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Synthesis, spectroscopic characterization of tribenzyltin(IV) complexes of polyaromatic carboxylic acid ligands: Crystal and molecular structures of $Bz_3Sn[O_2CC_6H_4\{N{=}N(C_6H_3\text{-}4\text{-}OH(C(H){=}NC_6H_4X\text{-}4))\}\text{-}o](OH_2)$ (X = –Cl, $–OCH_3$)

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Abstract

The tribenzyltin(IV) complexes of 2-[(*E*)-2-(3-formyl-4-hydroxyphenyl)-1-diazenyl]benzoic acid and 2-{(*E*)-4-hydroxy-3-[(*E*)-4-(aryl)iminomethyl]phenyldiazenyl}benzoic acids (aryls = 4-CH_3, 4-Br, 4-Cl, 4-OCH_3) have been synthesized and characterized by ^1H, ^{13}C, ^{119}Sn NMR, IR and ^{119m}Sn Mössbauer spectroscopic techniques in combination with elemental analysis. The crystal structures of two monomeric tribenzyltin(IV) complexes, $Bz_3Sn[O_2CC_6H_4\{N{=}N(C_6H_3\text{-}4\text{-}OH(C(H){=}NC_6H_4X\text{-}4))\}\text{-}o](OH_2)$ (X = –Cl and $–OCH_3$) are reported. The coordination environment in each complex is trigonal bipyramidal *trans*-Bz_3SnO_2.

Keywords: Tribenzyltin; Carboxylates; 2-{(*E*)-4-hydroxy-3-[(*E*)-4-(aryl)iminomethyl]phenyldiazenyl}benzoic acid; NMR; Mössbauer; Crystal structure

1. Introduction

Recently, we have been investigating the crystal structures of polyaromatic ligands, such as 4-[((*E*)-1-{2-hydroxy-5-[(*E*)-2-(2-carboxyphenyl)-1-diazenyl]phenyl}-methylidene)amino]aryls hereafter termed as 2-{(*E*)-4-hydroxy-3-[(*E*)-4-(aryl)iminomethyl] phenyldiazenyl}benzoic acids, L^1HH'–L^4HH' (Fig. 1), which contain both azo and imino linkages, owing to possible mesogenic properties. The structures of L^1HH' (4-CH_3) [1], L^2HH' (4-Br) [2] and L^3HH' (4-Cl) [3] reveal that the three-ring ligand system assumes an extended conformation, with both outer rings slightly twisted with respect to the central aromatic ring. The carboxylic acid group is coplanar with its parent phenyl ring. The metric parameters within the molecules are similar, except that L^1HH' exists in a zwitterionic form [1]. After having done the structural characterization of these ligands, their coordination behaviour towards organotin(IV) was investigated in order to investigate their possible uses as metallomesogens. Triorganotin(IV) complexes of the general formula $R_3Sn[O_2CC_6H_4\{N{=}N\text{-}(C_6H_3\text{-}4\text{-}OH(C(H){=}\ NC_6H_4X\text{-}4))\}\text{-}o]$ (R = ^{n}Bu and Ph; X = –CH_3, –Br, –Cl or $–OCH_3$), are of great interest because of their structural diversity in the crystalline state (Scheme 1) and their interesting biological activity. In the

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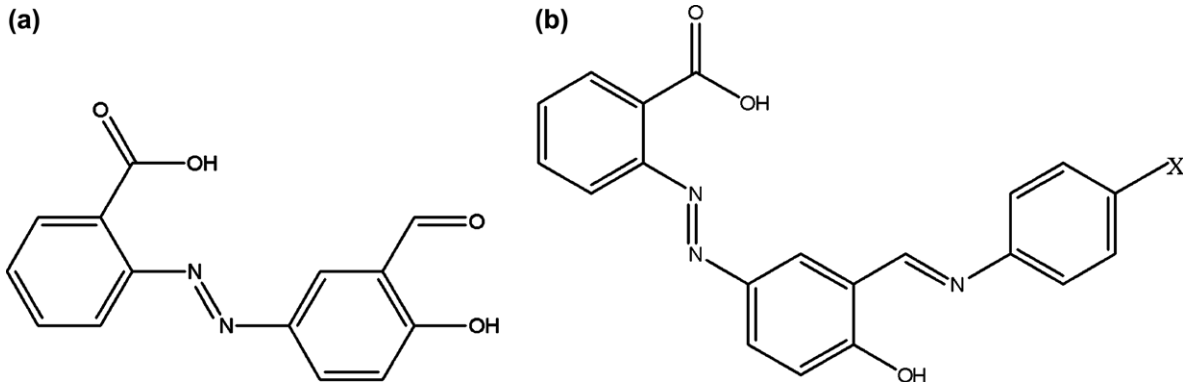
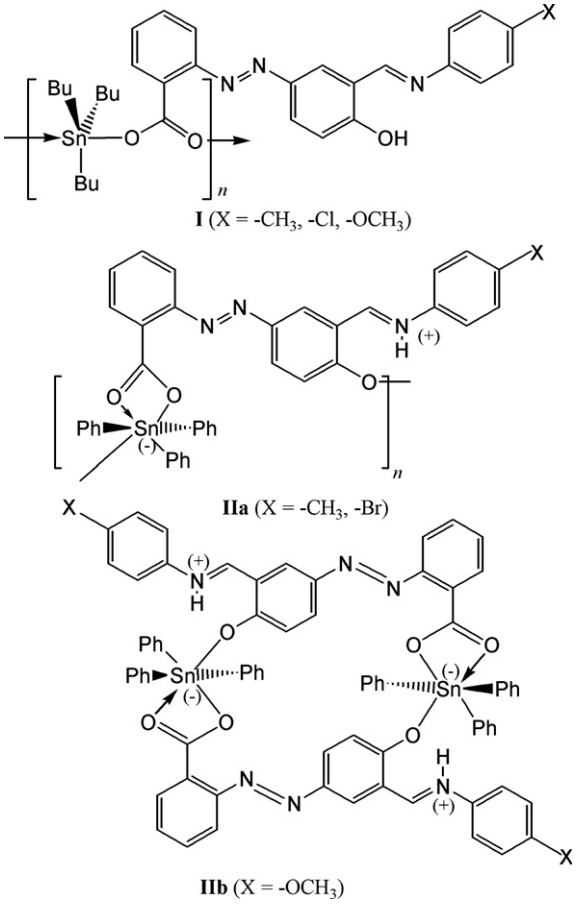


