

Synthesis, characterizations and crystal structures of di-*n*-butyltin(IV) complexes with heteroatomic (N, O or S) acid

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Abstract

Two types of di-*n*-butyltin(IV) complexes $\{[{}^n\text{Bu}_2\text{Sn}(\text{O}_2\text{CR})]_2\text{O}\}_2 \cdot \text{L}$ **1–4** and ${}^n\text{Bu}_2\text{Sn}(\text{O}_2\text{CR})_2\text{Y}$ **5–8** (when L = H₂O, R = 2-pyrazine **1**; L = 0, R = 2-pyrimidylthiomethylene **2**, 1-naphthoxymethylene **3**; L = C₆H₆, R = 2-naphthoxymethylene **4**; when Y = H₂O, R = 2-pyrazine **5**; Y = 0, R = 2-pyrimidylthiomethylene **6**, 1-naphthoxymethylene **7**, 2-naphthoxymethylene **8**) have been prepared in 1:1 or 1:2 molar ratios by reactions of di-*n*-butyltin oxide with the heteroatomic (N, O or S) carboxylic acids. The complexes **1–8** are characterized by elemental, IR, ¹H and ¹³C NMR spectra. And except for complexes **6** and **7**, the complexes **1–5** and **8** are also characterized by X-ray crystallography diffraction analyses, which reveal that the tin atom of complex **5** is seven-coordinated, while the complexes **1–4** and **8** are all hexa-coordinated. The nitrogen atom of the aromatic ring in complexes **1** and **5** participates in the interactions with the Sn atom.

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1. Introduction

Organotin carboxylates have been the subjects of interest for some time because of their biochemical and commercial applications [1]. In general, the biochemical activity of organotin carboxylates is influenced greatly by the structure of the molecule and the coordination number of the tin atoms [2–4]. Recent review on structures of organotin carboxylates has demonstrated that when a 1:1 (tin/ligand) ratio is used, there are five types of structure adopted in the crystalline state by the dimeric dicarboxylatorganodistannoxanes [1d,5]. A characteristic feature of these complexes in the solid state is their dimerization that results in the so-called ladder or staircase arrangement that contains a central planar Sn₂O₂ four-membered ring. When a 1:2 ratio is used, a diorganotin dicarboxylate is formed. They are mono-

structural and the Sn atom has skew-trapezoidal planar geometry [1d,6].

Despite such extensive studies being carried out on theme, the report on the formal coordination to the Sn atoms of additional hetero-atoms in these organotin carboxylates is rare [7,8]. Our current interest is whether or not the hetero-atoms (N, O or S) of the carboxylic acids are to influence the coordination mode and further help the self-assemble of these molecules. Out of above consideration, we design a series of experiments of di-*n*-butyltin oxide with 2-pyrazinecarboxylic acid, (2-pyrimidylthio)acetic acid, 1-naphthoxyacetic acid and 2-naphthoxyacetic acid, respectively. With 1:1 ratio (tin/ligand), we obtain four di-*n*-butyltin(IV) ladder complexes **1–4** of the type $\{[{}^n\text{Bu}_2\text{Sn}(\text{O}_2\text{CR})]_2\text{O}\}_2 \cdot \text{L}$ (L = H₂O, R = 2-pyrazine **1**; L = 0, R = 2-pyrimidylthiomethylene **2**, 1-naphthoxymethylene **3**; L = C₆H₆, R = 2-naphthoxymethylene **4**). With 1:2 ratio, another four mononuclear complexes **5–8** are obtained and the general formula is ${}^n\text{Bu}_2\text{Sn}(\text{O}_2\text{CR})_2\text{Y}$ (Y = H₂O, R = 2-pyrazine **5**; Y = 0, R = 2-pyrimidylthiomethylene **6**, 1-naphthoxymethylene, **7**, 2-naphthoxymethylene, **8**).

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2. Results and discussion

2.1. Synthesis

Reactions of di-*n*-butyltin oxide with 2-pyrazine-carboxylic acid, (2-pyrimidylthio)acetic acid, 1-naphthoxyacetic acid and 2-naphthoxyacetic acid in 1:1 or 1:2 stoichiometry in refluxing benzene, which afford air-stable complexes. The synthesis procedures are shown in Scheme 1.

2.2. Spectroscopic studies

2.2.1. IR spectra

The stretching frequencies of interest are those associated with the acid COO, Sn–C, Sn–O and Sn–O–Sn groups. The spectra of all the complexes **1–8** show some common characters. The explicit feature in the infrared spectra of all complexes **1–8** is the absence of the band in the region 2600–3436 cm⁻¹, which appears in the free-ligand as the ν(O–H) vibration, indicating metal–ligand bond formation through this site. While strong absorption appears at 474–492 cm⁻¹ in the respective spectra of the complexes **1–8**, which is absent in the spectra of the free ligand, is assigned to the Sn–O stretching mode of vibration. All these values are consistent with that detected in a number of organotin(IV)–oxygen derivatives [9,10]. The observation of two Sn–C absorption bands in the 532–576 cm⁻¹ regions reveals a non-linear *trans* configuration of the C–Sn–C moiety [11].

Some obvious differences among the spectra of the complexes **1–8** are also observed. A strong band in the 621–640 cm⁻¹ region for the {[ⁿBu)₂Sn(O₂CR)]₂O}₂·L complexes is assigned to ν(Sn–O–Sn), indicating a Sn–O–Sn bridged structure. For complexes **1** and **5**, new vibrations, which appear at about 445 and 461 cm⁻¹, attribute to Sn–N bonds and further testify their formation. Above these are also confirmed by an X-ray diffraction study.

2.2.2. NMR spectroscopic

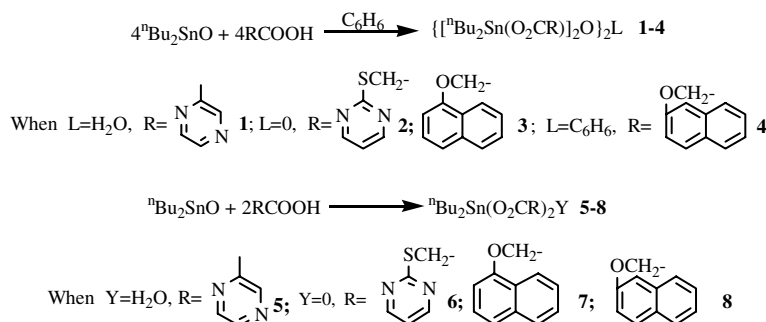
The ¹H NMR spectra show the expected integration and peak multiplicities. In the spectra of four free

ligands, single resonance are observed at 7.46, 8.51, 9.27 and 9.31 ppm, respectively, which is absent in the spectra of the complexes indicating the replacement of the carboxylic acid proton by a diorganotin moiety on complex formation. In addition, the resonance appears at 3.62 for complexes **2** and 3.61 ppm for complex **6** are attributed to the protons of (–S–CH₂) and the resonance at 4.41–4.53 ppm for complexes **3**, **4**, **7** and **8** is assigned to the protons of (–O–CH₂), which further testify their formations. Signals for the other groups appear at the same position as in the ligands.

