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Synthesis and characterization of some diorganotin(IV) complexes of Schiff bases derived from a non-protein amino acid. Crystal structures of $\{HO_2CC_6H_4[N{=}C(H)\}\{C(CH_3)CH(CH_3)\text{-}3\text{-}OH]\text{-}p\}$ and its di-*n*-butyltin(IV) complex $(^nBu_2Sn\{O_2CC_6H_4[N{=}C(H)\}\{C(CH_3)CH(CH_3)\text{-}3\text{-}OH]\text{-}p\}_2)$

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Diorganotin(IV) complexes $R_2Sn(LH)_2$ (R = Me, ^{n}Bu) and $\{[^nBu_2Sn(LH)]_2O\}_2$ (LH = 4-[(2*Z*)-(3-hydroxy-1-methyl-2-butenylidene)amino]benzoate and 4-[{(*E*)-1-(2-hydroxyphenyl)methylidene}mino]benzoate) have been reported. The complexes were characterized by elemental analysis, IR, NMR (^{1}H, ^{13}C, ^{119}Sn) and ^{119m}Sn Mössbauer spectroscopy. Crystal structures of a ligand $\{HO_2CC_6H_4[N{=}C(H)\}\{C(CH_3)CH(CH_3)\text{-}3\text{-}OH]\text{-}p\}$ and one of its di-*n*-butyltin(IV) complexes $(^nBu_2Sn\{O_2CC_6H_4[N{=}C(H)\}\{C(CH_3)CH(CH_3)\text{-}3\text{-}OH]\text{-}p\}_2)$ were determined. The spectroscopic data suggest that $R_2Sn(LH)_2$ complexes have skew-trapezoidal bipyramidal structure while $\{[^nBu_2Sn(LH)]_2O\}_2$ complexes adopt a dimeric tetraorganodistannoxane structure in the solid state and undergo complex exchange processes in deuterochloroform solution, as revealed by ^{119}Sn NMR spectroscopy.

Keywords: diorganotin; carboxylates; Schiff base; 4-[(2*Z*)-(3-hydroxy-1-methyl-2-butenylidene)amino]benzoic acid; 4-[{(*E*)-1-(2-hydroxyphenyl)methylidene}amino]benzoic acid; NMR; Mössbauer; crystal structure

Introduction

Recent years have seen a surge of activity aimed at attaching biological molecules to organometallic centers for medical purposes, prompting leading investigators to refer to the new field as bioorganometallic chemistry.[1] In this context, the coordination chemistry of organotin(IV) complexes of Schiff bases derived from amino acids has been investigated substantially by our group. Such Schiff bases have provided a great variety of molecular architectures, leading to diverged coordination modes, e.g. (a) the di-organotin(IV) complexes of the types (i) Ph_2SnL (monomeric 5-coordinate)[2,3] and (ii) $Vin_2SnL{\bullet}OH_2$ (monomeric 6-coordinate),[2] $[R_2SnL{\bullet}OH_2]_2$ (R = Me or ^{n}Bu; centrosymmetric dimer, 7-coordinate),[4] $[^nBu_2SnL]_3$ (cyclic trinuclear, 7-coordinate),[4] $[Ph_2SnL]_n$ (polymeric 6-coordinate),[4] $\{[^nBu_2Sn(LH)]_2O\}_2$ (centrosymmetric tetranuclear, 6-coordinate)[5] and $[Ph_2SnL.Phen]$ (monomeric 7-coordinate);[4] (b) the triorganotin(IV) complexes of the types (i) $[Bz_3SnLH]_2$ (centrosymmetric dimer, 5-coordinate)[6] and (ii) $[R_3SnLH]_n$ (R = Me, ^{n}Bu or Ph; polymeric 5-coordinate);[7] and (c) the dinuclear mixed organotin(IV) complexes of the type $R_2SnL.R_3SnCl$ (R = ^{t}Bu or Ph; both 5-coordinate).[2,8,9] This family of compounds, in particular

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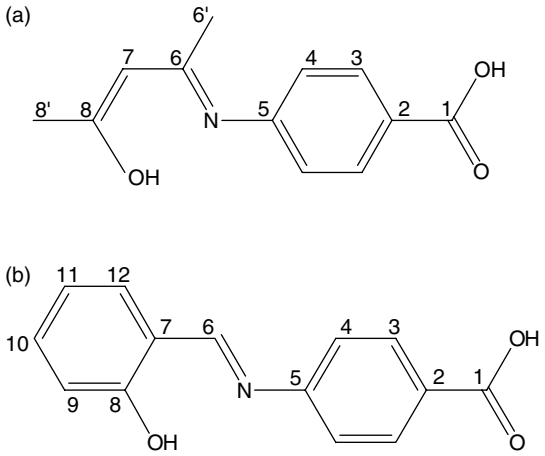


Figure 1. General structure of the ligands (abbreviations are in parentheses where H and H′ represent hydroxyl and carboxyl protons, respectively). (a) 4-[(2*Z*)-(3-hydroxy-1-methyl-2-butenylidene)amino]benzoic acid (L^1HH'). (b) 4-[{(*E*)-1-(2-hydroxyphenyl)methylidene}amino]benzoic acid (L^2HH').

$[Ph_3SnLH]_n$ and $Ph_2SnL.Ph_3SnCl$, has shown remarkable *in vitro* antitumor activity against seven well-characterized human tumor cell lines, *viz*., A498 (renal cancer), WIDR (colon cancer), M19 MEL (melanoma), IGROV (ovarian cancer), H226 (non-small cell lung cancer), MCF-7 and EVSA-T (breast cancer), using NCI protocols (T. S. Basu Baul and D. de Vos, unpublished results). A common obstacle in this work was the synthesis of Schiff bases derived from amino acids. It was not possible to prepare the preligands as free acids, and they were isolated as sodium or potassium salts, and these salts are stable for only a few days *in vacuo*. We chose to circumvent this obstacle by incorporating *p*-aminobenzoic acid with usual aldehyde or ketone and now they can be obtained in acid form and are stable for months.