Fig. 1. Generic structure of the ligand. *Abbreviations*. (a) LHH′ (pre-ligand) (b) L^1HH': X = –CH_3; L^2HH': X = –Br, L^3HH': X = –Cl, L^4HH': X = –OCH_3, where H and H′ represent hydroxy and carboxylic acid H atoms, respectively.



Scheme 1. Structural motifs in $R_3Sn[O_2CC_6H_4\{N{=}N(C_6H_3\text{-}4\text{-}OH\text{-}(C(H){=}NC_6H_4X\text{-}4))\}\text{-}o]$ complexes.

solid state, the three investigated tri-*n*-butyltin(IV) complexes (X = –Cl [4], –OCH_3 [5] or –CH_3 [6]) have the motif **I** structure. The complexes are one-dimensional polymers in which the two carboxylate O atoms of a single benzoate ligand bridge the adjacent $SnBu_3$ groups. The Sn atom has a slightly distorted *trans*-Bu_3SnO_2 trigonal-bipyramidal coordination geometry with O atoms from two different carboxylate ligands occupying the axial positions. In contrast to the tri-*n*-butyltin(IV) analogues, the carboxylate ligands in the triphenyltin(IV) complexes (X = –Br or –CH_3 [1]) were found to exist in a zwitterionic form as a result of the coordination of the phenoxide O atom to a Sn atom. Two structural motifs, **IIa** and **IIb**, were found. In motif **IIa**, a polymeric *trans*-Ph_3SnO_2 configuration was observed where the adjacent $SnPh_3$ moieties are bridged by a single carboxylate ligand through a carboxylate O atom and the phenoxide O atom. The pattern then continues indefinitely. Each Sn atom has a slightly distorted trigonal-bipyramidal coordination geometry with the carboxylate and phenoxide O atoms from two different carboxylate ligands occupying the axial positions. On the other hand, a subtle modification of the X-substituent in the ligand framework (from –CH_3 or –Br to –OCH_3) results in discrete cyclic centrosymmetric dimers where two $SnPh_3$ entities are bridged by two carboxylate anions through their carboxylate and phenoxide O atoms (motif **IIb**) [1]. Despite the dimerization instead of polymerization, the coordination geometry about the Sn atom is virtually the same as that found in motif **IIa**. The triorganotin(IV) complexes of the type $R_3Sn[O_2CC_6H_4\{N{=}N(C_6H_3\text{-}4\text{-}OH(C(H){=}NC_6H_4X\text{-}4))\}\text{-}o]$, particularly the tri-*n*-butyltin(IV) complexes, were screened for larvicidal activity against the second larval instar of the *Aedes aegypti* and *Anopheles stephensi* mosquito [4,5] as well as for embryo toxicity against the sea urchin (*Paracentrotus lividus* and *Sphaerechinus granularis*) early developmental stages [7]. These compounds have shown promise as larvicides but were found to be toxic against the sea urchin.

Given the synthetic and structural importance and the potential biological activity of the $R_3Sn[O_2CC_6H_4\{N{=}N(C_6H_3\text{-}4\text{-}OH(C(H){=}NC_6H_4X\text{-}4))\}\text{-}o]$ class of complexes, it is of interest to explore the chemistry of the analogous complexes of these ligands with Bz_3Sn(IV). The present contribution details the preparation and spectroscopic characterization of four complexes of this type, viz. $Bz_3Sn[O_2CC_6H_4\{N{=}N(C_6H_3\text{-}4\text{-}OH(C(H){=}NC_6H_4X\text{-}4))\}\text{-}o](OH_2)$ (X = –CH_3, –Br, –Cl, –OCH_3). The crystal structures of two aqua complexes, $Bz_3Sn[O_2CC_6H_4\{N{=}N(C_6H_3\text{-}4\text{-}OH(C(H){=}NC_6H_4X\text{-}4))\}\text{-}o](OH_2)$ (X = –Cl, –OCH_3), are also reported.

