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Synthesis, characterization and crystal structures of polymeric and dimeric triphenyltin(IV) complexes of 4-[((*E*)-1-{2-hydroxy-5-[(*E*)-2-(2-carboxyphenyl)-1-diazenyl]phenyl}methylidene)amino]aryls

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Abstract

The triphenyltin(IV) complexes of 4-[((*E*)-1-{2-hydroxy-5-[(*E*)-2-(2-carboxyphenyl)-1-diazenyl]phenyl}methylidene)amino]aryls (aryls = 4-CH_3, 4-Br, 4-Cl, 4-OCH_3) have been synthesized and characterized by ^{1}H-, ^{13}C-, ^{119}Sn-NMR, ESI mass spectrometry, IR and ^{119m}Sn Mössbauer spectroscopic techniques in combination with elemental analysis. The crystal structures of a representative carboxylate ligand (aryl = 4-CH_3) and three Sn complexes, viz., polymeric ($Ph_3Sn[O_2CC_6H_4\{N{=}N(C_6H_3$-4-OH$(C(H){=}NC_6H_4X-4))\}$-*o*$])_n$ (X = Me (**1**) and Br (**2**)) and dimeric ($Ph_3Sn[O_2CC_6H_4\{N{=}N(C_6H_3$-4-OH$(C(H){=}NC_6H_4X-4))\}$-*o*$])_2$ (X = OMe (**4**)) complexes are reported. The coordination environment in each complex is trigonal bipyramidal *trans*-Ph_3SnO_2. A single zwitterionic carboxylate ligand bridges adjacent Sn atoms via the carboxylate and phenoxide O atoms.

Keywords: Triphenyltin; Carboxylates; 4-[((*E*)-1-{2-hydroxy-5-[(*E*)-2-(2-carboxyphenyl)-1-diazenyl]phenyl}methylidene)amino]aryls; NMR; ESI-MS; Mössbauer; Crystal structure

1. Introduction

Recently, we have been investigating the 4-[((*E*)-1-{2-hydroxy-5-[(*E*)-2-(2-carboxyphenyl)-1-diazenyl]phenyl}methylidene)amino]aryl (Fig. 1) type of ligands, which contain both azo and imino linkages. These ligands structurally resemble the *N*-*p*-methoxybenzylidene-*p*-phenylazoaniline system, which is a mesogen and exhibits a nematic liquid-crystal phase [1]. The synthesis of liquid crystals based on organometallic or coordination compounds opens new perspectives in the design of mesogenic molecules. Consequently, there is currently much interest in the synthesis of metal-containing liquid crystals (metallomesogens) owing to the perceived advantages of combining the properties of a liquid-crystal system with those of transition metals [2–6]. However, to the best of our knowledge, the literature contains no report of a metallomesogen involving

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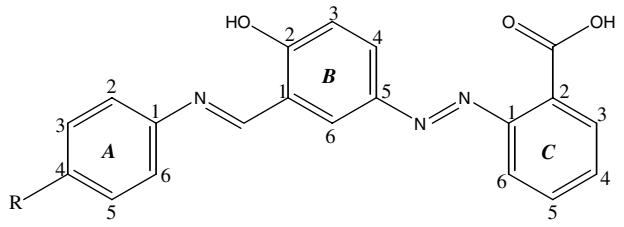

Fig. 1. Generic structure of the ligand. Abbreviations: L^1HH': R = $-CH_3$; L^2HH': R = –Br, L^3HH': R = –Cl, L^4HH': R = $-OCH_3$, where H and H′ represent hydroxyl and carboxyl protons, respectively.

tin(IV). In search of organic ligands/complexes having mesogenic behaviour, we have recently synthesized a number of 4-[((*E*)-1-{2-hydroxy-5-[(*E*)-2-(2-carboxyphenyl)-1-diazenyl]phenyl}methylidene)amino]aryl ligands and efforts have also been made to characterize these ligands by single crystal X-ray crystallographic techniques, for example, L^1HH' [this work], L^2HH' [7] and L^3HH' [1]. However, this family of ligands and its organotin(IV) derivatives await characterization as mesogens and the determination of other essential features such as thermotropic, lyotropic and macroscopic (e.g., optical) properties.

On the other hand, organotin compounds have been one of the most extensively studied class of antitumour compounds since the observation that triphenyltin acetate significantly reduced the growth rates of tumours [8,9]. Among the most active organotin antitumour agents are substituted triphenyltin benzoates, which exhibited exceptionally high in vitro activity against the human mammary tumour MCF-7 and a colon carcinoma, WiDr [10,11]. Recently, we have been examining the reactivity of 4-[((*E*)-1-{2-hydroxy-5-[(*E*)-2-(2-carboxyphenyl)-1-diazenyl]phenyl}methylidene)amino]aryls with $(Bu_3Sn)_2O$ and the structures of the resultant complexes. In the solid state, these complexes are polymeric in nature, being built from adjacent $SnBu_3$ moieties bridged by the two carboxylate O-atoms of a single aryl ligand, with the pattern then continuing indefinitely. The Sn atoms have slightly distorted trigonal bipyramidal *trans*-Bu_3SnO_2 coordination geometry with carboxylate O atoms occupying axial positions, one being from each of two aryl ligands [12]. These tributyltin(IV) complexes have shown promise as larvicides [12,13]. In addition, the tributyltin(IV) complexes were investigated by electrospray ionization (ESI) mass spectrometry [13], which is considered to be the softest and most suitable ionization technique for the analysis of organotin compounds [14], including complex structures with molecular weights (M_Ws) over 1000 Da and high polarity.

In view of the possible importance of these ligands and as a continuation of our studies of biological organotin compounds [12,13,15,16] and the structural chemistry of these complexes [12,13,15–29], we now report the synthesis and spectroscopic characterization of Ph_3SnLH complexes (where LH is the deprotonated ligand derived from 4-[((*E*)-1-{2-hydroxy-5-[(*E*)-2-(2-carboxyphenyl)-1-diazenyl]phenyl}methylidene)amino]aryls) ($L^{1-4}HH'$, Fig. 1). The complexes have been characterized in the solid state by means of ^{119m}Sn Mössbauer and IR spectroscopic techniques and in solution by ^{1}H-, ^{13}C-, ^{119}Sn-NMR and ESI mass spectrometric studies. The crystal and molecular structures of ligand L^1HH', Ph_3SnL^1H (**1**), Ph_3SnL^2H (**2**) and Ph_3SnL^4H (**4**) are also reported.

