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Synthesis and Characterization of Some Triphenyltin(IV) Complexes from Sterically Crowded [((*E*)-1-{2-Hydroxy-5-[(*E*)-2-(aryl)-1-diazenyl]phenyl}methylidene)amino]acetate Ligands and Crystal Structure Analysis of a Tetrameric Triphenyltin(IV) Compound

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Abstract Four new triphenyltin(IV) complexes containing [((*E*)-1-{2-hydroxy-5-[(*E*)-2-(aryl)-1-diazenyl]phenyl}methylidene)amino]acetate ligands (L) have been synthesized with formulations of Ph_3SnLH. They have been studied by multinuclear (^1H, ^{13}C, ^{119}Sn) NMR, ^{119}Sn Mössbauer and IR spectroscopy. A full characterization of one complex, Ph_3SnL^1H (**1**), was accomplished by single crystal X-ray crystallography, which revealed the compound to be a macrocyclic tetramer. In the tetramer, the five coordinate tin atoms have distorted trigonal bipyramidal geometries with the three phenyl groups occupying equatorial positions, while an oxygen atom of the carboxylate group of one L ligand and the oxide O-atom (formerly the hydroxy group) of a second L ligand in an apical positions. The carboxylate ligands bridge adjacent tin atoms and coordinate in the zwitterionic form with the phenolic proton moved to the nearby nitrogen atom. ^{119}Sn NMR results indicate that the tetrameric structures of the complexes in the solid state, in which the tin atoms are five-coordinated, dissociate in solution to yield four coordinate monomeric species.

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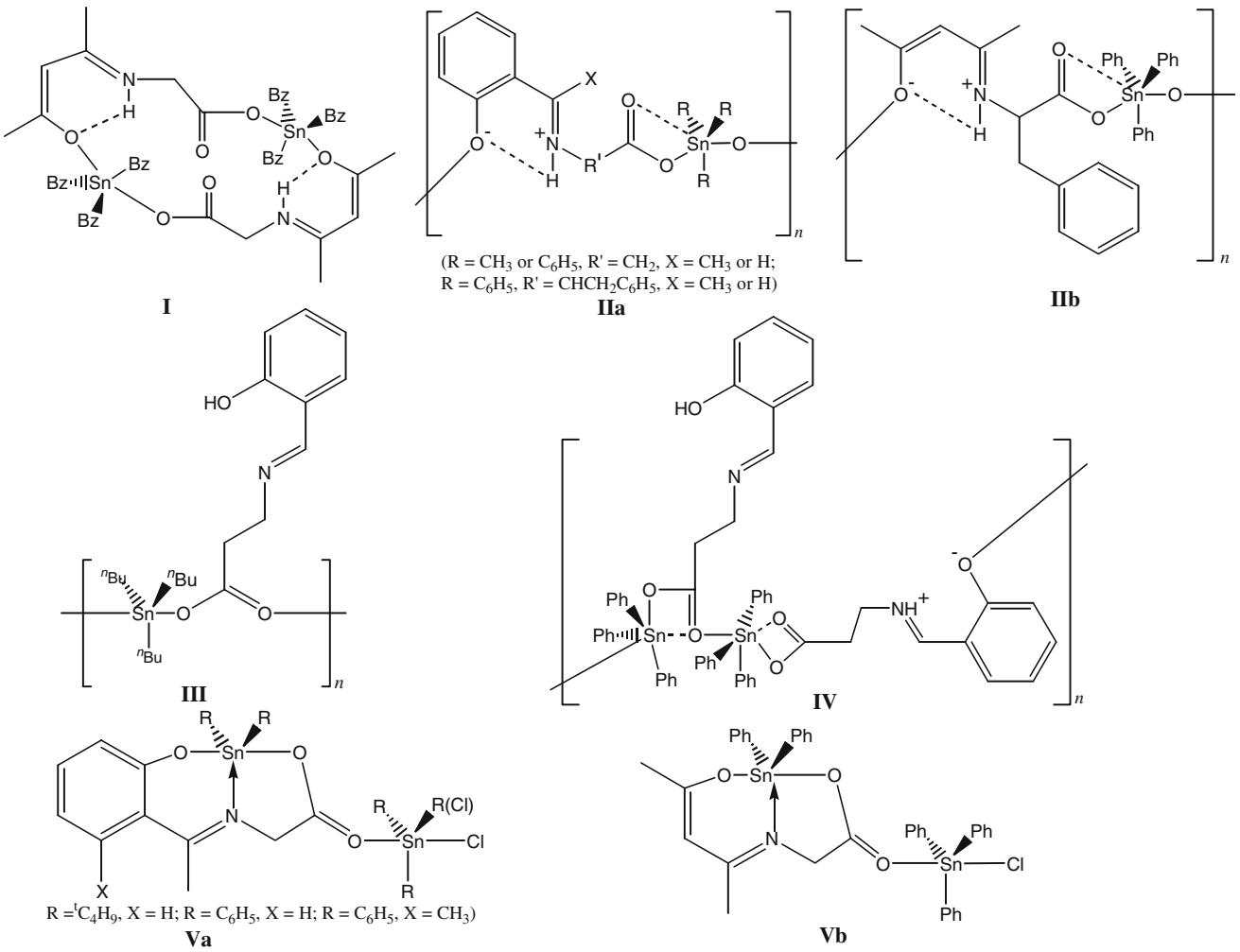
1 Introduction