2. Experimental

2.1. Materials

Bz_3SnOH was prepared as described by Sisido et al. [8]. The solvents used in the reactions were of AR grade and were dried using standard procedures. Toluene was distilled from sodium benzophenone ketyl. The ligands, 2-{(*E*)-4-hydroxy-3-[(*E*)-4-(aryl)iminomethyl] phenyldiazenyl}benzoic acids, $L^{1-4}HH'$, were prepared and characterized as described in our earlier report [4]. The compound $Bz_3SnLH \cdot OH_2$ (where $LH = O_2CC_6H_4(N{=}N(C_6H_3\text{-}4\text{-}OH\text{-}5\text{-}CHO)\text{-}o)$ [9]) has been included for the convenience of the discussion.

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 ^1H, ^{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 ^1H, ^{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 spectrometer in the acceleration mode with a moving source geometry. A 10 mCi $Ca^{119m}SnO_3$ source was used and counts of 30,000 or more were accumulated for each spectrum. The spectra were measured at 80 K using a liquid-nitrogen cryostat. 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.

2.3. Synthesis of the tribenzyltin(IV) complexes

A typical method is described below.

2.3.1. Synthesis of $Bz_3SnLH \cdot OH_2$ (1)

Compound **1** was synthesized by reacting LHH′ (0.38 g, 1.40 mmol) and Bz_3SnOH (0.58 g, 1.41 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 8 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 thoroughly, extracted into benzene and filtered. The crude product was obtained after evaporation and this was then recrystallized from benzene to yield dark-red crystals of the desired product. Yield: (0.36 g, 39%); m.p.: 73–75 °C. *Anal.* Calc. for $C_{35}H_{32}N_2O_5Sn$: C, 61.85; H, 4.70; N, 4.12. Found: C, 61.48; H, 4.53; N, 4.29%. IR (cm^{-1}): 1659 $\nu(OCO)_{asym}$. ^1H NMR ($CDCl_3$): 11.3 (brs, 1H, OH, D_2O exchangeable), 9.78 (s, 1H, C(H)=O), 2.68 (s, 6H, CH_2: Bz_3Sn), 6.72–7.60 (complex multiplets, 22H, remaining ligand and Bz_3Sn protons) ppm. ^{13}C NMR ($CDCl_3$): 196.5 (C(H)=O), 174.9 (CO_2), not detected (C–OH), 24.2 (CH_2: Bz_3Sn), 116.3–161.2 (complex nature of the remaining ligand and Bz_3Sn carbon signals which could not be identified with certainty owing to poor signal to noise ratio) ppm. ^{119}Sn Mössbauer: $\delta = 1.04$, $\Delta = 2.51$ mm s^{-1}, $\rho = 2.4$.

The other tribenzyltin(IV) complexes (**2**–**5**) were prepared by reacting Bz_3SnOH with the appropriate ligand (L^1HH'–L^4HH') following an analogous procedure. The characterization and spectroscopic data of the complexes are given below.

2.3.2. $Bz_3SnL^1H \cdot OH_2$ (2)

Orange-red crystals of compound **2** was obtained from a benzene–hexane mixture (1:3 v/v). Yield: 79%; m.p.: 96–98 °C. *Anal.* Calc. for $C_{42}H_{39}N_3O_4Sn$: C, 65.62; H, 5.11; N, 5.46. Found: C, 65.42; H, 4.83; N, 5.49%. IR (cm^{-1}): 1619 $\nu\ (OCO)_{asym}$. ^1H NMR ($CDCl_3$): 13.1 (brs, 1H, OH, D_2O exchangeable), 8.45 (s, 1H, C(H)=N), 2.69 (s, 6H, CH_2: Bz_3Sn), 2.42 (s, 3H, CH_3), 6.70–8.10 (26H, remaining ligand and Bz_3Sn protons) ppm. ^{13}C NMR ($CDCl_3$): 174.9 (CO_2), 164.5 (C–OH), 160.8 (C(H)=N), 24.3 (CH_2: Bz_3Sn), 20.9 (CH_3), 151.9, 145.7, 144.9, 138.6, 137.3, 131.3, 129.9, 129.1, 128.6, 128.3, 127.8, 127.2, 124.5, 120.9, 118.9, 118.1, 117.8 (remaining ligand and Bz_3Sn carbon signals) ppm. ^{119}Sn NMR (δ, ppm): −10.5. ^{119}Sn Mössbauer: $\delta = 1.39$, $\Delta = 3.07$ mm s^{-1}, $\rho = 2.2$.

