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Research paper

Perceptive variation of carboxylate ligand and probing the influence of substitution pattern on the structure of mono- and di-butylstannoxane complexes

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ABSTRACT

By reacting 2- and 3-aminobenzoic acids (HL¹ and HL², respectively), as well as 2-, 3- and 4-{(E)-2-[4-(dimethylamino)phenyl]diazenyl}benzoic acids (HL³, HL⁴ and HL⁵, in this order) with a *n*-butyltin(IV) source [^{*n*}BuSn(O)OH or ^{*n*}Bu₂SnO], the drum-type butylstannoxane complexes of general composition [^{*n*}Bu₆Sn₆O₆(L^{*n*})₆] [L^{*n*} = L¹ (1), L² (2) and L³ (3)] and the ladder-type compounds [^{*n*}Bu₈Sn₄O₂(L^{*n*})₄] [L^{*n*} = L³ (5), L⁴ (6) and L⁵ (7)] were obtained and fully characterized. By reacting 1 with 2-{(E)-[4-(dimethylamino)benzylidene]amino]benzoic acid (HL⁶), a co-crystal (4) was achieved which comprises the metal complex aggregate found in 1 and the neutral HL⁶ molecule. The solution properties of the compounds were assessed from ¹H and ¹³C NMR studies and, for the metal complexes, also from ¹¹⁹Sn NMR. The molecular structures of 1, 2, 4–7 were confirmed by single-crystal X-ray diffraction. Compounds 1–3 and the complex moiety of 4 display hexameric Sn₆O₆ clusters with drum-like structures, but 5–7 reveal Sn₄O₂ cores with ladder-type structural motifs. Besides the observed relationship between the ligand N-functional group and obtained (drum- or ladder-type) assemblies, the relative position of the carboxylate group in the ligand itself influences its coplanarity.

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1. Introduction

Organotin compounds have many sustainable chemistry applications, from wood preservation to organic syntheses, and more recently antitumor drugs [1–4] and carbon dioxide capture [5]. Organotin carboxylates in particular have found use as homogenous catalysts in PVC stabilisation, polyurethane formation and transesterification [6]. The structural chemistry of organotin carboxylates displays a rich diversity including monomers, dimers, tetrameric ladders, hexameric drums and polymers [7–9]. While significant structural changes are expected from altering the number of organic groups at tin, seemingly small differences in organic group or carboxylate ligand can also result in major changes. However, the 1:1 reaction of carboxylic acids with n-butylstannonic acid and di-n-butyltin oxide results predominantly in the hexanuclear drums, [n BuSn(O)O₂CR]₆ and tetranuclear ladders,

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http://dx.doi.org/10.1016/j.ica.2016.05.008 0020-1693/© 2016 Elsevier B.V. All rights reserved. {[${}^{n}Bu_{2}SnO_{2}CR$]₂O}₂, respectively. Reliable formation of these defined core structures has allowed variation of the carboxylate ligand in order to create interesting supramolecular structures through a range of intermolecular interactions including Sn···O, C—H···O, C—H···N, C—H··· π and π - π stacking [10–17]. Super gelators have even been obtained by assembly of supramolecular networks containing the organostannoxane drum core and alkoxy-substituted benzoate peripheries [18,19]. The organized self-assembly of organostannoxane ladders and drums has also resulted in them being used as supports for functional groups [20] including calixarenes [21], porphyrins [22], metallocenes [23–27] and photoactive substituents [28,29], as well as to create dendrimers with up to 24 fullerenes [30].

In this paper we report multinuclear organostannoxanes with drum- or ladder-type structural motifs (Scheme 1), the former with aminobenzoate ligands and the latter with related framework ligands where an azo group (—N—N—ArNMe₂) replaced the amino group. In the case of ladders, a systematic variation of the carboxy-late anchoring positions were accomplished. Such frameworks are of current interest due to their potential use in dye-sensitized solar cells [31–34], photoinduced azo dye-doped nematics [35–38] and

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Scheme 1. Generic structures of HLⁿ (n = 1-5), with numbering protocol, and of the drum- (A) and ladder-type (B) tin(IV) compounds.

others [39,40]. The pro-ligands used in this work comprise 2- and 3-aminobenzoic acids (HL¹ and HL², respectively), the 2-, 3- and 4-{(E)-2-[4-(dimethylamino)phenyl]diazenyl}benzoic acid, (HL³, HL⁴ and HL⁵ in this order), and also the 2-{(E)-[4-(dimethylamino)benzylidene]amino}benzoic acid (HL⁶) (Scheme 1).

Further, as part of a program to determine the structures arising from the coordination of the ligands L^{*n*-} to Sn⁴⁺, seven new butylstannoxane complexes were synthesized and characterized spectroscopically, viz. $[{}^{n}Bu_{6}Sn_{6}O_{6}(L^{1})_{6}]$. $C_{8}H_{10}$ (1), $[{}^{n}Bu_{6}Sn_{6}O_{6}(L^{2})_{6}]$ (2), $[{}^{n}Bu_{6}Sn_{6}O_{6}(L^{3})_{6}]$ (**3**), $[{}^{n}Bu_{6}Sn_{6}O_{6}(L^{1})_{6}] \cdot (HL^{6}) \cdot 2(C_{7}H_{8})$ (**4**), $[{}^{n}Bu_{8}Sn_{4} O_2(L^3)_4$] (**5**), [^{*n*}Bu₈Sn₄O₂(L⁴)₄] (**6**) and [^{*n*}Bu₈Sn₄O₂(L⁵)₄] (**7**). Detailed structural information on 1, 2, 4-7 has been obtained through single-crystal X-ray crystallographic analyses, which allowed assessing the influence of carboxylate coordination in hexanuclear organostannoxane drums and tetranuclear ladders, their solidstate molecular structures and supramolecular features.

2. Experimental

2.1. Materials

Anthranilic acid (Sigma-Aldrich), m-aminobenzoic acid, paminobenzoic acid, 4-N,N-dimethylaminobenzaldehyde (SRL), N, *N*-dimethylaniline (sd fine-chem), *n*-dibutyltin oxide and *n*-butylstannoic acid (Fluka) were used. The solvents used in the reactions were of AR grade and dried using standard procedures. Toluene was distilled from sodium.

2.2. Physical measurements

Melting points were measured using a Büchi melting point apparatus M-560 and are uncorrected. 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 Perkin Elmer Spectrum BX series FT-IR spectrophotometer with samples investigated as KBr discs.

¹H and ¹³C NMR spectra were recorded on a Bruker AMX 400 spectrometer and measured at 400.13 and 100.62 MHz, respectively. ¹¹⁹Sn NMR spectra were measured on a Jeol GX 270 spectrometer at 100.75 MHz. The ¹H, ¹³C and ¹¹⁹Sn chemical shifts were referenced to Me₄Si (δ 0.00 ppm), CDCl₃ (δ 77.00 ppm), and Me₄Sn (δ 0.00 ppm), respectively. The NMR data of complexes 1– 7 have been reported in Table 1. Absorption measurements were carried out on a Perkin-Elmer Lambda25 spectrophotometer at ambient temperature in freshly prepared benzene solutions.