2. Experimental

2.1. Materials

Ph_3SnOH was prepared from Ph_3SnCl (Fluka) by following the literature method [30]. Salicylaldehyde (Lancaster) and the substituted anilines (reagent grade) 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. The ligands 4-[((*E*)-1-{2-hydroxy-5-[(*E*)-2-(2-carboxyphenyl)-1-diazenyl]phenyl}methylidene)amino]aryls, $L^{1-4}HH'$ were prepared and characterized as described in our earlier report [12]. The compound $Ph_3SnL^5H \cdot OH_2$ (where L^5H = deprotonated $O_2CC_6H_4$ (N=N(C_6H_3-4-OH-5-CHO)-*o*)) (**5**) was prepared by the method described in [18]. This compound has been included for convenience of discussion of ^{119}Sn chemical shifts and Mössbauer spectra (Table 3) and ESI mass spectrometric data (Section 2.3.5).

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 BOMEM DA-8 FT-IR spectrophotometer with samples investigated as KBr discs. The ^{1}H- and ^{13}C-NMR spectra of the ligands were acquired on a Bruker Avance 500 spectrometer operating at 500.13 and 125.76 MHz, respectively. For the organotin compounds, the ^{1}H-, ^{13}C- and ^{119}Sn-NMR spectra were recorded on a Bruker AMX 400 spectrometer and measured at 400.13, 100.62 and 149.18 MHz, respectively. The ^{1}H, ^{13}C and ^{119}Sn chemical shifts were referred to Me_4Si set at 0.00 ppm, $CDCl_3$ set at 77.0 ppm and Me_4Sn set at 0.00 ppm, respectively. Mössbauer spectra were recorded on solid samples at liquid nitrogen temperature by using a conventional constant acceleration spectrometer, coupled with a multichannel analyser (a.e.n., Ponteranica (BG), Italy) equipped with a cryostat Cryo (RIAL, Parma, Italy). A $Ca^{119}SnO_3$ Mössbauer source, 10 mCi (from Ritverc, St. Petersburg, Russia) moving at room temperature with constant acceleration in a triangular waveform

was used. The velocity calibration was made using a ^{57}Co Mössbauer source, 10 mCi, and an iron foil as absorber (from Ritverc, St. Petersburg, Russia). Positive-ion and negative-ion electrospray ionization (ESI) mass spectra were measured on an ion trap analyser Esquire 3000 (Bruker Daltonics, Bremen, Germany) in the mass range m/z 50–1600. The samples were dissolved in 100% acetonitrile (HPLC grade, Merck, Darmstadt, Germany) and analysed by direct infusion at a flow rate of 5 μl/min. The ion source temperature was 300 °C, the tuning parameter compound stability 100%, the flow rate and pressure of nitrogen were 4 l/min and 10 psi, respectively. The selected precursor ions were further analysed by tandem mass spectrometry (MS/MS) experiments under the following conditions: isolation width $m/z = 8$ for ions containing one tin atom and $m/z = 12$ for ions containing more tin atoms, and the collision amplitude was in the range 0.7–1.0 V depending on the precursor ion stability.

2.3. Synthesis of the triphenyltin complexes

A typical method is described below.

2.3.1. Synthesis of Ph_3SnL^1H (1)

Compound **1** was synthesized by reacting L^1HH' (0.73 g, 2.04 mmol) and Ph_3SnOH (0.75 g, 2.04 mmol) in 50 ml of anhydrous toluene in a 100 ml flask equipped with a Dean-Stark moisture trap and water-cooled condenser. The reaction mixture was refluxed for 9 h and filtered while hot. 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 crude product was obtained after evaporation and this was then recrystallized from chloroform to yield orange crystals of the desired product. Yield (0.50 g, 34.5%); m.p.: 138–40 °C. Anal. Found: C, 66.12; H, 4.45; N, 6.02%. Calc. for $C_{39}H_{31}N_3O_3Sn$: C, 66.09; H, 4.40; N, 5.92. IR (cm^{-1}): 1619 $\nu(OCO)_{asym}$. $M_W = 709$. Positive-ion MS: m/z 1457 $[2*M + K]^+$; m/z 1441 $[2*M + Na]^+$; m/z 1060 $[M + SnPh_3]^+$; m/z 748 $[M + K]^+$, 100%; m/z 732 $[M + Na]^+$; m/z 710 $[M + H]^+$. MS/MS of m/z 1457: m/z 1100 $[M + K + HSnPh_3]^+$; m/z 748 $[M + K]^+$. MS/MS of m/z 1441: m/z 1084 $[M + Na + HSnPh_3]^+$; m/z 732 $[M + Na]^+$. MS/MS of m/z 1060: m/z 982 $[M - benzene + SnPh_3]^+$; m/z 904 $[M - 2*benzene + SnPh_3]^+$; m/z 650 $[M - Ph + H_2O]^+$; m/z 632 $[M - Ph]^+$; m/z 588 $[M - Ph - CO_2]^+$; m/z 554 $[M - Ph - benzene]^+$. MS/MS of m/z 732: m/z 364 $[M + Na - HOSnPh_3]^+$. MS/MS of m/z 710: m/z 632 $[M - benzene + H]^+$; m/z 588 $[M + H - benzene - CO_2]^+$; m/z 554 $[M + H - 2*benzene]^+$; m/z 342 $[M + H - HOSnPh_3]^+$. Negative-ion MS: m/z 720 $[L^1H + Ph_2SnCl_2 + H_2O]^-$; m/z 708 $[M - H]^-$; m/z 553; m/z 439 $[Ph_3SnCl + Cl + H_2O]^-$; m/z 358 $[L^1H]^-$, 100%; m/z 314 $[L^1H - CO_2]^-$; m/z 269 $[L^5H]^-$. MS/MS of m/z 720: m/z 358 $[L^1H]^-$; m/z 314 $[L^1H - CO_2]^-$. MS/MS of m/z 708: m/z 664 $[M - H - CO_2]^-$. MS/MS of m/z 439: m/z 351 $[Ph_3Sn]^-$. MS/MS of m/z 358: m/z 314 $[L^1H - CO_2]^-$.

The other triphenyltin complexes (**2**–**4**) were prepared by reacting Ph_3SnOH with the appropriate ligand (L^2HH', L^3HH' and L^4HH') by following an analogous procedure. The characterization data of the complexes are given below, while the spectroscopic data are presented in Tables 1–3.

