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Di-*n*-octyltin(IV) complexes with 5-[(*E*)-2-(aryl)-1-diazenyl]-2-hydroxybenzoic acid: Syntheses and assessment of solid state structures by ^{119}Sn Mössbauer and X-ray diffraction and further insight into the solution structures using electrospray ionization MS, ^{119}Sn NMR and variable temperature NMR spectroscopy

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Abstract

Reactions of 5-[(*E*)-2-(aryl)-1-diazenyl]-2-hydroxybenzoic acids (LHH′, where the aryl group is an R-substituted phenyl ring such that for L^1HH′:X = H; L^2HH′:X=2′-OCH_3; L^3HH′:X = 3′-CH_3; L^4HH′:X = 4′-CH_3; L^5HH′:X = 4′-Cl) with ^{n}Oct$_2$SnO in 2:1 and 1:1 molar ratios have been investigated.Two types of complexes, ^{n}Oct$_2$Sn(LH)$_2$ and {[^{n}Oct$_2$Sn(LH)]$_2$O}$_2$, were isolated and they have been characterized by ^{1}H, ^{13}C, ^{119}Sn NMR, ESI-MS, IR and ^{119m}Sn Mössbauer spectroscopic techniques in combination with elemental analyses. The crystal structures of ^{n}Oct$_2$Sn(L^1H)$_2$ (**1**), {[^{n}Oct$_2$Sn(L^2H)]$_2$O}$_2$ (**3**) and{[^{n}Oct$_2$Sn(L^3H)]$_2$O}$_2$ (**4**) were determined. The mononuclear complex **1** was found to adopt a skew-trapezoidal bipyramidal arrangement around the tin atom while **3** and **4** are centrosymmetric tetranuclear bis(dicarboxylatotetrabutyldistannoxane) complexes containing a planar Sn_4O_2 core in which two μ_3-oxo O-atoms connect an Sn_2O_2 ring to two exocyclic Sn-atoms. The solution structures were confirmed by ^{119}Sn NMR spectroscopy by observing one tin resonance in compound **1** and two tin resonances in {[^{n}Oct$_2$Sn(L^5H)]$_2$O}$_2$ (**5**). {[^{n}Oct$_2$Sn(L^2H)]$_2$O}$_2$ (**3**) and {[^{n}Oct$_2$Sn(L^3H)]$_2$O}$_2$ (**4**) undergo very complex exchange processes in deuteriochloroform solution, which has been confirmed by variable temperature ^{1}H NMR spectroscopy. The cleavage of the most labile bond in the molecule was studied by ESI mass spectrometry.

Keywords: Di-*n*-octyltin; Carboxylates; 5-[(*E*)-2-(aryl)-1-diazenyl]-2-hydroxybenzoic acid; NMR; ESI-MS; Mössbauer; Crystal structure

1. Introduction

Recently, we have been investigating the coordination behaviour of 5-[(*E*)-2-(aryl)-1-diazenyl]-2-hydroxybenzoic acids towards organotin(IV), owing to possible biological applications and their structural diversity in the crystalline state (Scheme 1). The triorganotin(IV) complexes of the

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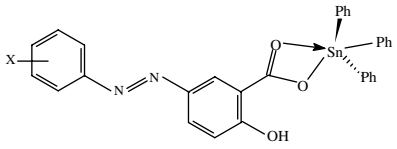
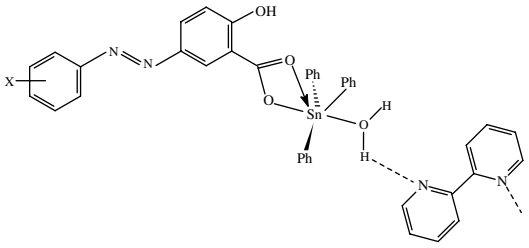
general formula $R_3Sn(O_2CC_6H_4(OH\text{-}2)(N{=}NC_6H_4(X)\text{-}5))$ (R = Me, ^{n}Bu or Ph; X = H, 2′-CH_3, 3′-CH_3, 4′-CH_3, 4′-Br, 4′-Cl, 4′-NO_2, 4′-OCH_3) have been investigated in great detail [1–3]. The triphenyltin(IV) compounds provided diffraction quality crystals and their solid state structures revealed a monomeric distorted tetrahedral



(X = H, 2'-CH_3, 3'-CH_3, 4'-CH_3, 4'-OCH_3, 4'-Cl)

I



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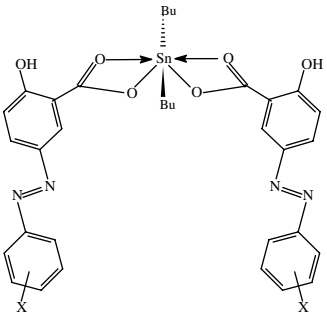
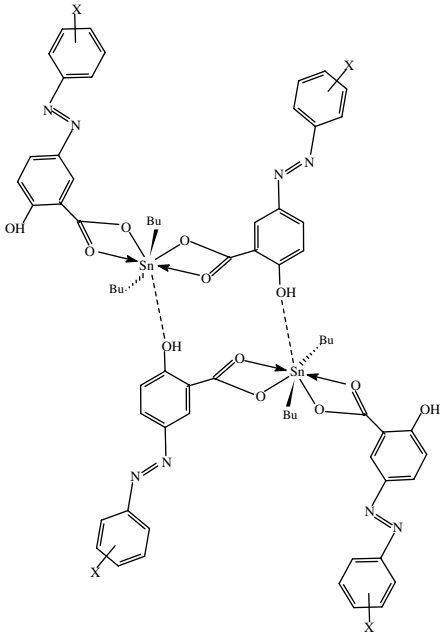
II



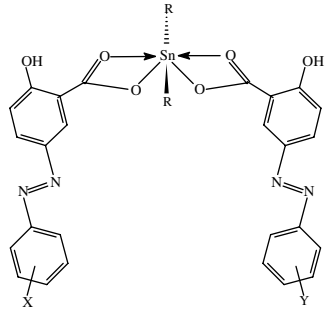
(X = H, 2'-CH_3, 3'-CH_3, 4'-CH_3, 4'-Cl, 4'-Br)

IIIa



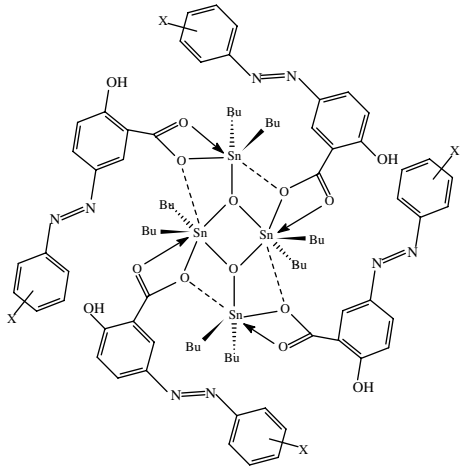
(X = H, 2'-CH_3, 3'-CH_3)

IIIb



(X = 4'-CH_3, 4'-Cl; Y = 4'-Cl, 4'-Br)

IIIc



(X = H, 4'-CH_3, 4'-Cl, 4'-Br)

IV

Scheme 1. An overview showing the coordination behaviour of 5-[(*E*)-2-(aryl)-1-diazenyl]-2-hydroxybenzoic acids towards organotin(IV).

