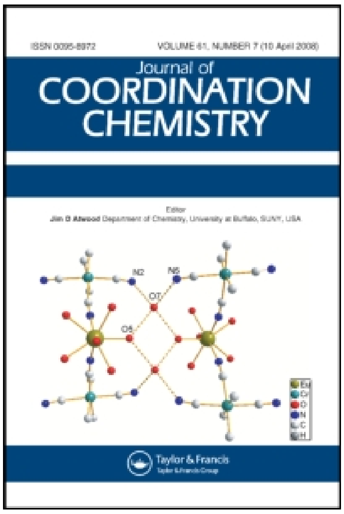

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Syntheses and crystal structures of mononuclear, tetranuclear and hexanuclear organotin compounds with derivatives of <i>p</i>-aminobenzoic acid

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Syntheses and crystal structures of mononuclear, tetranuclear and hexanuclear organotin compounds with derivatives of *p*-aminobenzoic acid

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Four organotin(IV) compounds, $[Bu_6Sn_6O_6(L^1)_6]$ (**1**), $[Bu_6Sn_6O_6(L^2)_4(L^3)_2]$ (**2**), $[Bu_8Sn_4O_2(L^2)_4]$ (**3**) and $[Ph_3Sn(L^2)]$ (**4**), were obtained by reactions of BuSnOH, Bu_2SnO and Ph_3SnOH with 4-((6-chloropyridin-3-yl)methylamino)benzonic acid (HL^1), 4-((pyridin-2-yl)methylamino) benzonic acid (HL^2) and *p*-aminobenzoic acid (HL^3). **1** is a hexameric cluster, existing in a drum-like structure with prismatic Sn_6O_6 core. Compound **2** is a mixed drum, containing two kinds of carboxylic acid anions. Compound **3** possesses a Sn_4O_4 ladder structure. In **2** and **3**, two-dimensional supramolecular structures are formed by the intermolecular hydrogen-bonding interactions. Compound **4** is a monomer with a dimer formed through π–π stacking between adjacent L^2 anions. Compounds **1**–**4** were characterized by elemental analyses and IR spectra.

Keywords: Organotin (IV); Crystal structures; Supramolecular structures; Carboxylate

1. Introduction

A variety of the organotin carboxylate compounds have been investigated for their intriguing molecular structures [1, 2], potential biological activities [3, 4] and industrial and agricultural applications [5–9]. Structures such as monomers, dimers, tetramers, ladders and hexameric drums have been reported [10–13]. However, prediction of either the composition or the structure of such products is difficult and architectures of organotin compounds with carboxylate acids remain a long-term challenge [14].

Ongoing research in our laboratory has been directed toward the design and synthesis of organooxotin clusters [15]. As an extension of our previous work, we select three ligands, HL^1, HL^2 and HL^3 (scheme 1) to react with organotin complexes. Four new compounds, $[Bu_6Sn_6O_6(L^1)_6]$ (**1**), $[Bu_6Sn_6O_6(L^2)_4(L^3)_2]$ (**2**), $[Bu_8Sn_4O_2(L^2)_4]$ (**3**) and $[Ph_3Sn(L^2)]$ (**4**), have been synthesized by azeotropic removal of water from the reactions. The crystal structures of these compounds will be represented and discussed in this article.

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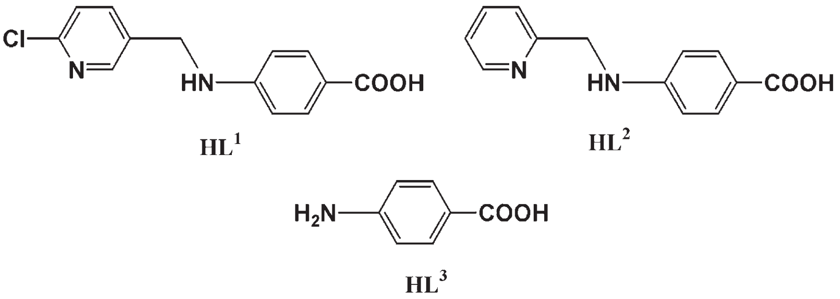

Scheme 1. Structures of the ligands.

2. Experimental

2.1. *Preparation*

2.1.1. Synthesis of the ligands HL^1. Anhydrous potassium carbonate (3.35 g, 24.24 mmol) was added to a solution of ethyl 4-aminobenzoate (4.00 g, 24.24 mmol) in acetonitrile (25 mL). After stirring for 30 min, a solution of 2-chloro-5-(chloromethyl)pyridine (3.93 g, 24.24 mmol) in acetonitrile (10 mL) was added. The reaction mixture was refluxed for 20 h, then cooled to room temperature, filtered, and a yellow filtrate was obtained. Solid HL^1 was obtained by slow evaporation of the solvent, and collected by filtration, washed with water and dried in air (3.05 g, yield: 48%), m.p. 210–212°C.

HL^2 HL^2 was prepared in the same way as HL^1 by using 2-chloromethylpyridine (3.98 g, 24.24 mmol) instead of 2-chloro-5-(chloromethyl)pyridine. The brown solid was washed with water and dried in air (3.32 g, yield: 60%), m.p. 196–197°C.

2.1.2. Synthesis of organotin compounds

[$Bu_6Sn_6O_6(L^1)_6$] (1): A mixture of *n*-butylstannoic acid (0.021 g, 0.10 mmol) and HL^1 (0.079 g, 0.30 mmol) in benzene (35 mL) was heated to reflux for 8 h with azeotropic removal of water via a Dean–Stark trap. Then DMF was added reaction continued for 4 h. After cooling to room temperature, the mixture was filtered, and the filtrate was evaporated to afford colorless crystals. (0.059 g, yield: 65%); Anal. Calcd. for $C_{102}H_{114}Cl_6N_{12}O_{18}Sn_6$: C, 45.02; H, 4.22; N, 6.18; found: C, 44.98; H, 4.18; N, 6.12%.