2.3.2. Ph_3SnL^2H (2)

Red crystals of compound **2** were obtained from a benzene–hexane mixture (1:3 v/v). Yield: 37.3%; m.p.: 132–134 °C. Anal. Found: C, 59.10; H, 3.70; N, 5.40%. Calc. for $C_{38}H_{28}BrN_3O_3Sn$: C, 58.99; H, 3.64; N, 5.42. IR (cm^{-1}): 1622 $\nu(OCO)_{asym}$. $M_W = 773$. Positive-ion MS: m/z 1585 $[2*M + K]^+$; m/z 1569 $[2*M + Na]^+$; m/z 812 $[M + K]^+$, 100%; m/z 796 $[M + Na]^+$; m/z 463. MS/MS of m/z 1585: m/z 1164 $[M + K + HSnPh_3]^+$; m/z 812 $[M + K]^+$. MS/MS of m/z 1569: m/z 1148 $[M + Na + HSnPh_3]^+$; m/z 796 $[M + Na]^+$. MS/MS of m/z 796: m/z 428 $[M + Na - HOSnPh_3]^+$. Negative-ion MS: m/z 772 $[M - H]^-$; m/z 439 $[Ph_3SnCl + Cl + H_2O]^-$; m/z 422 $[L^2H]^-$, 100%; m/z 378 $[L^2H - CO_2]^-$; m/z 269 $[L^5H]^-$. MS/MS of m/z 772: m/z 728 $[M - H - CO_2]^-$. MS/MS of m/z 439:

Table 1
^{1}H-NMR data (δ, ppm) for the triphenyltin complexes **1**–**4** in $CDCl_3$

Ring[a]/other/Sn–Ph[b] protons	Proton number	Compound			
		1	**2**	**3**	**4**
A	2	7.28	7.41	7.42	7.26
	3	7.19	7.12	7.19	6.98
	5	7.19	7.12	7.19	6.98
	6	7.28	7.41	7.42	7.26
B	3	6.99	6.90	7.00	6.98
	4	7.81	7.82	7.83	7.80
	6	7.91	7.91	7.91	7.91
C	3	7.81	7.82	7.83	7.80
	4	7.57	7.56	7.57	7.57
	5	7.41	7.56	7.42	7.40
	6	7.57	7.56	7.57	7.57
Other	C(H)=N	8.38	8.47	8.31	8.48
	OH	14.0	13.5	13.6	14.0
	CH_3/OCH_3	2.41	–	–	3.89
Sn–Ph	2*	7.75	7.75	7.75	7.75
	3*	7.41	7.41	7.42	7.40
	4*	7.41	7.41	7.42	7.40

[a] Refer to Fig. 1 for the numbering scheme of the ligand skeleton (Ring A, B and/or C) in compounds **1**–**4**.

[b] The numbering scheme for the Sn–Ph skeleton is as shown below:

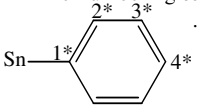

Table 2
^{13}C-NMR data (δ, ppm) for the triphenyltin **1**–**4** complexes in $CDCl_3$

Ring[a]/other/Sn–Ph[b] carbon	Carbon number	Compound			
		1	**2**	**3**	**4**
A	1	145.1	145.8	145.8	140.6
	2	121.1	122.9	122.5	122.4
	3	130.1	132.6	130.2	114.8
	4	138.4	120.9	138.4	159.4
	5	130.1	132.6	130.2	114.8
	6	121.1	122.9	122.5	122.4
B	1	118.8	118.7	118.6	118.9
	2	164.4	164.0	164.0	164.2
	3	118.1	118.1	118.1	118.0
	4	127.9	128.4	128.4	127.7
	5	145.7	146.9	146.4	145.6
	6	128.3	128.6	128.6	128.1
C	1	152.0	152.2	152.2	152.3
	2	130.5	130.5	130.6	130.6
	3	128.6	129.2	129.2	128.6
	4	129.2	129.3	129.7	129.2
	5	131.6	131.6	131.6	131.6
	6	118.7	118.6	118.3	118.7
Other	C(H)=N	161.2	162.7	162.6	159.9
	CH_3/OCH_3	21.1	–	–	55.6
	COO	174.6	174.3	174.5	174.8
Sn–Ph	1*	137.5	138.4	138.4	138.4
	2*	136.9	136.9	136.9	136.9
	3*	128.9	128.9	128.9	128.9
	4*	130.1	130.2	130.2	130.2

[a] Refer to Fig. 1 for the numbering scheme of the ligand skeleton (Ring A, B and/or C) in compounds **1**–**4**.
[b] The numbering scheme for the Sn–Ph skeleton is as shown in Table 1.

Table 3
^{119}Sn-NMR data (δ, ppm) and ^{119}Sn Mössbauer parameters (mm s^{-1}) for the triphenyltin complexes **1**–**5**

Compound	^{119}Sn-NMR data[a]	^{119}Sn Mössbauer data[b]				
		δ	Δ	$\rho = \Delta/\delta$	Γ_1	Γ_2
1	−109.7	1.24	3.00	2.42	0.90	0.92
2	−109.8	1.27	3.05	2.40	0.85	0.91
3	−109.7	1.26	2.97	2.36	0.88	0.87
4	−109.8	1.25	2.98	2.38	0.84	0.80
5[c]	−108.0	1.30	3.30	2.53	0.84	0.95

[a] In $CDCl_3$ solution.
[b] Parameters: δ, isomer shifts; Δ, quadrupole splitting; Γ_1 and Γ_2: line widths.
[c] ^{119}Sn-NMR and ^{119}Sn Mössbauer data for compound **5** ({Ph_3Sn-[$O_2CC_6H_4$(N=N(C_6H_3-4-OH-5-CHO))-*o*]OH_2}) [18] have now been obtained and included for convenience of discussion.

m/z 351 $[Ph_3Sn]^-$. MS/MS of *m/z* 422: *m/z* 378 $[L^2H - CO_2]^-$.

2.3.3. Ph_3SnL^3H (*3*)

Orange crystals of compound **3** were obtained from a benzene–hexane mixture (1:3 v/v). Yield: 35.6%; m. p.: 146–148 °C. Anal. Found: C, 62.40; H, 3.90; N, 5.80%. Calc. for $C_{38}H_{28}ClN_3O_3Sn$: C, 62.61; H, 3.87; N, 5.76. IR (cm^{-1}): 1616 $\nu(OCO)_{asym}$. $M_W = 729$. Positive-ion MS: *m/z* 1497 $[2*M + K]^+$; *m/z* 1481 $[2*M + Na]^+$; *m/z* 768 $[M + K]^+$, 100%; *m/z* 752 $[M + Na]^+$; *m/z* 463. MS/MS of *m/z* 1499: *m/z* 1120 $[M + K + HSnPh_3]^+$; *m/z* 768 $[M + K]^+$. MS/MS of *m/z* 1483: *m/z* 1104 $[M + Na + HSnPh_3]^+$; *m/z* 752 $[M + Na]^+$. MS/MS of *m/z* 752: *m/z* 384 $[M + Na - HOSnPh_3]^+$; *m/z* 351 $[SnPh_3]^+$. Negative-ion MS: *m/z* 728 $[M - H]^-$; *m/z* 439 $[Ph_3SnCl + Cl + H_2O]^-$; *m/z* 378 $[L^3H]^-$, 100%; *m/z* 334 $[L^3H - CO_2]^-$; *m/z* 269 $[L^5H]^-$. MS/MS of *m/z* 728: *m/z* 684 $[M - H - CO_2]^-$. MS/MS of *m/z* 439: *m/z* 351 $[Ph_3Sn]^-$. MS/MS of *m/z* 378: *m/z* 334 $[L^3H - CO_2]^-$.