2.3. Synthesis of pro-ligands

2.3.1. Synthesis of 2-{(E)-2-[4-(dimethylamino)phenyl]diazenyl} benzoic acid (HL³)

HL³ was prepared by following the method reported in Ref. [41] with slight modification. Anthranilic acid (3.25 g, 23.69 mmol) in a mixture of concentrated HCl (2.5 mL) and water (7 mL) was diazotized with cold NaNO₂ solution (1.80 g, 26.00 mmol, 3.5 mL water). A cold solution of *N*,*N*-dimethyl aniline (4.25 g, 35.00 mmol) was then added fairly rapidly to the cold diazonium salt solution and

Table 1

H, ${}^{13}C$ and ${}^{119}Sn$ NMR data of butyltin(IV) compounds 1-7 ^{a,b,c}	
	_

H/C no.	1		2		3		4 ^d		5		6		7	
	$\delta(^{1}H)$	δ(¹³ C)	$\delta(^{1}H)$	δ(¹³ C)	$\delta(^{1}H)$	δ(¹³ C)	$\delta(^{1}H)$	$\delta(^{13}C)$	$\delta(^{1}H)$	δ(¹³ C)	$\delta(^{1}H)$	δ(¹³ C)	$\delta(^{1}H)$	δ(¹³ C)
1	-	174.3	-	172.4	-	175.1	-	174.3	-	172.5	-	172.5	-	172.5
2	-	114.5	6.85	115.2	-	127.6	-	114.4	-	125.7	8.42	123.5	8.08	121.8
3	7.90	132.6	7.06	133.1	7.70	130.7	7.90	132.5	7.10-7.43	134.3	-	134.3	7.85	130.8
4	6.63	116.8	6.94	118.2	7.01	129.7	6.63	116.8	7.10-7.43	128.8	7.80-7.93	130.5	-	121.8
5	7.23	133.8	6.56	128.1	7.25	130.3	7.22	133.8	7.10-7.43	130.5	7.44	125.7	7.85	130.8
6	6.63	116.3	-	118.2	7.32	119.2	6.61	116.3	7.10-7.43	123.5	7.80-7.93	128.7	8.08	133.5
7	-	150.2	-	147.0	-	152.1	-	150.2	-	153.1	-	152.5	-	152.7
8	-	-	-	-	-	143.7	-	-	-	143.5	-	143.5	-	143.7
9	-	-	-	-	7.70	125.6	-	-	7.76	125.1	7.80-7.93	125.1	7.85	125.4
10	-	-	-	-	6.09	110.9	-	-	6.61	111.4	6.62	111.4	6.69	111.4
11	-	-	-	-	-	152.0	-	-	-	152.5	-	153.1	-	155.5
12	-	-	-	-	6.09	110.9	-	-	6.61	111.4	6.62	111.4	6.69	111.4
13	-	-	-	-	7.70	125.6	-	-	7.76	125.1	7.80-7.93	125.1	7.85	125.4
14	-	-	-	-	2.72	40.1	-	-	2.95-2.98	40.3	2.98	40.2	3.03	40.2
15	-	-	-	-	-	-	-	-	-	-	-	-	-	-
NH ₂	5.60	-	6.51	-	-	-	5.78	-	-	-	-	-	-	-
α	1.46-1.84	27.5	1.46-1.56	26.5	1.46-1.53	27.1	1.84	27.4	1.51-1.58	29.9, 28.6	1.72-1.59	29.9, 28.6	1.59-1.69	29.9, 28.4
β	1.46-1.84	27.3	1.13-1.30	26.1	1.21-1.25	27.0	1.44	27.3	1.16-1.21	27.5, 27.4	1.72-1.59	28.3,27.8	1.31-1.33	27.8, 27.5
γ	1.46-1.84	26.5	1.13-1.30	25.5	0.94-0.99	26.4	1.44	26.4	0.95-0.15	26.9, 26.8	1.32-1.22	26.8, 26.7	1.31-1.33	27.8, 27.5
δ	0.93	13.6	0.66	12.9	0.47	13.3	0.92	13.5	0.69-0.74	13.7, 13.6	0.79-0.69	13.7, 13.5	0.72, 0.80	13.7, 13.5
Sn		-481.1		-482.1		-480.2		-481.0		-199.2, -204.1		-206.8, -212.2		-211.7, -212.0

^a ¹H and ¹³C spectra of compounds **1**, **3**, **5**, **6**, **7** were recorded in CDCl₃ while **2** was recorded in CDCl₃/DMSO-*d*₆ mixture. ^b α , β , γ and δ represents the ¹H and ¹³C atom numbers in Sn⁻ⁿBu skeleton. ^c Tin NMR spectra of compounds (**1**-**7**) were recorded in CDCl₃ and δ (¹¹⁹Sn) values are placed at the end of the ¹³C NMR column of each compounds. ^d Only data for the drum portion of [ⁿBu₆Sn₆O₆(L¹)₆]·(HL⁶)·2(C₇H₈) (**4**) is included in the table owing to the complex nature of spectrum. Full ¹H and ¹³C NMR spectral details are given in Section 2.

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held at 0-5 °C in an ice-bath, with vigorous stirring. A deep-red precipitate developed almost immediately and the stirring was continued for 15 min and then an aqueous solution of sodium acetate (3.40 g in 5 mL water) was added and stirring was continued for 1 h. The reaction mixture was kept overnight in a refrigerator, followed by 2 h at room temperature. Sodium hydroxide solution (5 mL, 20%) was added to have a distinct odor of dimethylaniline and the reaction mixture was kept at room temperature for 1 h. The precipitate was filtered, washed with water, then acetic acid (10 mL, 10%) to remove excess dimethylaniline, again washed several times with water, and finally with methanol and then dried in air. The crude product was washed thoroughly with hexane to remove any tar-like material and then dissolved in toluene. Several recrystallizations from toluene yielded dark-red crystalline product in 61% yield; M.p.: 180-182 °C. Anal. Found. C, 66.78; H, 5.39; N, 15.50%. Calc. for C₁₅H₁₅N₃O₂: C, 66.90; H, 5.61; N, 15.60. IR (cm⁻¹): 1717 m v(OCO)_{asym}, 1601 s, 1547 w, 1529 w, 1483 w, 1466 w, 1365 s v(OCO)_{sym}, 1312 m, 1277 m, 1147 s, 1113 m, 942 m, 828 m, 766 w, 688 w, 636 w, 524 w. ¹H NMR (CDCl₃); $\delta_{\rm H}$: 14.3 [s, 1H, OH], 8.27 [d, 1H, H-3], 7.91 [d, 1H, H-6], 7.70 [d, 2H, H-9 & H-13], 7.54 [t, 1H, H-4], 7.42 [t, 1H, H-5], 6.66 [d, 2H, H-10 & H-12], 3.07 [s, 6H, H-14] ppm. ¹³C NMR (CDCl₃); δ_C: 167.3 [C-1], 153.9 [C-7], 150.3 [C-11], 141.7 [C-8], 133.4 [C-5], 132.4 [C-4], 129.7 [C-3], 126.9 [C-9 & C-13], 124.9 [C-2], 115.5 [C-6], 111.7 [C-10 & C-12], 40.2 [C-14] ppm. Electronic absorption data λ_{max} , nm; (ɛ [M⁻¹]): 453sh (6702), 482 (10,208).