[$Bu_6Sn_6O_6(L^2)_4(L^3)_2$] (2): Compound **2** was prepared similarly to **1** by using HL^2 (0.023 g, 0.10 mmol) and HL^3 (0.014 g, 0.10 mmol) instead of HL^1. The molar ratio of *n*-butylstannoic acid: HL^2: HL^3 is 2:1:1. Brown crystals suitable for X-ray diffraction were obtained by slow evaporation of the solvent. (0.055 g, yield: 48%); Anal. Calcd for $C_{90}H_{92}N_{10}O_{18}Sn_6$: C, 46.71; H, 4.01; N, 6.05; found: C, 46.69; H, 3.99; N, 6.04%.

[$Bu_8Sn_4O_2(L^2)_4$] (3): A mixture of di-n-butyltin oxide (0.037 g, 0.15 mmol) and HL^2 (0.068 g, 0.30 mmol) in benzene (35 mL) was heated to reflux for 6 h with azeotropic removal of water via a Dean–Stark trap. After cooling to room temperature, the mixture was filtered, and the filtrate was evaporated to afford the solid product which was then recrystallized from benzene–methanol (1 : 1, v/v) to give yellow crystals. (0.084 g, yield: 60%); Anal. Calcd for $C_{84}H_{110}N_8O_{10}Sn_4$: C, 54.05; H, 5.94; N, 6.00; found: C, 54.04; H, 5.92; N, 5.98%.

[$Ph_3Sn(L^2)$] (4): A mixture of triphenyltin hydroxide (0.068 g, 0.18 mmol) and HL^2 (0.042 g, 0.18 mmol) in benzene (20 mL) was heated to reflux for 12 h with azeotropic removal of water via a Dean–Stark trap. After cooling to room temperature, the mixture was filtered, and the filtrate was evaporated to give product which was then recrystallized from acetone–dichloromethane (1 : 1, v/v) to give yellow crystals. (0.058 g, yield: 56%); Anal. Calcd for $C_{31}H_{26}N_2O_2Sn$: C, 64.50; H, 4.54; N, 4.85; found: C, 64.35; H, 4.48; N, 4.92%.

2.2. *Physical Measurements and X-ray crystallography*

All materials were commercially available and used as received. The FT-IR spectra were recorded from KBr pellets from 4000–400 cm^{-1} on a Mattson Alpha-Centauri spectrometer. Elemental analyses were carried out with a Carlo Erba 1106 elemental analyzer. Experimental details of the X-ray analyses are provided in table 1. Diffraction intensities for **1**–**4** were collected on a Bruker Apex CCD diffractometer using ω-scan technique with graphite-monochromated Mo-Kα radiation ($\lambda = 0.71069$ Å). Absorption corrections were applied using multi-scan technique [16]. The structures were solved with the direct method of SHELXS-97 [17] and refined with full-matrix least-squares techniques using SHELXL-97 [18] within WINGX [19]. Non-hydrogen atoms were refined anisotropically. The H atoms on C were generated geometrically except H atoms on distorted *n*-butyl groups for **2**. Analytical expressions of neutral-atom scattering factors were employed, and anomalous dispersion corrections were incorporated [20].

3. Results and discussion

Compounds **1**–**4** were prepared using the same procedure. In the course of our investigations on the coordination ability of HL^1, HL^2 and HL^3 toward Sn(IV), it is found that the carboxylate ligands are bidentate chelating or isobidentate bridging ligands, while the imino and pyridine N atoms do not coordinate to tin.

3.1. *Crystal structure*

Selected geometric parameters for **1**–**4** are given in table 2 and hydrogen bond data are listed in table 3.

3.1.1. The structure of [$Bu_6Sn_6O_6(L^1)_6$] (1). Compound **1** consists of a drum-shaped Sn_6O_6 core which is held together by six L^1 anions on the periphery [21, 22]. There are two kinds of crystallographically independent Sn atoms and two μ_3-O^{2-} anions in the

Table 1. Crystal data and structure refinements for **1**–**4**.

	1	**2**	**3**	**4**
Formula	$C_{102}H_{114}Cl_6N_{12}O_{18}Sn_6$	$C_{90}H_{92}N_{10}O_{18}Sn_6$	$C_{84}H_{110}N_8O_{10}Sn_4$	$C_{31}H_{26}N_2O_2Sn$
Fw	2721.01	2314.00	1872.69	577.23
Temperature (K)	293(2)	293(2)	293(2)	293(2)
Crystal system	Cubic	Monoclinic	Triclinic	Orthorhombic
Space group	*Pa*-3	*C*2/*m*	$P\bar{1}$	*Pbca*
a (Å)	28.712(3)	18.7060(12)	12.1890(14)	8.706(5)
b (Å)	28.712(3)	25.6220(8)	14.0020(16)	17.476(5)
c (Å)	28.712(3)	14.1810(16)	14.4540(17)	34.724(5)
α (°)	90	90	67.086(2)	90
β (°)	90	110.877(5)	87.329(2)	90
γ (°)	90	90	78.161(2)	90
V (Å^{-3})	23670(5)	6350.5(8)	2222.4(4)	5283(3)
Z	8	2	1	8
D_{calcd} (g cm^{-3})	1.527	0.605	1.399	1.451
Absorption coefficient (mm^{-1})	1.446	0.607	1.168	0.997
$F(000)$	10848	1146	956	2336
θ range (°)	3.01–27.48	1.75–28.39	1.74–28.30	1.17–28.29
Reflns collected/unique	189415/8908	19645/7792	13738/10085	31446/6397
R_{int}	0.1121	0.0472	0.0199	0.0614
Data/restraints/parameters	8908/4/391	7792/8/301	10085/13/476	6397/0/329
Goodness-of-fit on F^2	1.202	0.979	0.977	0.978
Final R_1/wR_2 ($I > 2\sigma(I)$)	0.1153, 0.2203	0.0596, 0.1523	0.0506, 0.1261	0.0368, 0.0601
Max, min peaks (e Å^{-3})	2.327, −0.850	2.126, −0.512	0.619, −0.596	0.342, −0.411