2.3.4. Ph_3SnL^4H (*4*)

Red-brown crystals of compound **4** were obtained from benzene. Yield: 38%; m.p.: 136–138 °C. Anal. Found: C, 64.60; H, 4.27; N, 5.80%. Calc. for $C_{39}H_{31}N_3O_4Sn$: C, 64.67; H, 4.30; N, 5.80. IR (cm^{-1}): 1619 $\nu(OCO)_{asym}$. $M_W = 725$. Positive-ion MS: *m/z* 1489 $[2*M + K]^+$; *m/z* 1473 $[2*M + Na]^+$; *m/z* 1076 $[M + SnPh_3]^+$; *m/z* 764 $[M + K]^+$, 100%; *m/z* 748 $[M + Na]^+$; *m/z* 726 $[M + H]^+$. MS/MS of *m/z* 1489: *m/z* 1116 $[M + K + HSnPh_3]^+$; *m/z* 764 $[M + K]^+$. MS/MS of *m/z* 1473: *m/z* 1100 $[M + Na + HSnPh_3]^+$; *m/z* 748 $[M + Na]^+$. MS/MS of *m/z* 1076: *m/z* 998 $[M - benzene + SnPh_3]^+$; *m/z* 920 $[M - 2*benzene + SnPh_3]^+$; *m/z* 666 $[M - Ph + H_2O]^+$; *m/z* 648 $[M - Ph]^+$; *m/z* 604 $[M - Ph - CO_2]^+$. *m/z* 570 $[M - Ph - benzene]^+$. MS/MS of *m/z* 764: *m/z* 686 $[M + K - benzene]^+$; *m/z* 642 $[M + K - benzene - CO_2]^+$; *m/z* 396 $[M + K - HOSnPh_3]^+$; *m/z* 270. MS/MS of *m/z* 748: *m/z* 626 $[M + Na - benzene - CO_2]^+$; *m/z* 380 $[M + Na - HOSnPh_3]^+$. MS/MS of *m/z* 726: *m/z* 648 $[M + H - benzene]^+$; *m/z* 604 $[M + H - benzene - CO_2]^+$; *m/z* 570 $[M + H - 2*benzene]^+$; *m/z* 358 $[M + H - HOSnPh_3]^+$. Negative-ion MS: *m/z* 1099 $[M + ligand]^-$; *m/z* 736 $[L^4H + Ph_2SnCl_2 + H_2O]^-$; *m/z* 724 $[M - H]^-$; *m/z* 553; *m/z* 439 $[Ph_3SnCl + Cl + H_2O]^-$; *m/z* 374 $[L^4H]^-$, 100%; *m/z* 330 $[L^4H - CO_2]^-$; *m/z* 269 $[L^5H]^-$. MS/MS of *m/z* 1099: *m/z* 374 $[L^4H]^-$. MS/MS of *m/z* 736: *m/z* 374 $[L^4H]^-$; *m/z* 330 $[L^4H - CO_2]^-$; *m/z* 315 $[L^4H - CO_2 - CH_3]^{-\cdot}$. MS/MS of *m/z* 724: *m/z* 680 $[M - CO_2]^-$; *m/z* 665 $[M - CO_2 - CH_3]^{-\cdot}$. MS/MS of *m/z* 439: *m/z* 351 $[Ph_3Sn]^-$. MS/MS of *m/z* 374: *m/z* 330 $[L^4H - CO_2]^-$; *m/z* 315 $[L^4H - CO_2 - CH_3]^{-\cdot}$.

2.3.5. $Ph_3SnL^5H \cdot OH_2$ (*5*)

ESI-MS data: $M_W = 620$ (Ph_3SnL^5H). Positive-ion MS: *m/z* 659 $[M + K]^+$, 100%; *m/z* 643 $[M + Na]^+$; *m/z* 463. MS/MS of *m/z* 659: *m/z* 581 $[M + K - benzene]^+$; *m/z* 537 $[M + K - CO_2 - benzene]^+$; *m/z* 503 $[M + K - 2*benzene]^+$; *m/z* 291 $[M + K - HOSnPh_3]^+$. MS/MS of *m/z* 643: *m/z* 565 $[M + Na - benzene]^+$; *m/z* 521 $[M + Na - CO_2 - benzene]^+$; *m/z* 487 $[M + Na -$

Table 4
Crystallographic data and structure refinement parameters for the ligand **L^{1}HH′** and triphenyltin complexes **1**, **2** and **4**

	L^{1}HH′	**1**	**2**	**4**
Empirical formula	$C_{21}H_{17}N_3O_3 \cdot 0.5H_2O$	$C_{39}H_{31}N_3O_3Sn$	$C_{38}H_{28}BrN_3O_3Sn$	$C_{78}H_{62}N_6O_8Sn_2$
Formula weight	368.39	708.29	773.16	1448.58
Crystal size (mm)	$0.10 \times 0.2 \times 0.20$	$0.10 \times 0.12 \times 0.35$	$0.05 \times 0.22 \times 0.27$	$0.05 \times 0.20 \times 0.25$
Crystal shape	Prism	Tablet	Plate	Plate
Temperature (K)	160(1)	273(1)	160(1)	160(1)
Crystal system	Monoclinic	Monoclinic	Monoclinic	Triclinic
Space group	*C*2/*c*	$P2_1/c$	$P2_1/c$	$P\bar{1}$
a (Å)	13.0688(4)	9.5782(1)	9.9665(1)	9.3588(3)
b (Å)	21.8141(6)	15.7608(2)	15.5199(2)	11.1570(3)
c (Å)	12.5941(4)	22.0905(3)	21.4797(2)	16.0416(5)
α (°)	90	90	90	79.173(2)
β (°)	92.487(2)	98.8889(7)	101.2908(8)	80.388(1)
γ (°)	90	90	90	77.642(2)
V (Å^3)	3587.0(2)	3294.73(7)	3258.16(6)	1592.98(8)
Z	4	4	4	1
D_x (g cm^{-3})	1.364	1.428	1.576	1.510
μ (mm^{-1})	0.0948	0.817	2.056	0.849
Transmission factors (min,max)	–	0.820, 0.932	0.581, 0.912	0.835, 0.980
$2\theta_{max}$ (°)	55	55	60	60
Reflections measured	39,399	72,870	78,938	41,734
Independent reflections (R_{int})	4113 (0.079)	7563 (0.068)	9509 (0.094)	9281 (0.079)
Reflections with $I > 2\sigma(I)$	2633	5519	7292	6941
Number of parameters	263	420	419	429
$R(F)$ [$I > 2\sigma(I)$ reflections]	0.050	0.036	0.038	0.043
$wR(F^2)$ (all data)	0.136	0.093	0.094	0.091
GOF(F^2)	1.02	1.05	1.04	1.03
$\Delta\rho_{max,min}$ (e/Å^3)	0.29, −0.19	0.95, −0.65	0.90, −1.31	0.54, −1.15