The 3-{(E)-2-[4-(dimethylamino)phenyl]diazenyl}benzoic acid (HL⁴) and 4-{(E)-2-[4-(dimethylamino)phenyl]diazenyl}benzoic acid (HL⁵) were prepared in a similar way by reacting *m*-carboxy-benzenediazonium chloride or *p*-carboxybenzenediazonium chloride with *N*,*N*-dimethyl aniline under cold conditions. The characterization and spectroscopic data are presented below.

2.3.2. Synthesis of 3-{(E)-2-[4-(dimethylamino)phenyl]diazenyl} benzoic acid (HL^4)

A similar synthetic procedure to that used for HL³ was used except that anthranilic acid was replaced by *m*-aminobenzoic acid. The dry powder was recrystallized from methanol to give a brown yellow crystalline material in 60% yield. M.p.: 202-203 °C. Anal. Found. C, 66.98; H, 5.50; N, 15.70%. Calc. for C₁₅H₁₅N₃O₂: C, 66.90; H, 5.61; N, 15.60. IR (cm⁻¹): 1686 s v(OCO)_{asym}, 1601 s, 1563 w, 1519 s, 1485 w, 1444 w, 1366 s v(OCO)_{sym}, 1307 m, 1240 m, 1140 s, 946 m, 817 s, 787 w, 759 m, 671 m, 636 w, 507 w. ¹H NMR (DMSO- d_6 + CDCl₃); δ_H : 8.35 [s, 1H, H-2], 7.92 [m, 2H, H-4 & H-6], 7.77 [d, 2H, H-9 & H-13], 7.47 [t, 1H, H-5], 6.66 [d, 2H, H-10 & H-12], 3.00 [s, 6H, H-14] ppm. Signals for the carboxylic acid were exchanged due to presence of water in the solvent. ¹³C NMR (DMSO-*d*₆ + CDCl₃); δ_C: 167.3 [C-1], 152.4 [C-11], 152.2 [C-7], 142.6 [C-8], 131.5 [C-3], 129.6 [C-4], 128.5 [C-5], 125.7 [C-6], 124.7 [C-9 & C-13], 122.6 [C-2], 111.2 [C-10 & C-12], 39.3 [C-14] ppm. Electronic absorption data λ_{max} , nm; (ϵ [M⁻¹]): 418 (7,604).

2.3.3. Synthesis of 4-{(E)-2-[4-(dimethylamino)phenyl]diazenyl} benzoic acid (HL⁵)

A similar synthetic procedure to that used for HL^3 was used except that anthranilic acid was replaced by *p*-aminobenzoic acid. The crude product thus obtained was dissolved by boiling with excess sodium bicarbonate (around two equivalents) in water and filtered while hot. The clear reddish-yellow solution was acidified with dilute acetic acid and filtered. The precipitate was washed thoroughly with water and then methanol, which upon drying yielded orange red powder in 58% yield. M.p.: 255–256 °C. The compound could not be recrystallized due to poor solubility in common organic solvents, but can be dissolved in DMSO. *Anal.* Found. C, 66.90; H, 5.70; N, 15.78%. Calc. for C₁₅H₁₅N₃O₂: C, 66.90; H, 5.61; N, 15.60. IR (cm⁻¹): 1682 s $v(OCO)_{asym}$, 1597 s, 1559 w, 1523 w, 1421 m, 1366 s ν(OCO)_{sym}, 1301 m, 1254 w, 1139 s, 1122 w, 946 m, 821 m, 692 w, 534 w. ¹H NMR (DMSO-*d*₆ - + CDCl₃); δ_H: 8.04 [d, 2H, H-3 & H-5], 7.77 [m, 4H, H-2, H-6, H-9 & H-13], 6.70 [d, 2H, H-10 & H-12], 3.05 [s, 6H, H-14] ppm. Signals for the carboxylic acid were exchanged due to presence of water in the solvent. ¹³C NMR (DMSO-*d*₆ + CDCl₃); δ_C: 172.6 [C-1], 160.3 [C-11], 157.6 [C-7], 148.0 [C-8], 135.9 [C-4], 135.3 [C-3 & C-5], 130.1 [C-9 & C-13], 126.5 [C-2 & C-6], 116.2 [C-10 & C-12], 45.0 [C-14] ppm. Electronic absorption data λ_{max}, nm; (ε [M⁻¹]): 436 (3958).

2.3.4. Synthesis of 2-{(E)-[4-(dimethylamino)benzylidene]amino} benzoic acid (HL^{6})

A report describing the synthesis of a series of differently substituted Schiff bases including HL⁶ have appeared in the literature [42], while the present work was in an advanced stage. The literature method utilizes a solvent-free procedure under microwave irradiation and the efficiency of the method was compared to that observed in conventional synthesis, however the color and melting points of the reported Schiff bases are not mentioned in the report and hence the synthesize and characterization of L⁶H was undertaken. The present work utilizes a classical condensation method which is suitably modified and is described here. To a hot absolute ethanol solution (30 mL) containing anthranilic acid (0.50 g, 3.64 mmol) was added a solution of 4-N,N-dimethylaminobenzaldehyde (0.54 g, 3.64 mmol) in absolute ethanol (15 mL) whereupon the solution turned orange immediately. Then the reaction mixture was heated to reflux for 1 h using a Dean-Stark apparatus and filtered while hot. The filtrate was collected, the volatiles removed on a rotary evaporator and the red orange residue obtained was washed once with methanol and dried in vacuo. The residue was boiled with hexane $(3 \times 10 \text{ mL})$, filtered and dried in vacuo. The crude product was then recrystallized from methanol to give a red orange crystalline material in 68% yield. M.p.: 198-199 °C. Anal. Found. C, 71.50; H, 5.80; N, 10.68%. Calc. for C₁₆H₁₆N₂O₂: C, 71.62; H, 6.01; N, 10.44. IR (cm⁻¹): 1695 m, 1587 s, 1532 m, 1453 w, 1441 w, 1373 s, 1321 w, 1233 w, 1168 s, 1066 w, 944 m, 829 m, 768 m, 694 w, 636 w, 572 w, 546 w, 525 w. Electronic absorption data λ_{max} , nm; (ε [M⁻¹]): 416 (6979).