Table 2. Selected bond lengths (Å) and angles (°) for **1**–**4**.[a]

1			
Sn(1)–O(5)#1	2.086(6)	Sn(2)–O(4)#1	2.082(6)
Sn(2)–O(5)#1	2.083(7)	Sn(2)–C(27)	2.115(13)
Sn(1)–O(5)	2.086(6)	Sn(2)–O(1)	2.131(7)
Sn(1)–O(4)	2.089(7)	Sn(2)–O(2)	2.183(7)
Sn(1)–C(31)	2.111(13)	Sn(2)–O(4)	2.084(6)
C(1)–O(6)#1	1.256(13)	C(1)–O(1)	1.263(13)
Sn(1)–O(3)	2.121(7)	Sn(2)–Sn(1)#1	3.1963(10)
Sn(1)–O(6)	2.181(7)	Sn(1)–Sn(2)	3.2022(10)
Sn(1)–Sn(2)#2	3.1963(10)	O(5)#1–Sn(1)–Sn(2)#2	99.92(18)
O(5)#1–Sn(1)–O(5)	103.8(3)	O(5)–Sn(1)–Sn(2)#2	39.91(19)
O(5)#1–Sn(1)–O(4)	77.7(3)	O(4)–Sn(1)–Sn(2)#2	39.91(17)
O(5)–Sn(1)–O(4)	77.8(3)	C(31)–Sn(1)–Sn(2)#2	137.3(4)
O(5)#1–Sn(1)–C(31)	103.2(4)	O(3)–Sn(1)–Sn(2)#2	122.8(2)
O(5)–Sn(1)–C(31)	99.2(4)	O(6)–Sn(1)–Sn(2)#2	77.2(2)
O(4)–Sn(1)–C(31)	177.1(4)	O(5)#1–Sn(1)–Sn(2)	39.78(19)
O(5)#1–Sn(1)–O(3)	85.6(3)	O(5)–Sn(1)–Sn(2)	99.88(18)
O(5)–Sn(1)–O(3)	161.0(3)	O(4)–Sn(1)–Sn(2)	39.83(17)
O(4)–Sn(1)–O(3)	88.3(3)	C(31)–Sn(1)–Sn(2)	141.7(4)
C(31)–Sn(1)–O(3)	94.6(4)	O(3)–Sn(1)–Sn(2)	76.6(2)
O(5)#1–Sn(1)–O(6)	157.5(3)	O(3)–Sn(1)–Sn(2)	76.6(2)
O(5)–Sn(1)–O(6)	88.4(3)	Sn(2)#2–Sn(1)–Sn(2)	73.33(3)
O(4)–Sn(1)–O(6)	86.7(3)	O(4)#1–Sn(2)–O(5)#1	78.0(3)
C(31)–Sn(1)–O(6)	93.3(5)	O(4)#1–Sn(2)–O(4)	104.0(3)
O(3)–Sn(1)–O(6)	77.8(3)	O(5)#1–Sn(2)–O(4)	77.9(3)
O(5)#1–Sn(2)–C(27)	177.4(4)	O(6)#1–C(1)–O(1)	125.9(10)
O(6)#1–C(1)–C(2)	118.1(11)	O(2)–C(14)–O(3)	124.7(9)
O(4)#1–Sn(2)–C(27)	99.9(4)	O(4)–Sn(2)–C(27)	101.2(4)
O(4)#1–Sn(2)–O(1)	86.5(3)	C(27)–Sn(2)–Sn(1)#1	138.4(4)
O(5)#1–Sn(2)–O(1)	88.8(3)	O(1)–Sn(2)–Sn(1)#1	77.3(2)
O(4)–Sn(2)–O(1)	160.7(3)	O(2)–Sn(2)–Sn(1)#1	123.1(2)
C(27)–Sn(2)–O(1)	92.7(5)	O(4)#1–Sn(2)–Sn(1)	100.15(18)
O(4)#1–Sn(2)–O(2)	161.1(3)	O(5)#1–Sn(2)–Sn(1)	39.85(17)
O(5)#1–Sn(2)–O(2)	88.8(3)	O(4)–Sn(2)–Sn(1)	39.95(19)
O(4)–Sn(2)–O(2)	86.2(3)	C(27)–Sn(2)–Sn(1)	139.8(4)
C(27)–Sn(2)–O(2)	93.6(4)	O(1)–Sn(2)–Sn(1)	123.0(2)
O(1)–Sn(2)–O(2)	79.6(3)	O(2)–Sn(2)–Sn(1)	77.3(2)
O(4)#1–Sn(2)–Sn(1)#1	40.07(19)	Sn(1)#1–Sn(2)–Sn(1)	73.46(3)
O(5)#1–Sn(2)–Sn(1)#1	39.98(18)	O(4)–Sn(2)–Sn(1)#1	100.18(18)
2			
Sn(1)–O(3)	2.081(5)	Sn(2)–O(3)	2.086(2)
Sn(1)–O(4)	2.085(4)	Sn(2)–O(4)#2	2.088(4)
Sn(1)–O(4)#1	2.085(4)	Sn(2)–O(4)	2.090(4)
Sn(1)–C(18)	2.126(13)	Sn(2)–C(14)	2.146(7)
Sn(1)–O(1)	2.150(4)	Sn(2)–O(2)	2.150(4)
Sn(1)–O(1)#1	2.150(4)	Sn(2)–O(5)	2.155(5)
Sn(1)–Sn(2)#1	3.1999(6)	Sn(2)–Sn(2)#2	3.2083(8)
Sn(1)–Sn(2)	3.1999(6)	O(3)–Sn(1)–O(4)	78.01(14)
O(3)–Sn(1)–O(4)#1	78.01(14)	O(3)–Sn(2)–O(2)	86.19(17)
O(4)–Sn(1)–O(4)#1	103.9(2)	O(4)#2–Sn(2)–O(2)	160.59(16)
O(3)–Sn(1)–C(18)	179.2(4)	O(4)–Sn(2)–O(2)	88.75(15)
O(4)–Sn(1)–C(18)	101.5(3)	C(14)–Sn(2)–O(2)	94.4(3)
O(4)#1–Sn(1)–C(18)	101.5(3)	O(3)–Sn(2)–O(5)	160.14(18)
O(3)–Sn(1)–O(1)	88.38(15)	O(4)#2–Sn(2)–O(5)	85.82(16)
O(4)–Sn(1)–O(1)	86.67(16)	O(4)–Sn(2)–O(5)	87.91(16)
O(4)#1–Sn(1)–O(1)	160.46(16)	C(14)–Sn(2)–O(5)	97.2(2)
C(18)–Sn(1)–O(1)	92.2(3)	O(3)–Sn(2)–Sn(1)	39.78(14)
O(3)–Sn(1)–O(1)#1	88.38(15)	O(4)#2–Sn(2)–Sn(1)	100.02(11)