geometry where the carboxylate ligand coordinates to Sn in an usual monodentate fashion (Scheme 1, **I**). The reactivity of the tetrahedral triphenyltin(IV) complex $Ph_3Sn(O_2CC_6H_4(OH\text{-}2)(N{=}NC_6H_4$ (2′-CH_3)-5)) towards 2,2′-bipyridine (bipy) has been investigated to ascertain the ability of bipy to coordinate to the Sn-complex and the resultant changes in the molecular architecture. The crystal structure of the product revealed that the bipy moiety does not coordinate to the Sn atom, but forms a cyclic tetrameric adduct of formula $[Ph_3Sn(O_2CC_6H_4(OH\text{-}2)(N{=}NC_6H_4(2'\text{-}CH_3)\text{-}5))(H_2O)]_2 \cdot bipy_2$ through hydrogen bonding between the water ligand of $Ph_3SnL^1H(H_2O)$ and the bipy N atoms (Scheme 1, **II**) [3]. Furthermore, a series of di-*n*-butyltin(IV) complexes of the aforementioned ligands of the formulations of $^nBu_2Sn(O_2CC_6H_4(OH\text{-}2)(N{=}NC_6H_4(X)\text{-}5))_2$ (and mixed ligand complexes) and $\{[^nBu_2Sn(O_2CC_6H_4(OH\text{-}2)(N{=}NC_6H_4(X)\text{-}5))]_2O\}_2$ were prepared and their structures were determined. In general, the X-ray diffraction studies divulge that $^nBu_2Sn(O_2CC_6H_4(OH\text{-}2)(N{=}NC_6H_4(X)\text{-}5))_2$ (X = H, 2′-CH_3, 3′-CH_3, 4′-CH_3, 4′-Br, 4′-Cl) complexes [4–6] adopt a skew-trapezoidal bipyramidal arrangement around the tin atom (Scheme 1, **IIIa**). In addition, there are weak bridging intermolecular Sn···O contacts in the di-*n*-butyltin(IV) complexes (X = H, 3′-CH_3), but not in the 4′-substituted analogues. In the case of the di-*n*-butyltin(IV) complex with the substituent X = H, the Sn···O interaction links the molecules into polymeric chains, while in the other complex (X = 3′-CH_3), these interactions link pairs of molecules into head-to-head dimeric units. In these two structures, the open side of the Sn atom actually allows one of the hydroxy oxygen atoms from the 2-hydroxybenzoate moiety of one ligand of a neighboring molecule to form a bridge and coordinate very weakly with the Sn atom, thereby completing a seventh coordination site in the extended Sn coordination sphere (Scheme 1, **IIIb**) [6]. In all of the above-described instances, the Sn atom is always coordinated by two chemically equivalent carboxylates. Attempts were also made with two different carboxylic acids in order to obtain mixed ligand complexes with the $R_2Sn(O_2CC_6H_4(OH\text{-}2)(N{=}NC_6H_4(X)\text{-}5))(O_2CC_6H_4(OH\text{-}2)(N{=}NC_6H_4(Y)\text{-}5))$ formulation. The solid state structures of three such complexes (R = Me or ^{n}Bu, and X = 4′-Cl (held constant) and Y = 4′-CH_3 or 4′-Br) were accomplished by single crystal X-ray crystallography [7]. These complexes were found to adopt the usual dicarboxylato structural type with a skew-trapezoidal bipyramidal arrangement around the tin atom (Scheme 1, **IIIc**). On the other hand, the di-*n*-butyltin (IV) complexes of the type $\{[^nBu_2Sn(O_2CC_6H_4(OH\text{-}2)(N{=}NC_6H_4\text{-}(X)\text{-}5))]_2O\}_2$ (X = H, 2′-CH_3, 3′-CH_3, 4′-CH_3, 4′-Cl, 4′-Br) are centrosymmetric tetranuclear species containing a planar Sn_4O_2 core in which two μ_3-oxo O-atoms connect an Sn_2O_2 ring to two exocyclic Sn-atoms (Scheme 1, **IV**) [8].

The organotin(IV) complexes of the types $R_3Sn(O_2C\text{-}C_6H_4(OH\text{-}2))(N{=}NC_6H_4(X)\text{-}5)$ (R = ^{n}Bu or Ph) and $^nBu_2Sn(O_2CC_6H_4(OH\text{-}2)(N{=}NC_6H_4(X)\text{-}5))_2$ were screened for larvicidal activity against the second larval instar of the *Aedes aegypti* mosquito and have shown promise as larvicides [5]. On the other hand, the di-*n*-butyltin (IV) compounds of the type $\{[^nBu_2Sn(O_2CC_6H_4(OH\text{-}2)(N{=}NC_6H_4(X)\text{-}5))]_2O\}_2$ were found to be more active in vitro than $^nBu_2Sn(O_2CC_6H_4(OH\text{-}2)(N{=}NC_6H_4(X)\text{-}5))_2$ when investigated for cytotoxic potential against human tumour cell lines [8]. In addition, diorganotin(IV) compounds are used extensively as heat stabilizers for processing polyvinyl chloride. The three major types of tin stabilizers are distinguished by their respective alkyl groups, such as octyl, butyl, and methyl, and the ligands normally used are thioglycolic acid esters, reverse esters and carboxylic acids [9,10].

Given the synthetic and structural importance and the potential biological activity of the organotin(IV) complexes of 5-[(*E*)-2-(aryl)-1-diazenyl]-2-hydroxybenzoic acid, it is of interest to explore the chemistry of the analogous complexes of these ligands with ^{n}OctSn(IV). The present contribution details the preparation and spectroscopic characterization of some di-*n*-octyltin(IV) complexes of 5-[(*E*)-2-(aryl)-1-diazenyl]-2-hydroxybenzoic acid (Fig. 1), along with the crystal structures of three compounds, viz., $^nOct_2Sn(L^1H)_2$, $\{[^nOct_2\text{-}Sn(L^2H)]_2O\}_2$ and $\{[^nOct_2Sn(L^3H)]_2O\}_2$.

2. Experimental

2.1. Materials

Di-*n*-octyltin oxide (Fluka) was used as received. The solvents used in the reactions were of AR grade and were dried using the standard literature procedures. Toluene was distilled from sodium benzophenone ketyl.

2.2. Physical measurements

Carbon, hydrogen and nitrogen analyses were performed with a Perkin–Elmer 2400 series II instrument. IR spectra in the range 4000–400 cm^{-1} were obtained on a BOMEM DA-8 FT-IR spectrophotometer as KBr discs. The ^1H, ^{13}C and ^{119}Sn NMR spectra were recorded

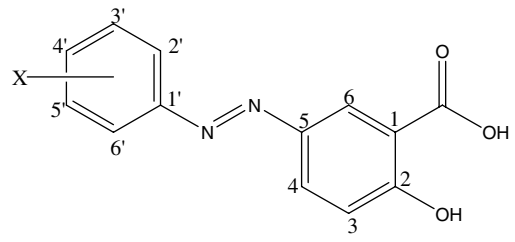


Fig. 1. Ligands used in the present work. Abbreviations: L^1HH': X = H; L^2HH': X = 2′-OCH_3; L^3HH': X = 3′-CH_3; L^4HH': X = 4′-CH_3; L^5HH': X = 4′-Cl, where H and H′ represent hydroxy and carboxylic acid H-atoms, respectively.

on a Bruker ACF 300 spectrometer and measured at 300.13, 75.47 and 111.92 MHz, respectively, or on a Mercury Plus Varian 400 NMR spectrometer measured at 400.44, 100.69 and 149.32 MHz, respectively. The ^{1}H, ^{13}C and ^{119}Sn chemical shifts were referenced to Me_4Si set at 0.00 ppm, $CDCl_3$ set at 77.0 ppm and Me_4Sn set at 0.00 ppm, respectively. Positive-ion and negative-ion electrospray ionization (ESI) mass spectra were measured on an ion trap analyzer Esquire 3000 (Bruker Daltonics, Bremen, Germany) in the range m/z 50–2600. The samples were dissolved in methanol (100%) and analyzed by direct infusion using a flow rate of 5 μl/min. The selected precursor ions were further analyzed by MS/MS analyses under the following conditions: an isolation width of $m/z = 8$ for ions containing one tin atom and $m/z = 12$ for ions containing multiple tin atoms, a collision amplitude in the range 0.7–1.0 V depending on the precursor ion stability, an ion source temperature of 300 °C, and a flow rate and pressure of nitrogen of 4 l/min and 10 psi, respectively. The tuning parameter "compound stability" was set to 100% in the positive-ion mode and 20% in the negative-ion mode. The software IsoPro 2.1 (freeware, http://members.aol.com/msmssoft/) was used for the theoretical calculation of relative isotopic abundances. 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).