The ¹³C NMR data for the complexes **1–4** are consistent with a dimeric tetraorganostannoxane structure. Although at least two different types of carboxylate groups are present, only single resonances are observed for the COO group in the ¹³C spectra. The possible reason is that either accidental magnetic equivalence of the carbonyl carbon atoms or the separations between the two sets of resonance are small to be resolved. Complementary information for several complexes is given by the values of the coupling constant. The ¹J_{SnC} value for **1** are 615 and 750 Hz, similar to that of the hexa-coordinated compound {[ⁿBu)₂Sn(2-pic)]₂O₂} [8a], and the calculated θ (C–Sn–C) by the Holeček and Lyčka equation [12] are 136.2° and 149.7°, which are close to the angles observed in the solid state for complex **1**. The same coincidence can be found in complexes **2**, **3**, **4** and **8**. The ¹J_{SnC} values, 622 Hz for **2**, 637 Hz for **3**, 631 and 710 Hz for **4**, 609 Hz for **8**, are in keep with those reported in hexa-coordinated compounds {[ⁿBu)₂Sn(OCOC₁₂H₈NO₂-4')]₂O₂} [13] and ⁿBu₂Sn(OCOC₄H₃Me-2)₂ [14]. And the calculated θ approach to the C–Sn–C angles in the solid state, too. So it can reasonably be assumed that the structure in solution of all these complexes are likely similar to that observed in the solid state.

2.3. X-ray crystallographic studies

Crystals were mounted in Lindemann capillaries under nitrogen. Diffraction data were collected on a Smart CCD area-detector with graphite monochromated Mo Kα radiation (λ = 0.71073 Å). A semiempirical



Scheme 1.

Table 1
Crystal, data collection and structure refinement parameters for complexes 1–5 and 8

Complex	1	2	3	4	5	8
Empirical formula	C ₅₂ H ₈₆ N ₈ O ₁₁ Sn ₄	C ₅₆ H ₉₂ O ₁₀ S ₄ Sn ₄	C ₈₀ H ₁₀₆ O ₁₄ Sn ₄	C ₈₈ H ₁₁₄ O ₁₄ Sn ₄	C ₁₈ H ₂₆ N ₄ O ₅ Sn	C ₃₂ H ₃₆ O ₆ Sn
Formula weight	1474.05	1640.38	1766.41	1870.55	497.12	635.30
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Triclinic	Triclinic	Monoclinic	Rhombohedral	Monoclinic
Space group	C2/c	P $\bar{1}$	P $\bar{1}$	C2/c	R $\bar{3}c$	Cc
Unit cell dimension						
<i>a</i> (Å)	17.309(8)	10.124(7)	11.938(14)	25.389(10)	25.132(19)	36.17(2)
<i>b</i> (Å)	19.505(8)	12.967(8)	13.569(15)	18.400(7)	25.132(19)	5.031(3)
<i>c</i> (Å)	19.083(9)	15.582(10)	13.837(16)	18.825(7)	17.699(19)	17.719(10)
α (°)	90	68.996(8)	103.934(16)	90	90	90
β (°)	94.222(9)	79.265(9)	104.769(16)	92.603(7)	90	114.062(8)
γ (°)	90	71.858(9)	99.691(17)	90	120	90
<i>Z</i>	4	1	1	4	18	4
Absorption coefficient (mm ⁻¹)	1.594	1.535	1.269	1.183	1.224	0.910
Crystal size (mm)	0.42×0.28×0.23	0.55×0.45×0.40	0.35×0.32×0.27	0.28×0.25×0.21	0.22×0.13×0.09	0.52×0.43×0.14
θ range for data collection (°)	2.35–25.02	2.36–25.03	1.82–25.03	2.46–25.03	2.49–25.02	2.31–25.02
Index ranges	–18 ≤ <i>h</i> ≤ 20, –23 ≤ <i>k</i> ≤ 18, –14 ≤ <i>l</i> ≤ 22	–8 ≤ <i>h</i> ≤ 12, –13 ≤ <i>k</i> ≤ 15, –18 ≤ <i>l</i> ≤ 18	–11 ≤ <i>h</i> ≤ 14, –15 ≤ <i>k</i> ≤ 16, –16 ≤ <i>l</i> ≤ 14	30 ≤ <i>h</i> ≤ 30, –15 ≤ <i>k</i> ≤ 21, –22 ≤ <i>l</i> ≤ 22	–28 ≤ <i>h</i> ≤ 29, –25 ≤ <i>k</i> ≤ 29, –21 ≤ <i>l</i> ≤ 20	–42 ≤ <i>h</i> ≤ 41, –5 ≤ <i>k</i> ≤ 5, –21 ≤ <i>l</i> ≤ 20
Reflections collected	16 609	9087	10 082	22 654	15 343	6985
Unique reflections (<i>R</i> _{int})	5632 (0.0617)	6062 (0.0322)	6968 (0.0240)	7744 (0.1489)	1868 (0.0568)	4098 (0.0492)
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents	Semi-empirical from equivalents	Semi-empirical from equivalents	Semi-empirical from equivalents	Semi-empirical from equivalents
Refinement method	Full-matrix least-squares on <i>F</i> ²	Full-matrix least-squares on <i>F</i> ²	Full-matrix least-squares on <i>F</i> ²	Full-matrix least-squares on <i>F</i> ²	Full-matrix least-squares on <i>F</i> ²	Full-matrix least-squares on <i>F</i> ²
Data/restraints/parameters	5632/74/314	6062/44/370	6968/44/442	7744/15/470	1868/6/132	4098/37/352
Goodness of fit on <i>F</i> ²	0.866	0.963	1.045	0.930	0.961	0.903
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0572, <i>wR</i> ₂ = 0.1381	<i>R</i> ₁ = 0.0542, <i>wR</i> ₂ = 0.1324	<i>R</i> ₁ = 0.0405, <i>wR</i> ₂ = 0.0872	<i>R</i> ₁ = 0.0608, <i>wR</i> ₂ = 0.1252	<i>R</i> ₁ = 0.0294, <i>wR</i> ₂ = 0.0653	<i>R</i> ₁ = 0.0464, <i>wR</i> ₂ = 0.0924
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.1381, <i>wR</i> ₂ = 0.1703	<i>R</i> ₁ = 0.0964, <i>wR</i> ₂ = 0.1601	<i>R</i> ₁ = 0.0810, <i>wR</i> ₂ = 0.1124	<i>R</i> ₁ = 0.1121, <i>wR</i> ₂ = 0.1519	<i>R</i> ₁ = 0.0492, <i>wR</i> ₂ = 0.0725	<i>R</i> ₁ = 0.0609, <i>wR</i> ₂ = 0.0969

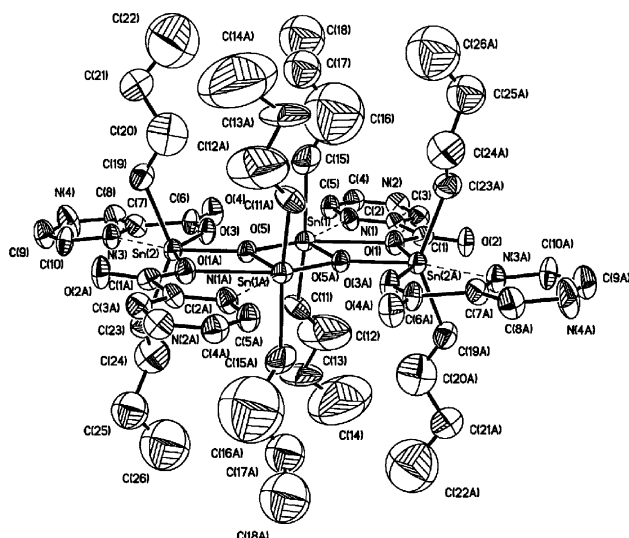


Fig. 1. Molecular structure of complex 1.

absorption correction was applied to the data. The structure was solved by direct methods using SHELXS-97 and refined against *F*² by full-matrix least-squares using SHELXL-97. Hydrogen atoms were placed in calculated positions. Crystal data and experimental details of the structure determinations are listed in Table 1.