(*Continued*)

Table 2. Continued.

O(4)–Sn(1)–O(1)#1	160.46(16)	O(4)–Sn(2)–Sn(1)	39.91(10)
O(4)#1–Sn(1)–O(1)#1	86.67(16)	C(14)–Sn(2)–Sn(1)	136.6(2)
C(18)–Sn(1)–O(1)#1	92.2(3)	O(2)–Sn(2)–Sn(1)	77.34(11)
O(1)–Sn(1)–O(1)#1	78.9(2)	O(5)–Sn(2)–Sn(1)	122.32(12)
O(3)–Sn(1)–Sn(2)#1	39.88(5)	O(3)–Sn(2)–Sn(2)#2	100.03(14)
O(4)–Sn(1)–Sn(2)#1	99.97(11)	O(4)#2–Sn(2)–Sn(2)#2	39.86(11)
O(4)#1–Sn(1)–Sn(2)#1	40.03(11)	O(4)–Sn(2)–Sn(2)#2	39.81(10)
C(18)–Sn(1)–Sn(2)#1	139.83(16)	C(14)–Sn(2)–Sn(2)#2	139.3(2)
O(1)–Sn(1)–Sn(2)#1	122.63(12)	O(2)–Sn(2)–Sn(2)#2	122.93(11)
O(1)#1–Sn(1)–Sn(2)#1	77.37(12)	O(5)–Sn(2)–Sn(2)#2	76.53(12)
O(3)–Sn(1)–Sn(2)	39.88(5)	Sn(1)–Sn(2)–Sn(2)#2	73.304(16)
O(4)–Sn(1)–Sn(2)	40.03(11)	O(2)–C(13)–O(1)	123.9(5)
O(4)#1–Sn(1)–Sn(2)	99.97(11)	O(2)–C(13)–C(10)	119.2(6)
C(18)–Sn(1)–Sn(2)	139.83(16)	O(1)–C(13)–C(10)	116.9(6)
O(1)–Sn(1)–Sn(2)	77.37(12)	C(13)–O(1)–Sn(1)	130.0(4)
O(1)#1–Sn(1)–Sn(2)	122.63(12)	C(13)–O(2)–Sn(2)	130.7(4)
Sn(2)#1–Sn(1)–Sn(2)	73.21(2)	Sn(1)–O(3)–Sn(2)#1	100.34(15)
O(3)–Sn(2)–O(4)#2	104.22(17)	Sn(1)–O(3)–Sn(2)	100.34(15)
O(3)–Sn(2)–O(4)	77.79(18)	Sn(2)#1–O(3)–Sn(2)	132.4(3)
O(4)#2–Sn(2)–O(4)	77.76(17)	Sn(1)–O(4)–Sn(2)#2	132.9(2)
O(3)–Sn(2)–C(14)	97.8(3)	Sn(1)–O(4)–Sn(2)	100.07(16)
O(4)#2–Sn(2)–C(14)	100.2(3)	Sn(2)#2–O(4)–Sn(2)	100.33(16)
O(4)–Sn(2)–C(14)	174.4(2)	C(22)–O(5)–Sn(2)	130.5(5)
3			
Sn(1)–O(3)	2.049(3)	Sn(2)–O(3)	2.015(3)
Sn(1)–C(35)	2.103(6)	Sn(1)–C(31)	2.115(6)
Sn(1)–O(3)#1	2.171(3)	Sn(1)–O(5)	2.226(4)
Sn(2)–C(27)	2.109(6)	Sn(2)–C(39)	2.117(8)
C(13)–O(1)	1.225(7)	C(13)–O(2)	1.295(6)
C(14)–O(4)	1.239(7)	C(14)–O(5)	1.252(7)
Sn(2)–O(2)	2.156(4)	Sn(2)–O(4)	2.243(4)
Sn(1)–O(2)#1	2.794	Sn(2)–O(1)	2.964
O(3)–Sn(1)–C(35)	107.3(2)	O(3)–Sn(1)–C(31)	109.4(2)
C(35)–Sn(1)–C(31)	143.2(3)	O(3)–Sn(1)–O(3)#1	76.56(13)
C(35)–Sn(1)–O(3)#1	93.9(2)	C(27)–Sn(2)–C(39)	138.2(3)
C(31)–Sn(1)–O(3)#1	96.6(2)	O(3)–Sn(2)–O(2)	80.62(13)
O(3)–Sn(1)–O(5)	91.44(15)	C(27)–Sn(2)–O(2)	98.3(2)
C(35)–Sn(1)–O(5)	90.9(3)	C(39)–Sn(2)–O(2)	95.3(3)
C(31)–Sn(1)–O(5)	86.0(2)	O(3)–Sn(2)–O(4)	91.20(15)
O(3)#1–Sn(1)–O(5)	167.9(2)	C(27)–Sn(2)–O(4)	82.9(3)
O(3)–Sn(2)–C(27)	111.3(2)	C(39)–Sn(2)–O(4)	89.2(3)
O(3)–Sn(2)–C(39)	109.8(3)	O(2)–Sn(2)–O(4)	171.6(2)
4			
Sn(1)–O(1)	2.086(2)	Sn(1)–C(4)	2.129(3)
Sn(1)–O(2)	2.560(2)	Sn(1)–C(12)	2.140(3)
O(2)–C(25)	1.245(4)	C(25)–O(1)	1.301(4)
Sn(1)–C(18)	2.125(3)	C(4)–Sn(1)–C(12)	107.53(13)
O(1)–Sn(1)–C(18)	104.86(11)	O(1)–Sn(1)–C(12)	93.77(11)
O(1)–Sn(1)–C(4)	115.80(11)	C(18)–Sn(1)–C(12)	111.00(13)
C(18)–Sn(1)–C(4)	120.66(12)	O(2)–C(25)–O(1)	118.9(3)