This paper reports the results of extending the organotin(IV) work to the stable 4-[(2*Z*)-(3-hydroxy-1-methyl-2-butenylidene) amino]benzoic acid (L^1HH') and 4-[{(*E*)-1-(2-hydroxyphenyl) methylidene}amino]benzoic acid (L^2HH') ligand system derived from *p*-aminobenzoic acid (Fig. 1), a non-protein amino acid. However, there is no report in the extant literature of organotin(IV) complexes having been synthesized, except a very recent report[10] involving L^2HH', which appeared while the present work was in progress. In view of this and recent reports, the present paper aims to evaluate the bonding mode(s) of the diorganotin(IV) complexes from a detailed analysis of their IR, NMR (^1H, ^{13}C, ^{119}Sn) and ^{119m}Sn Mössbauer spectra. Crystal and molecular structures of the ligand L^1HH' and its di-*n*-butyltin(IV) derivative $^nBu_2Sn(L^1H)_2$ (**2**) have been also reported.

Experimental

Materials

Me_2SnCl_2 (Aldrich), $^nBu_2SnCl_2$ (Merck), $^nBu_2SnO$ (Fluka), salicylaldehyde (Lancaster), and acetylacetone (Sisco) were used as received. The solvents used in the reactions were of AR grade and dried using standard procedures. Toluene was distilled from sodium benzophenone ketyl.

Measurements

Elemental analyses (C, H, N) 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, using proton decoupled modes at 300 K. The ^1H, ^{13}C and ^{119}Sn chemical shifts were referenced to Me_4Si set at 0.00 ppm, $CDCl_3$ at 77.0 ppm and Me_4Sn at 0.00 ppm. The ^{119}Sn Mössbauer spectra were recorded with a conventional spectrometer operating in the transmission mode. The source was $Ca^{119}SnO_3$ (Ritverc GmbH, St Petersburg, Russia; 10 mCi), moving at room temperature with constant acceleration in a triangular waveform. The driving system was from Halder (Seehausen, Germany), and the NaI (Tl) detector from Harshaw (De Meern, The Netherlands). The multichannel analyzer and the related electronics were from Takes (Bergamo, Italy). The solid absorber samples, containing ca. 0.5 mg ^{119}Sn cm^{-2}, were held at 77.3 K in a MNC 200 liquid-nitrogen cryostat (AERE, Harwell, UK). The velocity calibration was made using a ^{57}Co Mössbauer source (Ritverc GmbH, St Petersburg, Russia, 10 mCi), and an iron foil as absorber. The isomer shifts are relative to room temperature $Ca^{119}SnO_3$.

Syntheses of ligands

Preparation of 4-[(2Z)-(3-hydroxy-1-methyl-2-butenylidene)amino] benzoic acid (L^1HH')

To a warm ethanol solution (20 ml) of *p*-aminobenzoic acid (3.0 g, 21.87 mmol), an ethanol solution (10 ml) of acetylacetone (2.2 g, 21.97 mmol) was added and refluxed for 5 h. The reaction mixture was filtered while hot, reduced to one-half of its original solvent volume and left to crystallize at room temperature. The block-shaped light yellow crystals of L^1HH' were isolated from the mother liquor and dried *in vacuo*. Yield: 4.0 g (86%); m.p.: 178-180 °C. Anal. found: C, 65.81; H, 6.06; N, 6.72%; calcd for $C_{12}H_{13}NO_3$: C, 65.75; H, 5.97; N, 6.39%. IR (cm^{-1}): 1699 $\nu(OCO)_{asym}$, 1600 ν (C═N), 1288 ν [Ph(C–O)]. ^1H NMR ($CDCl_3$); δ_H: 12.68 [brs, 1H, OH, D_2O exchangeable], 8.01 [d (8.5 Hz), 2H, H4], 7.11 [d (8.5 Hz) 2H, H3], 5.21 [s, 1H, H7], 2.01 and 2.02 [s, 6H, H6′ and H8′], ppm. Signal for the carboxylic acid were exchanged due to the presence of water in the solvent. ^{13}C NMR ($CDCl_3$); δ_C: 195.2 [C1], 167.0 (C6), 157.4 [C8], 141.8 [C5], 130.3 [C4], 125.7 [C2], 121.2 [C3], 98.3 [C7], 28.3 [C6′], 19.2 [C8′], ppm.

Preparation of sodium 4-[(2Z)-(3-hydroxy-1-methyl-2-butenylidene) amino]benzoate (L^1HNa)

The sodium salt of 4-[(2*Z*)-(3-hydroxy-1-methyl-2-butenylidene) amino]benzoic acid (L^1HH') was prepared by reacting stoichiometric amounts of L^1HH' with a slight excess of $NaHCO_3$ in water. The reaction mixture was heated on a water-bath until the dissolution was complete and filtered while hot. The filtrate was evaporated to dryness on a water bath, triturated with methanol and dried *in vacuo*. The dried residue was extracted with anhydrous methanol, filtered and the filtrate was evaporated to dryness. The dried residue was then washed with diethyl ether and dried *in vacuo*. Yield, 4.0 g (80%); m.p., >250 °C. IR (cm^{-1}): 1650 $\nu(OCO)_{asym}$, 1600 ν (C═ N).

Preparation of 4-[{(E)-1-(2-hydroxyphenyl)methylidene}amino] benzoic acid (L^2HH')

To a warm ethanol solution (20 ml) of *p*-aminobenzoic acid (3.0 g, 21.87 mmol), ethanol solution (10 ml) containing salicylaldehyde (2.67 g, 21.85 mmol) was added drop-wise under stirring. An immediate thick yellow precipitation was noticed, 25 ml of ethanol was added and then the reaction mixture was allowed to reflux for 2 h to ensure the completion of the reaction. The reaction mixture was filtered; the residue was washed with ethanol, then with hexane and dried *in vacuo*. The crude product was dissolved in a large volume of methanol, reduced to one-half of its original solvent volume and left to crystallize at room temperature. Dark yellow needle-shaped crystals of L^2HH' were isolated from the mother liquor and dried *in vacuo*. Yield, 4.5 g (86%); m.p., 252–253 °C (193 °C decomp., the product was not characterized by microanalytical and spectroscopic means).[10] Anal. found: C, 69.95; H, 4.66; N, 6.02%; calcd for $C_{14}H_{11}NO_3$: C, 69.70; H, 4.59; N, 5.80%. IR (cm^{-1}): 1699 $\nu(OCO)_{asym}$, 1600 ν (C═N), 1287 ν [Ph(C–O)]. ^1H NMR ($CDCl_3$); δ_H: 12.95 [brs, 1H, COOH, D_2O exchangeable], 12.72 [brs, 1H, OH, D_2O exchangeable], 9.0 [s, 1H, H6], 8.04 [d (8.5 Hz), 2H, H4], 7.71[d (7.50 Hz), 1H, H9], 7.42 [m, 3H, H3 and H10], 7.01 [m, 2H, H11 and H12], ppm. ^{13}C NMR ($CDCl_3$); δ_C: 192.4 [C1], 166 [C6], 164.6 [C8], 160.4 [C5], 133.5 [C10], 132.6 [C12], 130.7 [C4], 128.8 [C2], 121.2 [C3], 119.0 [C7], 117.0 [C9], 116.6 [C11], ppm.