2*benzene]$^+$; *m/z* 351 [$SnPh_3$]$^+$; *m/z* 275 [M + Na − $HOSnPh_3$]$^+$; *m/z* 270. Negative-ion MS: *m/z* 619 [M − H]$^-$; *m/z* 439 [$Ph_3SnCl + Cl + H_2O$]$^-$; *m/z* 269 [L^5H]$^-$, 100%; *m/z* 225 [$L^5H - CO_2$]$^-$; *m/z* 197 [$L^5H - CO - CO_2$]$^-$. MS/MS of *m/z* 619: *m/z* 575 [M − H − CO_2]$^-$; *m/z* 547 [M − H − CO − CO_2]$^-$. MS/MS of *m/z* 439: *m/z* 351 [Ph_3Sn]$^-$. MS/MS of *m/z* 269: *m/z* 225 [$L^5H - CO_2$]$^-$; *m/z* 197 [$L^5H - CO - CO_2$]$^-$. MS/MS of *m/z* 225: *m/z* 197 [$L^5H - CO - CO_2$]$^-$. MS/MS of *m/z* 197: *m/z* 170 [$L^5H - CO - CO_2 - N_2$]$^{-\cdot}$; *m/z* 92 [$L^5H - CO - CO_2 - N_2$ − benzene]$^{-\cdot}$.

2.4. X-ray crystallography

Crystals of the compounds suitable for an X-ray crystal-structure determination were obtained from toluene (L^{1}HH′), chloroform (**1**), benzene/hexane (**2**) and benzene (**4**) by slow evaporation of the solvent at room temperature. All measurements were made at low temperature (except for **1**, the crystals of which did not survive cooling to 160 K) on a Nonius KappaCCD diffractometer [31] with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) and an Oxford Cryosystems Cryostream 700 cooler. Data reduction was performed with HKL Denzo and Scalepack [32]. The intensities were corrected for *Lorentz* and polarization effects, and an empirical absorption correction based on the multi-scan method [33] was applied, except in the case of L^{1}HH′. Equivalent reflections were merged. The data collection and refinement parameters are given in Table 4. Views of the structures are shown in Figs. 2–4. The structure of **4** was solved by heavy-atom Patterson methods [34],

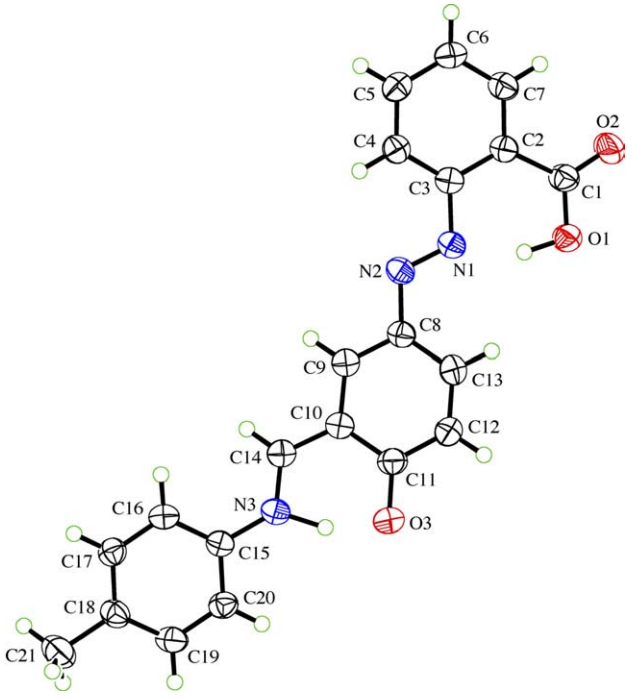

Fig. 2. View of the molecule of L^{1}HH′ showing the atom-labelling scheme (50% probability ellipsoids).

