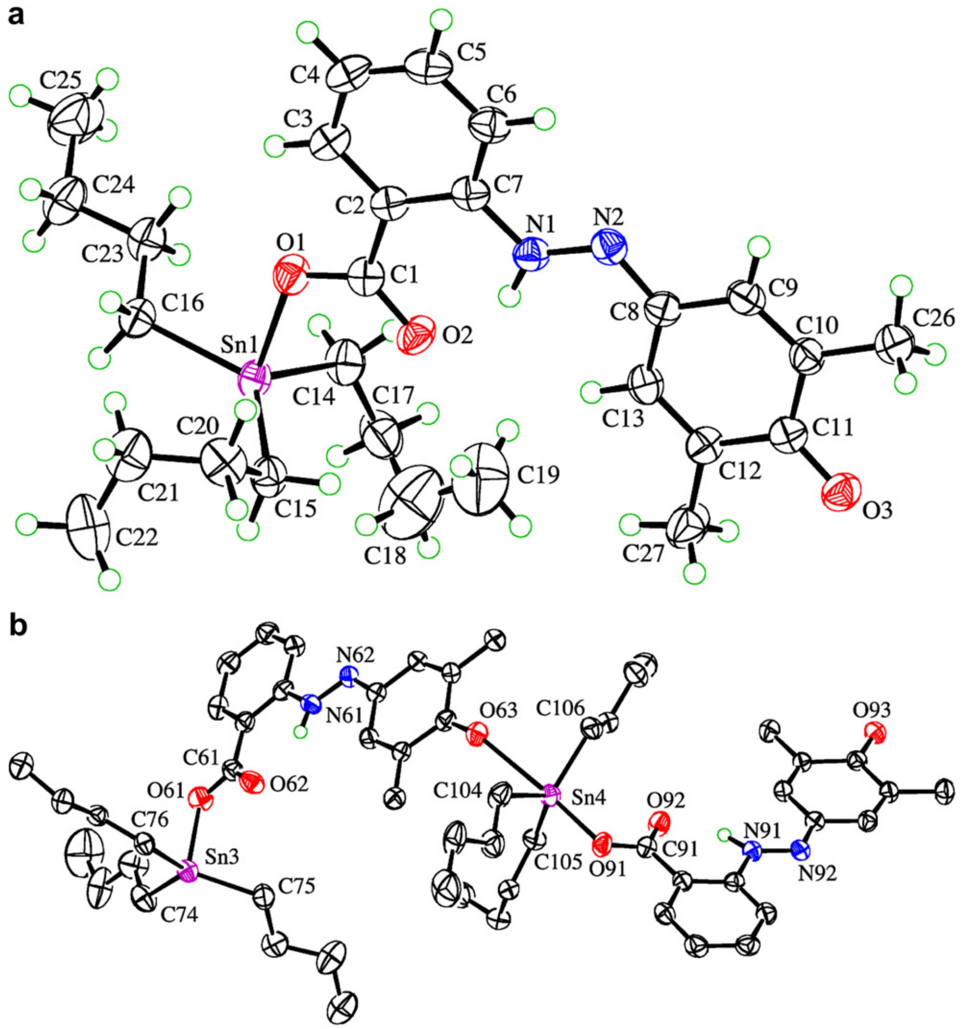

Fig. 4. (a) The crystallographically and chemically unique unit in one of the three symmetry-independent polymeric chains in the structure of $[Bu_3SnLH]_n$ 2 (50% probability ellipsoids); (b) Two continuous chemical but crystallographically unique units in one of the other symmetry-independent $[Bu_3SnLH]_n$ chains in **2** (50% probability ellipsoids).

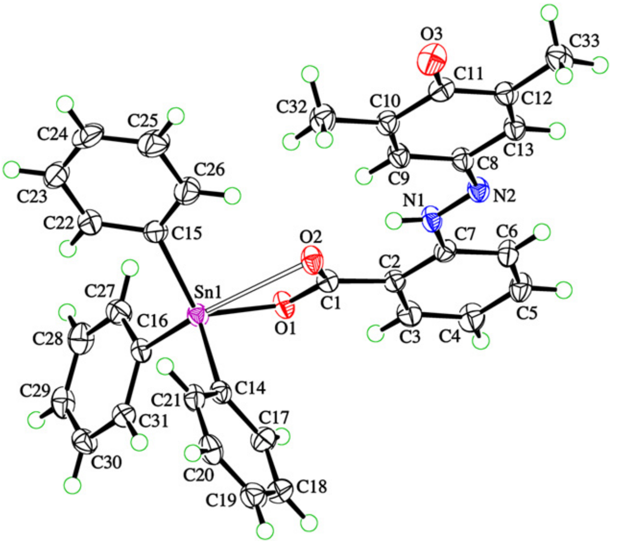

Fig. 5. The molecular structure of Ph_3SnLH **3** (50% probability ellipsoids).