2.3. Synthesis of 5-[(E)-2-(aryl)-1-diazenyl]-2-hydroxybenzoic acids

The 5-[(*E*)-2-(aryl)-1-diazenyl]-2-hydroxybenzoic acids (L^1HH', $L^{3-5}HH'$) were prepared as described in earlier reports [1,2,4,5] except for L^2HH' which is described here. The ligand, L^2HH' (5-[(*E*)-2-(2-methoxyphenyl)-1-diazenyl]-2-hydroxybenzoic acid) was prepared by a diazo-coupling reaction using *o*-anisidine and salicylic acid in alkaline medium [2]. The brown coloured precipitate was recrystallized from methanol to give pure L^2HH'. Yield: 31.5%, m.p.: 185–187 °C. Anal. Calc. for $C_{14}H_{12}N_2O_4Sn$: C, 43.01; H, 3.09; N, 7.17. Found: C, 43.09; H, 3.03; N, 7.12%. IR (KBr, cm^{-1}): 1661 $\nu(OCO)_{asym}$; ^{1}H NMR (DMSO-d_6, 300.13 MHz); δ_H: Ligand skeleton: 4.04 [s, 3H, OCH_3], 7.04 [ddd, 1H, H-3], 7.11 [dd, 2H, H-3′ and H-4′], 7.45 [ddd, 1H, H-5′], 7.68 [dd, 1H, H-6′], 8.14 [dd, 1H, H-4], 8.54 [d, 1H, H-6] ppm. Signals for the phenol and carboxylic acid were exchanged due to presence of water in the solvent. ^{13}C NMR (DMSO-d_6, 75.47 MHz); δ_C: Ligand skeleton: 56.0 [OCH_3], 112.7 [C-6′], 112.9 [C-1], 116.6 [C-3], 118.9 [C-6], 120.6 [C-5′], 127.4 [C-4], 128.2 [C-4′], 132.2 [C-3′], 141.8 [C-2′], 145.4 [C-5], 156.5 [C-1′], 164.0 [C-2], 172.3 [CO_2] ppm.

2.4. Synthesis of di-n-octyltin(IV) complexes

The di-*n*-octyltin(IV) complexes of composition $^{n}Oct_2Sn(LH)_2$ (**1**–**2**) and $\{[^{n}Oct_2Sn(LH)]_2O\}_2$ (**3**–**5**) were prepared by reacting the appropriate LHH′ with $^{n}Oct_2SnO$ in 2:1 and 1:1 molar ratios in anhydrous toluene under reflux conditions. A typical procedure is described below.

2.4.1. $^{n}Oct_2Sn(L^1H)_2$ (1)

A suspension of $^{n}Oct_2SnO$ (0.56 g, 1.54 mmol) and L^1HH' (0.75 g, 3.09 mmol) in 50 ml anhydrous toluene were refluxed for 6 h in a flask equipped with a Dean-Stark water separator and a water cooled condenser. After the reaction, an orange colored solution was obtained and filtered while hot. The solvent was concentrated on a hot plate and precipitated with petroleum ether. The orange colored precipitate was filtered and washed thoroughly with petroleum ether (60–80 °C) and dried *in vacuo*. The dried product was dissolved in anhydrous benzene–hexane (v/v 2:1), filtered off to remove any undissolved particles and the filtrate left to crystallize at room temperature. The orange crystals were isolated from the mother liquor and dried *in vacuo*. Yield: 1.15 g (89.8%), m.p.: 84–86 °C. Anal. Calc. for $C_{42}H_{52}N_4O_6Sn$: C, 60.9; H, 6.3; N, 6.8. Found: C, 61.2; H, 6.1; N, 6.5%. IR (KBr, cm^{-1}): 1630 $\nu(OCO)_{asym}$. ^{1}H NMR ($CDCl_3$, 300.13 MHz); δ_H: ligand skeleton: 7.13 [d, 1H, H-3], 7.49 [m, 3H, H-3′, H-4′ and H-5′], 7.93 [m, 2H, H-2′ and H-6′], 8.14 [dd, 1H, H-4], 8.66 [d, 1H, H-6], 11.03 [s, 1H, OH]; Sn-^{n}Oct skeleton: 0.83 [m, 3H, CH_3], 1.10–2.0 [m, 14H, CH_2], ppm. ^{13}C NMR ($CDCl_3$, 75.47 MHz); δ_C: ligand skeleton: 113.0 [C-1], 118.5 [C-3], 122.9 [C-2′ and C-6′], 128.7 [C-6], 129.1 [C-4], 129.3 [C-3′ and C-5′], 130.9 [C-4′], 145.7 [C-5], 152.7 [C-1′], 164.1 [C-2], 177.3 [CO_2]; Sn-^{n}Oct skeleton: 14.2 [CH_3], 22.7 [ηCH_2], 24.7 [ζCH_2], 27.4 [εCH_2], 28.1 [δCH_2], 28.3 [γCH_2], 31.9 [βCH_2], 33.1 [αCH_2], ppm. ^{119}Sn NMR ($CDCl_3$, 111.92 MHz); δ_{Sn}: −114.3 ppm. ESI-MS: MW = 828, $M_{mono} = 586 = L^1SnOct_2$-H. Positive-ion MS: m/z 1173 $[2^*M_{mono}+H]^+$, 100%; m/z 587 $[M_{mono}+H]^+$. MS/MS of m/z 587: m/z 569 $[M_{mono}+H-H_2O]^+$; m/z 543 $[M_{mono}+H-CO_2]^+$; m/z 361 $[M_{mono}+H-octene-octane]^+$; m/z 317 $[M_{mono}+H-octene-octane-CO_2]^+$; m/z 233 $[SnOct]^+$. Negative-ion MS: m/z 827 $[M-H]^-$, 100%; m/z 621 $[M_{mono}+Cl]^-$; m/z 241 $[L^1]^-$; m/z 197 $[L^1-CO_2]^-$. MS/MS of m/z 827: m/z 241 $[L^1]^-$. ^{119}Sn Mössbauer: $\delta = 1.46$, $\Delta = 3.41$, $\Gamma_1 = 0.83$, $\Gamma_2 = 0.82$ mm s^{-1}, $\rho = 2.34$, C–Sn–C = 142°.

2.4.2. $^{n}Oct_2Sn(L^4H)_2$ (2)

Compound **2** was prepared analogously by following the method and conditions described for **1** and using L^4HH' (0.75 g, 2.93 mmol) and $^{n}Oct_2SnO$ (0.53 g, 1.47 mmol).

The orange product was recrystallized from a benzene–hexane mixture. Yield: 1.16 g, 92.8%. m.p.: 124–126 °C. Anal. Calc. for $C_{44}H_{56}N_4O_6Sn$: C, 61.77; H, 6.60; N, 6.0. Found: C, 61.9; H, 6.7; N, 6.2%. IR (KBr, cm^{-1}): 1628 ν $(OCO)_{asym}$. ^1H NMR ($CDCl_3$, 300.13 MHz); δ_H: Ligand skeleton: 2.45 [s, 3H, CH_3], 7.13 [d, 1H, H-3], 7.32 [d, 2H, H-2′ and H-6′], 7.85 [d, 2H, H-3′ and H-5′], 8.12 [dd, 1H, H-4], 8.64 [d, 1H, H-6], 10.98 [s, 1H, OH]; Sn-^{n}Oct skeleton: 0.83 [m, 3H, CH_3], 1.10–2.0 [m, 14H, CH_2], ppm. ^{13}C NMR ($CDCl_3$, 75.47 MHz); δ_C: Ligand skeleton: 21.5 [CH_3], 112.9 [C-1], 118.3 [C-3], 122.8 [C-2′ and C-6′], 128.4 [C-6], 129.0 [C-4], 129.7 [C-3′ and C-5′], 141.2 [C-4′], 145.7 [C-5], 150.8 [C-1′], 163.7 [C-2], 177.5 [CO_2]; Sn-^{n}Oct skeleton: 14.0 [CH_3], 22.6 [ηCH_2], 24.5 [ζCH_2], 26.9 [εCH_2], 28.9 [δCH_2], 29.1 [γCH_2], 31.7 [βCH_2], 33.3 [αCH_2], ppm. ^{119}Sn NMR ($CDCl_3$, 111.92 MHz); δ_{Sn}: −115.0 ppm. ESI-MS: MW = 856. $M_{mono} = 600 = L^4SnOct_2$-H. Positive-ion MS: m/z 601 $[M_{mono}+H]^+$. MS/MS of m/z 601: m/z 583 $[M_{mono}+H-H_2O]^+$; m/z 557 $[M_{mono}+H-CO_2]^+$; m/z 443 $[M_{mono}+H-octane-CO_2]^+$; m/z 375 $[M_{mono}+H-octane-octene]^+$; m/z 331 $[M_{mono}+H-octane-octene-CO_2]^+$. Negative-ion MS: m/z 855 $[M-H]^-$; m/z 635 $[M_{mono}+Cl]^-$; m/z 255 $[L^4]^-$, 100%; m/z 211 $[L^4\text{-}CO_2]^-$. MS/MS of m/z 855: m/z 255 $[L^4]^-$. ^{119}Sn Mössbauer: $\delta = 1.49$, $\Delta = 3.51$, $\Gamma_1 = 0.80$, $\Gamma_2 = 0.83$ mm s^{-1}, $\rho = 2.36$, C–Sn–C = 143°.

