

Note

Structural chemistry of mononuclear, tetranuclear and hexanuclear organotin(IV) carboxylates from the reaction of di-*n*-butyltin oxide or diphenyltin oxide with rhodanine-*N*-acetic acid

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Abstract

Three new organotin(IV) carboxylates, $\{[n\text{-Bu}_2\text{Sn}(\text{O}_2\text{CC}_4\text{H}_4\text{NOS}_2)_2]_2\text{O}\}_2$ (**1**), $n\text{-Bu}_2\text{Sn}(\text{O}_2\text{CC}_4\text{H}_4\text{NOS}_2)_2$ (**2**) and $[\text{PhSn}(\text{O})\text{O}_2\text{CC}_4\text{H}_4\text{NOS}_2]_6 \cdot 3\text{H}_2\text{O}$ (**3**) were synthesized by the reaction of di-*n*-butyltin/diphenyltin oxide and rhodanine-*N*-acetic acid. The complexes **1–3** are characterized by elemental, IR, ¹H, ¹³C and ¹¹⁹Sn NMR and X-ray crystallography diffraction analyses. The complex **1** has a tetranuclear structure based on a planar four-membered Sn₂O₂ ring, while complex **2** is a hexa-coordinated monomer. As for complex **3**, it adopts the hexameric drum-shaped structure. The supramolecular structure of **1** has been found to consist of one-dimensional molecular chain built up by intermolecular non-bonded S···O interactions. The salient feature of the supramolecular structure of complex **2** is that of a one-dimensional polymer, in which intermolecular Sn···O, S···O and S···S interactions are recognized.

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1. Introduction

Organotin(IV) compounds have attracted much attention owing to their potential biocidal activities [1–3] as well as their industrial and agricultural applications [4,5]. In general, the biochemical activity of organotin compounds is influenced greatly by the structure of the molecule and the coordination number of the tin atoms [3–5]. Recently, we have investigated organotin compounds containing carboxylate ligands which have an additional hetero-donor atom (e.g. N, O or S) residing on the R' group, that is, potentially tridentate ligands, in order to examine what effect the presence of the heteroatom has on the structure adopted by these com-

pounds [6,7]. As a part of our continuing program in this area we have synthesized and structurally characterized organotin(IV) carboxylates of rhodanine-*N*-acetic acid, and the results of this study are reported herein.