2.3.3. $Bz_3SnL^2H \cdot OH_2$ (3)

Red crystals of compound **3** were obtained from a benzene–hexane mixture (1:3 v/v). Yield: 64%; m.p.: 72–74 °C. *Anal.* Calc. for $C_{41}H_{36}BrN_3O_4Sn$: C, 59.09; H, 4.35; N, 5.04. Found: C, 60.19; H, 4.26; N, 5.18%. IR (cm^{-1}): 1619 $\nu\ (OCO)_{asym}$. ^1H NMR ($CDCl_3$): 13.5 (brs, 1H, OH, D_2O exchangeable), 8.43 (s, 1H, C(H)=N), 2.63 (s, 6H, CH_2: Bz_3Sn), 6.70–7.99 (26H, remaining ligand and Bz_3Sn protons) ppm. ^{13}C NMR ($CDCl_3$): 173.4 (CO_2), 164.1 (C–OH), 162.3 (C(H)=N), 24.3 (CH_2: Bz_3Sn), 151.9, 146.6, 145.8, 138.5, 132.5, 131.4, 129.9, 129.5, 129.3, 128.8, 127.9, 127.0, 124.6, 122.8, 120.8, 118.8, 118.2, 117.6 (remaining ligand and Bz_3Sn carbon signals) ppm. ^{119}Sn NMR (δ, ppm): −9.82. ^{119}Sn Mössbauer: $\delta = 1.27$, $\Delta = 2.76$ mm s^{-1}, $\rho = 2.2$.

2.3.4. $Bz_3SnL^3H \cdot OH_2$ (4)

Red crystals of compound **4** were obtained from a toluene–hexane mixture (1:3 v/v). Yield: 49%; m.p.: 71–73 °C. *Anal.* Calc. for $C_{41}H_{36}ClN_3O_4Sn$: C, 62.43; H, 4.59; N, 5.33. Found: C, 62.01; H, 4.49; N, 5.40%. IR (cm^{-1}): 1617 $\nu(OCO)_{asym}$. ^1H NMR ($CDCl_3$): 13.6 (brs, 1H, OH, D_2O exchangeable), 8.49 (s, 1H, C(H)=N), 2.69 (s, 6H, CH_2: Bz_3Sn), 6.70–8.05 (26 H, remaining ligand and Bz_3Sn protons) ppm. ^{13}C NMR ($CDCl_3$): 173.2 (CO_2), 163.9 (C–OH), 162.2 (C(H)=N), 24.3 (CH_2: Bz_3Sn), 151.7, 146.1,

145.8, 139.8, 138.4, 132.8, 131.2, 129.9, 129.4, 129.2, 128.6, 127.8, 126.8, 124.5, 122.2, 118.7, 117.9, 117.5 (remaining ligand and Bz_3Sn carbon signals) ppm. ^{119}Sn NMR (δ, ppm): −10.2. ^{119}Sn Mössbauer: $\delta = 1.14$, $\Delta = 2.99$ mm s^{-1}, $\rho = 2.6$.

2.3.5. $Bz_3SnL^4H \cdot OH_2$ (5)

Red crystals of compound **5** were obtained from a benzene–hexane mixture (1:3 v/v). Yield: 75%; m.p.: 74–76 °C. *Anal.* Calc. for $C_{42}H_{39}N_3O_5Sn$: C, 64.30; H, 5.01; N, 5.36. Found: C, 64.50; H, 4.89; N, 5.28%. IR (cm^{-1}): 1617 $\nu(OCO)_{asym}$. ^1H NMR ($CDCl_3$): 14.1 (brs, 1H, OH, D_2O exchangeable), 8.53 (s, 1H, C(H)=N), 3.84 (s, 3H, OCH_3), 2.69 (s, 6H, CH_2: Bz_3Sn), 6.70–8.03 (26 H, remaining ligand and Bz_3Sn protons) ppm. ^{13}C NMR ($CDCl_3$): 173.2 (CO_2), 164.3 (C–OH), 159.5 (C(H)=N), 55.5 (OCH_3), 24.3 (CH_2: Bz_3Sn), 151.9, 145.8, 140.5, 138.6, 131.3, 130.3, 129.9, 129.2, 128.6, 128.4, 126.8, 124.5, 122.3, 119.1, 117.9, 117.7, 114.7 (remaining ligand and Bz_3Sn carbon signals) ppm. ^{119}Sn NMR (δ, ppm): −10.48. ^{119}Sn Mössbauer: $\delta = 1.39$, $\Delta = 3.13$ mm s^{-1}, $\rho = 2.3$.

2.4. X-ray crystallography

Crystals of compounds **4** and **5** suitable for an X-ray crystal-structure determination were obtained from a toluene–hexane and a benzene–hexane solution, respectively, by slow evaporation of the solvent at room temperature. All measurements were made at low temperature on a Nonius KappaCCD diffractometer [10] with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) and an Oxford Cryosystems Cryostream 700 cooler. Data reduction were performed with HKL DENZO and SCALEPACK [11]. The intensities were corrected for Lorentz and polarization effects, and an empirical absorption correction based on the multi-scan method [12] was applied. Equivalent reflections were merged. The data collection and refinement parameters are given in Table 1. Views of the molecular structures are shown in Figs. 3 and 4. The structures were solved by direct methods by using SIR-92 [13]. For each structure, the non-hydrogen atoms were refined anisotropically. The water ligand and phenoxy H atoms were placed in positions indicated by the 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 the methyl group in **5**). 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 complex **5**. One reflection, whose intensity was considered to be an extreme outlier, was omitted from the final refinement of **4**. All calculations were performed using the SHELXL-97 [14] program.