Syntheses of organotin(IV) complexes

*Preparation of $Me_2Sn(L^1H)_2$ (**1**)*

A methanol solution (5 ml) of Me_2SnCl_2 (0.4g, 1.32 mmol) was added drop-wise to a filtered methanol solution (15 ml) containing L^1HNa (0.64 g, 2.65 mmol). The reaction mixture was refluxed for 5 h and filtered while hot. The filtrate was then evaporated to dryness and the residue was dried *in vacuo*. The dried mass was washed thoroughly with hexane, dried *in vacuo*, extracted in chloroform (*ca* 20 ml) and filtered while hot. The filtrate was reduced to one-quarter of the original solvent volume and then precipitated with hexane to give a light yellow product. The crude product was washed with hexane and dried *in vacuo*. Recrystallization of the product from chloroform-hexane mixture (4 : 1 v/v) yielded a light yellow microcrystalline product of **1** in 65% (0.50 g) yield; m.p., 172-174 °C. Anal. found: C, 53.41; H, 5.09; N, 4.82%; calcd for $C_{26}H_{30}N_2O_6Sn$: C, 53.37; H, 5.17; N, 4.79%. IR (KBr, cm^{-1}): 1596 $\nu(OCO)_{asym} + \nu$ (C═N), 1279 ν [Ph(CO)]. ^1H NMR ($CDCl_3$) δ_H: ligands skeleton, 12.67 [brs, 2H, OH], 8.08 [d (8.5 Hz), 4H, H4], 7.15 [d (8.5 Hz) 4H, H3], 5.27 [s, 2H, H7], 2.12 and 2.13 [s, 12H, H6′ and H8′]; Sn–Me skeleton, 1.12 [s, 6H], ppm. ^{13}C NMR ($CDCl_3$) δ_C: Ligand skeleton, 197.0 [C1], 170.9 [C6], 158.4 [C8], 143.5 [C5], 132.7 [C4], 131.7 [C2], 122.6 [C3], 99.5 [C7], 29.3 [C6′], 20.3 [C8′]; Sn–Me skeleton, 4.7, ppm. ^{119}Sn NMR ($CDCl_3$) δ_{Sn}: −123.1, ppm. ^{119}Sn Mössbauer spectrum: $\delta = 1.20$, $\Delta = 3.42$, $\Gamma\pm = 0.83$ mm s^{-1}, $\rho = 2.85$, C–Sn–C angle: 140°.

C–Sn–C angles were calculated with p.q.s. [alkyl] = −1.03 mm s^{-1}. For the ^1H- and ^{13}C- NMR assignments, refer to Fig. 1 for the numbering scheme of the ligand skeleton, while for the Sn–^{n}Bu skeleton, the numbering is as shown below:

$$\underset{CH_3}{4*}\!\!-\!\!\underset{CH_2}{3*}\!\!-\!\!\underset{CH_2}{2*}\!\!-\!\!\underset{CH_2}{1*}\!\!-\!Sn$$

*Preparation of $^nBu_2Sn(L^1H)_2$ (**2**)*

This compound was prepared in the same manner as described for **1** using $^nBu_2SnCl_2$ (0.44 g, 1.45 mmol) and L^1HNa (0.70 g, 2.90 mmol). After work-up, the crude product was re-crystallized from hexane-chloroform mixture (1 : 1, v/v) which upon slow evaporation afforded a yellow crystalline product in 58% (0.56 g) yield; m.p., 126-127 °C. Anal. found: C, 57.57; H, 6.42; N, 4.12%; calcd for $C_{32}H_{42}N_2O_6Sn$: C, 57.42; H, 6.32; N, 4.18%. IR (KBr, cm^{-1}): 1625 $\nu(OCO)_{asym}$, 1581 ν (C═N), 1273 ν [Ph(CO)]. ^1H NMR ($CDCl_3$) δ_H: ligands skeleton, 12.60 [brs, 2H, OH], 8.20 [d (8.5 Hz), 4H, H4], 7.10 [d (8.5 Hz), 4H, H3], 5.20 [s, 2H, H7], 2.05 and 2.06 [s, 12H, H6′ and H8′]; Sn–^{n}Bu skeleton, 1.72 [m, 8H, H1* and H2*], 1.33 [m, 4H, H3*], 0.81 [t, 6H, H4*], ppm. ^{13}C NMR ($CDCl_3$) δ_C: ligand skeleton, 197.0 [C1], 175.3 [C6], 158.4 [C8], 143.6 [C5], 131.8 [C4], 126.1 [C2], 122.6 [C3], 99.5 [C7], 29.4 [C6′], 20.3 [C8′]; Sn–^{n}Bu skeleton, 26.7 [C1*], 26.3 [C2*], 25.5 [C3*] 13.5 [C4*], ppm. ^{119}Sn NMR ($CDCl_3$) δ_{Sn}: −151.3 ppm. ^{119}Sn Mössbauer spectrum: $\delta = 1.38$, $\Delta = 3.26$, $\Gamma\pm = 0.75$ mm s^{-1}, $\rho = 2.36$, C–Sn–C angle: 135°.