2.3.1. Crystal structure of $\{[{}^n\text{Bu}_2\text{Sn}(\text{O}_2\text{CN}_2\text{H}_3\text{C}_4)]_2\text{O}\}_2 \cdot \text{H}_2\text{O}$ (1)

The molecular structure is illustrated in Fig. 1, selected bond lengths (Å) and angles (°) are listed in Table 2. There have being significant intra- and intermolecular contacts in the crystal lattice. As observed for the related structure [1b,15,16], the core geometry of the molecule consists of a centrosymmetric planar four-membered Sn₂O₂ ring with two additional ⁿBu₂Sn(O₂CN₂H₃C₄) units attach at each bridging oxygen atom, with the result that these oxygen atoms are three

Table 2
Selected bond lengths (Å) and angles (°) for complexes 1–4

Bond lengths		Bonds angles		Bonds angles	
<i>Complex 1</i>					
Sn(1)–O(5)#1	2.061(7)	O(5)#1–Sn(1)–O(5)	73.9(3)	O(5)–Sn(2)–C(19)	110.2(5)
Sn(1)–O(5)	2.115(7)	O(5)#1–Sn(1)–C(11)	104.8(5)	O(5)–Sn(2)–C(23)	109.9(5)
Sn(1)–C(11)	2.137(13)	O(5)–Sn(1)–C(11)	98.9(5)	C(19)–Sn(2)–C(23)	135.4(7)
Sn(1)–C(15)	2.202(17)	O(5)#1–Sn(1)–C(15)	103.0(6)	O(5)–Sn(2)–O(3)	75.8(3)
Sn(1)–O(1)	2.461(8)	C(11)–Sn(1)–C(15)	150.9(7)	C(19)–Sn(2)–O(3)	99.7(5)
Sn(1)–N(1)	2.952(10)	O(5)#1–Sn(1)–O(1)	67.8(3)	C(23)–Sn(2)–O(3)	108.2(5)
Sn(2)–O(5)	2.006(7)	O(5)–Sn(1)–O(1)	141.7(3)	O(5)–Sn(2)–O(3)	75.8(3)
Sn(2)–C(19)	2.136(14)	C(11)–Sn(1)–O(1)	91.8(5)	C(19)–Sn(2)–O(1)#1	90.9(5)
Sn(2)–C(23)	2.148(14)	C(15)–Sn(1)–O(1)	90.5(6)	C(23)–Sn(2)–O(1)#1	84.9(5)
Sn(2)–O(3)	2.151(9)	O(5)#1–Sn(1)–N(1)	126.9(3)	O(3)–Sn(2)–O(1)#1	146.0(3)
Sn(2)–O(1)#1	2.383(8)	O(5)–Sn(1)–N(1)	159.1(3)	O(5)–Sn(2)–N(3)	140.5(3)
Sn(2)–N(3)	2.734(10)	C(11)–Sn(1)–N(1)	77.5(4)	O(5)–Sn(2)–O(3)	75.8(3)
		C(15)–Sn(1)–N(1)	78.9(6)	C(19)–Sn(2)–N(3)	80.3(5)
		O(1)–Sn(1)–N(1)	59.1(3)	C(23)–Sn(2)–O(3)	81.1(5)
		O(3)–Sn(2)–N(3)	64.8(3)	C(19)–Sn(2)–O(3)	99.7(5)
<i>Complex 2</i>					
Sn(1)–O(5)	2.035(4)	O(5)–Sn(1)–C(13)	109.3(3)	O(5)#1–Sn(2)–C(25)	107.7(3)
Sn(1)–C(13)	2.128(9)	O(5)–Sn(1)–C(17)	112.2(3)	O(5)#1–Sn(2)–C(21)	114.7(3)
Sn(1)–C(17)	2.148(11)	C(13)–Sn(1)–C(17)	138.3(4)	C(25)–Sn(2)–C(21)	136.6(4)
Sn(1)–O(1)	2.158(5)	O(5)–Sn(1)–O(1)	78.61(19)	O(5)#1–Sn(2)–O(5)	75.19(19)
Sn(1)–O(3)	2.261(6)	C(13)–Sn(1)–O(1)	99.9(3)	C(25)–Sn(2)–O(5)	100.8(3)
Sn(1)–O(2)	3.005(6)	C(17)–Sn(1)–O(1)	91.8(4)	C(21)–Sn(2)–O(5)	98.8(3)
Sn(2)–O(5)#1	2.039(5)	O(5)–Sn(1)–O(3)	89.6(2)	O(5)#1–Sn(2)–O(4)#1	89.7(2)
Sn(2)–C(25)	2.112(8)	C(13)–Sn(1)–O(3)	90.8(3)	C(25)–Sn(2)–O(4)#1	88.3(3)
Sn(2)–C(21)	2.144(9)	C(17)–Sn(1)–O(3)	85.9(4)	C(21)–Sn(2)–O(4)#1	82.9(3)
Sn(2)–O(5)	2.154(5)	O(1)–Sn(1)–O(3)	166.1(2)	O(5)–Sn(2)–O(4)#1	164.1(2)
Sn(2)–O(4)#1	2.323(5)	O(5)–Sn(1)–O(2)	125.55(18)	O(5)#1–Sn(2)–O(1)	139.70(18)
Sn(2)–O(1)	2.728(5)	C(13)–Sn(1)–O(2)	80.4(3)	C(25)–Sn(2)–O(1)	77.4(3)
		C(17)–Sn(1)–O(2)	78.8(4)	C(21)–Sn(2)–O(1)	76.7(3)
		O(1)–Sn(1)–O(2)	47.16(17)	O(5)–Sn(2)–O(1)	64.71(17)
		O(3)–Sn(1)–O(2)	144.78(18)	O(4)#1–Sn(2)–O(1)	130.62(19)
<i>Complex 3</i>					
Sn(1)–O(7)	2.026(4)	O(7)–Sn(1)–C(25)	111.1(2)	O(7)#1–Sn(2)–C(33)	112.3(3)
Sn(1)–C(25)	2.120(7)	O(7)–Sn(1)–C(29)	110.6(3)	O(7)#1–Sn(2)–C(37)	106.7(2)
Sn(1)–C(29)	2.130(8)	C(25)–Sn(1)–C(29)	137.3(3)	C(33)–Sn(2)–C(37)	140.6(4)
Sn(1)–O(4)	2.178(5)	O(7)–Sn(1)–O(4)	80.91(15)	O(7)#1–Sn(2)–O(7)	76.07(16)
Sn(1)–O(1)	2.252(5)	C(25)–Sn(1)–O(4)	95.9(3)	C(33)–Sn(2)–O(7)	97.2(3)
Sn(1)–O(5)	2.865(6)	C(29)–Sn(1)–O(4)	99.2(3)	C(37)–Sn(2)–O(7)	97.3(3)
Sn(2)–O(7)#1	2.054(4)	O(7)–Sn(1)–O(1)	90.42(15)	O(7)#1–Sn(2)–O(2)#1	891.02(18)
Sn(2)–C(33)	2.102(8)	C(25)–Sn(1)–O(1)	85.1(3)	C(33)–Sn(2)–O(2)#1	84.1(3)
Sn(2)–C(37)	2.106(7)	C(29)–Sn(1)–O(1)	85.9(3)	C(37)–Sn(2)–O(2)#1	89.9(3)
Sn(2)–O(7)	2.161(4)	O(4)–Sn(1)–O(1)	171.3(16)	O(7)–Sn(2)–O(2)#1	166.55(16)
Sn(2)–O(2)#1	2.296(7)	O(7)–Sn(1)–O(5)	130.21(17)	O(7)#1–Sn(2)–O(4)	140.82(14)
Sn(2)–O(4)	2.822(5)	C(25)–Sn(1)–O(5)	76.9(2)	C(33)–Sn(2)–O(4)	76.8(3)
		C(29)–Sn(1)–O(5)	83.3(3)	C(37)–Sn(2)–O(4)	76.8(2)
		O(4)–Sn(1)–O(5)	49.35(15)	O(7)–Sn(2)–O(4)	64.86(13)
		O(1)–Sn(1)–O(5)	139.14(16)	O(2)#1–Sn(2)–O(4)	128.16(15)
<i>Complex 4</i>					
Sn(1)–O(1)	2.010(4)	O(1)–Sn(1)–C(25)	111.9(3)	O(1)–Sn(2)–C(33)	106.1(2)
Sn(1)–C(25)	2.124(8)	O(1)–Sn(1)–C(29)	111.6(3)	O(1)–Sn(2)–C(37)	106.1(2)
Sn(1)–C(29)	2.161(11)	C(25)–Sn(1)–C(29)	136.6(4)	C(33)–Sn(2)–C(37)	146.7(3)
Sn(1)–O(5)	2.177(4)	O(1)–Sn(1)–O(5)	78.03(16)	O(1)–Sn(2)–O(1)#1	76.38(18)
Sn(1)–O(2)	2.215(5)	C(25)–Sn(1)–O(5)	94.5(3)	C(33)–Sn(2)–O(1)#1	98.1(2)
Sn(1)–O(6)	3.069(5)	C(29)–Sn(1)–O(5)	93.2(4)	C(37)–Sn(2)–O(1)#1	97.4(3)
Sn(2)–O(1)	2.066(4)	O(1)–Sn(1)–O(2)	91.80(18)	O(1)–Sn(2)–O(3)	88.55(17)
Sn(2)–C(33)	2.110(7)	C(25)–Sn(1)–O(2)	89.7(3)	C(33)–Sn(2)–O(3)	85.8(3)
Sn(2)–C(37)	2.115(8)	C(29)–Sn(1)–O(2)	90.1(4)	C(37)–Sn(2)–O(3)	86.8(3)
Sn(2)–O(1)#1	2.168(4)	O(5)–Sn(1)–O(2)	169.83(18)	O(1)#1–Sn(2)–O(3)	164.93(16)
Sn(2)–O(3)	2.294(5)	O(1)–Sn(1)–O(6)	124.53(15)	O(1)–Sn(2)–O(5)#1	142.43(16)
Sn(2)–O(5)#1	2.622(4)	C(25)–Sn(1)–O(6)	78.1(3)	C(33)–Sn(2)–O(5)#1	81.3(2)