intermolecular hydrogen-bonding patterns can be described by graph set motifs [24] of S(6) and C(12), respectively. Pairs of molecules related by a two-fold axis have their planes less than 3.5 Å apart, but the antiparallel nature of the molecules precludes any $\pi \cdots \pi$ interactions between adjacent phenyl rings. Nonetheless, azo N atoms in adjacent molecules come into close proximity: $N(1) \cdots N(1)^i = 3.2869(11)$; $N(1) \cdots N(2)^i = 3.4702(11)$ Å (symmetry code (i): $2 - x, y, 1/2 - z$). These pairs of molecules are further connected to form a stack of molecules parallel to the [001] direction by two weak $C{-}H \cdots \pi$ interactions between adjacent pairs related by a centre of inversion. Thus, methyl group C(14)–H(142) of the hydroxyphenyl ring interacts with the centroid of the phenyl

Table 2
Selected bond lengths (Å) and angles (°) for **LHH′**.

O(1)–C(1)	1.3254(11)	N(1)–N(2)	1.2636(11)
O(2)–C(1)	1.2176(11)	N(1)–C(7)	1.4239(11)
O(3)–C(11)	1.3519(11)	N(2)–C(8)	1.4035(11)
N(2)–N(1)–C(7)	115.01(8)	C(2)–C(7)–N(1)	117.62(8)
N(1)–N(2)–C(8)	116.27(8)	C(6)–C(7)–N(1)	122.23(8)
O(2)–C(1)–O(1)	119.62(8)	C(9)–C(8)–N(2)	125.94(8)
O(2)–C(1)–C(2)	122.19(8)	C(13)–C(8)–N(2)	114.53(8)
O(1)–C(1)–C(2)	118.18(8)		

Table 3
Hydrogen bonding geometry (Å, °) for **LHH′**.

D-H···A	D-H	H···A	D···A	D-H···A
O(1)–H(1)···N(1)	0.90(2)	1.73(2)	2.5733(10)	155.4(17)
O(3)–H(3)···O(2′)	0.89(2)	1.945(9)	2.7885(10)	157.0(19)

Primed atoms refer to the molecule in the symmetry-related position: $1 + x, -y, 1/2 + z$.

ring defined by atoms C(2) to C(7) in the molecule at the symmetry-related position $2 - x, -y, 1 - z$, and this latter molecule has an identical interaction back to the original molecule ($H\cdots\pi = 2.96$ Å, $C–H\cdots\pi = 151°$). Finally, two intermolecular C–H···O interactions serve to complete the three-dimensional supramolecular structure. The C(5)–H(5)···O(1)^{ii} interaction between the hydroxyphenyl ring and the carboxylic acid O-atom links the molecules into extended chains which run parallel to the [010] direction; graph set motif C(7) (H(5)···O(1)^{ii} = 2.50 Å, C(5)–H(5)···O(1)^{ii} = 160°; symmetry code (ii): $3/2 - x, y - 1/2, 1/2 - z$). The C(3)–H(31)···O(3)^{iii} interaction between the benzoate phenyl ring and the hydroxyphenyl O-atom also links the molecules into extended chains, this time running parallel to the [$\bar{1}$02] direction and producing a graph set motif of C(11) (H(31)···O(3)^{iii} = 2.35 Å, C(3)–H(31)···O(3)^{iii} = 163°; symmetry code (iii): $x - 1, -y, z - 1/2$).

The one-dimensional polymeric structures of compounds **1** and **2** are shown in Figs. 3 and 4, while selected geometric parameters are collected in Table 4. The crystal structures of complexes **1** and **2** are very similar and exhibit the same structural motif of a polymeric chain where a single carboxylate ligand bridges adjacent *trans*-R_3SnO_2 centres via its carboxylate and phenoxide O-atoms. It should be mentioned here that a neutral monomeric structure for a tributyltin(IV) complex with a *trans*-R_3SnO_2 motif was recently reported for an analogous ligand 2-[(*E*)-2-(4-hydroxy-3-methylphenyl)-1-diazenyl]benzoate. In this complex, the tributyltin centre is coordinated by both a carboxylate anion, which exists in a quinoid form, as well by the neutral form of the ligand, which coordinates as a ketone [9].