Table 1
Crystallographic data and structure refinement parameters for the tribenzyltin(IV) complexes **4** and **5**

	4	**5**
Empirical formula	$C_{41}H_{36}ClN_3O_4Sn$	$C_{42}H_{39}N_3O_5Sn$
Formula weight	788.80	784.39
Crystal size (mm)	0.10 × 0.17 × 0.32	0.12 × 0.17 × 0.28
Crystal shape	tablet	prism
Temperature (K)	160(1)	160(1)
Crystal system	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/n$
a (Å)	12.5388(1)	13.1825(2)
b (Å)	22.6661(2)	21.9417(4)
c (Å)	14.1787(2)	14.3594(2)
β (°)	114.8089(5)	115.9489(8)
V (Å^3)	3657.78(7)	3734.7(1)
Z	4	4
D_x (g cm^{-3})	1.432	1.395
μ (mm^{-1})	0.817	0.732
Transmission factors (minimum; maximum)	0.804; 0.925	0.759; 0.916
$2\theta_{max}$ (°)	60	55
Reflections measured	88 212	82 555
Independent reflections (R_{int})	10 662 (0.068)	8548 (0.091)
Reflections with $I > 2\sigma(I)$	8172	6020
Number of parameters	463	474
$R(F)$ ($I > 2\sigma(I)$ reflections)	0.037	0.039
$wR(F^2)$ (all data)	0.090	0.091
Goodness-of-fit (F^2)	1.05	1.05
Maximum, minimum $\Delta\rho$ (e Å^3)	1.61, −0.92	1.52, 0.67

3. Results and discussion

3.1. Synthetic aspect

Recently, we have investigated the reaction of Bz_3SnCl with sodium 2-[(*E*)-2-(3-formyl-4-hydroxyphenyl)-1-diazenyl]benzoate, LHNa (Fig. 1a) in anhydrous methanol. The reaction proceeded via debenzylation and oxidative decarbonylation [15]. This reaction afforded a cyclic dinuclear dibenzyltin(IV) complex, $[Bz_2\{O_2CC_6H_4\{N(H)=N=(C_6H_3\text{-}4(=O)\text{-}5\text{-}O)\}\text{-}o\}Sn]_2$ (Fig. 2) instead of the polymeric Me_3Sn(IV) [16] and Bu_3Sn(IV) [4] as well as the monomeric Ph_3Sn(IV) [9] analogues. In a similar way, the reactions of Bz_3SnCl with sodium 2-{(*E*)-4-hydroxy-3-[(*E*)-4-(aryl)iminomethyl]phenyldiazenyl}benzoates, L^1H-Na–L^4HNa (Fig. 1b) were attempted under identical

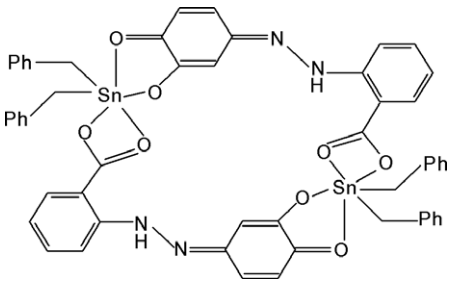


Fig. 2. Cyclic dibenzyltin(IV) complex: $[Bz_2\{O_2CC_6H_4\{N(H)\text{–}N=(C_6H_3\text{-}4(=O)\text{-}5\text{–}O)\}\text{-}o\}Sn]_2$.

reaction conditions, in the expectation of obtaining the corresponding $Bz_3Sn(IV)$ derivatives. Instead, the work-up of the reaction mixture yielded crystals of the same cyclic dibenzyltin(IV) dimer, i.e. $[Bz_2\{O_2CC_6H_4\{N(H)\text{—}N{=}(C_6H_3\text{-}4(=O)\text{-}5\text{-}O)\}\text{-}o\}Sn]_2$. The melting point, microanalytical, spectroscopic and crystallographic data of the two products were identical. In the latter reactions, cleavage of the H–C=N–Ar part from the ligand molecule and simultaneous debenzylation was noticed. At present, however, the exact mechanism of the cleavage/rearrangement is not clearly understood. On the other hand, attempted reactions of the free acids (LHH′ (pre-ligand) and L^1HH'–L^4HH') with Bz_3SnOH in anhydrous toluene afforded the desired products $Bz_3SnLH \cdot OH_2$ and $Bz_3SnL^{1-4}H \cdot OH_2$ in moderate to good yields, respectively. Attempted crystallization of these $Bz_3Sn(IV)$ complexes from an anhydrous benzene-methanol mixture again afforded crystals of the dimeric dibenzyltin complex (Fig. 2). Hence, the crystallization attempts were made using anhydrous benzene, benzene–hexane or toluene–hexane.

3.2. Spectroscopy

The diagnostically important infrared absorption frequencies for the carboxylate antisymmetric [ν_{asym}(OCO)] stretching vibration of the complexes 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 assignment of the band is based on comparison with the spectra of the free ligands. The antisymmetric [ν_{asym}(OCO)] stretching vibrations for the uncomplexed ligands have been detected at 1733 cm^{-1} in LHH′ [9] and around the 1725 cm^{-1} region for $L^{1-4}HH'$ [4]. In the complexes, the carbonyl stretching frequencies are found to be shifted to lower wavenumber, which is ascribed to carboxylate coordination in accordance with earlier reports [1,4,17,18].