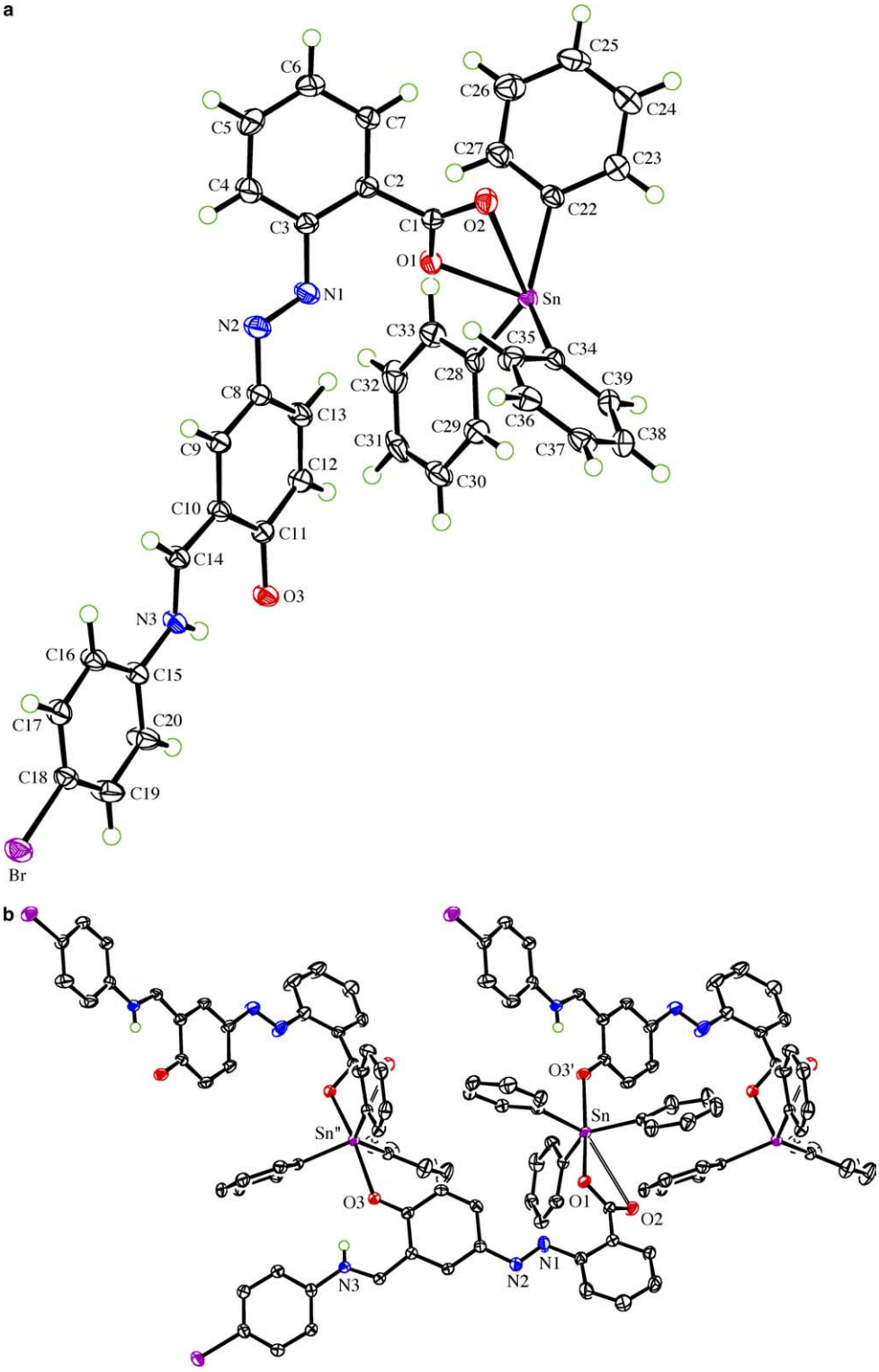

Fig. 3. (a) The asymmetric unit of $[Ph_3SnL^2H]_n$ (**2**) showing the atom-labelling scheme (50% probability ellipsoids). (b) A three-unit segment of the polymeric $[Ph_3SnL^2H]_n$ chain in **2** (50% probability ellipsoids).

followed by the Fourier expansion routine of DIRDIF94 [35]. The other structures were solved by direct methods by using SIR92 [36]. For each structure, the non-hydrogen atoms were refined anisotropically.

In L^1HH', the asymmetric unit contains one molecule of the carboxylic acid in a general position plus a water molecule that sits on a C_2-axis. In **4**, the dinuclear molecule sits across a crystallographic centre of inversion.

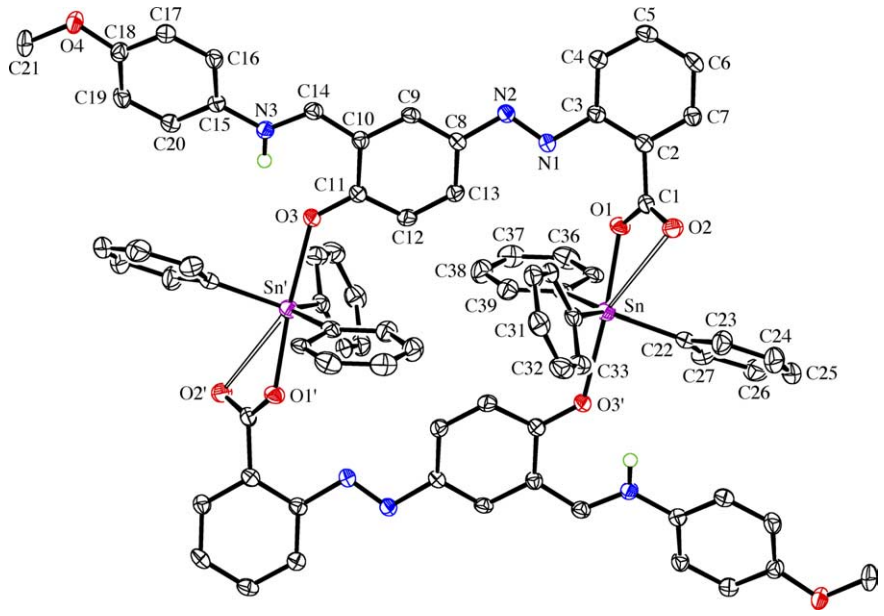

Fig. 4. The cyclic dinuclear moiety of $[Ph_3SnL^4H]_2$ (**4**) with the atom-labelling scheme (50% probability ellipsoids).

The symmetry-unique H-atom of the water molecule and the carboxylic acid H-atom of L^1HH', as well as the H-atom of the protonated imine group of **1**, **2** and **4** were placed in the positions indicated by a difference electron density map and their positions were allowed to refine together with individual isotropic displacement parameters. All remaining H-atoms in each structure 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 $1.2U_{eq}$ of its parent atom ($1.5U_{eq}$ for methyl groups). The refinement of each structure was carried out on F^2 using full-matrix least-squares procedures, which minimized the function $\sum w(F_o^2 - F_c^2)^2$. A correction for secondary extinction was applied in the case of L^1HH'. Three reflections, whose intensities were considered to be extreme outliers, were omitted from the final refinement of L^1HH' and **1**. All calculations were performed using the SHELXL97 [37] program.

3. Results and discussion

3.1. Spectroscopy

Diagnostically important infrared absorption frequencies for the carboxylate antisymmetric [ν_{asym}(OCO)] stretching vibration of the triphenyltin complexes (**1**–**4**) are given in Section 2. 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 ligands ($L^{1-4}HH'$) appears at $\sim$1725 cm^{-1} [12]. In the triphenyltin complexes, the carbonyl stretching frequency appears at $\sim$1620 cm^{-1}. The shift of the band relative to its position for the free ligand is ascribed to carboxylate coordination in accordance with earlier reports [12,24,25].

The ^{1}H- and ^{13}C-NMR data of $L^{1-4}HH'$ are reported in our earlier [12] and 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 (Tables 1 and 2, respectively) of the triphenyltin moiety are straightforward from the multiplicity patterns, resonance intensities and also by examining the $^nJ(^{13}C–^{119/117}Sn)$ coupling constants [22,24,25]. The ^{1}H-NMR integration values were completely consistent with the formulation of the products. The ^{119}Sn-NMR chemical shifts of the triphenyltin complexes (**1**–**4**) in $CDCl_3$ solution are listed in Table 3. The complexes exhibit a single sharp resonance at ca. −109 ppm, suggesting that the complexes are isostructural in solution where the tin atom is four-coordinate [22,24,38]. In contrast, the solid-state polymeric structures found for complexes **1** and **2**, and the dimeric structure observed for complex **4** reveal five-coordinate tin atoms (vide infra). It is anticipated that the multi-nuclear structures break down in solution to generate a monomeric four-coordinate tetrahedral structure [22].