*Preparation of $\{[^nBu_2Sn(L^1H)]_2O\}_2$ (**3**)*

Compound **3** was synthesized by reacting L^1HH' (0.35 g, 1.60 mmol) and $^nBu_2SnO$ (0.40 g, 1.60 mmol) in 50 ml of anhydrous toluene. The reaction mixture was refluxed using a Dean–Stark moisture trap and water-cooled condenser for 5 h. It was then filtered while still hot. The filtrate was collected and the volatiles were removed using a rotary evaporator. The dried mass was washed with a small amount of hexane and dried *in vacuo*. The yellow powder was dissolved in chloroform and filtered to remove any undissolved particles, precipitated with hexane and dried *in vacuo*. The crude product was recrystallized from benzene-hexane mixtures (2 : 1 v/v), which afforded a yellow crystalline product of **3** (crystals effloresce and become amorphous but it retains its chemical composition as revealed from microanalytical and IR data) in 67% (0.49 g) yield; m.p., 110-112 °C. Anal. found: C, 52.37; H, 6.66; N, 3.12%; calcd for $C_{80}H_{120}N_4O_{14}Sn_4$: C, 52.31; H, 6.58; N, 3.05%. IR (KBr, cm^{-1}): 1626 $\nu(OCO)_{asym}$, 1601 ν (C═N), 612 $\nu(Sn–O–Sn)_{asym}$. ^1H NMR ($CDCl_3$) δ_H: ligands skeleton, 12.64 [brs, 1H, OH], 8.0 [d (8.5 Hz), 2H, H4], 7.10 [d, (8.5 Hz) 2H, H3], 5.25 [s, 1H, H7], 2.12 [s, 6H, H6′ and H8′]; Sn–^{n}Bu Skeleton, 1.78-1.53 [m, 8H, H1* and H2*], 1.43-1.24 [m, 4H, H3*], 0.93-0.72 [m, 6H, H4*], ppm. ^{13}C NMR ($CDCl_3$) δ_C: ligand skeleton, 196.7 [C1], 172.1 [C6], 158.8 [C8], 142.5 [C5], 130.9 [C4], 126.1 [C2], 122.8 [C3], 99.0 [C7], 29.6 [C6′], 20.2 [C8′]; Sn–^{n}Bu skeleton, 27.7 and 27.4 [C1*], 26.3 and 26.1 [C2*], 25.4 [C3*], 13.6 [C4*], ppm. ^{119}Sn NMR ($CDCl_3$) δ_{Sn}: −210.5, −211.3, −213.2, −214.6 (signal intensity ratios: 0.8 : 1 : 1 : 0.8), ppm. ^{119}Sn Mössbauer spectrum: $\delta = 1.30$, $\Delta = 3.32$, $\Gamma\pm = 0.83$ mm s^{-1}, $\rho = 2.55$, C–Sn–C angle: 137°.

*Preparation of $^nBu_2Sn(L^2H)_2$ (**4**)*

Preparation of compound **4** was accomplished according to the procedure used for **3** by reacting $^nBu_2SnO$ and L^2HH' in 1 : 2 molar ratios except that the reaction mixture was refluxed for 12 h. The yellow microcrystalline material of the desired product was obtained after evaporation of the chloroform solution in 80% (1.20 g) yield; m.p., 187-189 °C. Anal. found: C, 60.75; H, 5.36; N, 3.90%; calcd for $C_{36}H_{38}N_2O_6Sn$: C, 60.61; H, 5.37; N, 3.93%. IR (KBr, cm^{-1}): 1620 $\nu(OCO)_{asym}$, 1600 ν (C═N). ^1H NMR ($CDCl_3$) δ_H: ligands skeleton, 12.9 [brs, 2H, OH], 8.66 [s, 2H, H6], 8.22 [d (8.5 Hz), 4H, H4], 7.44 [d (7.50 Hz), 2H, H9], 7.39 [m, 6H, H3 and H10], 6.99 [m, 4H, H11 and H12]; Sn–^{n}Bu skeleton, 1.76 [m, 8H, H1* and H2*],

1.43 [m, 4H, H3*], 0.89 [t, 6H, H4*], ppm. ^{13}C NMR ($CDCl_3$) δ_C: ligand skeleton, 198.0 [C1], 175.7 [C6], 164.4 [C8], 161.5 [C5], 134.0 [C10], 132.9 [C12], 132.3 [C4], 128.5 [C2], 121.3 [C3], 119.5 [C7], 119.2 [C9], 117.7 [C11]; Sn–^{n}Bu skeleton, 26.9 [C1*], 26.6 [C2*], 25.7 [C3*] 13.8 [C4*], ppm. ^{119}Sn NMR ($CDCl_3$) δ_{Sn}: −150.0 ppm. ^{119}Sn Mössbauer spectrum: $\delta = 1.37$, $\Delta = 3.24$, $\Gamma\pm = 0.80$ mm s^{-1}, $\rho = 2.36$, C–Sn–C angle: 134°.

Preparation of $\{[^nBu_2Sn(L^2H)]_2O\}_2.0.5C_7H_8$ (**5**)

An identical method to that of **3** was followed to synthesize **5** using $^nBu_2SnO$ and with L^2HH' in equimolar ratios. Yellow prismatic crystals of compound were obtained from toluene in 78% yield; m.p., 144-145 °C. (147-149 °C for the unsolvated form of **5**).[10] Anal. found: C, 55.76; H, 6.01; N, 2.80%; calcd for $C_{91.5}H_{116}N_4O_{14}Sn_4$: C, 55.78; H, 5.93; N, 2.84%. IR (KBr, cm^{-1}): 1619 ν(OCO)$_{asym}$, 1595 ν (C═N), 635 ν(Sn–O–Sn)$_{asym}$. ^{1}H NMR ($CDCl_3$) δ_H: ligands skeleton, 13.1 [brs, 1H, OH], 8.71 [s, 1H, H6], 8.12 [d (8.5 Hz) 2H, H4], 7.47 [d (7.50 Hz), 1H, H9], 7.39 [m, 3H, H3 and H10], 7.03 [m, 2H, H11 and H12]; Sn–^{n}Bu skeleton, 1.75-1.63 [m, 8H, H1* and H2*], 1.43-1.37 [m, 4H, H3*], 0.94-0.83 [m, 6H, H4*], ppm. ^{13}C NMR ($CDCl_3$) δ_C: ligand skeleton, 196.8 [C1], 172.5 [C6], 164.0 [C8], 161.5 [C5], 134.0 [C10], 132.8 [C12], 131.5 [C4], 128.5 [C2], 121.3 [C3], 119.5 [C7], 119.2 [C9], 117.7 [C11]; Sn–^{n}Bu skeleton, 28.6 and 28.0 [C1*], 27.7 and 27.0 [C2*], 25.8 [C3*], 13.8 [C4*], ppm. ^{119}Sn NMR ($CDCl_3$) δ_{Sn}: −212.1, −212.5, −213.6, −214.2 (signal intensity ratios: 0.8 : 1 : 1 : 0.8), ppm. ^{119}Sn Mössbauer spectrum: $\delta = 1.33$, $\Delta = 3.44$, $\Gamma\pm = 1.02$ mm s^{-1}, $\rho = 2.60$, C–Sn–C angle: 141°.