The ^1H and ^{13}C NMR data of LHH′ and $L^{1-4}HH'$ have been reported earlier [4,9] and the conclusions drawn from the ligand assignments were then subsequently extrapolated to the complexes owing to the data similarity for at least a few signals. The ^1H NMR integration values were completely consistent with the formulation of the products. Individual assignments of the ^1H and ^{13}C signals of the tribenzyltin(IV) moiety and most parts of the ligand skeleton could not be made owing to serious signal overlap resulting in complex patterns. The ^{119}Sn NMR chemical shifts of the tribenzyltin(IV) complexes (**2**–**5**) in $CDCl_3$ solution are listed in Section 2.3. The complexes exhibit a single sharp resonance at around −10.0 ppm, suggesting that the complexes are isostructural in solution. The ^{119}Sn NMR resonances fall within the range from +55.0 to −25.0 ppm, which is usually indicative of four-coordinate tribenzyltin(IV) species in solution [19]. This indicates that the five-coordinate structure of the solid (see X-ray discussion, vide infra) breaks up in solution [20], presumably by loss of the water ligand.

The Mössbauer results from the complexes are listed in Section 2.3. The ratio of the quadrupole splitting (Δ) value to the isomer shift (δ) value ($\rho = \Delta/\delta$) can be used to distinguish between the different coordination states of the central tin atom [21]. 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. Complexes **2**–**5** (slightly lower in the case of **1**) have similar δ and Δ parameters, and the ρ values are greater than 2.1 suggesting that the complexes are isostructural with a coordination number greater than four. Trigonal-bipyramidal triorganotin(IV) complexes with organic groups in the equatorial plane [22] have been reported to have Δ values between 3.00 and 4.00 mm s^{-1}. This value has also been found to change as a function of the axial bond distances [22]. The tribenzyltin(IV) complexes in the present investigation exhibited Δ values of ~3.00 mm s^{-1} which correspond with a trigonal-bipyramidal geometry around the tin atom with equatorial benzyl groups, [20,23–25] and is in agreement with the structures determined by X-ray crystallography (see Section 3.3).

3.3. X-ray crystallography

The crystal structures of complexes **4** and **5** are very similar and the principal geometric parameters do not differ significantly (Table 2). In contrast to the polymeric tri-*n*-butyltin(IV) [4–6] and polymeric and dimeric triphenyltin(IV) [1] analogues (Scheme 1), both of the tribenzyltin(IV)

Table 2
Selected bond lengths (Å) and angles (°) for **4** and **5**

	4	**5**
Sn–O(1)	2.150(1)	2.164(2)
Sn–O(4)	2.399(2)	2.396(2)
Sn···O(2)	3.056(2)	3.008(2)
Sn–C(21)	2.150(2)	2.151(3)
Sn–C(28)	2.148(2)	2.147(3)
Sn–C(35)	2.143(2)	2.139(3)
O(1)–C(1)	1.278(3)	1.288(3)
O(2)–C(1)	1.238(3)	1.234(3)
N(1)–N(2)	1.252(3)	1.254(3)
N(1)–C(3)	1.425(3)	1.421(4)
N(2)–C(8)	1.429(3)	1.429(4)
O(1)–Sn–O(4)	173.58(6)	172.64(8)
O(1)–Sn–C(21)	89.12(8)	89.05(9)
O(1)–Sn–C(28)	96.40(8)	96.4(1)
O(1)–Sn–C(35)	99.12(7)	98.98(9)
O(4)–Sn–C(21)	85.22(8)	84.1(1)
O(4)–Sn–C(28)	83.66(8)	84.2(1)
O(4)–Sn–C(35)	86.13(7)	86.58(9)
C(21)–Sn–C(28)	118.19(9)	114.9(1)
C(21)–Sn–C(35)	116.35(9)	117.9(1)
C(28)–Sn–C(35)	123.18(9)	124.9(1)
Sn–O(1)–C(1)	116.4(1)	114.1(2)
N(2)–N(1)–C(3)	114.3(2)	115.3(2)
N(1)–N(2)–C(8)	113.2(2)	113.2(2)
O(1)–C(1)–O(2)	123.6(2)	123.5(2)
O(1)–C(1)–C(2)	117.0(2)	116.7(2)
O(2)–C(1)–C(2)	119.4(2)	119.8(2)

complexes, **4** and **5**, exhibit the same monomeric *trans*-R_3SnO_2 structural motif, as illustrated in Figs. 3 and 4. The structures are also shown in Scheme 2 for clarity. The Sn atom has a slightly distorted trigonal-bipyramidal coordination geometry with equatorial benzyl groups and the axial positions occupied by an O atom from the carboxylate ligand and the O atom from the water ligand. A monomeric structure with a similar mode of coordination and geometry about the Sn atom was observed in the triphenyltin(IV) complex of the pre-ligand i.e. $Ph_3Sn[O_2CC_6H_4(N{=}N(C_6H_3$-4-OH-5-CHO))-*o*$](OH_2)$ [9]. The carbonyl O atom of the carboxylate ligand in **4** and **5** also coordinates very weakly to the Sn atom with long Sn···O(2) distances of 3.056(2) and 3.008(2) Å, respectively. Although the 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 principal trigonal bipyramidal Sn-coordination geometry as a result of this contact. A similar additional weak Sn···O coordination was also observed in the structures of related polymeric $[R_3SnLH]_n$ (R = ^{n}Bu, Ph) derivatives [1,4–6]. The Sn atom coordination geometry found for complexes **4** and **5** is in good agreement with that