2.4.3. $\{[^nOct_2Sn(L^2H)]_2O\}_2$ (3)

Orange prismatic crystals of compound **3**, m.p. 74–76 °C, were obtained from petroleum ether in 50% yield. Anal. Calc. for $C_{120}H_{180}N_8O_{18}Sn_4$: C, 57.71; H, 7.26; N, 4.49. Found: C, 57.65; H, 7.30; N, 4.52%. IR (KBr, cm^{-1}): 1622 $\nu(OCO)_{asym}$, 620 ν(Sn–O–Sn). For NMR: refer to Section 3.2 for specific comments. ESI-MS: MW = 2500. $M_{mono} = 616 = L^2SnOct_2$-H. Positive-ion MS: m/z 1233 $[2^*M_{mono}+H]^+$; m/z 927 $[M_{mono}+K+L^2H]^+$; m/z 911 $[M_{mono}+Na+L^2H]^+$; m/z 655 $[M_{mono}+K]^+$; m/z 639 $[M_{mono}+Na]^+$; m/z 617 $[M_{mono}+H]^+$. MS/MS of m/z 617: m/z 599 $[M_{mono}+H-H_2O]^+$; m/z 573 $[M_{mono}+H-CO_2]^+$; m/z 391 $[M_{mono}+H-octene-octane]^+$; m/z 347 $[M_{mono}+H-octene-octane-CO_2]^+$. Negative-ion MS: m/z 2517 $[M-H+H_2O]^-$; m/z 2499 $[M-H]^-$; m/z 2391 $[3^*M_{mono}+L^2+L^2H]^-$; m/z 2119 $[3^*M_{mono}+L^2]^-$; m/z 1775 $[2^*M_{mono}+L^2+L^2H]^-$; m/z 1539 $[2^*M_{mono}+Cl+L^2H]^-$; m/z 1503 $[2^*M_{mono}+L^2]^-$; m/z 1267 $[2^*M_{mono}+Cl]^-$; m/z 1159 $[M_{mono}+L^2+L^2H]^-$; m/z 887 $[M_{mono}+L^2]^-$; m/z 651 $[M_{mono}+Cl]^-$; m/z 271 $[L^2]^-$, 100%; m/z 227 $[L^2\text{-}CO_2]^-$; m/z 212 $[L^2-CH_3OH-N_2]^-$. MS/MS of m/z 2499: m/z 2481 $[M-H-H_2O]^-$; m/z 2227 $[M-H-L^2H]^-$; m/z 1883 $[M-H-M_{mono}]^-$; m/z 1865 $[M-H-M_{mono}-H_2O]^-$; m/z 1611 $[M-H-L^2H-M_{mono}]^-$; m/z 1249 $[M-H\text{-}2^*M_{mono}\text{-}H_2O]^-$; m/z 887 $[M_{mono}+L^2]^-$. MS/MS of m/z 2391: m/z 2119 $[3^*M_{mono}+L^2]^-$; m/z 1775 $[2^*M_{mono}+L^2+L^2H]^-$; m/z 1503 $[2^*M_{mono}+L^2]^-$; m/z 887 $[M_{mono}+L^2]^-$. MS/MS of m/z 887: m/z 271 $[L^2]^-$. ^{119}Sn Mössbauer: $\delta = 1.33$, $\Delta = 3.41$, $\Gamma_1 = 0.78$, $\Gamma_2 = 0.78$ mm s^{-1}, $\rho = 2.56$, C–Sn–C = 140°.

2.4.4. $\{[^nOct_2Sn(L^3H)]_2O\}_2$ (4)

Orange prismatic crystals of compound **4**, m.p. 74–76 °C, were obtained from benzene–acetonitrile (v/v 2:1) in 65.6% yield. Anal. Calc. for $C_{120}H_{180}N_8O_{14}Sn$: C, 59.24; H, 7.47; N, 4.61. Found: C, 59.30; H, 7.51; N, 4.65%. IR (KBr, cm^{-1}): 1628 $\nu(OCO)_{asym}$, 623ν(Sn–O–Sn). For NMR: refer to Section 3.2 for specific comments. ESI-MS: MW = 2436. $M_{mono} = 600 = L^3SnOct_2$-H. Positive-ion MS: m/z 601 $[M_{mono}+H]^+$. MS/MS of m/z 601: m/z 583 $[M_{mono}+H-H_2O]^+$; m/z 557 $[M_{mono}+H-CO_2]^+$; m/z 443 $[M_{mono}+H-octane-CO_2]^+$; m/z 375 $[M_{mono}+H-octane-octene]^+$; m/z 331 $[M_{mono}+H-octane-octene-CO_2]^+$. Negative-ion MS: m/z 2453 $[M-H+H_2O]^-$; m/z 2435 $[M-H]^-$; m/z 2311 $[3^*M_{mono}+L^3+L^3H]^-$; m/z 2055 $[3^*M_{mono}+L^3]^-$; m/z 1711 $[2^*M_{mono}+L^3+L^3H]^-$; m/z 1491 $[2^*M_{mono}+Cl+L^3H]^-$; m/z 1455 $[2^*M_{mono}+L^3]^-$; m/z 1235 $[2^*M_{mono}+Cl]^-$; m/z 855 $[M_{mono}+L^3]^-$; m/z 635 $[M_{mono}+Cl]^-$; m/z 255 $[L^3]^-$, 100%; m/z 211 $[L^3\text{-}CO_2]^-$. MS/MS of m/z 2435: m/z 2417 $[M-H-H_2O]^-$; m/z 2179 $[M-H-L^3H]^-$; m/z 1817 $[M-H-M_{mono}-H_2O]^-$; m/z 1579 $[M-H-L^3H-M_{mono}]^-$; m/z 1217 $[M-H-2^*M_{mono}-H_2O]^-$; m/z 855 $[M_{mono}+L^3]^-$. MS/MS of m/z 2055: m/z 1455 $[2^*M_{mono}+L^3]^-$; m/z 855 $[M_{mono}+L^3]^-$. MS/MS of m/z 855: m/z 255 $[L^3]^-$. ^{119}Sn Mössbauer: $\delta = 1.37$, $\Delta = 3.46$, $\Gamma_1 = 0.81$, $\Gamma_2 = 0.81$ mm s^{-1}, $\rho = 2.53$, C–Sn–C = 141°.