Table 2 (continued)

Bond lengths	Bonds angles	Bonds angles	Bonds angles
C(29)–Sn(1)–O(6)	76.7(3)	C(37)–Sn(2)–O(5)#1	78.3(2)
O(5)–Sn(1)–O(6)	46.50(14)	O(1)#1–Sn(2)–O(5)#1	66.07(15)
O(2)–Sn(1)–O(6)	143.65(17)	O(3)–Sn(2)–O(5)#1	129.00(16)

coordination. The two crystallographically unique 2-pyrazinecarboxylic ligands coordinate in different ways. The ligand contains the O(1) and O(2) atoms bridging two tin atoms only via the O(1) atom, Sn(1)–O(1) 2.461(8) Å and Sn(2)–O(1A) 2.383(8) Å. Although the O(2A) oxygen is 3.659(4) Å from the Sn(2) atom, a distance is slightly less than the sum of the van der Waal's radii for Sn and O of 3.74 Å [17], it is not indicative of a significant bonding interaction. The C–O bond distance which associates with the oxygen atom bridging the two tin atoms of 1.315(13) Å is significantly longer than the other C–O bond distance of 1.211(14) Å that suggests a partial localization of π -electron density in the C(1)–O(2) bond, and it consists with the non-coordination of the O(2) atom to Sn(2A). The nitrogen atom from the 2-pyrazine ring of this ligand makes a close contact with Sn(1) at 2.952(10) Å, which is significantly less than the sum of the van der Waal's radii for Sn and N of 3.74 Å [17] and should be considered as a bonding interaction. The O(3) of the second ligand in $\{[{}^n\text{Bu}_2\text{Sn}(\text{O}_2\text{CN}_2\text{H}_3\text{C}_4)]_2\text{O}\}_2$ forms a strong bond to Sn(2), 2.151(9) Å, and is 2.828(4) Å from Sn(1). The O(4) atom does not make any significant contacts with the tin atoms. As for the first ligand, the C(6)–O(4) 1.196(14) Å bond is shorter than the C(6)–O(3) 1.283(14) Å. The weak Sn \cdots N interactions exist between the Sn atom and the adjacent nitrogen atom, thereby forming a chelate with a five-membered ring. Beside, co-crystallization is found in the crystals and the co-crystallized solvent is water with the molar ratio of $\{[{}^n\text{Bu}_2\text{Sn}(\text{O}_2\text{CN}_2\text{H}_3\text{C}_4)]_2\text{O}\}_2 \cdot \text{H}_2\text{O}$ is 1:1. The weak hydrogen bonds are formed between $\{[{}^n\text{Bu}_2\text{Sn}(\text{O}_2\text{CN}_2\text{H}_3\text{C}_4)]_2\text{O}\}_2$ and H_2O which help the construction of one dimension infinite chain.

The endocyclic tin atom, Sn(1), is five-coordinate to a first approximation and exists in a distorted trigonal bipyramidal environment, with the two *n*-butyl groups and the centrosymmetrically related bridging oxygen atom defining an approximate trigonal plane. The apical position is occupied by C(11) and C(15) atom from the ligand. The C(11)–Sn–C(15), is 150.9(7)°. If the weakly bonded N(1) atom is included in the coordination polyhedron, the geometry about the tin atom can be consisted as being distorted octahedron. The exocyclic tin atom, Sn(2), forms four short bonds, a longer bond to O(5) and a weak interaction. The geometry is highly distorted, the coordination sphere can be thought of as distorted octahedron, similar to Sn(1) atom.

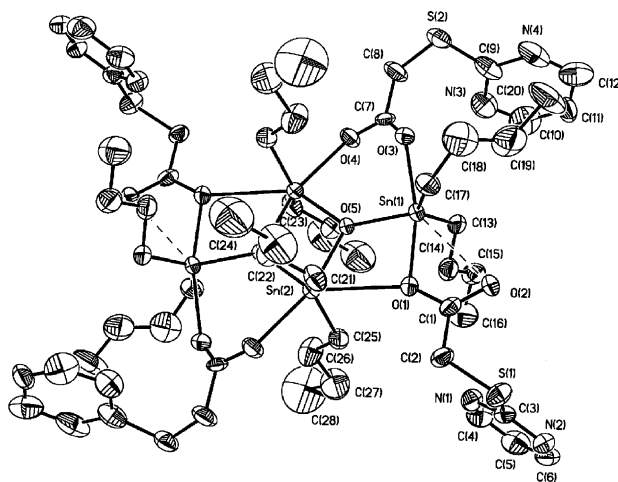


Fig. 2. Molecular structure of complex 2.