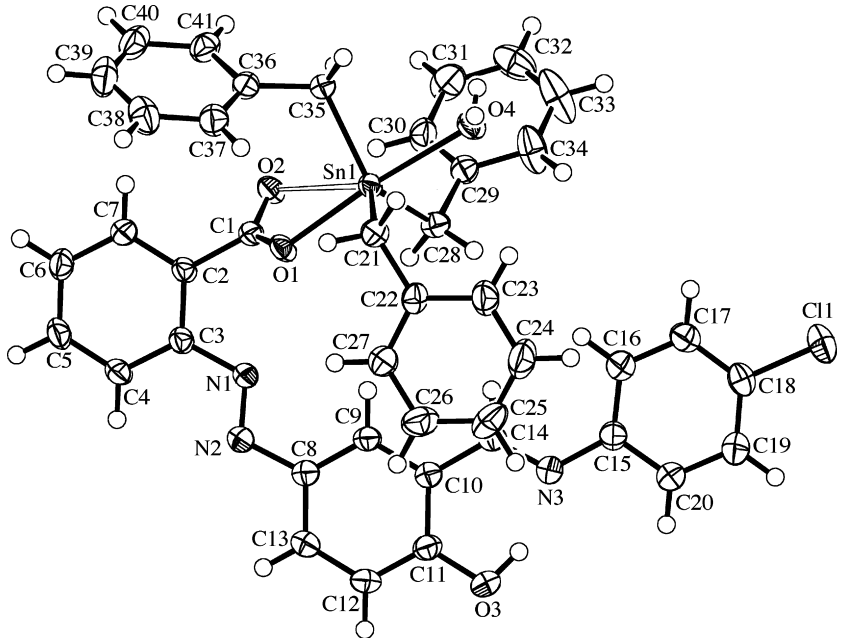


Fig. 3. The molecular structure of $Bz_3SnL^3H \cdot OH_2$ (**4**) showing the atom-labelling scheme (50% probability ellipsoids).

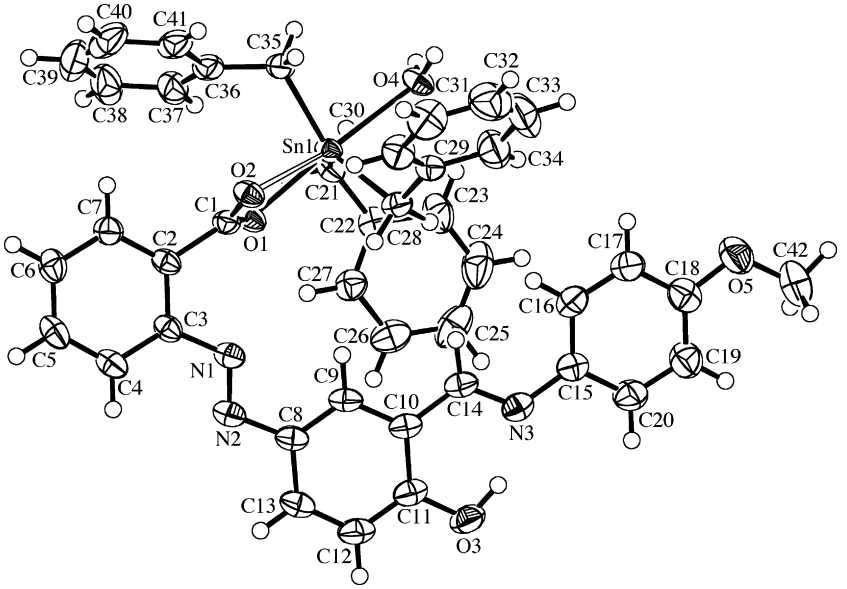
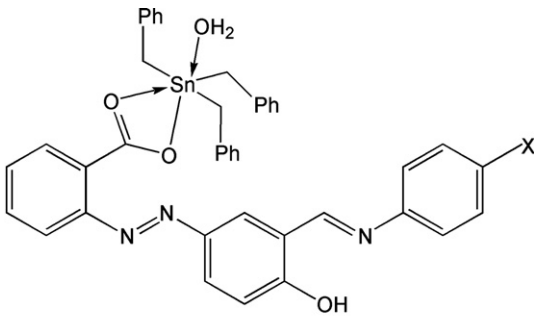


Fig. 4. The molecular structure of $Bz_3SnL^4H \cdot OH_2$ (**5**) showing the atom-labelling scheme (50% probability ellipsoids).