2.4.5. $\{[^nOct_2Sn(L^5H)]_2O\}_2$ (5)

Compound **5** was prepared by following the method and conditions described for **1** and using L^5HH' (0.50 g, 1.81 mmol) and $^nOct_2SnO$ (0.65 g, 1.81 mmol). The dried orange product was recrystallized from hot hexane. Yield: 0.61 g, 55%. m.p.: 74–76 °C. Anal. Calc. for $C_{116}H_{168}N_8O_{12}Cl_4Sn_4$: C, 56.11; H, 6.82; N, 4.51. Found: C, 56.15; H, 6.86; N, 4.54%. IR (KBr, cm^{-1}): 1628 $\nu(OCO)_{asym}$ 615ν(Sn–O–Sn). ^1H NMR ($CDCl_3$, 300.13 MHz); δ_H: Ligand skeleton: 7.08 [d, 1H, H-3], 7.30 [d, 2H, H-2′ and H-6′], 7.73 [d, 2H, H-3′ and H-5′], 8.10 [dd, 1H, H-4], 8.37 [d, 1H, H-6], 11.75 [brs, 1H, OH]; Sn-^{n}Oct skeleton: 0.77 [brm, 6H, CH_3], 0.80–2.0 [brm, 28H, CH_2], ppm. ^{13}C NMR ($CDCl_3$, 75.47 MHz); δ_C: Ligand skeleton: 114.4 [C-1], 118.6 [C-3], 124.0 [C-2′ and C-6′], 126.7 [C-6], 129.3 [C-3′ and C-5′], 136.5 [C-4], 145.1 [C-4′], 150.6 [C-5], 155.3 [C-1′], 164.7 [C-2], 175.5 [CO_2]; Sn-^{n}Oct skeleton: 14.3 [CH_3], 22.7, 25.2, 25.4, 25.7, 27.4, 29.3, 29.8, 30.2, 31.9, 33.9, 34.0 [CH_2 carbons], ppm. ^{119}Sn NMR ($CDCl_3$, 111.92 MHz); δ_{Sn}: −187.2 and −189.7 ppm. ESI-MS: MW = 2516. $M_{mono} = 620 = LSnOct_2$-H. Positive-ion MS: m/z 621 $[M_{mono}+H]^+$; m/z 459 $[SnOct_3]^+$. Negative-ion MS: m/z 2533 $[M-H+H_2O]^-$; m/z 2515 $[M-H]^-$; m/z 2411 $[3^*M_{mono}+L^5+LH]^-$; m/z 2249 $[2^*M_{mono}+L^5+L^5SnOct_3]^-$; m/z 2135 $[3^*M_{mono}+L^5]^-$; m/z 1791 $[2^*M_{mono}+L^5+L^5H]^-$; m/z 1629 $[M_{mono}+L^5+L^5SnOct_3]^-$; m/z 1551 $[2^*M_{mono}+Cl+L^5H]^-$; m/z 1515 $[2^*M_{mono}+L^5]^-$; m/z 1275 $[2^*M_{mono}+Cl]^-$; m/z 1009 $[L^5SnOct_3+L^5]^-$; m/z 895 $[M_{mono}+L^5]^-$; m/z 655 $[M_{mono}+Cl]^-$; m/z 275 $[L^5]^-$, 100%; m/z 231 $[L^5-CO_2]^-$. MS/MS of m/z 2515: m/z 2497 $[M-H-H_2O]^-$; m/z 2239

$[M-H-L^5H]^-$; *m/z* 1877 $[M-H-M_{mono}-H_2O]^-$; *m/z* 1619 $[M-H-L^5H-M_{mono}]^-$; *m/z* 1257 $[M-H-2^*M_{mono}-H_2O]^-$; *m/z* 895 $[M_{mono}+L^5]^-$. MS/MS of *m/z* 895: *m/z* 275 $[L^5]^-$. ^{119}Sn Mössbauer: $\delta = 1.34$, $\Delta = 3.45$, $\Gamma_1 = 0.82$, $\Gamma_2 = 0.82$ mm s^{-1}, $\rho = 2.57$, C–Sn–C = 141°.

2.5. X-ray crystallography

Crystals of compounds **1**, **3** and **4** suitable for an X-ray crystal-structure determination were obtained from benzene-*n*-hexane (v/v 2:1), petroleum ether and benzene–acetonitrile (v/v 2:1), respectively. The measurements were made at 293 K (**1**), 110 K (**3**) and 160 K (**4**) and with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). For **1**, a Nonius CAD4 diffractometer was used and an empirical absorption correction based on azimuthal scans [11] was applied. For **3**, a Bruker SMART APEX CCD diffractometer and an Oxford Cryosystems Cryostream 800 cooler were employed. Data reduction was performed with SAINT [12] and a multi-scan absorption correction was applied using SADABS [13]. For **4**, a Nonius KappaCCD diffractometer [14] and an Oxford Cryosystems Cryostream 700 cooler were employed and data reduction was performed with HKL DENZO and SCALEPACK [15]. An absorption correction based on the multi-scan method was applied using SORTAV [16]. For each structure, the intensities were corrected for Lorentz and polarization effects, equivalent reflections were merged and the structures were solved by direct methods using SHELXS97 [17]. In **3** and **4**, the molecule of the tetranuclear Sn-complex sits about a crystallographic centre of inversion. The octyl residues are disordered in all three compounds. In complex **1**, all atoms of the octyl groups were treated as disordered over two closely neighbouring equally occupied positions. In **3**, equally occupied split positions were defined for the terminal methyl group of one octyl residue and for all atoms of two other alkyl chains. In **4**, for the two octyl groups on the exocyclic Sn-atoms, two sets of positions were defined for all atoms of one octyl group and for the terminal ethyl segment in the other octyl group. The site occupation factors of the major conformations of these groups refined to 0.539(6) and 0.71(5), respectively. In addition, the *m*-tolyl substituent in the carboxylate ligand that bridges one endocyclic and one exocyclic Sn-centre is disordered over two equally occupied conformations. In each structure, similarity restraints were applied to the bond lengths and angles involving the disordered C atoms, while neighbouring C atoms along the disordered alkyl chains in **1** and **4** were restrained to have similar atomic displacement parameters. All disordered atoms in **3** were assigned isotropic displacement parameters.

In all structures, 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 1.2 U_{eq} of its parent atom (1.5 U_{eq} for the methyl and hydroxy groups). The orientation of each hydroxy O–H vector was optimised to correspond with the direction that would bring the H-atom closest to the nearest hydrogen bond acceptor. The refinement of each structure was carried out on F^2 using full-matrix least-squares procedures, which minimised the function $\Sigma w(F_o^2 - F_c^2)^2$. One reflection in **4**, whose intensity was considered to be an extreme outlier, was omitted from the final refinement. All calculations were performed using the SHELXL97 program [18]. The data collection and refinement parameters are given in Table 1 and views of the molecules of **1**, **3** and **4** are shown in Figs. 2–4.

3. Results and discussion

3.1. Synthesis

The 5-[(*E*)-2-(aryl)-1-diazenyl]-2-hydroxybenzoic acids (LHH′) react with di-*n*-octyltin(IV) oxide in anhydrous toluene in a 2:1 and 1:1 molar ratio to give compounds with the formulations ^{n}Oct$_2$Sn(LH)$_2$ (**1**–**2**) and {[^{n}Oct$_2$Sn(LH)]$_2$O}$_2$ (**3**–**5**). The complexes were isolated as orange crystalline solids in moderate yield and are stable in air. They are soluble in common organic solvents. Compounds **3** and **4** slowly decompose in chloroform solution.

3.2. Spectroscopy

Diagnostically important infrared absorption frequencies for the carboxylate antisymmetric [ν_{asym}(OCO)] stretching vibration of the di-*n*-octyltin(IV) complexes appears at around 1628 cm^{-1}. The assignment of the symmetric [ν_{sym}(OCO)] stretching vibration band could not be made owing to the complex pattern of the spectra. In addition, a strong broad band at around 620 cm^{-1} was detected for the complexes **3**–**5**, which was assigned to the ν(Sn–O–Sn) mode [8,19,20].