X-ray crystallography

Single crystals of L^1HH' and $^nBu_2Sn(L^1H)_2$ (**2**) suitable for an X-ray crystal structure determination were obtained from the slow evaporation of ethanol and benzene solutions, respectively. Intensity data for both compounds were collected at 100.0(1) K on a Bruker SMART APEX2 CCD area detector diffractometer with MoK_α radiation ($\lambda = 0.71073$ Å) equipped with an Oxford Cryosystem Cobra low-temperature attachment. The intensities were corrected for *Lorentz* and polarization effects, and an empirical absorption correction based on a multi-scan method was applied.[11] The structures were solved by direct-methods using SHELXTL[12] and the non-hydrogen atoms were refined with anisotropic atomic displacement parameters using the least-squares method[12] on F^2. Hydroxyl- and amine-H atoms were located from difference maps and refined isotropically. The remaining H atoms were included in their calculated positions. The data collection and refinement parameters are given in Table 1, and views of the molecular structures of L^1HH' and (**2**) are shown in Figs 3 and 4, respectively.

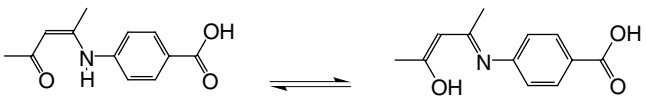
Results and Discussion

Synthetic aspects

The 4-[(2*Z*)-(3-hydroxy-1-methyl-2-butenylidene)amino]benzoic acid (L^1HH') and 4-[{(*E*)-1-(2-hydroxyphenyl)methylidene}amino]benzoic acid (L^2HH') were prepared by condensing acetylacetone or salicylaldehyde with *p*-aminobenzoic acid in ethanol. The diorganotin(IV) complexes of the type (i), $R_2Sn(LH)_2$, were prepared either by reacting sodium salts of the ligand LHNa with appropriate R_2SnCl_2 in methanol or by reacting LHH′ with R_2SnO in toluene, in a 2 : 1 molar ratio and those of type (ii), $\{[^nBu_2Sn(LH)]_2O\}_2$, were obtained by dehydration reaction of LHH′ with $^nBu_2SnO$ in 1 : 1 molar ratio in refluxing toluene. Spectroscopic properties for all complexes are given in the Experimental section. The complexes were obtained in good yield and purity. They were stable in air and soluble in all common organic solvents.

Table 1. Crystallographic data and structure refinement parameters for L^1HH' and $^nBu_2Sn(L^1H)_2$ (**2**)

	L^1HH'	$^nBu_2Sn(L^1H)_2$ (**2**)
Empirical formula	$C_{12}H_{13}NO_3$	$C_{32}H_{42}N_2O_6Sn$
Formula weight	219.23	669.37
Temperature (K)	100.0(1)	100 .0(1)
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1$	$C2/c$
a (Å)	7.6273(2)	29.9796(9)
b (Å)	8.8051(2)	6.7555 (2)
c (Å)	16.1761(2)	31.1310(9)
β (deg)	90.8850(10)	92.2580 (10)
V (Å^3)	1086.24(4)	6300.0 (3)
Z	4	8
D_x (g cm^{-3})	1.341	1.411
μ (mm^{-1})	0.097	0.856
$2\theta_{max}$ (deg)	1.3–28.8	1.3–30.0
Reflections measured	12102	47018
Reflections with $I > 2\sigma(I)$	3016	9204
Number of parameters	309	384
Number of restraints	1	0
$R(F)$ [$I > 2\sigma(I)$reflns]	0.043	0.023
$wR(F^2)$ (all data)	0.091	0.055
GOF (F^2)	1.05	1.12



I II

Figure 2. The tautomeric equilibrium: *keto-enamine* (**I**) and *enol-imine* (**II**) in L^1HH'.

Spectroscopy

The ligand L^1HH' can exist in the *keto-enamine* (**I**) and *enol-imine* (**II**) tautomeric forms, as shown in Fig. 2. The tautomeric form **I** was found to be predominant in the solid state, where the phenolic proton moved to near the imine N-atom [see Fig. 3(a) for crystal structure]. This was also reflected in the IR spectrum, where a medium intensity band at around 3370 cm^{-1} was detected due to ν NH vibration. The existence of the tautomeric form **II** was evident from the ^{1}H NMR data of L^1HH' in $CDCl_3$, which displayed a broad singlet at 12.68 ppm (OH, D_2O exchangeable, see the Experimental) owing to possible migration of the H-atom to the oxygen atom. On the other hand, L^2HH' existed predominantly in *enol-imine* tautomeric form **II** both in solution and in solid state, which was reflected in the ^{1}H NMR spectra of L^2HH' and also in its complex $\{[^nBu_2Sn(L^2H)]_2O\}_2$ (unsolvated form of **5**),[10] for which the crystal structure is available.

Relevant diagnostically important infrared absorption frequencies due to the carboxylate antisymmetric [ν_{asym}(OCO)] stretching