2.4. Synthesis of organotin(IV) complexes

2.4.1. Synthesis of butylstannoxanes of composition $[{}^{n}Bu_{6}Sn_{6}O_{6}(L^{n})_{6}]$

A general method was followed for the synthesis of complexes **1–3**. In a typical procedure, a mixture of ^{*n*}BuSn(O)OH and the appropriate ligands (HL^1 , HL^2 or HL^3) in a 6:6 stoichiometric ratio was heated to reflux in anhydrous toluene (50 mL) for 8 h in a round bottom flask equipped with a Dean–Stark apparatus and a water cooled condenser. The reaction mixture was filtered while hot and the solvent was removed using a rotary evaporator. The residue was washed, boiled with hexane, filtered and dried *in vacuo*. The residue upon crystallization using appropriate solvent (s) yielded the desired product. The specific details pertaining to reactants, analytical and characterization data for the complexes are given below.

2.4.1.1. Synthesis of [${}^{n}Bu_{6}Sn_{6}O_{6}(L^{1})_{6}$]. $C_{8}H_{10}$ (**1**). ${}^{n}BuSn(O)OH$ (0.53 g, 2.54 mmol); HL¹ (0.35 g, 2.55 mmol). Recrystallized from *p*-xylene to give pale yellow microcrystalline product in 85% yield. M.p.: 315–317 °C. The chloroform solvated complex [${}^{n}Bu_{6}Sn_{6}O_{6}(L^{1})_{6}$]. CHCl₃ was reported earlier, which had M.p.: 215–216 °C (decomp) [14]. *Anal.* Found. C, 43.28; H, 5.20; N, 4.20%. Calc. for C₇₄H₁₀₀N₆-O₁₈Sn₆: C, 42.86; H, 4.86; N, 4.05. IR (cm⁻¹): 3496 m, 3386 m, 1619 s $v(OCO)_{asym}$, 1578 s, 1540 s, 1513 s, 1484 w, 1455 s, 1398 s, 1340 m, 1301 m, 1257 s, 1161 s, 965 w, 871 w, 752 s, 704 m, 622 s v(Sn-O-Sn), 527 w, 469 w. Electronic absorption data λ_{max} , nm; (ε [M⁻¹]): 340 (14,583).

2.4.1.2. Synthesis of $[{}^{n}Bu_{6}Sn_{6}O_{6}(L^{2})_{6}]$ (2). ${}^{n}BuSn(O)OH$ (0.53 g, 2.54 mmol); HL² (0.35 g, 2.55 mmol). Recrystallized from toluene to give a pale yellow microcrystalline product in 81% yield. M.p.: 308–310 °C. Anal. Found. C, 40.58; H, 4.50; N, 4.70%. Calc. for C₆₆-H₉₀N₆O₁₈Sn₆: C, 40.29; H, 4.61; N, 4.27. IR (cm⁻¹): 3478 m, 3386 m, 1624 m ν (OCO)_{asym}, 1602 s, 1545 w, 1510 m, 1406 s, 1304 m, 1179 s, 1149 w, 1126 w, 846 w, 781 m, 701 w, 670 w, 638 w, 612 s ν (Sn–O–Sn), 527 w, 503 w. Electronic absorption data λ_{max} , nm; (ϵ [M⁻¹]): 322 (2500).

2.4.1.3. Synthesis of $[{}^{n}Bu_{6}Sn_{6}O_{6}(L^{3})_{6}]$ (3). ${}^{n}BuSn(O)OH$ (0.39 g, 1.86 mmol); L³H (0.50 g, 1.85 mmol). Recrystallized from toluene to give a red orange microcrystalline product in 79% yield. M.p.: 200–202 °C. Anal. Found. C, 50.08; H, 5.50; N, 8.87%. Calc. for C₁₁₄-H₁₃₈N₁₈O₁₈Sn₆: C, 49.60; H, 5.04; N, 9.13. IR (cm⁻¹): 1601 s ν (OCO)_{asym}, 1567 w, 1533 w, 1518 m, 1442 w, 1408 m, 1364 m ν (OCO)_{sym}, 1312 m, 1262 w, 1230 w, 1146 s, 945 m, 875 w, 823 m, 764 m, 670 w, 619 m ν (Sn–O–Sn), 544 w, 522 w, 458 w. Electronic absorption data λ_{max} , nm; (ϵ [M⁻¹]): 424 (11,919).

2.4.1.4. Synthesis of $[{}^{n}Bu_{6}Sn_{6}O_{6}(L^{1})_{6}] \cdot (HL^{6}) \cdot 2(C_{7}H_{8})$ (4). Toluene solutions of **1** (0.40 g, 0.20 mmol, 40 mL) and HL^{6} (0.05 g, 0.19 mmol, 10 mL) were combined with stirring and the reaction mixture refluxed for 8 h. The pale yellow solution was filtered to remove any suspended particles and upon concentration provided an orange colored crystalline material. The solid was boiled with hexane and dried in vacuo. The dried material was recrystallized from toluene to give an orange microcrystalline product in 65% yield. M.p.: 235-237 °C (dec.). Anal. Found. C, 49.88; H, 5.10; N, 5.17%. Calc. for $C_{112}H_{138}N_{10}O_{22}Sn_6$: C, 50.04; H, 5.17; N, 5.21. IR (cm⁻¹): 3475 m, 3385 m, 3321 m, 1697 m v(OCO)_{asym} [HL⁶], 1616 s v(OCO)_{asym} [L¹H], 1579 m, 1539 m, 1512 m, 1454 m, 1397 m, 1343 w, 1302 m, 1258 s, 1163 s, 944 w, 870 m, 818 m, 753 s,706 m, 672 m, 622 s, 564 m, 527 m, 469 m. ¹H NMR (CDCl₃); δ_H: 9.75 [s, 1H, N=CH], 7.90 [d, 6H, Ar], 7.75 [d, 2H, Ar], 7.17-7.29 [m, 10H, Ar], 6.60–6.71 [m, 14H, Ar], 5.78 [br s, 12H, NH₂], 3.07 [s, 6H, NMe₂], 1.84 [m, 12H, Bu], 1.44 [m, 24H, Bu], 0.92 [t, 18H, Bu] ppm. ¹³C NMR (CDCl₃); $\delta_{\rm C}$: 190.35 (CO₂H), 174.31 (²J $({}^{13}\text{C} - {}^{117/119}\text{Sn}) = 30 \text{ Hz})$ (L¹), 154.31, 151.02, 150.17 (L¹), 137.83 (PhMe), 133.80 (L¹), 132.52 (L¹), 132.03, 129.00 (PhMe), 128.30, 128.19 (PhMe), 125.26 (PhMe), 125.08, 116.81 (L¹), 116.53, 116.28 (L¹), 114.42 (L¹), 110.94, 40.01 (NMe₂), 27.44 (Bu), 27.33 (Bu), 26.44 (Bu), 21.41 (Tol), 13.51 (Bu) ppm. PhMe refers to the solvated toluene. Electronic absorption data λ_{max} , nm; (ε [M⁻¹]): 346 sh (5656), 399 (8181).