The ^{1}H and ^{13}C NMR data of the ligands are reported in Refs. [1,2]. The signals were assigned by the use of correlated spectroscopy (COSY), heteronuclear single-quantum correlation (HSQC) and Constant time Inverse-detection Gradient Accordion Rescaled (CIGAR) heteronuclear multiple-bond connectivities (HMBC) [21] experiments using gradient coherence selection. Rotating-frame Overhauser enhancement spectroscopy (ROESY) spectra were required in order to assign the aromatic protons adjacent to the methyl groups of the ligands. The conclusions drawn from the ligand assignments were subsequently extrapolated to the spectra of the complexes owing to the similarity of the spectra. The ^{1}H and ^{13}C chemical shift assignments of the octyltin moiety are readily deducible from the multiplicity patterns and resonance intensities. The assignments of the signals for compounds **1**, **2** and **5** are reported in Section 2.4.

The solution ^{119}Sn NMR resonances for the compounds of the type ^{n}Oct$_2$Sn(LH)$_2$ (**1**–**2**) in $CDCl_3$ solution are around −114 ppm and the values are consistent with those

Table 1
Crystallographic data and structure refinement parameters for the di-*n*-octyltin(IV) complexes **1**, **3** and **4**

	1	**3**	**4**
Empirical formula	$C_{42}H_{52}N_4O_6Sn$	$C_{120}H_{180}N_8O_{18}Sn_4$	$C_{120}H_{180}N_8O_{14}Sn_4$
Formula weight	827.57	2497.48	2433.18
Crystal size (mm)	$0.10 \times 0.30 \times 0.30$	$0.06 \times 0.19 \times 0.49$	$0.07 \times 0.27 \times 0.27$
Crystal color, habit	Orange, plate	Orange, plate	Orange, plate
Temperature (K)	293(2)	110(2)	160(1)
Crystal system	Triclinic	Monoclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/c$	$P2_1/c$
a (Å)	9.7452(14)	16.2650(8)	18.9370(4)
b (Å)	11.658(4)	20.1517(9)	17.9197(3)
c (Å)	19.413(5)	18.7260(9)	18.8501(3)
α (°)	95.12(2)	90	90
β (°)	102.673(15)	93.6520(10)	107.664(1)
γ (°)	102.50(2)	90	90
V (Å^3)	2079.0(9)	6125.3(5)	6095.1(2)
Z	2	2	2
D_x (g cm^{-3})	1.322	1.354	1.326
μ (mm^{-1})	0.664	0.871	0.870
Transmission factors (min, max)	0.826, 0.937	0.68, 0.95	0.809, 0.956
$2\theta_{max}$ (°)	52	54.5	50
Reflections measured	16066	60247	79934
Independent reflections (R_{int})	8131 (0.046)	13628 (0.076)	10715 (0.054)
Reflections with $I > 2\sigma(I)$	4839	10324	8360
Number of parameters	528	661	825
Number of restraints	365	286	424
$R(F)$ ($I > 2\sigma(I)$ reflections)	0.049	0.054	0.042
$wR(F^2)$ (all data)	0.105	0.115	0.124
Goodness-of-fit (F^2)	1.02	1.09	1.11
Max, min $\Delta\rho$ (e/Å^3)	0.57, −0.31	1.13, −0.80	0.97, −0.70

reported for $R_2Sn(O_2CR')_2$ systems [6,22–24]. On the other hand, the ^{119}Sn NMR spectrum for compound **5**, which is of the $\{[^nOct_2Sn(LH)]_2O\}_2$ type, displays a pair of resonances of equal intensities at −187.2 and −189.7 ppm, which confirms the presence of *endo*- and *exo*-cyclic tin atoms [25,26]. Although it is difficult to assign coordination with certainty to the tin atoms on the basis of their ^{119}Sn chemical shifts, values of δ (^{119}Sn) in the ranges −200 to −400, −90 to −190 and 200 to −60 ppm have been associated with six-, five- and four-coordinate tin centres bearing *n*-alkyl groups, respectively [27]. On this basis, two chemically different five-coordinate tin centres (endocyclic and exocyclic) are present in solution for the di-*n*-octyltin complex **5**. ^{119}Sn Mössbauer data for complexes **3**, **4** and **5** are of the same order of magnitude (see Section 2), indicating that they are isostructural in the solid state which is also reflected in the crystal structures of compounds **3** and **4** (vide infra). On the other hand, compounds **3** and **4** deserve specific mention. In the ^{1}H NMR spectra of these compounds, signals both for acidic, aromatic and aliphatic protons were considerably broadened. The acidic proton part of the ^{1}H NMR spectrum of compounds **3** and **4** measured in the temperature range 223–323 K are shown in Fig. 5. The aromatic and aliphatic proton signals behaved similarly. It is, thus, clear that both samples undergo very complex exchange processes in deuteriochloroform solution. Each particular resonance in the ^{13}C NMR spectra of compounds **3** and **4** consisted of several lines differing in tenths or hundredths of ppm or the signal was rather broadened. Proton exchange between the hydroxy and the benzoic groups is likely with concomitant rearrangement of ligand coordination around the tin atom, which generates different isomers. The exchange is quenched at low temperature where more than six different signals for the acidic protons are detected. However, the presence of two or more broad signals also at 323 K in the ^{1}H NMR spectrum of **3** and **4** and the presence of several resonances of different relative intensities and different line half-widths in the range of −120.3 to −195.6 ppm and in the range of −155.0 to −189.8 ppm, in the ^{119}Sn NMR spectra of **3** and **4**, respectively, in accordance with the presence of different tin centers, indicates also the occurrence of decomposition or hydrolytic cleavage reactions generating different species [28–32].

First-order positive-ion ESI mass spectra provide characteristic molecular adducts for the determination of molecular weights. The interpretation is complicated by the fact that unusual adducts with tin-containing fragment ions are observed as well. The characteristic neutral losses observed in tandem mass spectra, such as octane, octene, CO_2, etc., confirm the presence of these functional features in the structure. The complementary information is provided by negative-ion mode, where the ion of the deprotonated molecule $[M-H]^-$ is the most important for the interpretation of all studied compounds. Moreover, the dimeric and trimeric ions probably formed during the ionization process are identified

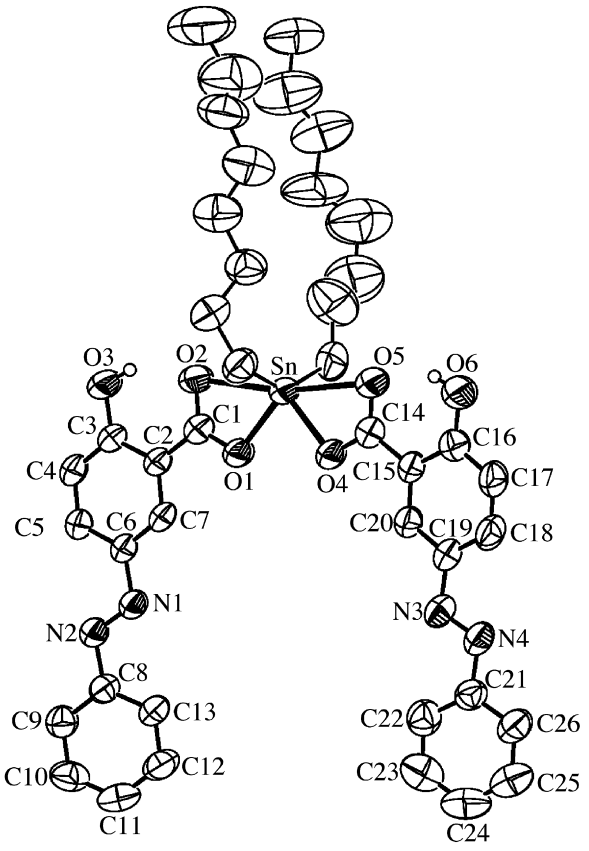


Fig. 2. The molecular structure of $^{n}Oct_2Sn(L^1H)_2$ (**1**) with 50% probability ellipsoids, carbon-bonded H-atoms omitted for clarity, and only one of the disordered arrangements of the ^{n}Oct lilgands shown.