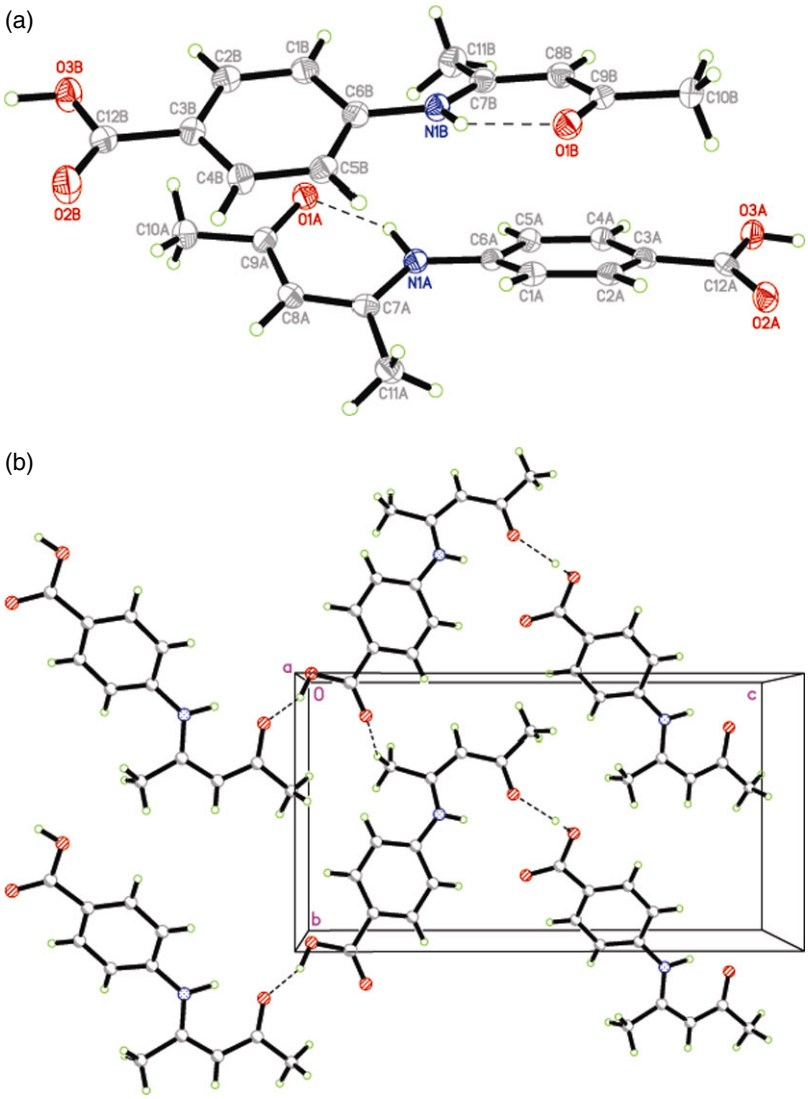


Figure 3. (a) The molecular structures of the two independent molecules of L^1HH' showing the atom-labeling scheme (50% probability ellipsoids); N–H···O intramolecular are shown as dashed lines. (b) Packing diagram of L^1HH' viewed along the *a*-axis; O–H···O hydrogen bonds are drawn as dashed lines.

vibration of the ligands and their complexes with diorganotin(IV) are given in the Experimental section. The assignment of the symmetric [ν_{sym}(OCO)] stretching vibration band was not straightforward owing to overlap with other absorptions due to the ligand. The [ν_{asym}(OCO)] stretching vibration for the ligands (L^1HH' and L^2HH') occurred at 1699 cm^{-1} as a very strong, sharp band. In the diorganotin(IV) complexes, the carbonyl stretching frequency shifted to ~1600–1625 cm^{-1} and such a shift was ascribed to the carboxylate coordination to Sn atom in accordance with earlier reports.[2,4,5]

The ^1H and ^{13}C NMR data of L^1HH' and L^2HH' are given in the Experimental section. The conclusions drawn from the ligand assignments were then subsequently extrapolated to complexes owing to their data similarity, and it was possible to detect all proton and carbon signals for compounds **1**–**5**. The ^1H NMR integration values and the number of ^{13}C signals corresponded to the proposed formulations of the products. The ^1H and ^{13}C chemical shift assignment of the diorganotin(IV) moiety was straightforward from the multiplicity patterns and resonance intensities. The difference in the chemical shift (i.e. Δ) of corresponding protons and carbons between the free ligand and the organotin complex is evidence of the existence of complexes in solution. For the dimethyltin(IV) complex **1**, the $^2J(^{119}Sn-^1H)$ coupling constant value (88 Hz) was in agreement with values reported for dimethyltin(IV) complexes (85–110 Hz) containing chelating unsymmetric O_2-donor ligand.[13] Using Lockhart's equation {Me–Sn–Me = $0.0161[|^2J(^{119}Sn,^1H)|]^2 - 1.32[^2J(^{119}Sn,^1H)] + 133.4$}, the C–Sn–C angle for **1** was estimated to be 141.4°.[14] The $^1J(^{13}C-^{119}Sn)$ coupling constant of **1** was 740 Hz and the calculated C–Sn–C angle was found to be 141.9° by applying the equation reported in the text. The calculated C–Sn–C value perfectly matched value calculated by Lockhart equation on the tin-proton coupling constant and Mössbauer data. The C–Sn–C angles for complexes **2** and **4** were calculated using the equation[15] $^1J(^{119}Sn,^{13}C) = 10.7\theta - 778$ with the $^1J(^{119}Sn,^{13}C)$ values of 581 and 580 Hz, respectively and, the corresponding calculated angles were 127.0 and 126.9°, respectively. Similarities of the calculated angles indicated that both the di-*n*-butyltin(IV)

complexes **2** and **4** were isostructural in solution, which was also reflected in the ^{119}Sn NMR chemical shifts. However, the calculated angles showed somewhat divergence compared with the values detected in the X-ray crystal structure of **2**. In the ^{13}C NMR spectra for the compounds **3** and **5**, a pair of resonances was observed for the C1* and C2* of the Sn–^{n}Bu skeletons. Although two structurally different carboxylate groups were also expected to be present in the complexes, occurrence of only a signal resonance due to CO_2 in ^{13}C NMR spectra revealed that the carboxylate groups were similar in solution on an NMR time scale.

The ^{119}Sn NMR chemical shifts of the diorganotin(IV) complexes **1**–**5** in $CDCl_3$ solution are listed in the Experimental. The diorganotin(IV) complexes of the type $R_2Sn(LH)_2$ **1, 2** and **4** exhibited a single sharp resonance in the range −123 to −150 ppm. The δ (^{119}Sn) values were in the range reported for five- to six-coordinated tin compounds.[16–19] The ^{119}Sn NMR values were consistent with those reported for the diorganotin(IV) diacetates and dibenzoates,[15,20–24] i.e. the tin atom was six-coordinated with two bis-chelated carboxylate ligands. If the δ(^{119}Sn) values are compared with those found for $R_2Sn(\beta$-diketonate$)_2$ complexes,[25–28] it is evident that in **1, 2** and **4** the secondary Sn–O bond are weaker in solution. It is well known that the extent of the δ(^{119}Sn) chemical shift of complexes having the same coordination number depends primarily on the types of substituent on the tin atom.[29,30] The δ (^{119}Sn), as expected, was greater for $^{n}Bu_2Sn(LH)_2$ with respect to $Me_2Sn(LH)_2$ complexes. On the other hand, the ^{119}Sn-NMR spectra of the complexes of the type $\{[^{n}Bu_2Sn(LH)]_2O\}_2$ **3** and **5**, displayed four resonances of variable intensities with at least two strongest signals at around −211 and −214 ppm. The spectra of compounds **3** and **5** were typical of species containing more than one tin center. The complexity of the tin NMR spectra also suggests dissociation in solution or formation of different isomers.[31] Although it is difficult to assign coordination numbers and geometry 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-coordinated tin centers bearing *n*-butyl groups, respectively.[32]