The Mössbauer results from the complexes are listed in Table 3. The ratio of the quadrupole splitting (Δ) value to isomer shift (δ) value ($\rho = \Delta/\delta$) can be used to distinguish between the different coordination states of the central tin atom [39]. Tin compounds which are four coordinate have ρ values less than 1.8 while ρ values larger than 2.1 would indicate compounds with greater than four coordination. All the complexes have similar

δ, Δ parameters and ρ values greater than 2.1 suggesting that the complexes are isostructural with a coordination number greater than four. Furthermore, the triphenyltin complexes exhibited Δ values of 3.00 mm s^{-1} which correspond with a trigonal bipyramidal geometry around the tin atom [40–42] and is in agreement with structures determined from X-ray crystallography (see Section 3.2) after ignoring the long Sn···O contact, which has no effect on the trigonal bipyramidal geometry.

The ESI mass spectra of the triphenyltin(IV) complexes (**1**–**5**; see Section 2.3) are very complex due to the formation of various unexpected adducts and the presence of a wide range of fragment ions in the first-order mass spectra, which complicates the interpretation of the spectra [43–47]. The assignments of the individual ions are therefore based on the combination of measurements of positive-ion, negative-ion and multistage tandem mass spectrometric (MS^n) experiments, which provide the most comprehensive and reliable results for the structure confirmation [48–51]. The typical ions in the first-order positive-ion ESI mass spectra are the sodium and potassium ion adducts with the molecule, which is used for the determination of the molecular weights (M_W) of the organotin compounds **1**–**5**. Moreover, the dimeric ions $[2*M + K]^+$ and $[2*M + Na]^+$ with significantly lower relative abundances are present as well. The presence of these dimeric ions, together with their tandem mass spectra, is a useful tool for the confirmation of the M_W. The formation of other unusual adducts is observed, such as adducts with the triphenyltin fragment ion (e.g., $[M - benzene + SnPh_3]^+$), water or Ph_2SnCl_2. The correctness of these assignments was supported by comparison of the theoretical and experimental isotopic distributions and tandem mass spectrometric experiments. The formation of similar adducts has already been reported in the literature [43]. The base peaks of the first-order negative ESI mass spectra are the $[ligand]^-$ ions (i.e., $[M - SnPh_3]^-$ written in the different notation), which are formed by cleavage of the most labile bond between the tin and oxygen atoms. The deprotonated molecule $[M - H]^-$ is also observed in the spectra and confirm the MS assignment. The characteristic neutral losses in the tandem mass spectra, such as CO, CO_2, acetic acid, benzene, $HOSnPh_3$, etc., show the presence of these functionalities in the structures.

3.2. X-ray crystallography

In the crystal structure of L^1HH', the asymmetric unit contains one molecule of the carboxylic acid in a general position plus a water molecule that sits on a C_2-axis, thereby giving a carboxylic acid:water ratio of 2:1. The three ring system of L^1HH' has an extended conformation with both external rings slightly twisted with respect to the central aromatic ring (Fig. 2). The bond lengths and angles (Table 5) within the molecule are similar to those found in the 4-Cl analogue (L^3HH') [1]. The carboxylic acid group is coplanar with its parent phenyl ring [O(1)–C(1)–C(2)–C(7) = 174.8(1)°]. The carboxylic acid molecule appears to be a zwitterion. The electron density peak associated with the expected phenolic H-atom was found to be closer to the imine N-atom (Table 6), although a plotted difference *Fourier* map of the region suggested that the electron density due to this H-atom is quite smeared out. Plots of difference *Fourier* maps with the H-atom position idealized firstly on the O-atom and then on the N-atom showed that neither idealized position fitted the observed electron density optimally, although a better match was obtained when the N-atom was considered to be protonated.

The carboxylic acid hydroxy group in L^1HH' forms an intramolecular hydrogen bond with the nearest adjacent azo N-atom, while the protonated imine N–H atom forms an intramolecular hydrogen bond with the adjacent deprotonated phenolic hydroxy O-atom. Both of these interactions form six-membered loops with a graph set motif [52] of S(6). In addition, one H-atom of the water molecule forms an intermolecular hydrogen bond with the carbonyl O-atom of the carboxylic acid group of one L^1HH' molecule. The C_2-symmetry of

Table 5
Selected bond lengths (Å) and angles (°) for **L^1HH'**

C(18)–C(21)	1.504(2)
O(1)–C(1)	1.329(2)
O(2)–C(1)	1.211(2)
O(3)–C(11)	1.303(2)
N(1)–N(2)	1.270(2)
N(1)–C(3)	1.424(2)
N(2)–C(8)	1.403(2)
N(3)–C(14)	1.295(2)
N(3)–C(15)	1.415(2)
N(2)–N(1)–C(3)	115.0(1)
N(1)–N(2)–C(8)	115.6(1)
C(14)–N(3)–C(15)	125.2(1)
O(2)–C(1)–O(1)	119.6(2)
O(2)–C(1)–C(2)	122.3(2)
O(1)–C(1)–C(2)	118.2(1)
C(4)–C(3)–N(1)	122.2(1)
C(2)–C(3)–N(1)	117.5(1)
C(9)–C(8)–N(2)	115.6(1)
N(3)–C(14)–C(10)	120.5(1)
C(16)–C(15)–N(3)	123.6(1)
C(20)–C(15)–N(3)	117.0(1)

Table 6
Hydrogen bonding geometry (Å,°) for **L^1HH'**

D–H···A	D–H	H···A	D···A	D–H···A
O(1)–H(1)···N(1)	1.00(3)	1.63(3)	2.582(2)	156(2)
N(3)–H(3)···O(3)	1.17(3)	1.42(3)	2.533(2)	156(2)
O(22)–H(22)···O(2′)	0.99(2)	1.89(3)	2.866(2)	169(2)

Primed atoms refer to the molecule in the symmetry related position: $2 - x$, y, $\frac{1}{2} - z$.

the water molecule means that the second H-atom of the water molecule forms an identical intermolecular hydrogen bond with a second carboxylic group of another L^1HH' molecule. The net result is the formation of a discrete hydrogen-bonded trimeric unit consisting of one water molecule and two molecules of the ligand molecules.