Organotin(IV) carboxylates have been found to show a variety of interesting molecular architectures [1, 2]. The construction of multidimensional architectures depends on the combination of several factors including the type of organic ligands, tin-R groups, tin coordination geometry preferences and metal-to-ligand molar ratio. The self-assembly of organotin(IV) complexed Schiff bases containing the amino acetate moiety is particularly attractive, since it can be accomplished in one-pot reactions, and the complexes have attracted much interest owing to their novel structural possibilities and therapeutic activity [3–14]. Recent reports on the structures of such complexes [3–14] show that Schiff base-amino acid systems are very versatile ligands, with considerable configurational flexibility creating the possibility of a variety of coordination modes, which are well-characterised. Thus, such Schiff bases are important building-blocks in the design of extended structures because of the type and position of the donor atoms that allow tin atoms to be linked together in diverse coordination modes. An overview showing the coordination behaviour of Schiff bases with amino acids towards the triorganotin(IV) moiety (motifs **I–V**) is shown in Scheme 1. Considering this important information and continuing our studies on tin carboxylates, we further report on the synthesis of some triphenyltin(IV) complexes of composition Ph_3SnLH where the ligand, LH, is [((*E*)-1-{2-hydroxy-5-[(*E*)-2-(aryl)-1-diazenyl]phenyl}methylidene)amino]acetate (Scheme 2),



Scheme 1 An overview showing the coordination behaviour of Schiff bases with amino acids towards the triorganotin(IV) moiety

which is sterically crowded**.** The complexes have been characterized by spectroscopic methods and in a representative case by single crystal X-ray crystallography.

2 Experimental Section

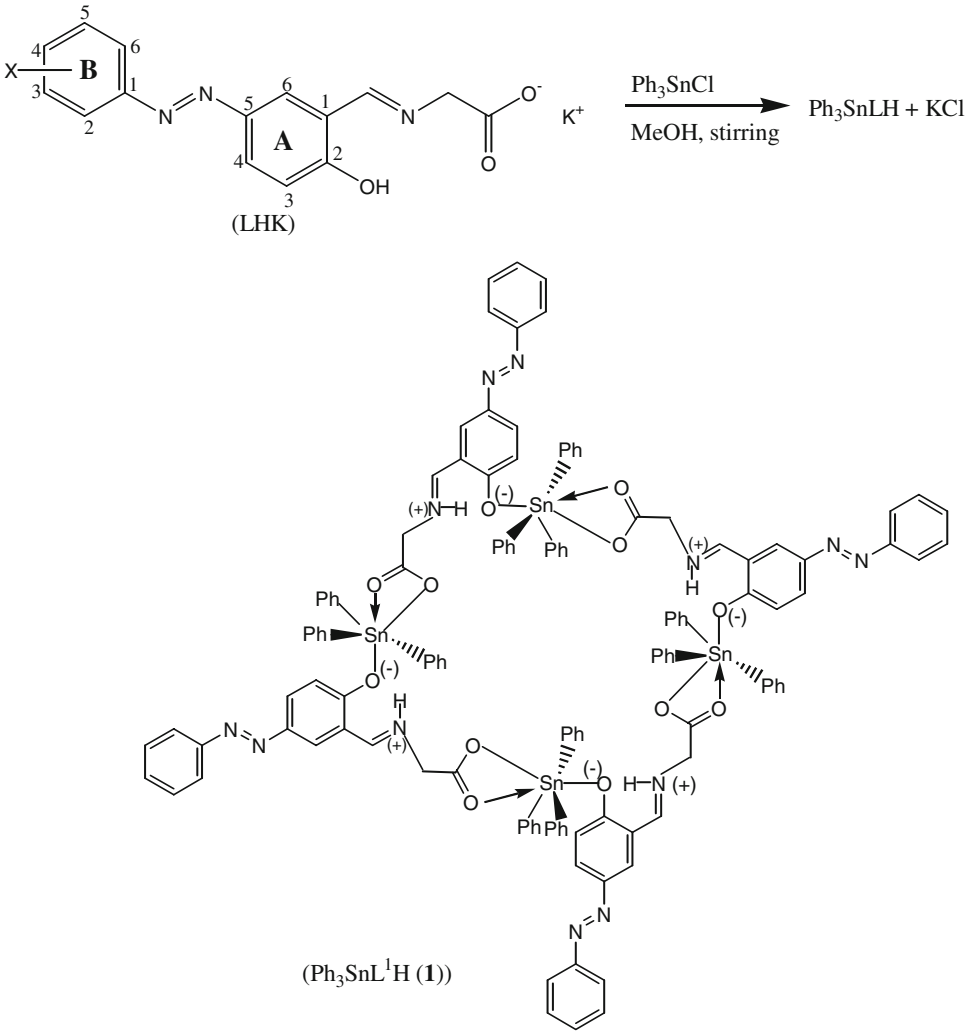
2.1 Materials and Measurement

Triphenyltin chloride (Fluka AG) and glycine (Aldrich) were used as received. Various pre-ligands, viz., 2-hydroxy-5-[(*E*)-phenyldiazenyl]benzaldehyde, 2-hydroxy-5-[(*E*)-(2-methyl phenyl)diazenyl]benzaldehyde, 2-hydroxy-5-[(*E*)-(3-methyl-phenyl)diazenyl]benzaldehyde and 2-hydroxy-5-[(*E*)-(4-methylphenyl)diazenyl]benzaldehyde were prepared by reacting the appropriate aryldiazonium chloride with salicylaldehyde by a previously reported method [15, 16] and the purities were established by their characterization and spectroscopic data prior to use. The solvents used in the reactions were of AR grade and dried using standard literature procedures.

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-, ^{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. 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. The Mössbauer spectra of the 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 m Ci $Ca^{119m}SnO_3$ source was used, and counts of 30,000 or more were accumulated for each

Scheme 2 The generic structure of the ligand, numbering scheme, abbreviations (L^1HK: X = H; L^2HK: X = 2-CH_3; L^3HK: X = 3-CH_3; L^3HK: X = 4-CH_3) and synthesis and structure of triphenyltin(IV) complexes



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 mm s^{-1}). The resultant spectra were analyzed using the Web Research software package (Web Research Co., Minneapolis, MN).

2.3 Synthesis of Ligands

A typical procedure is described below.