[a] Symmetry operations: For **1**: #1 $x-1/2$, $-y+1/2$, $-z+1$; #2 $-x+1$, $y+1/2$, $-z+1/2$; For **2**: #1 x, $-y+1$, z; #2 $-x+1$, y, $-z+1$; For **3**: #1 $-x+1$, $-y$, $-z+2$.

Table 3. Hydrogen-bond geometries for **2** and **3** (lengths in Å and angles in degrees).[b]

D–H···A	D–H	H···A	D···A	∠D–H···A
2				
N(2)–H(2N)···N(1)#3	1.00(5)	2.22(9)	2.997(1)	134(9)
3				
N(3)–H(3N)···O(1)#2	0.84(4)	2.19(5)	2.906(7)	143(6)
N(2)–H(2N)···N(4)#3	0.98(6)	2.13(7)	2.99(1)	144(8)

[b] Symmetry operations: For **2**: #3 $-x+1/2$, $-y+3/2$, $-z+2$; For **3**: #2 $-x+1$, $-y$, $-z+1$; #3 $x-1$, $y-1$, $z+1$.

unit cell. Sn1 is coordinated by O4, O5, O3, O5#1 and O6 with distances of 2.089(7), 2.086(6), 2.121(7), 2.086(6) and 2.181(7) Å, respectively, and O4#1, O1, O5#1, O2 and O4 coordinate to Sn2 with distances of 2.082(6), 2.131(7), 2.083(7), 2.183(7) and 2.082(6) Å, respectively. The Sn–O bonds lie within the normal ranges [23]. Each Sn is coordinated by one C of *n*-butyl and two O atoms of two carboxylate acid anions and three μ_3-O^{2-} anions to finish an O_5C donor set (figure 1). The Sn–O skeleton of the molecule can be described as a drum with top and bottom faces each being comprised of a six-membered Sn_3O_3 tristannoxane ring. The drum faces are joined together by six Sn–O bonds containing μ_3-O^{2-} anions. The sides of the drum are thus comprised of six four-membered Sn_2O_2 distannoxane rings, each of which is spanned by a carboxylate group that forms a symmetrical bridge between two Sn atoms. The bond angles found in the drum structure are in accord with reported values [24–26].

The distannoxane ring sides of the drum are not planar but are folded along the Sn–Sn vectors such that the μ_3-O^{2-} anions are directed toward the interior of the cavity. Similarly, the tristannoxane ring faces of the drum are not planar but have the μ_3-O^{2-} anions directed toward the interior of the cavity, relative to the Sn atoms. Thus, the interior of the cavity is defined by a crown of six μ_3-O^{2-} anions, in a trigonal-antiprismatic arrangement, and the entrance to the cavity is defined by μ_3-O^{2-} anions arranged as an approximate equilateral triangle. The carboxylates bridge alternate Sn atoms by an isobidentate bridging coordination mode. In **1**, the L^1 anions are not planar, and the dihedral angle between the benzene ring and pyridine ring is 92.8°.

3.1.2. The structure of $[Bu_6Sn_6O_6(L^2)_4(L^3)_2]$ (2).

The framework of **2** is similar to that of **1** except that **2** shows a mixed drum structure. Figure 2 shows the alternate coordination of the two kinds of anions of L^2 and L^3 around the outside of the mixed drum.

There exist extensive intermolecular N–H···N hydrogen bonding interactions in **2**. Each stannoxane drum interacts with four neighboring drum molecules *via* N–H···N hydrogen bonds. The N···N distance of 2.997(1) Å and the N–H···N angle of 134(9)° are in normal ranges [27, 28]. The cumulative effect of these interactions is generation of a two-dimensional supramolecular grid-like structure (figure 3).