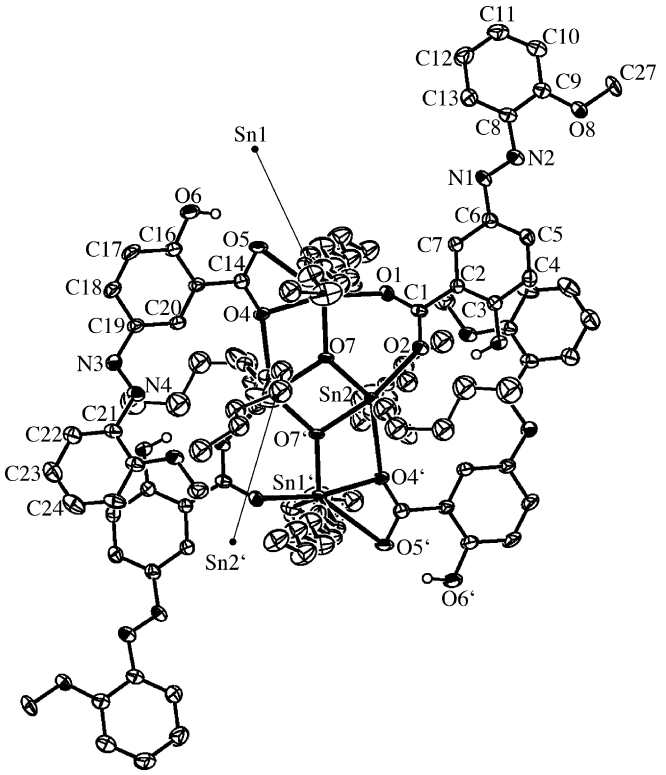


Fig. 3. The molecular structure of $\{[^{n}Oct_2Sn(L^2H)]_2O\}_2$ (**3**) with 50% probability ellipsoids, carbon-bonded H-atoms omitted for clarity, and only one of the disordered arrangements of the ^{n}Oct lilgands shown.

by their m/z values and the comparison with theoretically calculated isotopic patterns. Among other ions listed in Section 2.4, the negative-ion spectra also show the presence of adducts with the ligand and the neutral losses of ligand during the fragmentation in tandem mass spectrometric experiments.

^{119m}Sn Mössbauer spectra of complexes **1**–**5**, in the solid state, all show a well resolved single doublet with Γ values 0.78–0.83 mm s^{-1}. The Mössbauer parameter isomer shift (δ) is 1.46 and 1.49 mm s^{-1}, respectively for complexes **1** and **2**, with formula $^{n}Oct_2Sn(LH)_2$, which is typical of quadrivalent organotin derivatives, and the full width of half maximum ($\Gamma\pm$) of these resonance absorptions are approximately 0.80 mm s^{-1}, further suggesting the presence of a single tin centre in the complexes [33]. The quadrupole splitting (Δ) value for complexes **1** and **2** is 3.41 and 3.51 mm s^{-1}, respectively, consistent with hexa-coordinated tin atoms with a distorted *trans*-R_2Sn octahedral geometry [5,33]. This conclusion is in agreement with the structures determined by X-ray crystallography (see below). Both complexes display similar Mössbauer parameters, which further indicate that they are isostructural in the solid state. Using the Parish relationship between the Δ parameter value and the C–Sn–C bond angle [34], the calculated angles are 142° and 143° for **1** and **2**, respectively, which indicate a distortion from the ideal *trans*-R_2Sn octahedral structure and the angle for **1** corresponds closely with the value found in the crystal structure determination (Table 2). The ^{119m}Sn Mössbauer data for the complexes **3**, **4** and **5** are of the same order of magnitude (see Section 2), which indicates that they are isostructural in the solid state. This conclusion is also reflected in the crystal structures of compounds **3** and **4** (vide infra). These complexes with formula $\{[^{n}Oct_2Sn(LH)]_2O\}_2$ all show one well resolved single doublet with $\Gamma\pm$ values of 0.78–0.82 mm s^{-1}, which indicates that the four tin centres present in the molecule have a similar environment. The Δ values lie in the narrow range of 3.41–3.46 mm s^{-1}, which is consistent with a five-coordinate or a six-coordinate tin atom [33]. The isomer shifts of the complexes were found in the restricted range 1.33–1.37 mm s^{-1}, which is typical of quadrivalent tin centres [33]. Furthermore, the ratio of the Δ value to δ value ($\rho = \Delta/\delta$) indicates a coordination number greater than four [35]. A similar Δ range was observed recently for the di-*n*-butyltin(IV) complexes of analogous ligands having a R_2SnO_4 arrangement, which were also characterized by X-ray crystallography [7,8]. Thus, the Mössbauer results are consistent with hexa-coordinated tin atoms with a distorted *trans*-R_2Sn octahedral geometry. Furthermore, the Mössbauer results for the present investigation neither distinguish the *exo*- and *endo*-cyclic tin centres nor their calculated C–Sn–C angles (the median value was about 141°) obtained from the Parish approach [34].

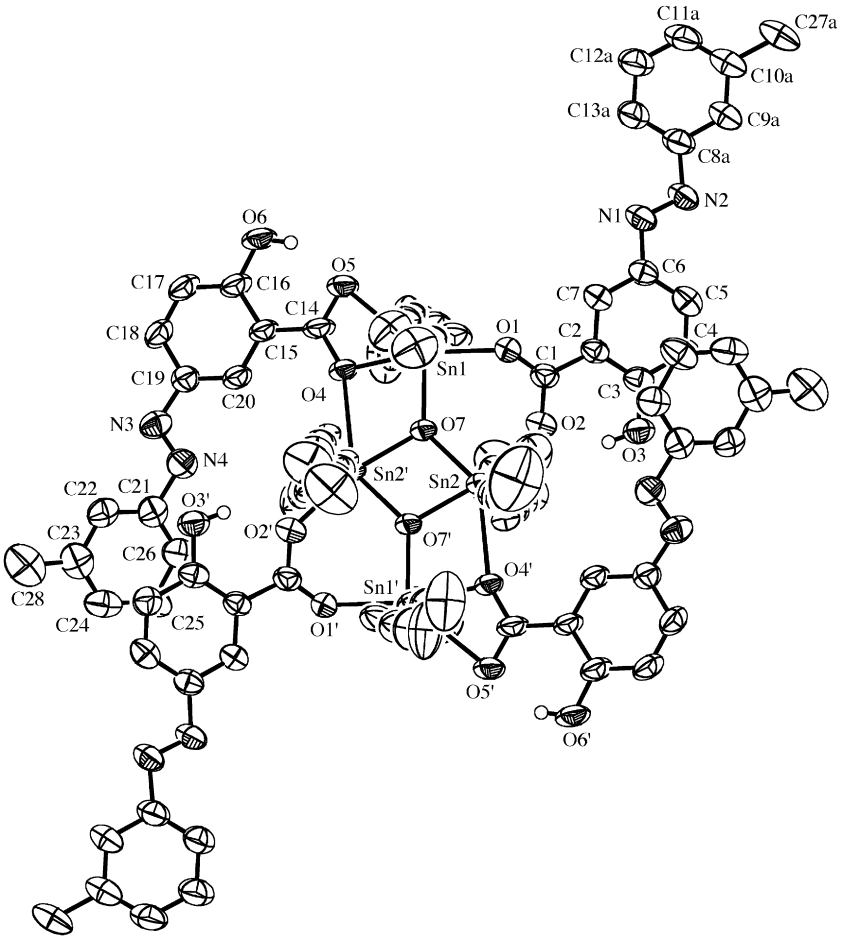


Fig. 4. The molecular structure of $\{[^{n}Oct_2Sn(L^3H)]_2O\}_2$ (**4**) with 50% probability ellipsoids, most H-atoms omitted for clarity, and only one disordered conformation shown.