*2.3.1 Synthesis of Potassium [((E)-1-{2-Hydroxy-5-[(E)-2-phenyl-1-diazenyl]phenyl}-methylidene)amino] acetate (**L^1HK**)*

An anhydrous methanol solution (25 mL) of KOH (0.24 g, 4.27 mmol) was added slowly to a suspension of glycine (0.32 g, 4.26 mmol) in anhydrous methanol (20 mL) with continuous stirring for an hour. To this clear solution, a solution of 2-hydroxy-5-[(*E*)-phenyldiazenyl]benzaldehyde (0.96 g, 4.24 mmol) in anhydrous methanol (40 mL) was added drop-wise and the stirring was continued for 8 h. Then, the volatiles were removed carefully in vacuo and thereby a yellow–orange mass was obtained which was stirred in petroleum ether and filtered. The residue was dried in vacuo, dissolved in anhydrous methanol and filtered. The filtrate was concentrated which afforded the crude potassium salt. Repeated crystallizations from anhydrous methanol afforded yellow–orange coloured L^1HK in 76% (0.91 g) yield. m.p.: >300 °C. Anal. Found: C, 55.81; H, 3.66; N, 13.24%. Calc. for $C_{15}H_{12}N_3O_3K$: C, 56.06; H 3.76; N; 13.08%. IR (cm^{-1}): 1646 $\nu(OCO)_{asym}$.

The other potassium salts (Fig. 1), *viz*., potassium-[((*E*)-1-{2-hydroxy-5-[(*E*)-2-(2-methylphenyl)-1-diazenyl] phenyl}methylidene)amino]acetate (**L^2HK**), potassium-[((*E*)-1-{2-hydroxy-5-[(*E*)-2-(3-methylphenyl)-1-diazenyl] phenyl}methylidene)amino]acetate (**L^3HK**) and potassium-[((*E*)-1-{2-hydroxy-5-[(*E*)-2-(4-methylphenyl)-1-diazenyl]phenyl}methylidene)amino]acetate (**L^4HK**) were

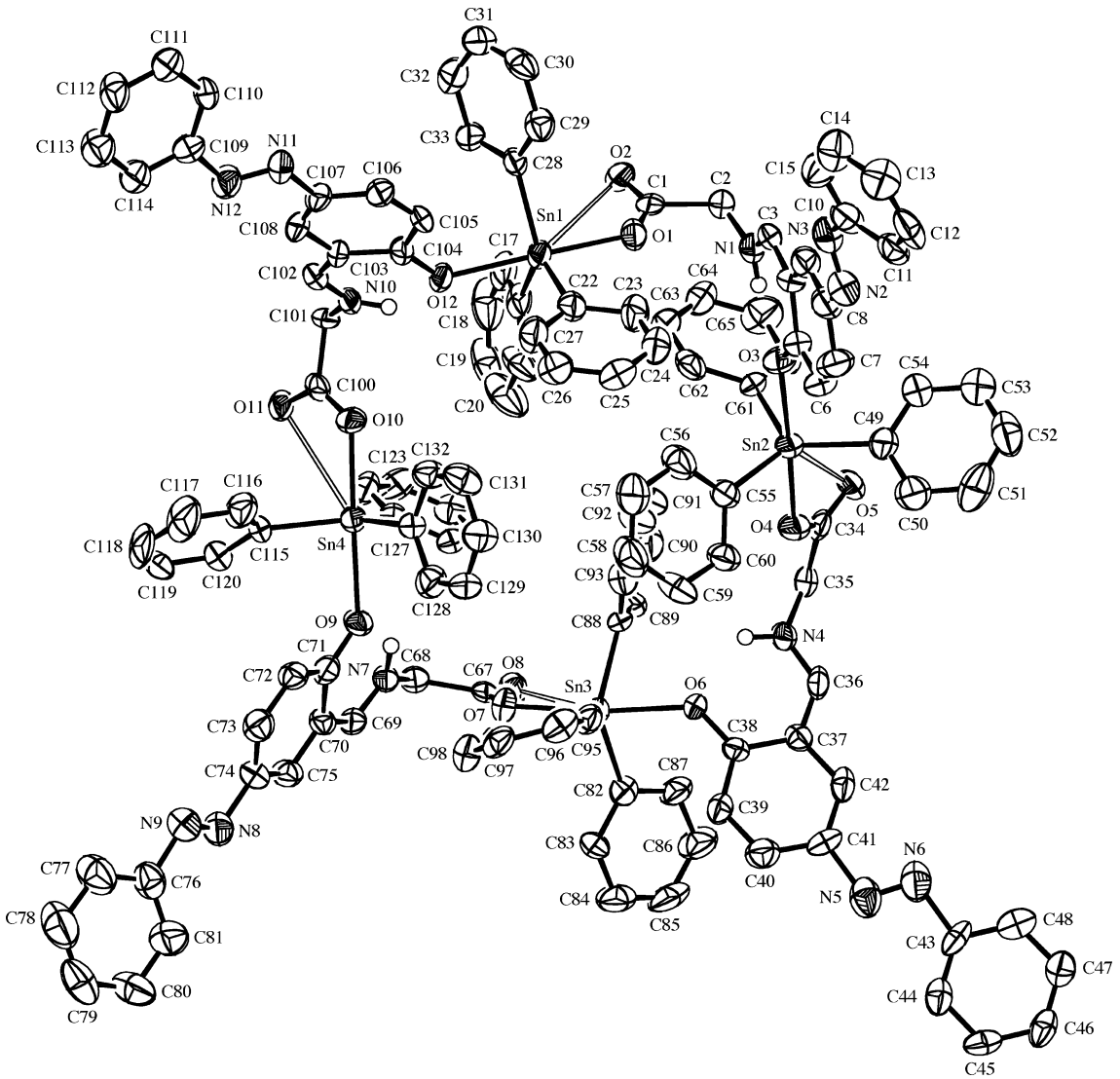


Fig. 1 The cyclic tetranuclear molecule of $[Ph_3SnL^1H]_4$ (**1**) with the atom-labelling scheme (50% probability ellipsoids). Most of the H-atoms have been omitted for clarity

prepared analogously by reacting appropriate 2-hydroxy-5-[(*E*)-(aryl)-diazenyl]benzaldehyde (pre-ligands) with glycine.