The asymmetric unit in **1** contains one chemical repeat of the polymer, plus one molecule of chloroform, while four independent chemical repeat units (designated A, B, C and D) from each of three symmetry-independent polymeric chains is present in the asymmetric unit of **2**. Fragments A and B form independent chains each composed of just A or B residues. Fragments C and D alternate within the third independent chain. Residue B has disordered positions for the methyl group of one butyl ligand. There is possible disorder in a second butyl ligand, but this was not modelled. The primary coordination sphere of the Sn-atom is trigonal bipyramidal with the Sn–R (R = Me or Ph) ligands in the equatorial plane and axial positions occupied by one O-atom from the carboxylate group of one ligand and the phenoxide O-atom (formerly the hydroxy group, see the structure of **LHH′** in Fig. 2) of the next carboxylate ligand in the chain. The formal hydroxy group of the azo ligand **LHH′** in these complexes has lost its H-atom, so is negatively charged. Instead, the azo N-atom nearest the carboxylate group is protonated, thus leading to a quinoid type zwitterionic ligand. This N–H group forms an intramolecular hydrogen bond with the carboxylate carbonyl O-atom. The carbonyl O-atom of the carboxylate group coordinates very weakly via a very long bond to the Sn-atom (3.081(2) Å in **1** and in the range 3.045(2)–3.079(3) Å in **2**). In **1** and **2**, the second O-atom of the carboxylate group is thus not involved in the primary coordination sphere of the Sn-atom, although these distances are still within the sum of the van der Waals radii of the respective atoms (ca. 3.6 Å). There are only very small distortions of the trigonal bipyramidal Sn-coordination geometry as a result of the Sn···O(2) contact (Table 2). A polymeric structure with a similar mode of coordination and geometry about the Sn-atom was observed in the triorganotin(IV) complexes with {[(*E*)-1-(2-hydroxyphenyl)methylidene]amino}acetate [25], 2-{[(2*Z*)-(3-hydroxy-1-methyl-2-butenylidene)]amino}phenylpropionate [26], 2-{[(*E*)-1-(2-hydroxyphenyl)methylidene]-amino}phenylpropionate [26], 2-{[(*E*)-1-(2-hydroxyphenyl)ethylidene]amino}phenylpropionate [26], 2-{[(2*Z*)-(3-hydroxy-1-methyl-2-butenylidene)]amino}-4-methyl-pentanoate [27], 2-{[(*E*)-1-(2-hydroxyphenyl)alkylidene]amino}-4-methylpentanoates [27] and 4-[(2Z)-(3-hydroxy-1-methyl-2-butenylidene)amino]benzoates [28].

Table 4
Selected bond lengths (Å) and angles (°) for **1**–**3**.[a]

	1	**2**[b]	**3**
Sn(1)–O(1)	2.137(2)	2.157(2)	2.075(1)
Sn(1)–O(3)^{i}	2.551(2)	2.625(2)	–
Sn(1)···O(2)	3.081(2)	3.079(3)	2.778(1)
Sn(1)–C(14)	2.123(3)	2.143(4)	2.119(2)
Sn(1)–C(15)	2.126(3)	2.138(4)	2.126(2)
Sn(1)–C(16)	2.113(4)	2.143(4)	2.136(2)
O(1)–Sn(1)–O(3)^{i}	176.29(8)	173.07(9)	–
O(1)–Sn(1)–C(14)	91.2(1)	98.1(1)	101.00(6)
O(1)–Sn(1)–C(15)	97.7(1)	98.0(1)	118.35(6)
O(1)–Sn(1)–C(16)	96.1(1)	89.9(1)	97.50(6)
O(3)^{i}–Sn(1)–C(14)	85.6(1)	86.5(1)	–
O(3)^{i}–Sn(1)–C(15)	85.3(1)	83.9(1)	–
O(3)^{i}–Sn(1)–C(16)	83.9(1)	83.5(1)	–
C(14)–Sn(1)–C(15)	115.4(2)	120.9(2)	117.47(7)
C(15)–Sn(1)–C(16)	126.2(2)	123.5(1)	111.17(7)
C(16)–Sn(1)–C(14)	116.0(2)	113.0(2)	109.18(7)

[a] Atom labels with superscript “i” refer to atoms from the next symmetry-related ligand in the polymeric chain of **1** (Symmetry code: $-x, y - 1/2, -z + 1/2$) and **2** (Symmetry code: $1 - x, y + 1/2, 3/2 - z$).