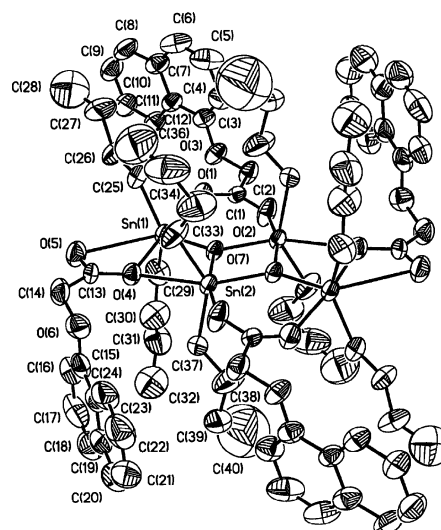


Fig. 3. Molecular structure of complex 3.

2.3.2. Crystal structures of $\{[{}^n\text{Bu}_2\text{Sn}(\text{O}_2\text{CCH}_2\text{SN}_2\text{H}_3\text{C}_4)]_2\text{O}\}_2$ (2), $\{[{}^n\text{Bu}_2\text{Sn}(\text{O}_2\text{CCH}_2\text{OH}_7\text{C}_{10})]_2\text{O}\}_2$ (3) and $\{[{}^n\text{Bu}_2\text{Sn}(\text{O}_2\text{CCH}_2\text{OH}_7\text{C}_{10})]_2\text{O}\}_2 \cdot \text{C}_6\text{H}_6$ (4)

The crystal structure of complexes 2, 3 and 4 are illustrated in Figs. 2–4, respectively, selected bond lengths and bond angles in Table 2. Significantly, there are no intramolecular interactions between the Sn and S or O atoms. The complexes are centrosymmetric dimer built up about the central cyclic Sn₂O₂ units. Two tin atoms are linked to this four-membered ring with two

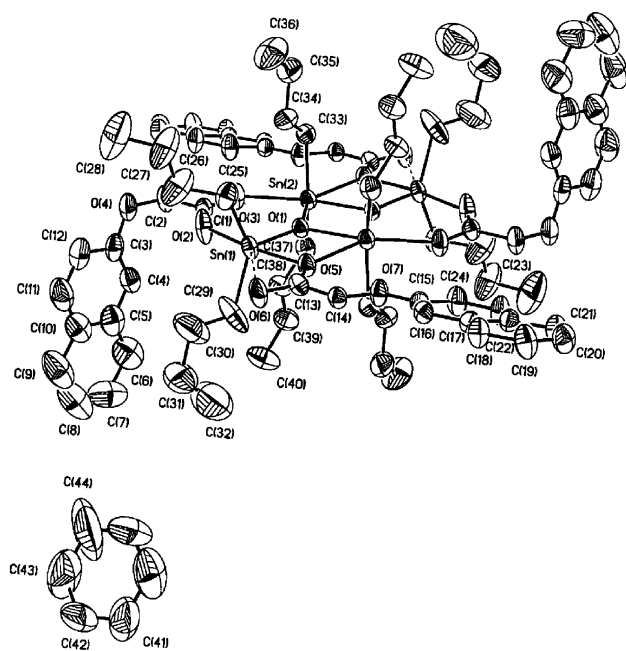


Fig. 4. Molecular structure of complex 4.

additional ${}^n\text{Bu}_2\text{Sn}(\text{O}_2\text{CR})$ units attach at each of the bridging oxygen atoms, with the result that the oxygen atoms of this ring are three-coordination. Although there are two types of tin atom, the geometry about two types is essentially identical. The weakly coordinating oxygen atom approaches the coordinating sphere of tin through one of the trigonal bipyramidal faces, making the coordination number of all tin atoms achieve six. The geometry of the tin atom is distorted octahedron.

For complex **2**, the Sn(2) atom is bonded to two carbon and to four oxygen atoms, the longest Sn–O bond is 2.728(5) Å, Sn(2)–O(1), while the others are between 2.332(5) and 2.039(5) Å. Two of the carboxylates ligands are bidentate and bridge a pair of tin atoms and the two other carboxylates are monodentate and coordinate each exocyclic tin atom. The coordination geometry of the tin atom Sn(2) is a distorted octahedron. C(21) and C(25) atoms occupy the apical sites and C(21)–Sn(2)–C(25), is 136.6(4)°. Sn(2), O(1), O(5), O(5A) and O(4A) are almost coplanar with the tin atom deviating from the best plane by 0.0206 Å. The sum of angles between the tin atom and the equatorial atoms is 360.22°. Compared to the ideal octahedral value of 360°, this further testifies the atoms in the same plane. The coordination sphere of Sn(1) consists of two carbon and three oxygen atoms, with Sn(1)–O bond lengths of 2.035(4)–3.261(6) Å. There are, in addition, an intramolecular weak interaction, Sn(1)–O(2), 3.005(5) Å, which derives from the monodentate carboxylate group. Interestingly, the directionality of this weak interaction involving the exocyclic tin atom Sn almost mimics that of the endocyclic tin. The angles in the central Sn₂O₂ ring are 75.19(19)° and 104.81(19)°.

For complex **3** and **4**, similar to the complex **2**, the Sn(2) atoms are bonded to two carbon and to four oxygen atoms, the longest Sn–O bonds are 2.822(5) Å, Sn(2)–O(4) and 2.622(4) Å, Sn(2)–O(5), respectively. Two of the carboxylates ligands are bidentate and bridge a pair of tin atoms and the two other carboxylates are monodentate and coordinate each exocyclic tin atom. The coordination geometry of the tin atom Sn(2) are a distorted octahedron. The coordination sphere of Sn(1) consists of two carbon, three oxygen atoms and an intramolecular weak interaction which derives from the monodentate carboxylate group. The directionality of this weak interaction involving the exocyclic tin atom Sn almost mimics that of the endocyclic tin. The angles in the central Sn₂O₂ ring are 76.07(16)° and 103.93(16)° for complex **3**, 76.38(18)° and 103.62(18)° for complex **4**. Specially, for complex **4**, co-crystallization is found in the crystals and the co-crystallized solvent is benzene with the molar ratio of $\{[{}^n\text{Bu}_2\text{Sn}(\text{O}_2\text{CCH}_2\text{OH}_7\text{C}_{10})_2\text{O}_2]_2 \cdot \text{C}_6\text{H}_6\}$ is 1:1.

2.3.3. Crystal structure of ${}^n\text{Bu}_2\text{Sn}(\text{O}_2\text{CN}_2\text{H}_3\text{C}_4)_2(\text{H}_2\text{O})$ (**5**)

The crystal structure of complex **5** is shown in Fig. 5, selected bond lengths and bond angles in Table 3. Complex **5** contains a seven-coordinated tin atom and has a pentagonal bipyramidal environment with C(6) and C(6A) atoms occupying the axial sites and the axial–Sn–axial, C(6)–Sn–C(6A) is 171.6(2)°. The tin atom lies on a crystallographic twofold structure. Sn(1), O(1), O(1A), N(1) and N(1A) are completely coplanar with the tin atom existing in the plane. The sum of angles between the tin atom and the equatorial atoms is 360°, consistent with the ideal value of 360°. In the structure, two carbons atoms and two nitrogen atoms of 2-pyrazinecarboxylic acid and the oxygen atom of water are covalently linked to the tin. The Sn–N bond length (Sn(1)–N(1) and Sn(1)–N(1)#1, 2.553(4) Å) is longer than those in ${}^n\text{Bu}_2\text{Sn}(\text{OOC}_5\text{H}_4\text{N}-2)_2(\text{H}_2\text{O})$ (2.2522(6)

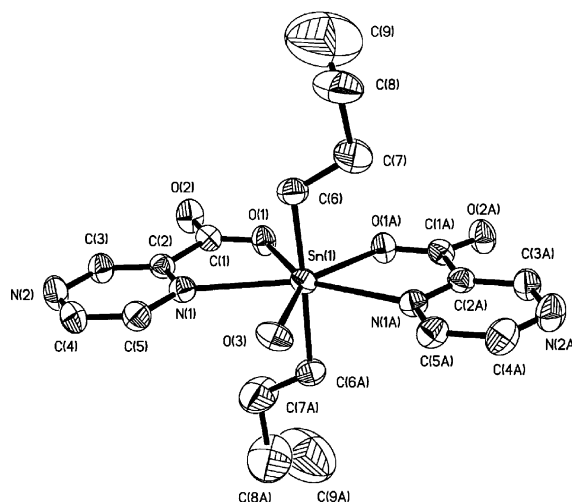


Fig. 5. Molecular structure of complex 5.