The (Sn_6O_6) core of **2** is supported by a periphery of four L^2 and two L^3 bridging anions. A mixed-drum composition, $[(MeSn(O)O_2CMe)(MeSn(O)O_2P(t\text{-}Bu)_2)]_3$ has been reported [29], but organotin compounds containing two kinds of carboxylic acid have not been reported.

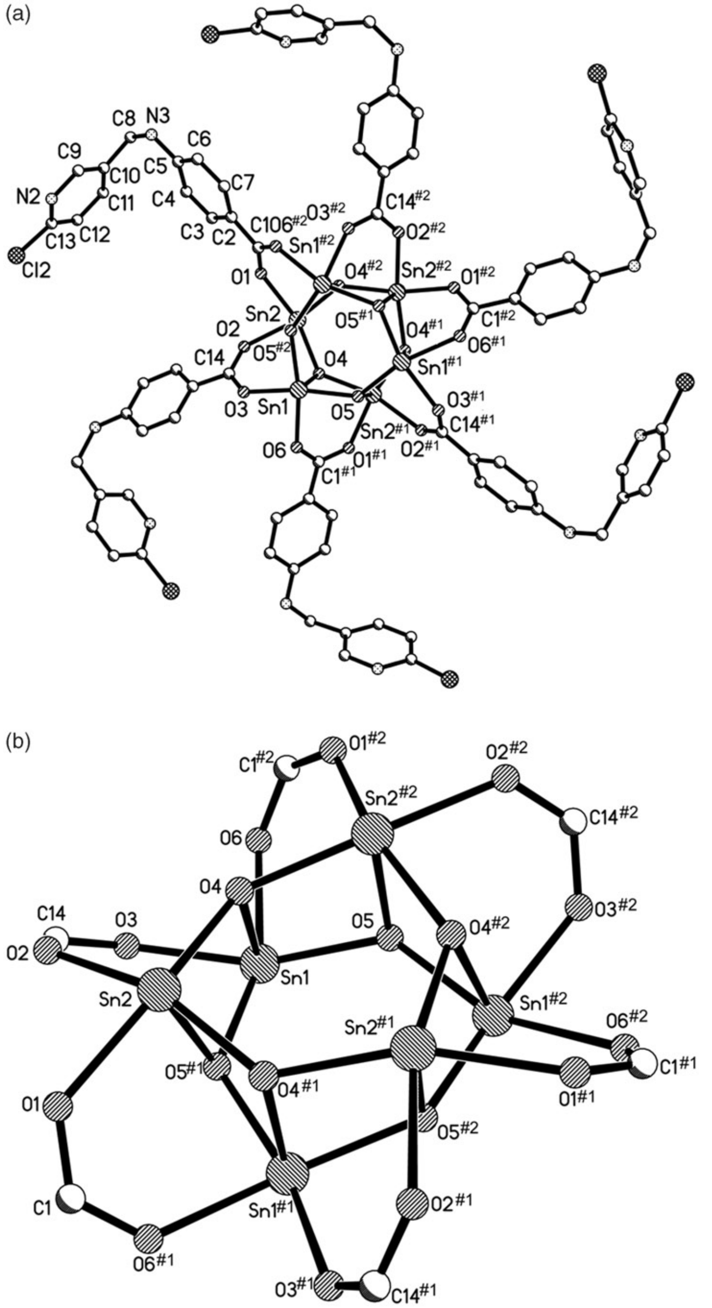

Figure 1. (a) Molecular structure of **1** (*n*-Butyl groups on the Sn atoms and H atoms are omitted for clarity). (b) View of the Sn_6O_6 core.

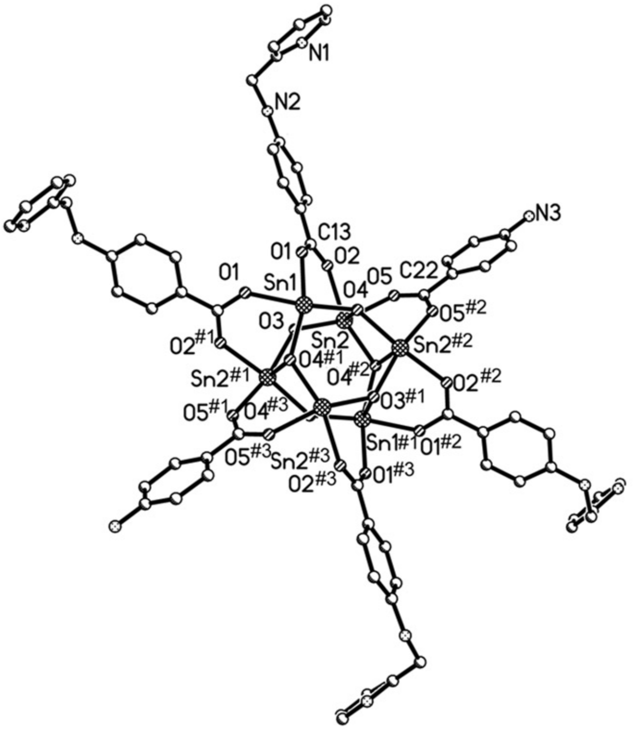

Figure 2. Molecular structure of **2** (*n*-Butyl groups on the Sn atoms and H atoms are omitted for clarity).