[b] Only the parameters for one of the four independent fragments of **2** are given; the corresponding parameters for the other three fragments are very similar.

The polymeric structures found for **1** and **2** are not repeated in the structure of **3** in which discrete monomeric Sn-complex molecules are present (Fig. 5). The Sn-atom is coordinated by one of the carboxylate group oxygen atoms of the ligand and three phenyl groups. Thus, the tin atom in **3** is four coordinate with a distorted tetrahedral geometry defined by a C_3O donor set (Table 4). The range of the tetrahedral angles at the Sn atom is 97.50(6) to 118.35(6)°. The carboxylate carbonyl O-atom, O(2), interacts only weakly with the Sn-atom at a distance of 2.778(1) Å and this is reflected in the disparity in the C(1)–O(1) and C(1)–O(2) bond distances, i.e. 1.306(2) and 1.244(2) Å, respectively. This interaction is the cause of the distortion of the tetrahedral primary coordination sphere, but the Sn(1)···O(2) distance is considered to be too long for the Sn atom to be described as truly five-coordinate. In addition, the bond angles around the Sn atom in **3** are more consistent with a tetrahedral environment than with a trigonal bipyramidal five-coordinate environment. Similar tetrahedral geometry about the Sn atom to that of **3** was observed in triphenyltin(IV) complexes with 2-[(*E*)-2-(2-hydroxy-5-methylphenyl)-1-diazenyl]benzoate and its acetone solvated complex [29,30], 5-[(E)-2-(aryl)-1-diazenyl]-2-hydroxybenzoates [21,22,31], 2-[(E)-(5-tert-Butyl-2-hydroxyphenyl)-diazenyl]benzoate, 4-[(E)-(5-tert-Butyl-2-hydroxyphenyl)-diazenyl]benzoate and 4-[(*E*)-2-(2-hydroxy-5-methylphenyl)-1-diazenyl]benzoate [10].

The carboxylate ligands of pairs of molecules related by a centre of inversion lie parallel and head-to-tail and exhibit $\pi\cdots\pi$ interactions between the phenyl rings with a distance between the centres of gravity of the rings being 3.5800(12) Å. The interplanar separation is approximately 3.35 Å. The carboxylate ligand in **3** also exists in a quinoid type zwitterionic form and shows the usual

Table 5
Hydrogen bonding geometry (Å, °) for **1**–**3**.[a]

D–H···A	D–H	H···A	D···A	D–H···A
N(1)–H(1)···O(2)	0.87(4)	1.87(4)	2.611(4)	143(3)
	[(0.88(4)]	[1.83(4))]	[2.601(4)]	[146(4)]
	(0.82(2))	(1.96(2))	(2.641(2))	(140(2))
N(31)–H(31)···O(32)	[0.90(3)]	[1.85(3)]	[2.606(4)]	[140(3)]
N(61)–H(61)···O(62)	[0.87(3)]	[1.88(3)]	[2.621(4)]	[142(3)]
N(91)–H(91)···O(92)	[0.97(4)]	[1.76(4)]	[2.612(4)]	[144(3)]

[a] The H-bonding parameters for the four independent fragments of complex **2** are in square brackets while those of complex **3** are in parentheses.

intramolecular hydrogen bond involving the carboxylate carbonyl O-atom and the protonated azide N–H group, as observed in its methyltin(IV) (**1**) and butyltin(IV) (**2**) analogues (vide supra) (Table 5). In contrast, the neutral **LHH**′ molecule does not present itself in the quinoid form. The preference for the formation of the zwitterionic form of the ligand in complexes may be a result of the coordination of the phenoxide O-atom to the Sn-atom in **1** and **2** while a steric reason could be ascribed for **3** where such coordination is absent. However, quinoid or zwitterionic forms are quite commonly encountered in similar systems [25–28].

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Appendix. Supplementary material

CCDC 824668–824671 contain the supplementary crystallographic data for **LHH**′ and complexes **1**–**3**, respectively. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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