Table 3
Selected bond lengths (Å) and angles (°) for complexes **5** and **8**

Bond lengths		Bonds angles		Bonds angles	
<i>Complex 5</i>					
Sn(1)–C(6)	2.121(4)	C(6)–Sn(1)–C(6)#1	171.6(2)	C(6)#1–Sn(1)–N(1)#1	87.31(13)
Sn(1)–C(6)#1	2.121(4)	C(6)–Sn(1)–O(1)#1	94.71(13)	O(1)#1–Sn(1)–N(1)#1	68.04(10)
Sn(1)–O(1)#1	2.232(3)	C(6)#1–Sn(1)–O(1)#1	92.01(13)	O(1)–Sn(1)–N(1)#1	142.72(9)
Sn(1)–O(1)	2.232(3)	C(6)–Sn(1)–O(1)	92.00(13)	O(3)–Sn(1)–N(1)#1	74.62(7)
Sn(1)–O(3)	2.384(4)	O(1)#1–Sn(1)–O(1)	74.68(14)	C(6)–Sn(1)–N(1)	87.31(13)
Sn(1)–N(1)#1	2.553(4)	C(6)–Sn(1)–O(3)	85.78(11)	C(6)#1–Sn(1)–N(1)	90.45(13)
Sn(1)–N(1)	2.553(4)	C(6)#1–Sn(1)–O(3)	85.78(11)	O(1)#1–Sn(1)–N(1)	142.72(9)
		O(1)#1–Sn(1)–O(3)	142.66(7)	O(1)–Sn(1)–N(1)	68.04(10)
		O(1)–Sn(1)–O(3)	142.66(7)	O(3)–Sn(1)–N(1)	74.62(7)
		C(6)–Sn(1)–N(1)#1	90.45(13)	N(1)#1–Sn(1)–N(1)	149.24(14)
<i>Complex 8</i>					
Sn(1)–C(29)	2.057(15)	C(29)–Sn(1)–O(1)	100.6(8)	O(5)–Sn(1)–C(13)	26.9(5)
Sn(1)–O(1)	2.103(16)	C(29)–Sn(1)–C(25)	137.4(3)	O(4)–Sn(1)–O(5)	53.3(5)
Sn(1)–C(25)	2.144(9)	O(1)–Sn(1)–C(25)	111.6(7)	O(2)–Sn(1)–O(5)	172.48(17)
Sn(1)–O(4)	2.152(14)	C(29)–Sn(1)–O(4)	110.1(7)	O(4)–Sn(1)–O(2)	134.2(5)
Sn(1)–O(2)	2.519(15)	O(1)–Sn(1)–O(4)	79.3(2)	C(29)–Sn(1)–O(5)	87.1(6)
Sn(1)–O(5)	2.581(15)	C(25)–Sn(1)–O(4)	102.7(6)	C(25)–Sn(1)–C(13)	96.4(5)
Sn(1)–C(13)	2.667(12)	C(29)–Sn(1)–O(2)	89.1(6)	O(1)–Sn(1)–O(5)	131.3(5)
		O(1)–Sn(1)–O(2)	55.9(5)	C(25)–Sn(1)–O(5)	91.6(5)
		C(25)–Sn(1)–O(2)	86.9(6)	O(4)–Sn(1)–C(13)	26.6(6)

Å) [18] but much shorter than the sum of the van der Waals radii of Sn and N, 3.74 Å [17], and Sn–O(3) 2.383(4) Å also approaches the sum of the covalent radii of Sn and O (2.13 Å) [17]. The valence extension is possibly preformed via the two nitrogen atoms and the oxygen atom of water. The intermolecular interactions exist between the water and two adjacent molecules and result in hydrogen bonds O(3)–H···O(2) (1.775 Å). Through these, a three-dimensional hydrogen bonded network is formed.

2.3.4. Crystal structure of $n\text{Bu}_2\text{Sn}(\text{O}_2\text{CCH}_2\text{OH}_7\text{C}_{10})_2$ (**8**)

The crystal structure of complex **8** is shown in Fig. 6, selected bond lengths and bond angles in Table 3. From Fig. 6, we find that the Sn atom exists in a skew-trapezoidal planar geometry. The four O atoms, which derive from two chelating carboxylate ligands, define the basal plane. The $n\text{Bu}–\text{Sn}–n\text{Bu}$ angle of $137.4(3)^\circ$ lies in the range of C–Sn–C angles of $122.6^\circ–156.9^\circ$ found for diorganotin chelates in which the organo substituents do not adopt *cis*- or *trans*-geometries about the tin atom [19]. The carboxylate ligands chelate the Sn center with

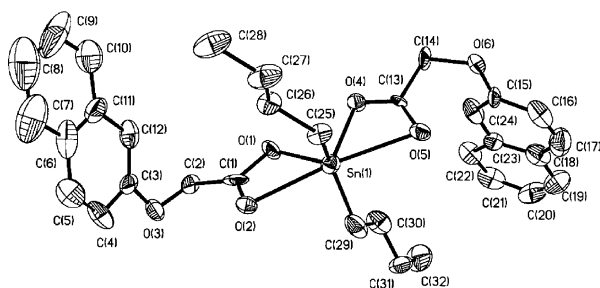


Fig. 6. Molecular structure of complex **8**.

asymmetric Sn–O bond distances and this asymmetry is reflected in the associated with the shorter Sn–O bonds. The degree of asymmetry in the Sn–O bond distances is not equal with the difference between Sn–O bond distance for the two carboxylate ligands being 0.416 and 0.429 Å, respectively. The anisobidentate mode of coordination of the carboxylate group is also reflected in the disparity of the associated carbon–oxygen bonds. Although the Sn(1)–O(2) 2.519(15) Å and Sn(1)–O(5) 2.581(15) Å bond lengths is longer than the sum of the covalent radii of the tin and oxygen 2.13 Å, it is nevertheless significantly below the sum of the van der Waal's radii of these atoms, 3.68 Å [17].

Besides, intermolecular non-bonded Sn···O interactions are recognized in the crystallographic analysis of complex **8**. The Sn···O bond length (3.624 Å) is longer than that reported in [Et₂Sn(O₂CC₄H₃S)] (2.891 Å), but similar to that of Ph₂Sn(O₂CCH₂Cl)₂ (3.552 Å) [20,21]. Due to the very weak intermolecular interaction, one chain is constructed. However, there is no evidence that the presence or absence of the additional intermolecular Sn···O interactions have any other great effect on the molecular geometry of complex **8**.