III (X = -Cl, -OCH_3)

Scheme 2. Structures of the complexes **4** and **5**.

inferred from ^{119m}Sn Mössbauer spectroscopy (see Section 3.2).

In complexes **4** and **5**, the phenoxy H atom forms an intramolecular hydrogen bond with the imine N atom, thereby creating a loop with a graph set motif [26,27] of S(6). The H atoms of the water ligand form intermolecular hydrogen bonds with the phenoxy O atom of one neighbouring molecule and with the weakly coordinating carboxylate O atom of a different neighbouring molecule (Table 3). The former interaction links the molecules into extended chains which run parallel to the [0 1 0] direction and can be described by a graph set motif of C(14). The

Table 3
Hydrogen bonding geometry (Å, °) for **4**[a] and **5**[b]

D–H···A	D–H	H···A	D···A	D–H···A
O(3)–H(3)···N(3)	0.90(3) [0.95(5)]	1.72(3) [1.69(5)]	2.562(3) [2.572(4)]	155(3) [151(4)]
O(4)–H(41)···O(3′)	0.80(4) [0.79(3)]	1.98(4) [1.89(3)]	2.783(3) [2.678(3)]	172(4) [171(3)]
O(4)–H(42)···O(2″)	0.83(4) [0.84(4)]	1.85(4) [1.97(4)]	2.668(3) [2.779(3)]	174(3) [162(4)]

Primed atoms refer to the molecule in the following symmetry related positions.
The H-bonding geometrical parameters for complex **5** are in parentheses.
[a] For **4**: ′ $\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$ and ″ $x-\frac{1}{2}, \frac{1}{2}-y, z-\frac{1}{2}$.
[b] For **5**: ′ $x, \frac{1}{2}-y, z-\frac{1}{2}$ and ″ $1-x, \frac{1}{2}+y, \frac{1}{2}-z$.

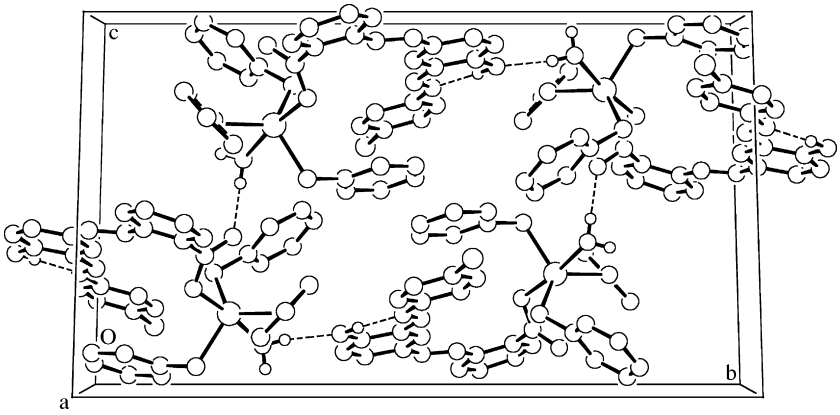


Fig. 5. The molecular packing of $Bz_3SnL^3H \cdot OH_2$ (**4**) showing the intra- and inter-molecular hydrogen bonding. The hydrogen bonding interactions are shown as dashed lines.

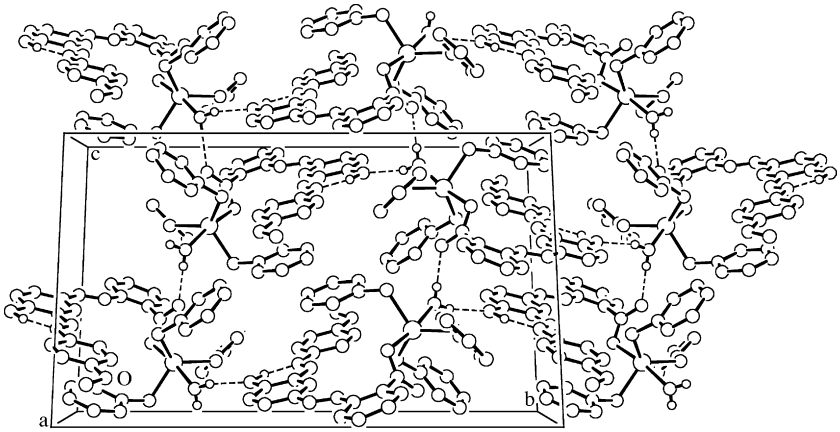


Fig. 6. The molecular packing of $Bz_3SnL^4H \cdot OH_2$ (**5**) showing the intra- and inter-molecular hydrogen bonding. The hydrogen bonding interactions are shown as dashed lines.

latter interaction links the molecules into extended chains which can be described by a graph set motif of C(4) and which run parallel to the [1 0 1] direction in **4** and the [0 0 1] direction in **5**. Together, the intermolecular interactions link the molecules into two-dimensional networks. In the case of **4**, these networks lie parallel to the $(10\bar{1})$ plane (Fig. 5), while in **5**, they lie parallel to the (1 0 0) plane (Fig. 6).

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Appendix A. Supplementary material

CCDC-604414–CCDC-604415 contain the supplementary crystallographic data for complexes **4** and **5**, respectively. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.poly.2006.06.026.

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