2.3.2 L^2HK

Recrystallized from methanol to give a yellow–orange precipitate in 69% yield. m.p.: >300 °C. Anal. Found: C, 57.51; H, 4.66; N, 13.04%. Calc. for $C_{16}H_{14}N_3O_3K$: C, 57.30; H 4.21; N; 12.53%. IR (cm^{-1}): 1644 $\nu(OCO)_{asym}$.

2.3.3 L^3HK

Recrystallized from methanol to give a yellow–orange precipitate in 60% yield. m.p.: >300 °C. Anal. Found: C, 57.41; H, 4.16; N, 12.64%. Calc. for $C_{16}H_{14}N_3O_3K$: C, 57.30; H 4.21; N; 12.53%. IR (cm^{-1}): 1651 $\nu(OCO)_{asym}$.

2.3.4 L^4HK

Recrystallized from methanol to give a yellow–orange precipitate in 65% yield. m.p.: >300 °C. Anal. Found: C, 57.61; H, 4.44; N, 12.74%. Calc. for $C_{16}H_{14}N_3O_3K$: C, 57.30; H, 4.21; N, 12.53%. IR (cm^{-1}): 1638 $\nu(OCO)_{asym}$.

2.4 Synthesis of the Triphenyltin(IV) Complexes

2.4.1 Ph_3SnL^1H (1)

A warm solution of Ph_3SnCl (0.58 g, 1.50 mmol) in anhydrous methanol (ca. 20 mL) was added drop-wise to a

warm solution of L^1HK (0.52 g, 1.55 mmol) in anhydrous methanol (ca. 30 mL) under stirring conditions. The reaction mixture was stirred for 8 h at an ambient temperature, then filtered and the filtrate was then evaporated to dryness and the residue was dried in vacuo. The dried mass was washed thoroughly with petroleum ether, dried in vacuo, extracted in benzene and filtered while hot. The filtrate upon concentration afforded orange colour product which was dried in vacuo. The dried mass was re-crystallized from benzene which deposited orange crystals of **1** in 63% (0.49 g) yield. m.p.: 138–140 °C. Anal. Found: C, 62.81; H, 4.44; N, 6.80%. Calc. for $C_{33}H_{27}N_3O_3Sn$: C, 62.68; H 4.30; N; 6.65%. IR (cm^{-1}): 1646 $\nu(OCO)_{asym}$. ^1H NMR ($CDCl_3$); δ_H: 4.53 [s, 2H, CH_2], 7.05 [d, 8.4 Hz, 1H, A-H3], 7.46 [m, 12H, B-H4, B-H3/H5 and Sn–Ph (*meta-* + *para-*)], 7.72 [m, 6H, Sn–Ph (*ortho-*)], 7.90 [m, 3H, B-H2/H6, A-H4], 8.0 [d, 2.4 Hz, 1H, A-H6], 8.42 [s, 1H, CHN], 13.8 [s, 1H, OH] ppm. ^{13}C NMR ($CDCl_3$); δ_C: 60.1 [CH_2], 167.1 [CHN], 174.2 [CO_2], Other aromatic carbons: 118.1, 122.5, 123.8, 127.0, 127.8, 130.3, 145.0, 152.7; Sn–Ph: 137.9 [*ipso-*], 136.4 [*ortho-*], 129.0 [*meta-*], 130.7 [*para-*] ppm. ^{119}Sn NMR ($CDCl_3$ solution): −83.5 ppm. ^{119}Sn Mössbauer: $\delta = 1.15$, $\Delta = 2.94$, $\Gamma\pm = 1.18$ mm s^{-1}, $\rho = 2.55$.

Other triphenyltin(IV) compounds, viz., Ph_3SnL^2H (**2**), Ph_3SnL^3H (**3**) and Ph_3SnL^4H (**4**) were prepared in the same manner as described for **1** by using Ph_3SnCl and appropriate LHK.

2.4.2 Ph_3SnL^2H (2)

Orange crystalline materials of compound **2** were obtained from ethanol in 57% yield. m.p.: 132–133 °C. Anal. Found: C, 63.31; H, 4.40; N, 6.78%. Calc. for $C_{34}H_{29}N_3O_3Sn$: C, 63.18; H, 4.52; N, 6.50%. IR (cm^{-1}): 1645 $\nu(OCO)_{asym}$. ^1H NMR ($CDCl_3$); δ_H: 2.72 [s, 3H, CH_3], 4.53 [s, 2H, CH_2], 7.11 [d, 8.4 Hz, 1H, A-H3], 7.25 [dt, 1.8 and 7.8 Hz, 1H, B-H5], 7.55 [m, 11H, B-H3/H4 and Sn–Ph (*meta-* + *para-*)], 7.65 [dd, 1.8 and 7.8 Hz, 1H, B-H6], 7.70 [m, 6H, Sn–Ph (*ortho-*)], 7.93 [dd, 2.4 and 8.4 Hz, 1H, A-H4], 8.20 [d, 2.4 Hz, 1H, A-H6], 8.45 [s, 1H, CHN], 13.8 [s, 1H, OH] ppm. ^{13}C NMR ($CDCl_3$); δ_C: 17.4 [CH_3], 57.4 [CH_2], 170.1 [CHN], 172.8 [CO_2], Other aromatic carbons: 115.4, 118.6, 123.8, 129.1, 130.3, 131.2, 131.5, 137.6, 144.9, 150.8; Sn–Ph: 137.4 [*ipso-*], 136.5 [*ortho-*], 128.7 [*meta-*], 130.8 [*para-*] ppm. ^{119}Sn NMR ($CDCl_3$ solution): –83.7 ppm. ^{119}Sn Mössbauer: $\delta = 1.17$, $\Delta = 2.99$, $\Gamma \pm = 1.16$ mm s^{-1}, $\rho = 2.55$.