2.4.2. Synthesis of butylstannoxanes of composition $[{}^{n}Bu_{8}Sn_{4}O_{2}(L^{n})_{4}]$

A general method was followed for the synthesis of complexes **5–7**. A similar synthetic procedure to that used for the synthesis of butylstannoxanes of composition $[{}^{n}Bu_{6}Sn_{6}O_{6}(L^{n})_{6}]$ was employed for obtaining the products of composition $[{}^{n}Bu_{8}Sn_{4}O_{2}(L^{n})_{4}]$ where n = 3-5. The reaction time was 10 h and the residue upon crystallization using appropriate solvent(s) yielded the desired product. The specific details pertaining to reactants, analytical and characterization data for the complexes are given below.

2.4.2.1. Synthesis of butylstannoxanes of composition $[^{n}Bu_{8}Sn_{4}O_{2}(L^{3})_{4}]$ (5). The synthesis of **5**, using ethanol as the reaction medium, is available in the literature [43], however the yield is lower and the melting point not reported, so the synthesis and characterization of **5** was carried out again. However, the spectroscopic data of **5** closely matches that reported. ⁿBu₂SnO (0.46 g, 1.85 mmol); HL³ (0.50 g, 1.85 mmol). Recrystallized from benzene to give a crimson coloured microcrystalline product in 84% yield. M.p.: 206–208 °C. *Anal.* Found. C, 53.98; H, 6.50; N, 8.60%. Calc. for C₉₂H₁₂₈N₁₂O₁₀Sn₄: C, 54.25; H, 6.33; N, 8.25. IR (cm⁻¹): 1602 s v(OCO)_{asym}, 1560 m, 1522 m, 1478 w, 1444 w, 1403 m, 1367 s ν(OCO)_{sym}, 1253 m, 1232 w, 1143 s, 1090 w, 947 m, 857 w, 819 m, 757 m, 663 w, 634 m ν(Sn–O–Sn), 543 m, 487 m. Electronic absorption data λ_{max} , nm; (ε [M⁻¹]): 432sh (3402), 480 (6428).

2.4.2.2. Synthesis of butylstannoxanes of composition [${}^{n}Bu_{8}Sn_{4}O_{2}(L^{4})_{4}$] (**6**). ${}^{n}Bu_{2}SnO$ (0.46 g, 1.85 mmol); HL⁴ (0.50 g, 1.85 mmol). Recrystallized from toluene to give an orange microcrystalline product in 72% yield. M.p.: 226–227 °C. *Anal.* Found. C, 54.48; H, 6.20; N, 8.61%. Calc. for C₉₂H₁₂₈N₁₂O₁₀Sn₄: C, 54.25; H, 6.33; N, 8.25. IR (cm⁻¹): 1621 s ν (OCO)_{asym}, 1602 s, 1551 m, 1519 m, 1478 w, 1397 s, 1365 s ν (OCO)_{sym}, 1328 w, 1242 w, 1189 w, 1130 s, 945 m, 878 w, 815 s, 771 m, 729 m, 675 m, 635 m ν (Sn–O–Sn), 556 w, 487 m. Electronic absorption data λ_{max} , nm; (ϵ [M⁻¹]): 416 (6938).

2.4.2.3. Synthesis of butylstannoxanes of composition [${}^{n}Bu_{8}Sn_{4}O_{2}(L^{5})_{4}$] (7). ${}^{n}Bu_{2}SnO$ (0.46 g, 1.85 mmol); HL⁵ (0.50 g, 1.85 mmol). Recrystallized from benzene to give a yellow-brown microcrystalline product in 76% yield. M.p.: 246–248 °C. *Anal.* Found. C, 53.88; H, 6.02; N, 8.50%. Calc. for C₉₂H₁₂₈N₁₂O₁₀Sn₄: C, 54.25; H, 6.33; N, 8.25. IR (cm⁻¹): 1622 s ν (OCO)_{asym}, 1599 s, 1542 m, 1520 m, 1493 w, 1444 w, 1390 m, 1364 s, 1333 w, 1248 m, 1138 s, 945 w, 871 w, 854 w, 816 m, 786 m, 725 w, 686 w, 646 m ν (Sn–O–Sn), 540 w, 492 m. Electronic absorption data λ_{max} , nm; (ϵ [M⁻¹]): 432 (4489).

2.5. X-ray crystallography

Crystals of butyltin(IV) compounds $[{}^{n}Bu_{6}Sn_{6}O_{6}(L^{1})_{6}] \cdot C_{8}H_{10}$ (1), $[{}^{n}Bu_{6}Sn_{6}O_{6}(L^{2})_{6}]$ (2), $[{}^{n}Bu_{6}Sn_{6}O_{6}(L^{3})_{6}]$ (3), $[{}^{n}Bu_{6}Sn_{6}O_{6}(L^{1})_{6}]$ (HL⁶) 2 (C_7H_8) (**4**), $[{}^{n}Bu_8Sn_4O_2(L^3)_4]$ (**5**), $[{}^{n}Bu_8Sn_4O_2(L^4)_4]$ (**6**) and $[{}^{n}Bu_8Sn_4 O_2(L^5)_4$ (7) suitable for single-crystal X-ray diffraction analysis were grown from xylene (1 and 3), toluene (2, 4 and 6), and benzene (5 and 7) solutions by slow evaporation at room temperature. Diffraction data were recorded at low temperature (150 K) on a Bruker AXS-KAPPA APEX II Photon 100 detector diffractometer (1 and 2), or at ambient temperature on an Agilent Technologies Gemini area-detector diffractometer [44] (4–7) using Mo Ka radiation ($\lambda = 0.71073$ Å). Data for **1** and **2** were collected using omega scans of 0.5° per frame and full sphere of data were obtained. Cell parameters were retrieved using Bruker SMART [45] software and refined using Bruker SAINT [45] on all the observed reflections. Absorption corrections were applied using sadabs [46]. Data reductions for compounds **4–7** were performed with CrysAlisPro [44], and intensities were corrected for Lorentz and polarization effects and empirical absorption corrections using spherical harmonics were applied [44].