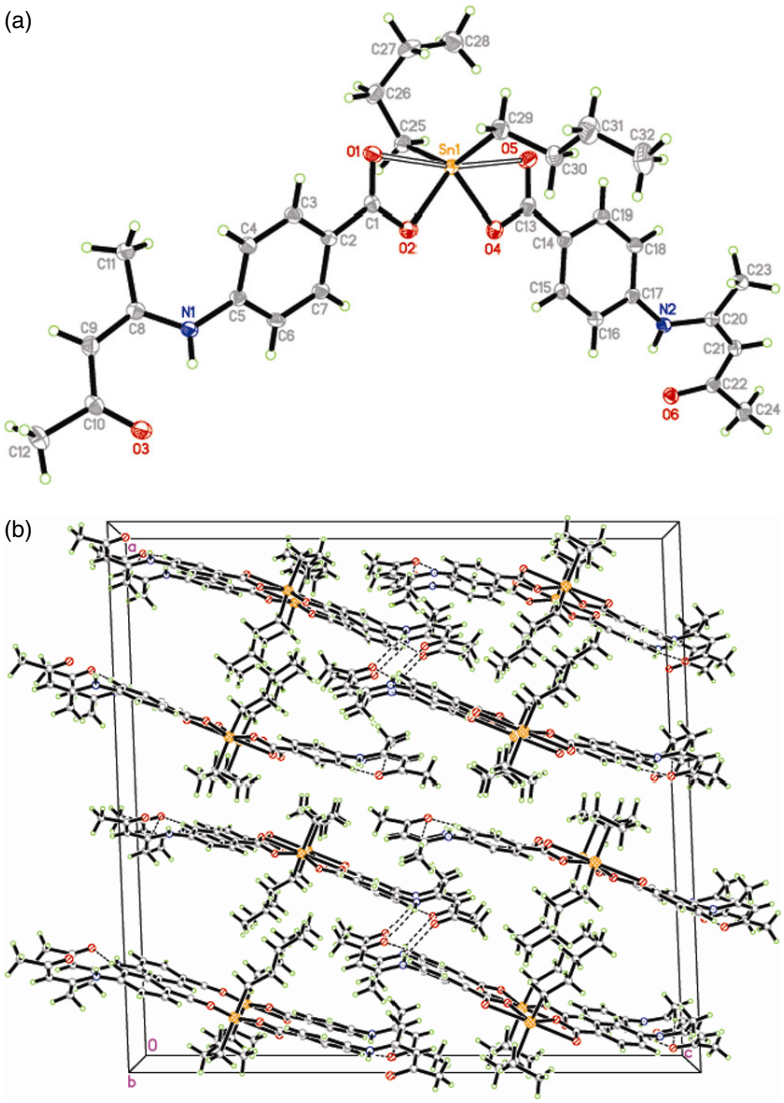


Figure 4. (a) The molecular structure of $^{n}Bu_2Sn(L^1H)_2$ (**2**) showing the atom-labeling scheme (50% probability ellipsoids). (b) Packing diagram of $^{n}Bu_2Sn(L^1H)_2$ viewed along the *b*-axis, showing molecular sheets parallel to the *ac*-plane. Hydrogen bonds are drawn as dashed lines. The molecules are also stacked into columns down the *b*-axis.

If two of the peaks found in the spectra of **3** and **5** are considered to be due to *endo* and *exo* species, the other two, which are very close to each other and smaller in intensities, but different with respect to those found in **2** and **4**, could be assigned to different isomeric forms. The δ (^{119}Sn) values were close to that reported for analogous tetraorganostannoxane complexes[5,33] and the results were consistent with the X-ray crystal structure described by Yin *et al*.[10] This demonstrates that the coordination environment of the tin atoms in the solid state is at least partly retained in solution. Thus, the ^{13}C- and ^{119}Sn-NMR data for the complexes **3** and **5** provide reasonable support for the formation of a dimeric tetraorganodistannoxane structure.[33,34]

The quadrupole splitting (Δ) values in the Mössbauer spectra for complexes of the type $R_2Sn(LH)_2$ **1, 2** and **4** lie in the range 3.24-3.42 mm s^{-1}, which is consistent with a five-coordinated or a six-coordinated tin atom, and the isomer shifts (δ) values are found in the range 1.20-1.38 mm s^{-1}, which is typical of quadrivalent tin centers.[35] Further, the ratio of the quadrupole splitting value to isomer shift value ($\rho = \Delta/\delta$) indicates coordination greater than four.[36] An octahedral configuration at the tin atom with *trans*- alkyl groups[23,37] can be postulated. In fact, this conclusion is in excellent agreement with the Mössbauer data of ^{n}Bu$_2$Sn{O$_2$CC$_6$H$_4$(OH-2)(N=NC$_6$H$_4$(X) − 5)}$_2$ (X = various nuclear substituents) complexes, which were recently characterized by crystallography.[23,37] Using the Parish relationship between Δ parameter value and C–Sn–C bond angle,[38] the latter was calculated. The calculated angles were 140° (**1**), 135° (**2**) and 134° (**4**), which indicate a distortion from the ideal *trans*-R$_2$Sn octahedral structure, and the C–Sn–C bond angle of **2** closely matched the value found in the crystal structure determination (see Table 2). The ^{119}Sn Mössbauer spectra of {[^{n}Bu$_2$Sn(LH)]$_2$O}$_2$ **3** and **5** showed one well-resolved single doublet with $\Gamma\pm$ values 0.83 and 1.02 mm s^{-1}, which indicates that the four tin centers present in the molecule have a similar environment. The Δ values are 3.32 and 3.44 mm s^{-1}, respectively, were consistent with a five-coordinate or a six-coordinated tin atom.[35] A similar Δ range was observed recently for the analogous di-*n*-butyltin(IV) complexes {[^{n}Bu$_2$Sn{*O*$_2$CC$_6$H$_4$(OH-2)(N=NC$_6$H$_4$(X) − 5)}]$_2$O}$_2$ (X = various nuclear substituents) having a bis[dicarboxylatotetraorganodistannoxane] unit, which were also characterized by X-ray crystallography.[38] Thus, the Mössbauer results are consistent with hexa-coordinated tin atoms with a distorted *trans*-R$_2$Sn octahedral geometry. Both complexes (**3** and **5**) display similar Mössbauer parameters, which further indicate that they are isostructural in the solid state. Furthermore, the Mössbauer results for complexes **3** and **5** of the present investigation could not distinguish the *exo*- and *endo*- cyclic tin centers in the complexes.