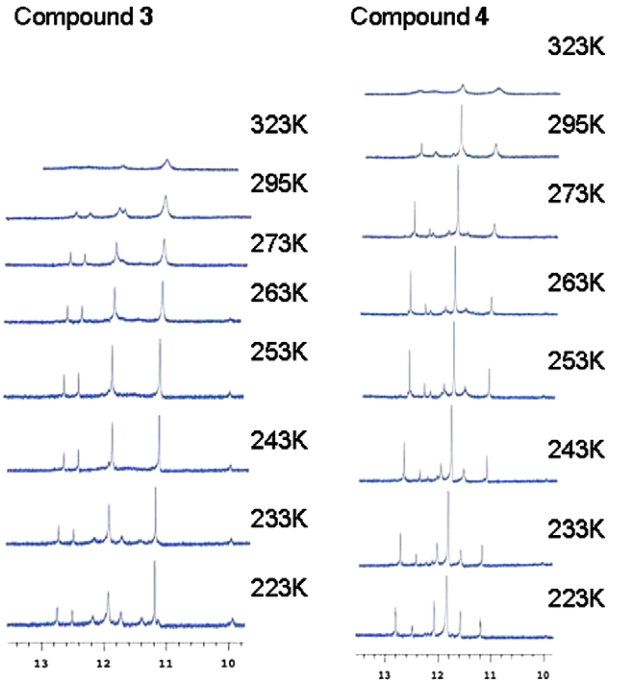


Fig. 5. Acidic proton part of the ^{1}H NMR spectra of compounds **3** and **4** measured from 223 to 323 K.

3.3. X-ray crystallography

The results of the X-ray crystallographic study on compound **1** are fully consistent with the other spectroscopic evidence described in Section 3.2. The molecular structure of compound **1** is depicted in Fig. 2, while selected geometric parameters are given in Table 2. The compound has a monomeric six-coordinate structure very similar to the

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

Sn–O(1)	2.089(3)	O(1)–C(1)	1.281(5)
Sn–O(2)	2.586(3)	O(2)–C(1)	1.253(5)
Sn–O(4)	2.089(3)	O(4)–C(14)	1.277(5)
Sn–O(5)	2.623(4)	O(5)–C(14)	1.251(5)
Mean Sn–C	2.109(9)		
O(1)–Sn–O(2)	54.57(11)	Mean O(4)–Sn–C	105.1(8)
O(1)–Sn–O(4)	82.80(11)	Mean O(5)–Sn–C	88.2(9)
O(1)–Sn–O(5)	136.72(11)	Mean C–Sn–C	139.3(10)
Mean O(1)–Sn–C	104.9(10)	C(1)–O(1)–Sn	104.3(3)
O(2)–Sn–O(4)	137.32(11)	C(1)–O(2)–Sn	81.8(3)
O(2)–Sn–O(5)	168.65(11)	C(14)–O(4)–Sn	105.2(3)
Mean O(2)–Sn–C	87.8(9)	C(14)–O(5)–Sn	80.8(3)
O(4)–Sn–O(5)	53.92(11)		

Table 3
Selected bond lengths (Å) and angles (°) for **3** and **4**

	3[a]	**4**[a]		**3**	**4**
Sn(1)–O(1)	2.232(3)	2.262(3)	Sn(2)–O(2)	2.374(3)	2.350(3)
Sn(1)–O(4)	2.197(3)	2.199(3)	Sn(2)–O(4)^{i}	2.760(3)	2.800(3)
Sn(1)–O(5)	2.799(3)	2.825(3)	Sn(2)–O(7)	2.051(3)	2.053(3)
Sn(1)–O(7)	2.042(3)	2.045(2)	Sn(2)–O(7)^{i}	2.134(3)	2.133(3)
Mean Sn(1)–C	2.133(4)	2.132(8)	Mean Sn(2)–C	2.119(6)	2.131(5)
Sn(2)···Sn(2)^{i}	3.2961(6)	3.2924(6)			
O(1)–Sn(1)–O(4)	164.92(11)	168.63(10)	O(2)–Sn(2)–O(7)	88.46(11)	88.14(11)
O(1)–Sn(1)–O(5)	143.15(10)	140.68(10)	O(2)–Sn(2)–O(7)^{i}	162.96(10)	163.05(11)
O(1)–Sn(1)–O(7)	88.14(11)	90.47(11)	O(7)–Sn(2)–O(7)^{i}	76.11(11)	76.29(11)
O(4)–Sn(1)–O(5)	50.65(9)	50.20(9)	Mean C–Sn(2)–C	139.6(4)	137.70(19)
O(4)–Sn(1)–O(7)	77.82(11)	78.63(10)	Sn(1)–O(7)–Sn(2)	134.04(14)	133.77(14)
O(5)–Sn(1)–O(7)	128.48(10)	128.81(10)	Sn(1)–O(7)–Sn(2)^{i}	120.91(13)	120.99(13)
Mean C–Sn(1)–C	140.16(18)	138.9(12)	Sn(2)–O(7)–Sn(2)^{i}	103.89(11)	103.71(11)

[a] Symmetry operation "i" moves the specified atom through the molecular crystallographic centre of inversion to the position $1-x, -y, -z$ in **3** and to $1-x, 1-y, -z$ in **4**.

structures of $^{n}Bu_2Sn(O_2CC_6H_4(OH\text{-}2)\ (N{=}NC_6H_4(X)\text{-}5))_2$ compounds [4–7]. The carboxylate groups on the ligands act as bidentate chelating agents, giving an equatorial plane around the tin of four asymmetrically coordinated oxygen atoms, whereas the octyl groups are in the axial positions, but pinned back somewhat to produce a skew-trapezoidal bipyramidal structure. The shorter Sn–O bonds are <2.1 Å and the longer Sn–O bonds are >2.5 Å, while the two octyl substituents are disposed over the longer Sn–O vectors with a C–Sn–C angle of 140.1(2)°. Each hydroxy group forms a hydrogen bond with the carbonyl O-atom of the adjacent carboxylate group within the same ligand.

The compounds **3** and **4** are centrosymmetric tetranuclear bis(dicarboxylatotetrabutyldistannoxane) complexes containing a planar Sn_4O_2 core in which two μ_3-oxo O-atoms connect an Sn_2O_2 ring to two exocyclic Sn-atoms to give a $R_8Sn_4O_2$ central unit. Views of the molecular structures of **3** and **4** are shown in Figs. 3 and 4, while selected geometric parameters are collected in Table 3. In both the structures, the molecule sits across a crystallographic centre of inversion. The molecule is a tetranuclear Sn-complex of the same type and molecular structure as that recently described for $\{[^{n}Bu_2Sn(2\text{-}OHC_6H_4C(CH_3){=}N(CH_2)_2COO)]_2O\}_2$ and its analogue [26]. The following specific details are given for the structure of **4**, but the comments apply equally well to the structure **3**. Each Sn-atom has six coordination, excluding the central Sn···Sn contact of 3.2924(6) Å. The *exo*-Sn···*endo*-Sn distances are 3.6371(4) and 3.7689(4) Å. The molecule contains two O-atoms which each bridge three Sn-centres, these being the two endocyclic and one of the exocyclic Sn-atoms. Two carboxylate ligands each bridge one endocyclic to one exocyclic Sn-centre via the two carboxylate O-atoms, with the Sn–O distances being quite similar. Two additional carboxylate ligands each have asymmetric bidentate coordination via the two carboxylate O-atoms to an exocyclic Sn-atom, with the longer Sn···O interactions being very long [2.825(3) Å]. Additionally, the other carboxylate O-atom in each of these ligands coordinates via a second long Sn···O bond [2.800(3) Å] to an endocyclic Sn-atom. Each Sn-atom is also coordinated by two octyl groups. The Sn-atoms and carboxylate ligands form an essentially planar system with the octyl groups extending roughly perpendicular to this plane. Some of the octyl groups in complexes **3** and **4** are disordered, while, in complex **4**, the *m*-toluyl substituent in the carboxylate ligand that bridges one endocyclic to one exocyclic Sn-centre is disordered over two approximately equally occupied conformations which result from a small rotation of the ring plane (see Section 2.5 for further details). Each hydroxy group forms a hydrogen bond with the carbonyl O-atom of the adjacent carboxylate group within the same ligand, thereby creating six-membered loops.

4. Supplementary material

CCDC 643300, 643301 and 643302 contain the supplementary crystallographic data for **1**, **3** and **4**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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