2.4. Conclusion

In summary, we conclude that the difference of coordination mode was derived from the residing position of the heteroatoms. For nitrogen donors in **1** and **5**, they exist in the ring systems that would orient to make easy coordination to tin. However, the ligands including S or O are linear types that are not ease to make coordination to tin.

3. Experimental

3.1. Materials and measurements

Di-*n*-butyltin oxide, 2-pyrazinecarboxylic acid, (2-pyrimidylthio)acetic acid, 1-naphthoxyacetic acid and 2-naphthoxyacetic acid are commercially available, and they are used without further purification. The melting points were obtained with Kofler micro-melting point apparatus and were uncorrected. Infrared-spectra were recorded on a Nicolle-460 spectrophotometer using KBr discs and sodium chloride optics. ^1H and ^{13}C NMR spectra were recorded on a Bruker AMX-300 spectrometer operating at 300 and 75.3 MHz, respectively. The spectra were acquired at room temperature (298 K) unless otherwise specified; ^{13}C spectra are broadband proton decoupled. The chemical shifts were reported in ppm with respect to the references and were stated relative to external tetramethylsilane (TMS) for ^1H and ^{13}C NMR. Elemental analyses were performed with a PE-2400II apparatus.

3.2. Synthesis

3.2.1. Synthesis of $\{[{}^n\text{Bu}_2\text{Sn}(\text{O}_2\text{CN}_2\text{H}_3\text{C}_4)]_2\text{O}\}_2 \cdot \text{H}_2\text{O}$ (**1**)

The reaction is carried out under nitrogen atmosphere. The di-*n*-butyltin oxide (0.496 g, 2 mmol) and the 2-pyrazinecarboxylic acid (0.248, 2 mmol) are added to the solution of dry benzene (30 ml) in a Schlenk flash. The mixture gives a clear solution within 10–15 min. Refluxing was continued for 10 h, the solvent is gradually removed by evaporation under vacuum until solid product is obtained. The solid is then recrystallized from ethyl ether and the white crystal is obtained. Buff crystal complex **1** is formed. Yield: 81%. m.p. 106–108 °C. Anal. Found: C, 42.18; H, 6.00; N, 7.69. Calc. for $\text{C}_{52}\text{H}_{86}\text{N}_8\text{O}_{11}\text{Sn}_4$: C, 42.37; H, 5.88; N, 7.60%. IR (KBr, cm^{-1}): $\nu_{\text{as}}(\text{COO})$, 1667; $\nu_{\text{s}}(\text{COO})$, 1377; $\nu(\text{Sn}-\text{C})$, 576; $\nu(\text{Sn}-\text{O})$, 476; $\nu(\text{Sn}-\text{O}-\text{Sn})$, 621, $\nu(\text{Sn}-\text{N})$, 445. ^1H NMR (CDCl_3 , ppm): δ 0.80(t, CH_3), 1.34–1.67(m, $\text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2$). ^{13}C NMR (CDCl_3 , ppm): δ 26.6 (αCH_2 , $^1J(^{119}\text{Sn}-^{13}\text{C})$, 615 Hz), 27.2 (αCH_2 , $^1J(^{119}\text{Sn}-^{13}\text{C})$, 750 Hz), 26.3 (βCH_2), 26.5 (βCH_2), 25.6 (γCH_2), 25.5 (γCH_2), 12.8 (CH_3), 13.3 (CH_3), 174.2 (COO).

3.2.2. Synthesis of $\{[{}^n\text{Bu}_2\text{Sn}(\text{O}_2\text{CCH}_2\text{SN}_2\text{H}_3\text{C}_4)]_2\text{O}\}_2$ (**2**)

The complex **2** is prepared in the same way as that of complex **1**, by adding di-*n*-butyltin oxide (0.496 g, 2 mmol) to (2-pyrimidylthio)acetic acid (0.340, 2 mmol). The solid is then recrystallized from ethyl ether and the light-yellow crystal is obtained. Buff crystal complex **2** is formed. Yield: 78%; m.p. 86–88 °C. Anal. Found: C, 40.96; H, 5.62; N, 6.64. Calc. for $\text{C}_{56}\text{H}_{92}\text{N}_8\text{O}_{10}\text{S}_4\text{Sn}_4$: C,

41.00; H, 5.65; N, 6.83%. IR (KBr, cm^{-1}): $\nu_{\text{as}}(\text{COO})$, 1653; $\nu_{\text{s}}(\text{COO})$, 1384; $\nu(\text{Sn}-\text{C})$, 558; $\nu(\text{Sn}-\text{O})$, 492; $\nu(\text{Sn}-\text{O}-\text{Sn})$, 640. ^1H NMR (CDCl_3 , ppm): δ 0.82(t, CH_3), 1.30–1.77(m, $\text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2$), 3.62 (s, $-\text{CH}_2\text{S}-$). ^{13}C NMR (CDCl_3 , ppm): δ 27.5 (αCH_2 , $^1J(^{119}\text{Sn}-^{13}\text{C})$, 622 Hz), 26.8 (βCH_2), 26.3 (γCH_2), 13.6 (CH_3), 175.1 (COO).

3.2.3. Synthesis of $\{[{}^n\text{Bu}_2\text{Sn}(\text{O}_2\text{CCH}_2\text{OH}_7\text{C}_{10})]_2\text{O}\}_2$ (**3**)

The complex **3** is prepared in the same way as that of complex **1**, by adding di-*n*-butyltin oxide (0.496 g, 2 mmol) to 1-naphthoxyacetic acid (0.404, 2 mmol). The solid is then recrystallized from ethyl ether and the purple crystal is obtained. Buff crystal complex **3** is formed. Yield: 70%; m.p. 110–112 °C. Anal. Found: C, 54.23; H, 5.97. Calc. for $\text{C}_{80}\text{H}_{106}\text{O}_{14}\text{Sn}_4$: C, 54.40; H, 6.05%. IR (KBr, cm^{-1}): $\nu_{\text{as}}(\text{COO})$, 1632; $\nu_{\text{s}}(\text{COO})$, 1376; $\nu(\text{Sn}-\text{C})$, 572; $\nu(\text{Sn}-\text{O})$, 474; $\nu(\text{Sn}-\text{O}-\text{Sn})$, 622. ^1H NMR (CDCl_3 , ppm): δ 0.88(t, CH_3), 1.35–1.80(m, $\text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2$), 4.41 (s, $-\text{CH}_2\text{O}-$). ^{13}C NMR (CDCl_3 , ppm): δ 26.8 (αCH_2 , $^1J(^{119}\text{Sn}-^{13}\text{C})$, 637 Hz), 26.5 (βCH_2), 26.3 (γCH_2), 13.5 (CH_3), 166.8 (COO).

3.2.4. Synthesis of $\{[{}^n\text{Bu}_2\text{Sn}(\text{O}_2\text{CCH}_2\text{OH}_7\text{C}_{10})]_2\text{O}\}_2 \cdot \text{C}_6\text{H}_6$ (**4**)

The complex **4** is prepared in the same way as that of complex **1**, by adding di-*n*-butyltin oxide (0.496 g, 2 mmol) to 2-naphthoxyacetic acid (0.404, 2 mmol). The solid is then recrystallized from ethyl ether and the purple crystal is obtained. Buff crystal complex **4** is formed. Yield: 85%; m.p. 108–110 °C. Anal. Found: C, 56.35; H, 6.05. Calc. for $\text{C}_{88}\text{H}_{114}\text{O}_{14}\text{Sn}_4$: C, 56.51; H, 6.14%. IR (KBr, cm^{-1}): $\nu_{\text{as}}(\text{COO})$, 1631; $\nu_{\text{s}}(\text{COO})$, 1381; $\nu(\text{Sn}-\text{C})$, 532; $\nu(\text{Sn}-\text{O})$, 483; $\nu(\text{Sn}-\text{O}-\text{Sn})$, 637. ^1H NMR (CDCl_3 , ppm): δ 0.87(t, CH_3), 1.37–1.79(m, $\text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2$), 4.50 (s, $-\text{CH}_2\text{O}-$). ^{13}C NMR (CDCl_3 , ppm): δ 26.9 (αCH_2 , $^1J(^{119}\text{Sn}-^{13}\text{C})$, 631 Hz), 27.3 (αCH_2 , $^1J(^{119}\text{Sn}-^{13}\text{C})$, 710 Hz), 26.5 (βCH_2), 26.7 (βCH_2), 25.3 (γCH_2), 25.1 (γCH_2), 13.5 (CH_3), 13.6 (CH_3), 170.1 (COO).