X-ray crystallography

The results of the X-ray crystallographic studies on L^{1}HH′ and ^{n}Bu$_2$Sn(L^{1}H)$_2$ (**2**) were fully consistent with the other spectroscopic evidence presented above. L^{1}HH′ crystallizes in the monoclinic $P2_1$ space group with two independent molecules *A* and *B* in an asymmetric unit [Fig. 3(a)]; a test for higher symmetry did not indicate this possibility.[39] The dihedral angles between the aromatic ring and the mean plane through the N1/O1/C7–C11 moiety are 36.5(1) and 26.3(1)° in molecules *A* and *B*, respectively. The carboxylic groups in both molecules are coplanar with the mean planes of the attached aromatic rings. There are N–H···O intramolecular hydrogen bonds between amine and carbonyl groups [Fig. 3(a)]. In the crystal packing [Fig. 3(b)], the molecules are linked by intermolecular O–H···O hydrogen bonds (O3A–H3OA···;O1B; symmetry code: $1-x, -1/2+y, 1-z$; and O3B–H3OB···;O1A; symmetry code: $2-x, 1/2+y, -z$] into zig-zag chains along the *c*-axis. The adjacent chains are linked by weak C–H···;O intermolecular interactions [C11B–H11F···;O2B; symmetry code: $x, -1+y, z$] to form molecular sheets parallel to the *bc*-plane.

Compound ^{n}Bu$_2$Sn(L^{1}H)$_2$ (**2**) crystallizes in the monoclinic $C2/c$ space group and has a monomeric six-coordinate structure [Fig. 4(a)]. The carboxylate groups on the ligands act as bidentate chelating agents, giving a basal plane around the Sn(IV) of four unsymmetrically coordinated oxygen atoms with the Sn–O bond distances being 2.094(1), 2.099(1), 2.564(1) and 2.573(1) Å, whereas the two butyl groups are in the axial positions with Sn–C bond distances of 2.127(2) and 2.129(2) Å, but pinned back to produce a skew-trapezoidal bipyramidal structure (Table 2). Such a configuration is commonly encountered in diorganotin carboxylates which exhibit Sn–O1 values of $\leq$2.2 Å and Sn–O2 values of $\geq$2.5 Å.[23,24,40–42] In **2**, the C–Sn–C angle is 137.10(8)°. In the crystal structure of **2** [Fig. 4(b)], weak C–H···;O intermolecular interactions (C4–H4A···;O3, C18–H18A···;O6 and C23–H23A···;O6; symmetry code: $x, -1+y, z$) link molecules into molecular sheets parallel to the *ac*-plane (Table 3).

Based on structural inferences extracted and stoichiometry of the products, the complexes of the types $R_2Sn(LH)_2$ and {[^{n}Bu$_2$Sn(LH)]$_2$O}$_2$ (motif I)[37] in the solid state may be formulated as shown in Fig. 5.

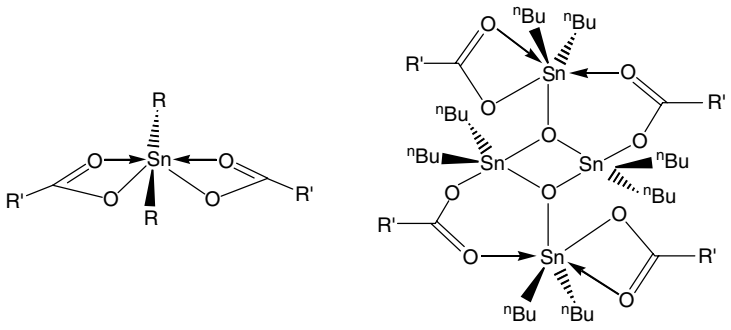
Table 2. Selected bond lengths (Å) and angles (deg) for ^{n}Bu$_2$Sn(L^{1}H)$_2$ (**2**)

Sn1–O2	2.099(1)	O4–Sn1–O2	80.87(4)
Sn1–O4	2.094(1)	O5–Sn1–O2	136.0(1)
Sn1–O1	2.573(1)	O1–Sn1–O2	55.4(1)
Sn1–O5	2.564(1)	C25–Sn1–O2	102.78(6)
Sn1–C29	2.127(2)	C29–Sn1–O2	109.42(6)
Sn1–C25	2.129(2)	O5–Sn1–O4	55.2(1)
O1–C1	1.245(2)	O1–Sn1–O4	135.9(1)
O2–C1	1.300(2)	C25–Sn1–O4	107.29(6)
O3–C10	1.245(2)	C29–Sn1–O4	105.20(6)
O4–C13	1.302(2)	C29–Sn1–C25	137.10(7)
O5–C13	1.242(2)	O5–Sn1–C29	86.6(1)
O6–C22	1.249(2)	O1–Sn1–C29	86.3(1)

Table 3. Hydrogen bonding geometry (Å, deg) for ^{n}Bu$_2$Sn(L^{1}H)$_2$ (**2**)

D–H···A	D–H	D–H···.A	D···.A	< D–H–A
N2–H1N2···O6	0.83(3)	1.97(2)	2.6717(18)	141(2)
N1–H1N1···O3	0.84(2)	2.01(2)	2.6953(18)	138.7(17)
N1–H1N1···O3^{i}	0.84(2)	2.47(2)	3.0862(17)	130.5(16)
C4–H4···O3^{ii}	0.93	2.4543	3.3111(19)	153
C18–H18A···O6^{ii}	0.93	2.5047	3.3751(18)	156
C23–H23B···O6^{ii}	0.96	2.5325	3.488(2)	173

Symmetry code: (i) $1/2-x, 5/2-y, -z$; (ii) $x, -1+y, z$.



Compounds: **1** (R = Me), **2** and **4** (R = ^{n}Bu) **3** and **5**

Figure 5. The structures of the diorganotin(IV) complexes.

Supplementary material

CCDC-646867 and CCDC-646868 contain the supplementary crystallographic data for L^1HH' and $^{n}Bu_2Sn(L^1H)_2$ (**2**), respectively. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

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