Structures were solved by direct methods by using sir-97 [47] and refined with SHELXL-2014 [48]. Calculations were performed using the wingx-Version 2014.01 [49]. All non-hydrogen atoms were found from the difference Fourier syntheses. The hydrogen atoms attached to carbon atoms were placed at geometrically calculated positions and included in the refinement using the ridingmodel approximation; $U_{iso}(H)$ were defined as 1.2 U_{eq} of the parent carbon atoms for phenyl and methylene residues and $1.5 U_{eq}$ of the parent carbon atoms for the methyl groups. The hydrogen atoms of the amine groups were not located from the final difference Fourier map; they were inserted in calculated positions and then allowed to refine with their isotropic thermal parameters set at 1.5 times the average thermal parameters of the belonging nitrogen atoms. Their isotropic thermal parameters were set at 1.5 times the average thermal parameters of the corresponding nitrogen atoms. In one of the 2-aminobenzoate ligands in 4, the amino group is disordered over two positions in the aromatic ring and were refined with the use of PART instruction. The occupancy refined to a ratio of 0.77:0.23. The structures of 1, 2 and 4 contain disordered molecules that could not be modelled and PLATON/Squeeze [50] was used

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to correct the data. The void treatment indicated *ca.* 102, 23 and 104 electrons, respectively, in void volumes of 186.8, 130 and 414 Å³, in this order. While the electron count in **2** could not be ascertained, in the other cases it fits well for one molecule of xylene in **1** and two molecules of toluene in **4**, which were included in the respective final refinements. The data collection and

refinement parameters are given in Table 2, while a comparison of selected bond distances and angles are shown in Table 3. The perspective views of the molecular structures are shown in Figs. 1–6. No publishable results could be derived from the observed diffraction data for compound **3**, however, the raw data appear to indicate the drum structure.

Table 2

Crystal data and	1 structure	refinement	details	for	butyltin(IV)	compounds	1, 2	and	4-	7
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	1	2	4	5	6	7
Empirical formula	C74H100N6O18Sn6	C66H90N6O18Sn6	C ₁₁₂ H ₁₃₈ N ₁₀ O ₂₂ Sn ₆	C ₉₂ H ₁₂₈ N ₁₂ O ₁₀ Sn ₄	C ₉₂ H ₁₂₈ N ₁₂ O ₁₀ Sn ₄	C ₉₂ H ₁₂₈ N ₁₂ O ₁₀ Sn ₄
Formula weight	2073.73	1967.57	2688.46	2036.82	2036.82	2036.82
Crystal size (mm)	$0.20 \times 0.19 \times 0.13$	$0.23 \times 0.12 x 0.10$	$0.24 \times 0.17 \times 0.09$	$0.23 \times 0.15 \times 0.10$	$0.25 \times 0.15 \times 0.10$	$0.21 \times 0.13 \times 0.06$
Crystal shape	prism	prism	block	block	block	block
T (K)	150(2)	150(2)	296(2)	294(2)	298(2)	293(2)
Crystal system	triclinic	triclinic	triclinic	monoclinic	triclinic	triclinic
Space group	ΡĪ	ΡĪ	ΡĪ	$P2_1/n$	ΡĪ	ΡĪ
Unit cell dimensions						
a (Å)	11.6363(9)	12.4104(7)	13.3148(4)	17.1977(5)	12.0568(6)	10.5320(10)
b (Å)	13.2044(11)	12.5877(7)	13.8032(4)	14.6480(4)	13.0523(8)	13.8950(11)
<i>c</i> (Å)	14.2746(10)	14.6506(9)	17.4049(5)	20.1829(5)	17.8207(10)	17.7530(10)
α (°)	100.590(4)	114.290(2)	110.361(3)	90	105.572(5)	80.131(4)
β(°)	108.900(3)	108.315(3)	92.340(2)	98.952(3)	98.423(4)	87.565(3)
γ (°)	101.776(4)	93.739(3)	101.032(3)	90	111.208(5)	70.858(4)
V (Å ³)	1956.0(3)	1929.7(2)	2923.39(16)	5022.4(2)	2424.1(3)	2417.8(3)
Ζ	1	1	1	2	1	1
D_{Calc} (g cm ⁻³)	1.760	1.693	1.527	1.347	1.395	1.399
μ (mm $^{-1}$)	1.957	1.978	1.332	1.041	1.078	1.081
F (000)	1030	972	1356	2088	1044	1044
Reflections measured	19251	55700	24520	27754	18317	20216
Independent reflections (R_{int})	7761 (0.0612)	8193 (0.0392)	13211 (0.0290)	11614 (0.379)	10885 (0.0352)	10974 (0.0321)
Reflection with $I > 2\sigma(I)$	5167	6673	9458	7395	5411	7490
Number of parameters	454	454	634	556	520	534
$R_1^{a} (I \ge 2\sigma)$	0.0473	0.0735	0.0417	0.0520	0.0852	0.0409
$wR_2^{\rm b} (I \ge 2\sigma)$	0.1043	0.1494	0.1128	0.1054	0.2286	0.0910
Goodness of fit (GOF) on F^2	0.986	1.132	1.052	1.121	1.040	1.071

^a $R_1 = \Sigma ||F_0| - |F_c|| / \Sigma |F_0|$.

^b $wR_2 = [\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)^2]]^{1/2}.$

Table 3

Sn coordination geometry and selected geometrical parameters for the butyltin(IV) compounds 1, 2, and 4-7.

	1	2	4	5	6	7		
Tin coordination number	6	6	6	5 and 6	5 and 6	5 and 6		
Tin coordination sphere ^a and geometry indices	C ₁ O ₅	C ₁ O ₅	C ₁ O ₅	$C_2O_3 (\tau_5 = 0.58)$ and C_2O_4	$C_2O_3 \ (\tau_5 = 0.56) \text{ and} \\ C_2O_4$	C ₂ O ₃ ($ au_5$ = 0.53) and C ₂ O ₄		
Sn—O bond length range (Å)	2.070(4)- 2.181(5)	2.071(6)- 2.186(6)	2.082(3)-2.176 (3)	2.028(3)-2.288(3)	2.014(6)-2.245(7)	2.016(2)-2.274(3)		
C—Sn—C angle (°)	-	-	_	135.8(2) 144.6(2)	137.4(6) 142.0(6)	136.52(16) 147.00(19)		
Intramolecular Sn Sn								
Minimum	3.1888(8)	3.1917(10)	3.1891(4)	3.3212(5)	3.2988(10)	3.3029(6)		
Maximum	4.9893(9)	4.9859(10)	4.9660(5)	3.7614(5)	3.7635(10)	3.7762(6)		
Intermolecular SnSn								
Minimum	8.460(1)	8.572(1)	11.1727(5)	9.6841(5)	8.141(1)	7.7477(7)		
Involving the diazo or monoazo species (fr	ee or as ligands)							
N=N bond length	-	-	_	1.246(5)	1.154(11)	1.207(5)		
0				1.251(5)	1.226(14)	1.252(5)		
$\angle l.s. Ph_{COO} - Ph_{NOO} (^{\circ})^{b}$	-	-	2.32	5.82 (bm)	5.51 (bm)	19.02 (bm)		
				2.85 (bc)	20.33 (bc)	3.41 (bc)		
\angle l.s. COO– <i>Ph</i> _{COO} (°) ^c	-	-	1.45	84.76 (bm)	7.18 (bm)	9.43 (bm)		
				72.89 (bc)	12.38 (bc)	6.27 (bc)		
Involving the aminebenzocarboxylate ligands								
$\angle 1.s. COO-Ph_{COO} (\circ)^c$	11.12	11.34	2.40					
	11.94	13.08	9.74	_	-	-		
	20.62	16.45	13.59					

^a For the definition of τ_5 , see Ref. [53].