2.4.3 Ph_3SnL^3H (3)

Orange crystalline materials of compound **3** were obtained from ethanol in 55% yield. m.p.: 128–130 °C. Anal. Found: C, 62.89; H, 4.38; N, 6.58%. Calc. for $C_{34}H_{29}N_3O_3Sn$: C, 63.18; H 4.52; N; 6.50%. IR (cm^{-1}): 1653 $\nu(OCO)_{asym}$. ^1H NMR ($CDCl_3$); δ_H: 2.48 [s, 3H, CH_3], 4.52 [s, 2H, CH_2], 7.08 [d, 8.4 Hz, 1H, A-H3], 7.25 [dt, 7.8 and 1.8 Hz, 1H, B-H4], 7.45 [m, 12H, B-H5,B-H2/6 and Sn–Ph (*meta-* + *para-*)], 7.77 [m, 7H, A-H4 and Sn–Ph (*ortho-*)], 7.92 [d, 2.4 Hz, 1H, A-H6], 8.45 [s, 1H, CHN], 13.8 [s, 1H, OH] ppm. ^{13}C NMR ($CDCl_3$); δ_C: 21.3 [CH_3], 59.4 [CH_2], 167.5 [CHN], 172.8 [CO_2], Other aromatic carbons: 118.2, 120.1, 120.3, 122.7, 127.0, 129.1, 130.1, 152.9; Sn–Ph: 138.8 [*ipso-*], 136.7 [*ortho-*], 128.9 [*meta-*], 130.7 [*para-*] ppm. ^{119}Sn NMR ($CDCl_3$ solution): −83.9 ppm. ^{119}Sn Mössbauer: $\delta = 1.17$, $\Delta = 2.94$, $\Gamma\pm = 1.13$ mm s^{-1}, $\rho = 2.51$.

2.4.4 Ph_3SnL^4H (4)

Orange crystalline materials of compound **4** were obtained from ethanol in 42% yield. m.p.: 130–131 °C. Anal. Found: C, 63.29; H, 4.68; N, 6.70%. Calc. for $C_{34}H_{29}N_3O_3Sn$: C, 63.18; H, 4.52; N, 6.50%. IR (cm^{-1}): 1630 $\nu(OCO)_{asym}$. ^1H NMR ($CDCl_3$); δ_H: 2.45 [s, 3H, CH_3], 4.52 [s, 2H, CH_2], 7.05 [d, 8.4 Hz, 1H, A-H3], 7.28 [AA′ portion of AA′XX′, 2H, B-H3/H5], 7.45 [m, 9H, Sn–Ph (*meta-* + *para-*)], 7.72 [m, 6H, Sn–Ph (*ortho-*)], 7.84 [XX′ portion of AA′XX′, 2H, B-H2/H6], 7.94 [dd, 8.4 and 2.4 Hz, 1H, A-H4], 7.98 [d, 2.4 Hz, 1H, A-H6], 8.42 [s, 1H, CHN], 13.8 [s, 1H, OH] ppm. ^{13}C NMR ($CDCl_3$); δ_C: 21.4 [CH_3], 59.3 [CH_2], 167.5 [CHN], 174.4 [CO_2], Other aromatic carbons: 118.2, 122.5, 126.4, 127.0, 129.6, 130.6, 131.0, 150.9; Sn–Ph: 140.8 [*ipso-*], 136.6 [*ortho-*], 129.9 [*meta-*], 128.8 [*para-*] ppm. ^{119}Sn NMR ($CDCl_3$ solution): −83.9 ppm. ^{119}Sn Mössbauer: $\delta = 1.18$, $\Delta = 2.96$, $\Gamma\pm = 1.18$ mm s^{-1}, $\rho = 2.50$.

2.5 Crystal Structure Determination

Orange crystals of compound (**1**) suitable for an X-ray crystal-structure determination were obtained from a benzene solution of the compound. Measurements were made using graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) with a Nonius KappaCCD diffractometer [17] and an Oxford Cryosystems Cryostream 700 cooler. Data reduction was performed with HKL Denzo and Scalepack [18]. The intensities were corrected for Lorentz and polarization effects, and an absorption correction based on the multi-scan method [19] was applied. The space group was uniquely determined by the systematic absences. Equivalent reflections were merged. The data collection and refinement parameters are given in Table 1, and a view of the molecular structure is shown in Fig. 1.

The structure was solved by direct methods using SHELXS97 [20], which revealed the positions of most non-hydrogen atoms. All remaining non-hydrogen atoms were located in a subsequent difference Fourier map. The asymmetric unit

Table 1 Crystallographic data and structure refinement parameters for **1**

Empirical formula	$C_{132}H_{108}N_{12}O_{12}Sn_4{\cdot}2C_6H_6{\cdot}0.38H_2O$
Formula weight	2691.85
Crystal size (mm)	0.02 × 0.15 × 0.17
Crystal shape	Plate
Temperature (K)	160(1)
Crystal system	Monoclinic
Space group	$P2_1/n$
a (Å)	21.4915 (4)
b (Å)	25.5778 (6)
c (Å)	23.0705 (5)
β (°)	93.585 (1)
V (Å^3)	12657.2 (5)
Z	4
D_x (g cm^{-3})	1.412
μ (mm^{-1})	0.847
Transmission factors (min, max)	0.881; 0.982
$2\theta_{max}$ (°)	50
Reflections measured	215728
Independent reflections; R_{int}	22328; 0.238
Reflections with $I > 2\sigma(I)$	10670
Number of parameters	1559
$R(F)$ [$I > 2\sigma(I)$reflns]	0.0892
$wR(F^2)$ (all data)	0.1548
GOF(F^2)	1.090
$\Delta\rho_{max,\ min}$ (e Å^{-3})	0.75; −0.72

contains one molecule of the tetranuclear complex, two benzene molecules and one site for a water molecule that is only partially occupied. Refinement of the site occupation factor for the water O-atom yielded a value of 0.38(3).