The crystal structures of complexes **1** and **2** are isostructural and the principal geometric parameters do not differ significantly (Table 7). Both compounds exhibit the same polymeric *trans*-R_3SnO_2 structural motif, in which adjacent $SnPh_3$ moieties are bridged by a single carboxylate ligand via one carboxylate O-atom and the phenoxide O-atom, with the pattern then continuing indefinitely, as illustrated in Fig. 3(a) and (b). Each Sn-atom has a slightly distorted trigonal bipyramidal coordination geometry with equatorial phenyl groups and the carboxylate and phenoxide O atoms from two different carboxylate ligands occupying axial positions. A polymeric structure with a similar mode of coordination and geometry about the Sn-atom was observed in $Ph_3Sn(2\text{-}OHC_6H_4C(H){=}NCH_2COO)_n$ [41]. The carbonyl O-atom of the carboxylate group of the carboxylate ligand in **1** and **2** also coordinates very weakly to the Sn-atom via long Sn···O(2) bonds of 3.071(2) and 3.092(2) Å, respectively. 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. Similar additional weak Sn···O coordination was also observed in the structures of related polymeric $[Bu_3SnLH]_n$ derivatives [12,13].

Table 7
Selected bond lengths (Å) and angles (°) for **1**, **2** and **4**[a]

	1	2	4
Sn–O(1)	2.155(2)	2.163(2)	2.161(2)
Sn–O(3)^{i}	2.380(2)	2.370(2)	2.367(2)
Sn···O(2)	3.071(2)	3.092(2)	3.253(2)
Sn–C(22)	2.130(3)	2.136(3)	2.133(3)
Sn–C(28)	2.141(3)	2.138(3)	2.145(3)
Sn–C(34)	2.142(3)	2.144(3)	2.141(3)
O(1)–Sn–O(3)^{i}	170.70(7)	172.71(7)	173.11(6)
O(1)–Sn–C(22)	90.38(9)	89.42(8)	100.36(8)
O(1)–Sn–C(28)	89.17(9)	89.26(8)	95.38(9)
O(1)–Sn–C(34)	97.25(9)	96.38(8)	83.01(8)
O(3)^{i}–Sn–C(22)	86.42(9)	89.74(8)	83.98(8)
O(3)^{i}–Sn–C(28)	84.74(8)	84.75(8)	87.23(8)
O(3)^{i}–Sn–C(34)	91.31(9)	89.50(8)	90.31(8)
C(22)–Sn–C(28)	118.8(1)	118.2(1)	117.5(1)
C(22)–Sn–C(34)	132.9(1)	132.9(1)	115.1(1)
C(28)–Sn–C(34)	107.8(1)	108.6(1)	126.7(1)

[a] Atom labels with superscript "i" refer to atoms from (i) the next symmetrically related ligand in the polymeric chain for **1** and **2** (symmetry code: $1-x, \frac{1}{2}+y, \frac{1}{2}-z$) and (ii) the centrosymmetrically related ligand in the dinuclear moiety for **4** (symmetry code: $-x, 1-y, 1-z$).

Although the same slightly distorted trigonal bipyramidal *trans*-R_3SnO_2 structural motif is found in complex **4**, the polymeric structures found for **1** and **2** are not repeated in the structure of **4**. Instead, the structure of **4** consists of discrete cyclic centrosymmetric dimers with two Ph_3Sn entities being bridged by two carboxylate anions through their carboxylate and phenoxide O-atoms (Fig. 4). Despite the dimerization instead of polymerization, the coordination geometry about the Sn-atom is virtually the same as that found for complexes **1** and **2** (Table 7), including the presence of the additional weak Sn···O(2) interaction of 3.253(2). The tin atom coordination geometry found for complexes **1**, **2** and **4** is in good agreement with that inferred from ^{119m}Sn Mössbauer spectroscopy (see Section 3.1).

The bridging of the Sn-atoms via one carboxylate and the phenoxide O-atoms of the carboxylate ligand in the structures of complexes **1**, **2** and **4** is in stark contrast to the mode present in the structures of the related polymeric $[Bu_3SnLH]_n$ derivatives [12,13], where both carboxylate O-atoms are involved in the bridge and the phenolic O-atom is non-coordinating. As the LH ligands are closely related in all of these structures, the change in ligand coordination mode must be influenced by the steric influence of the core R_3Sn moiety. The flexible and less bulky Bu_3Sn moieties allow coordination by both carboxylate O-atoms of the carboxylate ligand, so that there is only a short O–C–O spacer between adjacent Sn-atoms. In such arrangements, known as the type **II** polymeric motif for R_3SnO_2CR' compounds [22], the Sn···Sn distance has been found to be in the range of 5.1–5.6 Å [12,53]. The more bulky arrangement caused by the phenyl groups about the Ph_3Sn core does not allow sufficient room for adjacent Sn-atoms to be separated by only an O–C–O spacer, so the much larger 11 atom spacer offered by the use of the phenoxide O-atom as the second coordinating atom of the ligand in complexes **1**, **2** and **4** is preferred. The coordination mode observed in complexes **1**, **2** and **4** results in much larger Sn···Sn distances of 8.2725(3), 8.0508(3) and 7.9219(4) Å, respectively. These results suggest that the preferred coordination mode of 4-[((*E*)-1-{2-hydroxy-5-[(*E*)-2-(2-carboxyphenyl)-1-diazenyl]phenyl}methylidene)amino]aryl and related ligands is via both carboxylate O-atoms when steric conditions permit.

The carboxylate ligand in complexes **1**, **2** and **4** is in a zwitterionic form similar to that found for the structure of L^1HH', as the H-atom was clearly located and refined to a position close to the imine N-atom, rather than being near to the phenolic O-atom. The N(3)–H and H···O(3) distances are in the range 0.77–0.83 and 1.92–1.95 Å and show that the imine N–H group forms an intramolecular hydrogen bond with the phenoxide O(3) atom. The zwitterionic nature of the ligand in these triphenyltin complexes is in contrast to the arrangement found in the tributyltin analogues where the phenolic H-atom remains associated with the phenolic O-atom

[12,13]. The preference for the formation of the zwitterionic form of the ligand in complexes **1**, **2** and **4** may be a result of the coordination of the phenoxide O-atom to the Sn-atom, whereas the phenolic O-atom is not involved in coordination in the tributyltin analogues. Nonetheless, zwitterionic forms are quite commonly encountered in similar systems [41,54–56].

4. Supplementary material

CCDC-265053–CCDC-265056 contain the supplementary crystallographic data for L^1HH' and complexes **1**, **2** and **4**, 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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