^b Angle between the least-square planes defined by the COO— and the NOO— containing aromatic rings; distinct values are obtained when such planes involve the bridging monodentate (bm) or the bridging chelate (bc) carboxylate groups.

^c Angle between the least-square planes defined by the COO- atoms and the COO- containing aromatic ring. See also footnote b.

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Fig. 1. Ball and stick representations (arbitrary views) of the central drum- (A) and ladder-type (B) tin-oxygen cores existent in compounds **1**, **2** and **4** (**A**) and in **5–7** (**B**). The metal coordination spheres are also shown, together with the carboxylate binding modes. Colours: tin in violet; oxygen in red and light pink; carbon in light grey. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)



Fig. 2. Ball and stick representation (arbitrary view) of the molecular structure of **1** with partial atom labelling scheme. The symmetry generated half of the compound is depicted as grey sticks with the Sn(IV) cations as grey balls. Hydrogen atoms are omitted for clarity. Symmetry code: 1 - x, -y, 1 - z.



Fig. 3. Ball and stick representation (arbitrary view) of the molecular structure of **2** with partial atom labelling scheme. The symmetry generated half of the compound is depicted as grey sticks with the Sn(IV) cations as grey balls. Hydrogen atoms are omitted for clarity. Symmetry code: -x, 1 - y, 1 - z.



Fig. 4. Ball and stick representation (arbitrary view) of the molecular structure of **4** with partial atom labelling scheme. The symmetry generated half of the compound is depicted as grey sticks with the Sn(IV) cations as grey balls. Hydrogen atoms are omitted for clarity and only one of the disordered components is shown. Symmetry code: -x, -y, -z.

3. Results and discussion

3.1. Synthesis and characterization of ligands and their mono- and dibutyl-stannoxane complexes

Compound HL^3 was synthesized by diazotization of anthranilic acid, followed by coupling with *N*,*N*-dimethyl aniline under cold conditions [41], and an analogous procedure was adopted to synthesize HL^4 and HL^5 by reacting *m*-carboxybenzenediazonium chloride or *p*-carboxybenzenediazonium chloride with *N*,*N*dimethyl aniline. HL^6 was prepared by condensing anthranilic acid and 4-*N*,*N*-dimethylaminobenzaldehyde. Hexanuclear butylstannoxanes of composition [^{*n*}Bu₆Sn₆O₆(L^n)₆] (where *n* = 1–3) and tetranuclear butylstannoxanes of composition [^{*n*}Bu₈Sn₄O₂(L^n)₄] (where *n* = 3–5) were obtained by reacting the appropriate HL^n with tin(IV) precursors ^{*n*}BuSn(O)OH and ^{*n*}Bu₂SnO in 6:6 and



Fig. 5. Ball and stick representation (arbitrary view) of the molecular structure of **5** with partial atom labelling scheme. Hydrogen atoms are omitted for clarity and only one of the disordered components is shown. Symmetry code: 1 - x, -y, 1 - z.

4:4 molar ratios at reflux temperature, respectively. On the other hand, in an attempt to perceive the reactivity of **1** with HL^6 in a 1:1 molar ratio, a product of equimolar proportions *i.e.* [$^nBu_6Sn_6-O_6(L^1)_6$]·(HL^6)·2(C_7H_8) (**4**) was obtained. The complexes are soluble in common organic solvents, furnishing single crystals of the respective compounds suitable for diffraction studies and provided consistent elemental analyses. The behavior of the ligands in the presence of metal centres with different coordination geometries and numbers of available coordination sites was assessed from the results of spectroscopic and X-ray diffraction data. Pro-ligands have been characterized by IR, 1H and ^{13}C spectroscopic techniques, and their complexes also by ^{119}Sn NMR.

In the IR spectra of 1–7, the asymmetric stretching $v_{asym}(OCO)$ vibration for the ligands were detected in the range 1601–1624 cm⁻¹ which is lower than those found for the respective pro-ligands as a result of the coordination of the carboxylate group to the tin atoms, in accordance with earlier reports [51]. In compound **4**, an IR band at 1697 cm⁻¹ was also detected which corresponds to the $v_{asym}(OCO)$ vibration of neutral HL⁶ (see X-ray discussion). A medium to strong intensity band in the range 610–650 cm⁻¹ detected for compounds 1–7 is assigned to the v (Sn–O–Sn) vibration [51]. The ¹H and ¹³C data for 1–7 are given



Fig. 6. Ball and stick representation (arbitrary view) of the molecular structure of **6** with partial atom labelling scheme. Hydrogen atoms are omitted for clarity. Symmetry code: 1 - x, 1 - y, -z.



Fig. 7. Ball and stick representation (arbitrary view) of the molecular structure of **7** with partial atom labelling scheme. Hydrogen atoms are omitted for clarity. Symmetry code: 1 - x, -y, 1 - z.

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in Table 1. The presence of two sets of ¹H and ¹³C signals for the butyl resonances in 5-7 is in agreement with the pairwise heterotopic non-equivalence of the exocyclic and endocyclic ⁿBu₂Sn moieties [51]. Since the butyl protons of the compounds are not well defined showing broad signals, the tin satellite peaks were obscured. The aromatic protons of the ligands were also broad and hence coupling constants could not be determined. The ¹¹⁹Sn NMR spectra of the monobutyltin(IV) complexes 1-4 displayed a single resonance at ca. - 480 ppm, indicative of the equivalence of the six tin atoms, and this is generally observed for the drum structures [14,26,18]. For the dibutyltin(IV) complexes 5-7, the ¹¹⁹Sn NMR spectra display a pair of almost equally intense resonances in the range - 199 to - 212 ppm, which is in accordance with the presence of two types of tin atoms, *i.e.* the *endo* and the exo [51,52]. The hexanuclear drum- and tetranuclear ladder-type structures have been confirmed from the results of single crystal X-ray crystallography of 1, 2, 4–7 (vide infra).