The non-hydrogen atoms were refined anisotropically. Except for the H-atoms of the water molecule, which were not included in the model, all of the 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 $1.2U_{eq}$ of its parent atom. The refinement of the structure was carried out on F^2 using full-matrix least-squares procedures, which minimized the function $\Sigma w(F_o^2 - F_c^2)^2$. A correction for secondary extinction was not applied. Calculations were performed using the SHELXL97 program [21].

3 Results and Discussion

3.1 Synthetic Aspects

Triphenyltin(IV) complexes Ph_3SnLH (**1**–**4**) were prepared by reacting the appropriate potassium salt (LHK) with Ph_3SnCl in 1:1 M ratios in anhydrous methanol, as shown in Scheme 2. The spectroscopic properties of the complexes are given in Sect. 2.4. The complexes were obtained in good yield and purity. They are stable in air and soluble in all common organic solvents.

3.2 Crystal Structure

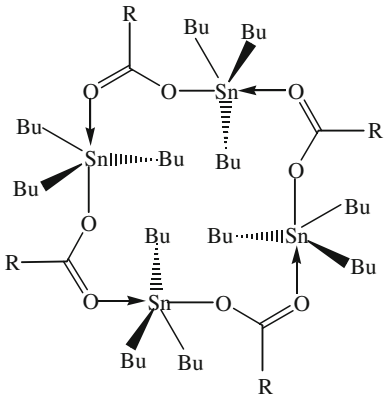
Triphenyltin [((*E*)-1-{2-hydroxy-5-[(E)-2-phenyl-1-diazenyl]phenyl}methylidene)-amino]acetate (**1**) crystallizes from ethanol as a L^1-bridged, cyclic tetramer. The molecular structure of compound **1** is shown in Fig. 1 (see Scheme 2 for line diagrams), while selected geometric parameters are collected in Table 2. The asymmetric unit contains one molecule of the tetranuclear complex, two benzene molecules and one site for a water molecule that is only approximately one-third occupied. The crystal structure of **1** reveals that the carboxylate ligand bridges two Sn-atoms via a carboxylate O-atom and the phenoxide O-atom, in a similar way to the related compounds (type **II** polymeric chain structural motif; Scheme 1) described for triphenyltin(IV)-2-{[(*E*)-1-(2-hydroxyphenyl)methylidene]amino}acetate [6], 2-{[(2*Z*)-(3-hydroxy-1-methyl-2-butenylidene)]amino}phenylpropionate [13], 2-{[(*E*)-1-(2-hydroxyphenyl)methylidene]amino}phenylpropionate [13], 2-{[(*E*)-1-(2-hydroxyphenyl)ethylidene]amino}phenylpropionate [13], 2-{[(2*Z*)-(3-hydroxy-1-methyl-2-butenylidene)]amino}-4-methyl-pentanoate [14] and 2-{[(*E*)-1-(2-hydroxyphenyl)ethylidene]amino}-4-methyl-pentanoate [14]. However, instead of extended chains of type **II**, four repeats of the primary unit close into a discrete loop in complex **1**, so that one molecule is a cyclic tetranuclear Sn-complex. Each Sn-atom in the molecule is coordinated by the O-atoms of the carboxylate group of one L^1 ligand, the oxide O-atom (formerly the hydroxy group) of a second L^1 ligand and three phenyl groups. The formal hydroxy group has lost its H-atom, so is negatively charged. Instead the N-atom of the imino group is protonated, thus leading to a zwitterionic ligand. This N^+–H group forms a strong intraligand hydrogen bond with the oxide O-atom, with the H···O distances in the four ligands ranging from 1.93 to 1.99 Å.

The carbonyl O-atom of the carboxylate group coordinates *via* a very long bond to the Sn-atom. Across the four independent sites within the molecule there is quite some variation in this Sn···O distance of 3.24–3.55 Å. Although these long Sn···O 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 observed in the structures of related polymeric $[Ph_3SnLH]_n$ derivatives [6, 13, 14, 22]. Ignoring this long Sn···O interaction, each Sn-atom in the molecule has