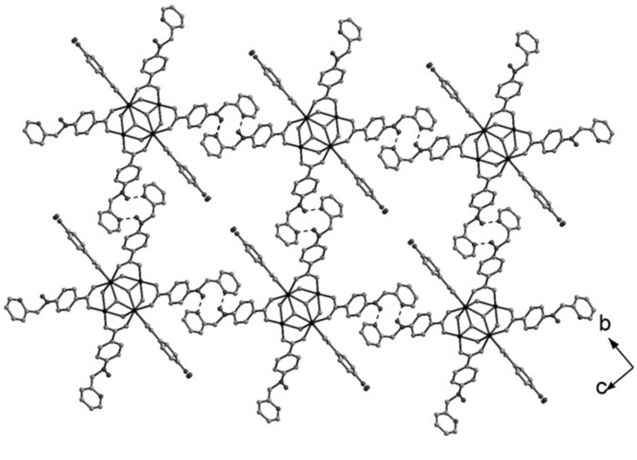

Figure 3. Two-dimensional supramolecular network of **2** through the intermolecular hydrogen bonds (*n*-Butyl groups on the Sn atoms are omitted for clarity).

3.1.3. The structure of [$Bu_8Sn_4O_2(L^2)_4$] (3).

The molecular structure of **3** is shown in figure 4. Compound **3** possesses a Sn_4O_4 ladder structure with two kinds of Sn atoms. The exo Sn center shows a distorted octahedral geometry composed of two C atoms from two *n*-butyl groups and four O atoms from one μ_3-O^{2-} anion and three

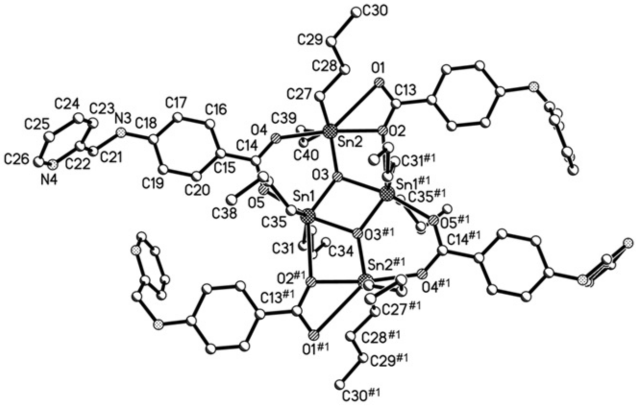

Figure 4. Molecular structure of **3** (The H atoms are omitted for clarity).

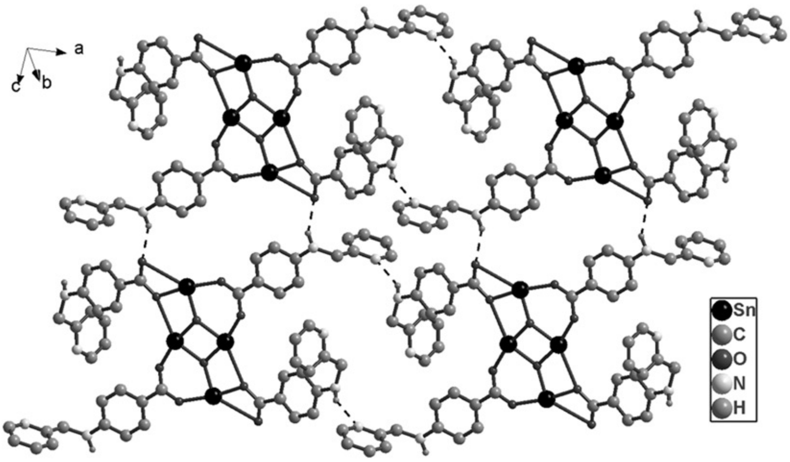

Figure 5. Two-dimensional supramolecular network of **3** through the intermolecular hydrogen bonds (*n*-Butyl groups on the Sn atoms are omitted for clarity).

carboxylates. The endo Sn center can be also regarded as six-coordinate, showing a distorted octahedral geometry composed of two C atoms from two *n*-butyl groups, and four O atoms from two μ_3-O^{2-} anions and two carboxylates.

Compound **3** is a tetranuclear centrosymmetric compound with a central Sn_2O_2 four-membered ring. The μ_3-O^{2-} anion (O3) is tridentate, linking one exo-cyclic (Sn2) and two endo-cyclic (Sn1) Bu_2Sn groups. Additional links between the endo- and exo-cyclic Sn atoms are provided by bidentate carboxylate ligands that form essentially symmetrical bridges. Each exocyclic Sn atom is also coordinated by an anisobidentate chelating carboxylate. The Sn–O distances of 2.794 and 2.964 Å (for Sn1–$O2^{\#1}$ and Sn2–O1, respectively) are slightly longer than the normal bond length, but still lie in the range of 2.61–3.02 Å reported for intramolecular $Sn \cdots O$ bond distances [30].

There exist two kinds of intermolecular hydrogen-bonding interactions. The lengths of $N \cdots N$ and $N \cdots O$ are 2.99(1) and 2.906(7) Å, respectively. The parameters

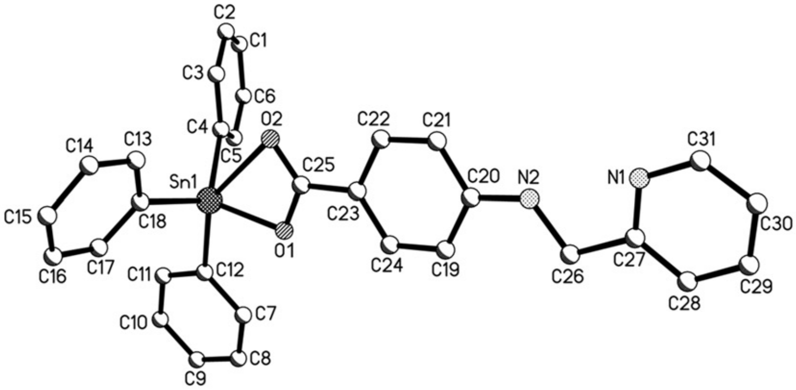

Figure 6. View of the molecular structure of **4** (The H atoms are omitted for clarity).