3.2. Description of the X-ray crystal structures

Compounds 1, 2 and 4 belong to the family of drum-type organostannoxane compounds which include a Sn_6O_6 core (Scheme 1, A and Figs. 1–4) made of two fused Sn_3O_3 (the hexagonal faces of the drum) and six lateral faces comprising four-membered Sn_2O_2 [1]. All tin atoms are hexacoordinate and held together by carboxylate groups from six aminobenzocarboxylate ligands that bind alternate Sn atoms in a bridging chelating mode. The butyl moieties are displayed above and below the basal faces of the drum and the aminobenzocarboxylate groups spread-out from the drum faces, since the $O_{carboxylate}$ atoms bridge between tin atoms of the two basal planes.

Compounds **5–7** display ladder-type structural motifs (Scheme 1, B and Figs. 5–7) consisting of four tin atoms and four L⁻ ligands that bind the tin atoms through bridging-chelating and bridging-monodentate carboxylate groups. The butyl groups and the L⁻ ligands are displayed above and below the tin-containing planes.

All the Sn atoms in 1, 2 and 4 present octahedral C_1O_5 geometries. In **5–7**, the *endo*-Sn atoms are clearly C₂O₄ hexacoordinate, while the exo-Sn atoms are C₂O₃ pentacoordinate (τ_5 [53] in the range 0.53– 0.58). The different geometries around the tin atoms influences the C-Sn-C angles, which are five to ten degrees shorter in the latter (Table 3). However, the contact interactions between the exo-Sn and the detached O-atom of the bridging-monodentate carboxylate (in the 2.895–2.946 Å range) may convert the geometries of those metals into highly distorted octahedral ones. The relative positions of the carboxylate and amine (in 1 and 2) or azo (in 5–7) groups have an influence in the twisting of the ligands, as measured by the angle between the least square planes of the carboxylate group and that of the attached aromatic ring (Table 3). In compound 5, those planes are nearly orthogonal, while in the other complexes such angles vary between 2.85° and 20.62°. The large twisting of the carboxylate moiety in 5 is probably related with steric constraints derived from the bulky azo-substituent in ortho position; the flatness of the ligand is here unsuited with the ladder-type structure. Comparing 1 and 4, which both have 2-aminobenzocarboxylate ligands, the presence of non-coordinated molecules in the structure of the latter flattens the ligand and enlarges the separation between adjacent hexanuclear molecules (increase of the minimum intermolecular Sn...Sn distances, Table 3). In addition, for 5–7, the angle between the least square planes of the aromatic rings depends on the type of coordination mode (bridging-chelate or bridging-monodentate) of the carboxylate groups of the L- ligand, with the greatest discrepancy occurring for 6 and 7 (Table 3).

Hydrogen bond interactions appear to play important roles in the stabilization of the drum structures (**1**, **2** and **4**). In **1** and **4**, the relevant contacts involve every amine atom (as donor) and the vicinal carboxylate (as acceptor) of the same ligand, thus giving rise to 6-membered rings (Figs. 8 and 9). In addition, intermolecular interactions are also established in **4** between the amine H-atoms and the benzoic acid derivative.

In the structure of **2**, and as a result of the relative positions of the amine substituents, the intramolecular contacts are established between those groups which can simultaneously behave as donors and as acceptors (Fig. 10). The intermolecular interactions found in **2**, link the non-coordinated carboxylate O-atoms as well as the



Fig. 8. Hydrogen bond interactions $[d_{D...A}$ (Å), $\angle_{D-H...A}$ (°)] in **1**: N1–H1N1···O2 [2.673(10), 132(8)], N2–H2N1···O3 [2.699(10), 110(4)], N3–H3N1···O6 [2.668(9), 134(5)]. For clarity, only the asymmetric unit is presented and hydrogen atoms not involved in the contacts are omitted.



Fig. 9. Hydrogen bond interactions $[d_{D...A}$ (Å), $\angle_{D-H}\cdots_A$ (°)] in compound **4**: 02–H2···N1 [2.516(7), 154], N3A–H3B···O3 [2.664(9), 152], N3B–H3C···O4 [2.63 (2), 146], N4–H4A···O1 [2.8583(10), 152], N4–H4B···O5 [2.675(7), 102)], N5B–H5C···O8 [2.70(3), 141]. For clarity, only the components in the asymmetric unit are presented and only one of the disordered amine constituents; hydrogen atoms not involved in the contacts are omitted. Symmetry code: (i) 1 - x, 1 - y, -z.



Fig. 10. Hydrogen bond interactions $[d_{D...A}(Å), \angle_{D-H...A}(^{\circ})]$ in **2**: N1–H12N···N2 [3.181(17), 143(18)], N3–H31N···N1 [3.291(16), 161(10)]. For clarity, only the asymmetric unit is presented, and hydrogen atoms not involved in the contacts are omitted. Symmetry codes: (i) 1 - x, 2 - y, 1 - z; (ii) x, y, -1 + z; (iii) x, y, 1 + z.

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Fig. 11. A fragment of an H-bond derived 2D network found in 2, viewed down the crystallographic a axis.

amine groups with amine groups in vicinal molecules, led to 2D frameworks (Fig. 11). The presence of classical intra- and intermolecular H-bond interactions in **1**, **2** and **4** may be important for the stabilization of drum-type structures in comparison to **5**–**7** (ladder type) where such interactions are absent. The relevant $\pi \cdots \pi$ contacts were detected only in the structure of **2**, which link the C9–C14 aromatic rings of adjacent molecules (*centroid* \cdots *centroid* distance of 3.783 Å).

4. Conclusion

The present paper reports the syntheses, characterization and crystal structures of three monobutyl- and three dibutyl-stannoxanes of the types $[{}^{n}Bu_{6}Sn_{6}O_{6}(L^{n})_{6}]$ and $[{}^{n}Bu_{8}Sn_{4}O_{2}(L^{n})_{4}]$, respectively, and a co-crystal consisting of a monobutylstannoxane and a neutral Schiff base. The solid-state structures of all the complexes have been established from single crystal X-ray crystallography while the solution structures were deduced from the δ (¹¹⁹Sn NMR) data. The relative positions of the carboxylate groups of the L⁻ ligands have a considerable influence on the angle between the least square planes of the carboxylate group and that of the attached aromatic ring, and may reach orthogonality. The flatness of the ligand is prevented by a bulky substituent in *ortho* position of the coordinated benzoate group and is thus unsuited for a ladder-type structure. Variation of the carboxylate position on the L³, L⁴ and L⁵ ligands was shown to have a profound influence on the structure of the tetraorganodistannoxane ladder compounds and this is reflected in the structures of compounds 5 through 7, where the ligand L³ is held close to the ladder core while L⁵ protrude significantly. Intramolecular H-bond contacts are relevant in the drum-type structures but virtually absent in the ladder-type ones.

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Appendix A. Supplementary material

CCDC 1456007–1456012 contains the supplementary crystallographic data for (1), (2), (4)–(7) this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.ica.2016.05.008.

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