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

Sn(1)–O(1)	2.173(6)	Sn(3)–O(6)	2.312(6)
Sn(1)···O(2)	3.404(8)	Sn(3)–O(7)	2.181(7)
Sn(1)–O(12)	2.268(6)	Sn(3)···O(8)	3.551(7)
Sn(1)–C(16)	2.10(1)	Sn(3)–C(82)	2.12(1)
Sn(1)–C(22)	2.13(1)	Sn(3)–C(88)	2.11(1)
Sn(1)–C(28)	2.11(1)	Sn(3)–C(94)	2.10(1)
Sn(2)–O(3)	2.283(7)	Sn(4)–O(9)	2.299(6)
Sn(2)–O(4)	2.161(7)	Sn(4)–O(10)	2.182(6)
Sn(2)···O(5)	3.268(7)	Sn(4)···O(11)	3.240(7)
Sn(2)–C(49)	2.12(1)	Sn(4)–C(115)	2.119(9)
Sn(2)–C(55)	2.11(1)	Sn(4)–C(121)	2.13(1)
Sn(2)–C(61)	2.12(1)	Sn(4)–C(127)	2.12(1)
O(1)–Sn(1)–O(12)	178.6(2)	O(7)–Sn(3)–O(6)	173.9(2)
O(12)–Sn(1)···O(2)	139.6(2)	O(6)–Sn(3)···O(8)	142.3(2)
O(1)–Sn(1)–C(16)	95.2(3)	O(7)–Sn(3)–C(82)	97.1(3)
O(1)–Sn(1)–C(22)	88.9(3)	O(7)–Sn(3)–C(88)	94.0(3)
O(1)–Sn(1)–C(28)	94.0(3)	O(7)–Sn(3)–C(94)	85.7(3)
O(12)–Sn(1)–C(16)	83.6(3)	O(6)–Sn(3)–C(82)	88.5(3)
O(12)–Sn(1)–C(22)	91.1(3)	O(6)–Sn(3)–C(88)	80.7(3)
O(12)–Sn(1)–C(28)	87.3(3)	O(6)–Sn(3)–C(94)	94.1(3)
O(2)···Sn(1)–C(16)	76.1(4)	O(8)···Sn(3)–C(82)	80.3(3)
O(2)···Sn(1)–C(22)	129.2(3)	O(8)···Sn(3)–C(88)	76.7(3)
O(2)···Sn(1)–C(28)	74.0(3)	O(8)···Sn(3)–C(94)	123.3(3)
C(16)–Sn(1)–C(28)	120.1(5)	C(94)–Sn(3)–C(88)	119.1(4)
C(16)–Sn(1)–C(22)	118.5(5)	C(94)–Sn(3)–C(82)	115.5(4)
C(28)–Sn(1)–C(22)	120.7(4)	C(88)–Sn(3)–C(82)	124.8(4)
O(4)–Sn(2)–O(3)	177.6(3)	O(10)–Sn(4)–O(9)	176.4(2)
O(3)–Sn(2)···O(5)	138.3(2)	O(9)–Sn(4)···O(11)	134.6(2)
O(4)–Sn(2)–C(49)	95.6(3)	O(10)–Sn(4)–C(115)	93.0(3)
O(4)–Sn(2)–C(55)	85.9(3)	O(10)–Sn(4)–C(121)	95.2(3)
O(4)–Sn(2)–C(61)	99.0(3)	O(10)–Sn(4)–C(127)	88.9(3)
O(3)–Sn(2)–C(49)	86.7(3)	O(9)–Sn(4)–C(115)	89.4(3)
O(3)–Sn(2)–C(55)	92.4(3)	O(9)–Sn(4)–C(121)	81.1(3)
O(3)–Sn(2)–C(61)	80.3(3)	O(9)–Sn(4)–C(127)	92.7(3)
O(5)···Sn(2)–C(49)	78.9(3)	O(11)···Sn(4)–C(115)	73.3(3)
O(5)···Sn(2)–C(55)	128.3(3)	O(11)···Sn(4)–C(121)	78.1(3)
O(5)···Sn(2)–C(61)	74.2(3)	O(11)···Sn(4)–C(127)	132.7(3)
C(55)–Sn(2)–C(61)	116.1(4)	C(115)–Sn(4)–C(127)	112.6(4)
C(55)–Sn(2)–C(49)	122.3(4)	C(115)–Sn(4)–C(121)	128.4(4)
C(61)–Sn(2)–C(49)	120.5(4)	C(127)–Sn(4)–C(121)	118.4(4)

essentially a trigonal bipyramidal coordination geometry with the phenyl groups in the equatorial plane and an O-atom from each of two different L^1 ligands occupying axial positions. The average O–Sn–O angle is 176.6°, which yields a *trans*-R_3SnO_2 geometry in the cyclic tetramer. Macrocyclic tetramers involving triorganotin(IV) and the carboxylate ligands with a similar mode of coordination and geometry about the Sn-atom have been observed in tributyltin(IV) 2,6-difluorobenzoate [23] and



[R: 2,6-$C_6H_3F_2$ and 4-$NO_2C_6H_4$]

Fig. 2 The structures of tributyltin(IV) complexes showing a macrocyclic structure involving a tetrameric tin assembly bridged by carboxylate oxygen connectors

tributyltin(IV) (*Z*)-3-(4-nitrophenyl)-2-phenyl-2-propenoate [24] (Fig. 2). In both the cases, the carboxylate group of each ligand bridges two tin atoms in the tetrameric ring assemblies giving rise to macrocyclic molecules containing 16 membered $Sn_4C_4O_8$ rings. In complex **1**, the [((*E*)-1-{2-hydroxy-5-[(E)-2-phenyl-1-diazenyl]phenyl}methylidene) amino]acetate bridging ligands adopt approximate *syn-anti* conformations and coordinate to adjacent tin atoms *via* a carboxylate O-atom and the phenoxide O-atom, giving rise to a 36-membered ring in the macrocyclic tetramer.

3.3 Spectroscopy

The Mössbauer spectra of the complexes **1**–**4** show a characteristic doublet absorption with narrow line width, Γ, indicating the occurrence of unique tin coordination sites. The isomer shift (δ) values of $\sim$1.17 mm s^{-1} are typical of quadrivalent organotin derivatives [25]. The quadrupole splitting (Δ) values ($\Delta = \sim$2.96 mm s^{-1}) for **1**–**4** are as expected for a trigonal bipyramidal geometry with the R groups in equatorial positions and axial electronegative ligands [25, 26] and also is in agreement with the X-ray diffraction data for **1**. The Δ values for the triphenyltin(IV) complexes **1**–**4** also match closely with the values found for the triphenyltin(IV)-2-{[(*E*)-1-(2-hydroxyphenyl)methylidene]amino}acetate [6], 2-{[(2*Z*)-(3-hydroxy-1-methyl-2-butenylidene)]amino}phenylpropionate [13], 2-{[(*E*)-1-(2-hydroxyphenyl)methylidene]amino}phenylpropionate [13] and 2-{[(*E*)-1-(2-hydroxyphenyl)ethylidene]amino} phenylpropionate [13], respectively, which were previously characterized crystallographically and showed to have ligands coordinated in the same way, but were linear chains. The solid-state IR spectra of the complexes display a strong sharp band at around 1615 cm^{-1} due to the [ν_{asym}(OCO)] stretching vibration of the coordinated carboxylate,