3.2.5. Synthesis of ${}^n\text{Bu}_2\text{Sn}(\text{O}_2\text{CN}_2\text{H}_3\text{C}_4)_2(\text{H}_2\text{O})$ (**5**)

The complex **5** is prepared in the same way as that of complex **1**, by adding di-*n*-butyltin oxide (0.496 g, 2 mmol) to 2-pyrazinecarboxylic acid (0.596, 4 mmol). The solid is then recrystallized from ethyl ether and the white crystal is obtained. Buff crystal complex **5** is formed. Yield: 86%; m.p. 186–188 °C. Anal. Found: C, 43.32; H, 5.11; N, 11.33. Calc. for $\text{C}_{18}\text{H}_{26}\text{N}_4\text{O}_5\text{Sn}$: C, 43.49; H, 5.27; N, 11.27%. IR (KBr, cm^{-1}): $\nu_{\text{as}}(\text{COO})$, 1640; $\nu_{\text{s}}(\text{COO})$, 1342; $\nu(\text{Sn}-\text{C})$, 536; $\nu(\text{Sn}-\text{O})$, 485; $\nu(\text{Sn}-\text{N})$, 461. ^1H NMR (CDCl_3 , ppm): δ 0.82(t, CH_3), 1.27–1.70(m, $\text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2$). ^{13}C NMR (CDCl_3 , ppm): δ 27.0 (αCH_2 , $^1J(^{119}\text{Sn}-^{13}\text{C})$, 891 Hz), 26.5 (βCH_2), 25.8 (γCH_2), 13.4 (CH_3), 174.5 (COO).

3.2.6. Synthesis of ${}^n\text{Bu}_2\text{Sn}(\text{O}_2\text{CCH}_2\text{SN}_2\text{H}_3\text{C}_4)_2$ (**6**)

The complex **6** is prepared in the same way as that of complex **1**, by adding di-*n*-butyltin oxide (0.496 g, 2 mmol) to (2-pyrimidylthio)acetic acid (0.680, 4 mmol). The solid is then recrystallized from ethyl ether and the light-yellow crystal is obtained. Buff crystal complex **6** is formed. Yield: 80%; m.p. 120–122 °C. Anal. Found: C, 41.85; H, 5.12; N, 9.67. Calc. for $\text{C}_{20}\text{H}_{28}\text{N}_4\text{O}_4\text{S}_2\text{Sn}$: C, 42.05; H, 4.94; N, 9.81%. IR (KBr, cm^{-1}): $\nu_{\text{as}}(\text{COO})$, 1656; $\nu_{\text{s}}(\text{COO})$, 1367; $\nu(\text{Sn}-\text{C})$, 542; $\nu(\text{Sn}-\text{O})$, 482. ${}^1\text{H}$ NMR (CDCl_3 , ppm): δ 0.81(t, CH_3), 1.43–1.80(m, $\text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2$), 3.61 (s, $-\text{CH}_2\text{S}-$). ${}^{13}\text{C}$ NMR (CDCl_3 , ppm): δ 27.7 (αCH_2 , ${}^1J(^{119}\text{Sn}-{}^{13}\text{C})$, 595 Hz), 26.7 (βCH_2), 26.1 (γCH_2), 13.5 (CH_3), 176.0 (COO).

3.2.7. Synthesis of ${}^n\text{Bu}_2\text{Sn}(\text{O}_2\text{CCH}_2\text{OH}_7\text{C}_{10})_2$ (**7**)

The complex **7** is prepared in the same way as that of complex **1**, by adding di-*n*-butyltin oxide (0.496 g, 2 mmol) to 1-naphthoxyacetic acid (0.816, 4 mmol). The solid is then recrystallized from ethyl ether and the purple crystal is obtained. Buff crystal complex **7** is formed. Yield: 90%; m.p. 127–129 °C. Anal. Found: C, 60.37; H, 5.57. Calc. for $\text{C}_{32}\text{H}_{36}\text{O}_6\text{Sn}$: C, 60.50; H, 5.71%. IR (KBr, cm^{-1}): $\nu_{\text{as}}(\text{COO})$, 1643; $\nu_{\text{s}}(\text{COO})$, 1359; $\nu(\text{Sn}-\text{C})$, 551; $\nu(\text{Sn}-\text{O})$, 490. ${}^1\text{H}$ NMR (CDCl_3 , ppm): δ 0.91(t, CH_3), 1.41–1.77(m, $\text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2$), 4.49 (s, $-\text{CH}_2\text{O}-$). ${}^{13}\text{C}$ NMR (CDCl_3 , ppm): δ 27.1 (αCH_2 , ${}^1J(^{119}\text{Sn}-{}^{13}\text{C})$, 611 Hz), 26.5 (βCH_2), 26.3 (γCH_2), 13.6 (CH_3), 172.1 (COO).

3.2.8. Synthesis of ${}^n\text{Bu}_2\text{Sn}(\text{O}_2\text{CCH}_2\text{OH}_7\text{C}_{10})_2$ (**8**)

The complex **8** is prepared in the same way as that of complex **1**, by adding di-*n*-butyltin oxide (0.496 g, 2 mmol) to 2-naphthoxyacetic acid (0.816, 4 mmol). The solid is then recrystallized from ethyl ether and the purple crystal is obtained. Buff crystal complex **8** is formed. Yield: 81%; m.p. 134–136 °C. Anal. Found: C, 60.49; H, 5.65. Calc. for $\text{C}_{32}\text{H}_{36}\text{O}_6\text{Sn}$: C, 60.50; H, 5.71%. IR (KBr, cm^{-1}): $\nu_{\text{as}}(\text{COO})$, 1630; $\nu_{\text{s}}(\text{COO})$, 1388; $\nu(\text{Sn}-\text{C})$, 542; $\nu(\text{Sn}-\text{O})$, 483. ${}^1\text{H}$ NMR (CDCl_3 , ppm): δ 0.89(t, CH_3), 1.39–1.83(m, $\text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2$), 4.53 (s, $-\text{CH}_2\text{O}-$). ${}^{13}\text{C}$ NMR (CDCl_3 , ppm): δ 27.9 (αCH_2 , ${}^1J(^{119}\text{Sn}-{}^{13}\text{C})$, 609 Hz), 26.6 (βCH_2), 26.2 (γCH_2), 13.6 (CH_3), 172.0 (COO).

4. Supplementary material

Crystallographic data (excluding structure factors) for the structure analysis of complexes **1–5** and **8** have been deposited with the Cambridge Crystallographic Data Center, CCDC Nos. 220167 (**1**), 221136 (**2**), 222377 (**3**), 220521 (**4**), 220168 (**5**) and 221138 (**8**). Copies of these information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033;

e-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>).

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