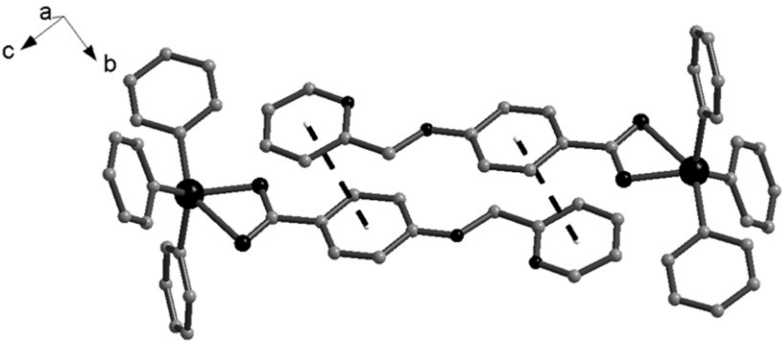

Figure 7. Packing diagram of the **4** (The H atoms are omitted for clarity).

observed for these hydrogen-bonding interactions are quite reasonable [31]. A two-dimensional supramolecular layer is formed by hydrogen-bonding interactions (figure 5).

3.1.4. The structure of [$Ph_3Sn(L^2)$] (4). As shown in figure 6, **4** is a monomer with Sn five-coordinated by three C atoms from three phenyl groups and two O atoms from one L^2 anion. The Sn–O distances are all in the normal ranges [32]. The Sn1–O1 distance (2.086 (2) Å) is significantly shorter than Sn1–O2 (2.560 Å), in accord with the stronger coordinative ability of the carboxylate O atom than the carbonyl O atom. The two C–O bond distances of the carboxylate group are unequal (1.245(4) and 1.301(4) Å) with the longer C–O distance associated with the shorter Sn–O bond. Therefore the carboxylate ligand coordinates to Sn in a chelating bidentate mode.

In addition, a dimer is formed through π–π stacking interactions (figure 7). The average face-to-face distance between phenyl ring and pyridine ring of adjacent L^2 anions is 3.546 Å (dihedral angle 7.4°). The π–π stacking interactions play an important role in stabilization of the stacked molecular units.

3.2. *Infrared spectrum*

The infrared spectra carried out on the solid samples show all the expected bands for the ligands and the Sn moieties. Weak absorptions in the range 3145–3170 cm^{-1} are due to the pyridine ring C–H stretching. In the spectra of free carboxylic acid ligands, the presence of $–CO_2H$ group is detected by an absorption between 1615 and 1411 cm^{-1}. These bands cannot be found in the spectra of the compounds, indicating coordination of deprotonated carboxylate groups to Sn. The $\nu_{asym}(OCO)$ and $\nu_{sym}(OCO)$ bands appear at 1604 and 1405 cm^{-1} for **1**, 1606 and 1363 cm^{-1} for **4**, respectively. The presence of the $\nu_{asym}(OCO)$ and $\nu_{sym}(OCO)$ is detected by intense absorptions at around 1633 and 1464 cm^{-1} for compounds **2** and **3**. The difference ($_{\Delta}v$) between $\nu_{asym}(OCO)$ and $\nu_{sym}(OCO)$ reflects the bridging bidentate coordination mode of the $–CO_2^-$ group [33]. Medium to weak bands in the region 410–492cm^{-1} are assigned to Sn–O and those in the region 526–611 cm^{-1} indicate the presence of Sn–C bands [23, 34, 35]. A strong to medium band at 620–701 cm^{-1} is assigned to Sn–O–Sn bridged structure for **1**, **2** and **3** [34] and around 729 cm^{-1} for **4**. These IR data are consistent with the X-ray structure analyses.

3.3. *Discussion*

Although organotin carboxylates have been extensively studied, reactions between organotin precursors and the benzoic acid derivatives containing pyridylmethylamino groups have not been reported. In this case, we have chosen HL^1, HL^2 and HL^3 as ligands and investigated their reactions with organotin precursors Bu_2SnO, BuSnOOH and Ph_3SnOH. The results indicate that these ligands coordinate through the O atoms of carboxylate groups. Although the N atoms of imino and pyridine groups do not coordinate to Sn, they are beneficial to formation of the supramolecular structure through hydrogen-bonding interactions. Due to the existence of the pyridylmethylamino groups, the organotin compounds may be connected through hydrogen bonds to form a variety of supramolecular structures (compounds **2** and **3**). In addition, the N atoms of pyridylmethylamino groups may further coordinate to other metal centers, and these organotin compounds may act as the multi-site coordination ligands [13]. Moreover, although many drum-like structures with an Sn_6O_6 core have been reported, **2** is the first drum-like structure containing two different kinds of carboxylic acids.

4. Conclusion

Four organotin(IV) compounds, $[Bu_6Sn_6O_6(L^1)_6]$, $[Bu_6Sn_6O_6(L^2)_4(L^3)_2]$, $[Bu_8Sn_4O_2(L^2)_4]$ and $[Ph_3Sn(L^2)]$, have been synthesized and their crystal structures determined by X-ray diffraction. The carboxylate groups are bidentate chelating or isobidentate bridging ligands, and the imino and pyridine N atoms do not coordinate to Sn. For compounds **2** and **3**, supramolecular frameworks are formed through N–H $\cdots$ N and N–H $\cdots$ O hydrogen bonds.

Supplementary data

X-ray crystallographic files in CIF format for compounds **1–4** have been deposited at the Cambridge Crystallographic Data Center with the deposition number CCDC 663493-663496. Copies of the data can be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge, CB2 IEZ, UK (Fax: t44-1223-336033; Email: deposit@ccdc.cam.ac.uk).

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