confirming O atom bonding to the Sn atom [6, 13, 14]. The ^{1}H NMR integration values for complexes **1–4** were completely consistent with the formulation of the products. All the complexes display a broad signal at around 13.8 ppm, assigned to phenolic hydroxylic proton. This confirms that the phenol function is retained in solution and does not bond to the Sn-atom (see tin NMR discussion). The phenyl group signals displayed the usual complex pattern in both ^{1}H and ^{13}C spectra. The solution-state structures of complexes **1–4** were derived from ^{119}Sn NMR chemical shifts. The complexes exhibit a single sharp ^{119}Sn resonance at around −84 ppm in $CDCl_3$, suggesting that the Sn-atoms in the complexes have the same four-coordinate environment [6, 13, 14, 27, 28]. These results testify that the tetrameric structures of **1–4** found in the solid state, in which the tin atoms are five-coordinated, is lost upon dissolution and that the ligand acts in solution as a monodentate O-donor, likely through the carboxylate arm owing to the collapse of the O (phenolic) to Sn interactions yielding monomeric species containing four coordinated tin.

4 Supplementary Materials

CCDC-751814 contains the supplementary crystallographic data 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.

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References

1. E.R.T. Tiekink, Appl. Organomet. Chem. **5**, 1 (1991)
2. E.R.T. Tiekink, Trends Organomet. Chem. **1**, 71 (1994)
3. D. Dakternieks, T.S. Basu Baul, S. Dutta, E.R.T. Tiekink, Organometallics **17**, 3058 (1998)
4. T.S. Basu Baul, E.R.T. Tiekink, Z. Kristallogr, NCS **214**, 361 (1999)
5. T.S. Basu Baul, S. Dutta, E. Rivarola, S. Choudhuri, Appl. Organomet. Chem. **15**, 947 (2001)
6. T.S. Basu Baul, S. Dutta, E. Rivarola, R. Butcher, F.E. Smith, J. Organomet. Chem. **654**, 100 (2002)
7. T.S. Basu Baul, S. Dutta, C. Masharing, E. Rivarola, U. Englert, Heteroatom. Chem. **14**, 149 (2003)
8. H. Yin, Q. Wang, S. Xue, J. Organomet. Chem. **689**, 2480 (2004)
9. T.S. Basu Baul, C. Masharing, R. Willem, M. Biesemans, M. Holčapek, R. Jirásko, A. Linden, J. Organomet. Chem. **690**, 3080 (2005)
10. A. Linden, T.S. Basu Baul, C. Masharing, Acta Crystallogr. **E61**, m557 (2005)
11. T.S. Basu Baul, C. Masharing, S. Basu, E. Rivarola, M. Holčapek, R. Jirásko, A. Lyčka, D. de Vos, A. Linden, J. Organomet. Chem. **691**, 952 (2006)
12. T.S. Basu Baul, C. Masharing, E. Rivarola, F.E. Smith, R. Butcher, Struct. Chem. **18**, 231 (2007)
13. T.S. Basu Baul, C. Masharing, G. Ruisi, R. Jirásko, M. Holčapek, D. de Vos, D. Wolstenholme, A. Linden, J. Organomet. Chem. **692**, 4849 (2007)
14. T.S. Basu Baul, S. Basu, D. de Vos, A. Linden, Invest. New Drugs **27**, 419 (2009)
15. K. Sarma, T.S. Basu Baul, W.L. Basaiawmoit, R. Saran, Spectrochim. Acta A **49**, 1027 (1993)
16. T.S. Basu Baul, P. Das, A.K. Chandra, S. Mitra, S.M. Pyke, Dyes Pigm. **82**, 379 (2009)
17. R. Hooft, *KappaCCD collect software* (Nonius BV, Delft, The Netherlands, 1999)
18. Z. Otwinowski, W. Minor, in *Methods in Enzymology,* ed. by C.W. Carter Jr., R.M. Sweet. Macromolecular Crystallography, Part A, vol 276 (Academic Press, New York, 1997), pp. 307–326
19. R.H. Blessing, Acta Crystallogr. A **51**, 33 (1995)
20. G.M. Sheldrick, *SHELXS97, Program for the Solution of Crystal Structures* (University of Göttingen, Germany, 1997)
21. G.M. Sheldrick, *SHELXL97, Program for the Refinement of Crystal Structures* (University of Göttingen, Germany, 1997)
22. T.S. Basu Baul, K.S. Singh, M. Holčapek, R. Jirásko, E. Rivarola, A. Linden, J. Organomet. Chem. **690**, 4232 (2005)
23. M. Gielen, A. El Khloufi, M. Biesemans, F. Kayser, R. Willem, B. Mahieu, D. Maes, J.N. Lisgarten, L. Wyns, A. Moreira, T.K. Chattopadhay, R.A. Palmer, Organometallics **13**, 2849 (1994)
24. S. Rehman, S. Ali, A. Badshah, A. Malik, E. Ahmed, G.X. Jin, E.R.T. Tiekink, Appl. Organomet. Chem. **18**, 401 (2004)
25. R. Barbieri, F. Huber, L. Pellerito, G. Ruisi, A. Silvestri, in *Chemistry of Tin: ^{119}Sn Mössbauer Studies on Tin Compounds*, ed. by P.J. Smith (Blackie, London, 1998), pp. 496–540
26. G.M. Bancroft, R.H. Platt, Adv. Inorg. Chem. Radiochem. **15**, 59 (1972)
27. J. Holeček, M. Nádvorník, K. Handlíř, A. Lyčka, J. Organomet. Chem. **241**, 177 (1983)
28. R. Willem, I. Verbruggen, M. Gielen, M. Biesemans, B. Mahieu, T.S. Basu Baul, E.R.T. Tiekink, Organometallics **17**, 5758 (1998)