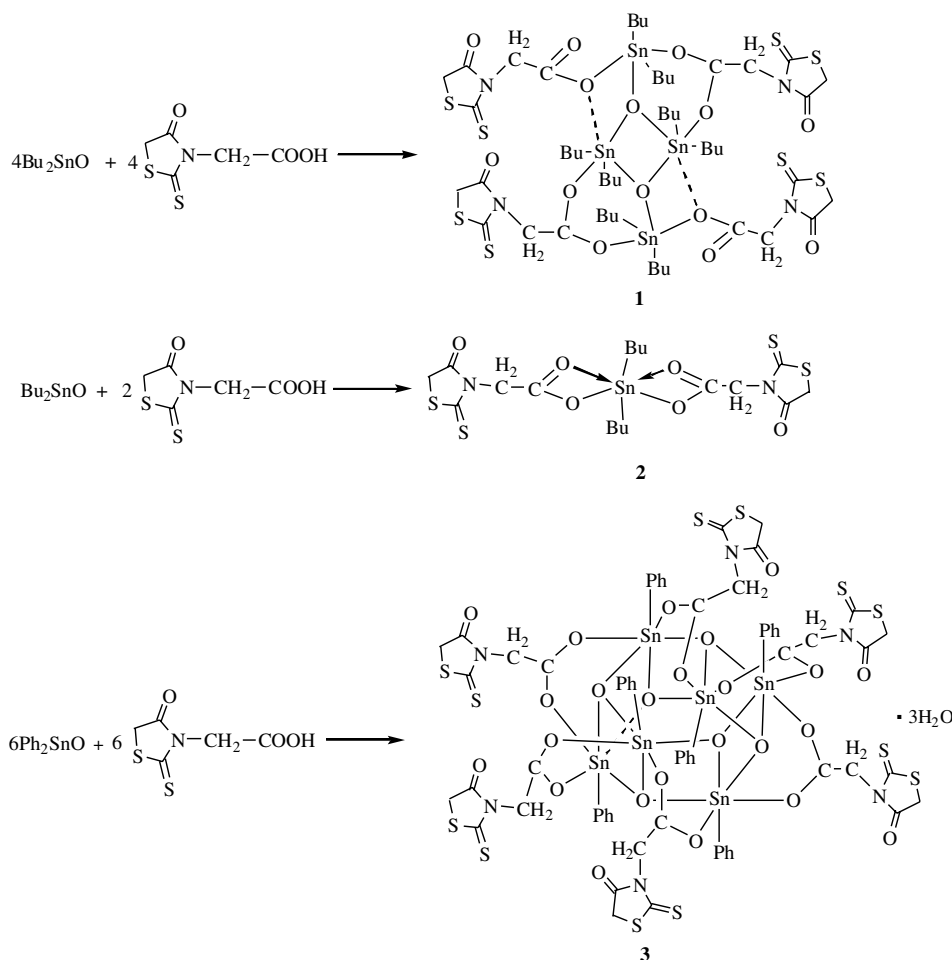
2. Results and discussion

2.1. Synthesis

Di-*n*-butyltin oxide react with rhodanine-*N*-acetic acid in 1:1 and 1:2 molar ratios to form $\{[n\text{-Bu}_2\text{Sn}(\text{O}_2\text{CC}_4\text{H}_4\text{NOS}_2)_2]_2\text{O}\}_2$ (**1**) and $n\text{-Bu}_2\text{Sn}(\text{O}_2\text{CC}_4\text{H}_4\text{NOS}_2)_2$ (**2**), respectively. Complex $[\text{PhSn}(\text{O})\text{O}_2\text{CC}_4\text{H}_4\text{NOS}_2]_6 \cdot 3\text{H}_2\text{O}$ (**3**) is however produced through the dearylation reaction of diphenyltin oxide and rhodanine-*N*-acetic acid in 1:1 molar ratio. The synthesis procedures are shown in Scheme 1.

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Scheme 1.

2.2. IR spectra

The stretching frequencies of interest are those associated with C=O, C=S, COO, Sn–O and Sn–O–Sn groups. The deprotonation of the carboxylic acid is evident from the disappearance of a broad band owing to the COOH group in the region 3200–2800 cm^{-1} of the ligand. In the spectrum of rhodanine-*N*-acetic acid the stretching modes of imido C=O and C=S are observed at 1740 and 1190 cm^{-1} , respectively, which shift little after complexation indicating the non-participation of the imido C=O and C=S groups in significant coordination to Sn. The $\Delta\nu$ values (where $\Delta\nu = \nu(\text{COO})_{\text{as}} - \nu(\text{COO})_{\text{s}}$) in the spectra of the complexes are lower than the value for the rhodanine-*N*-acetic acid ($\Delta\nu$ 350 cm^{-1}) and are comparable to that observed in the sodium salt of the ligand (200 cm^{-1}). These observations suggest the presence of bidentate carboxylate ligands [8]. A band in the 500–400 cm^{-1} region is assigned to the stretching frequency associated with the Sn–O bond. A strong band in the 640–620 cm^{-1} region for the complexes 1 and 3 is assigned to $\nu(\text{Sn–O–Sn})$, indicating a Sn–O–Sn bridged structure.

2.3. NMR spectra

The ^1H NMR spectra show the expected integration and peak multiplicities. In the spectrum of the free ligand a single resonance is observed at 9.25 ppm which is absent in the spectra of the complexes 1–3, indicating the replacement of the carboxylic acid proton by an alkyltin moiety on complex formation. Signals for the other groups appear at the same position as in the ligand. The ^{13}C NMR spectral pattern are consistent with the formulation of the complexes 1–3. ^{119}Sn NMR chemical shift values may be used to give tentative indications of the environment around tin atoms. Holeček et al. [9] have suggested δ values from +200 to –60 for four-coordinated, –90 to –190 for five-coordinated and –210 to –400 ppm for six-coordinated tin atoms in solution. The ^{119}Sn NMR spectrum of complex 1 exhibits two signals at δ –205.3 and –210.8 ppm, suggesting there are either five- or six-coordinate tin atoms in the distannoxane. For complex 2, the ^{119}Sn NMR data (–141.6 ppm) is consistent with those reported for the diorganotin dicarboxylates (–105 to –155 ppm) [10,11]. As for complex 3, the ^{119}Sn NMR spectrum

shows a single resonance at $\delta -505.9$ ppm, indicating the presence of only one type of tin atom. So it can reasonably be assumed that the structures in solution of complexes **1–3** are likely similar to those observed in the solid state.

2.4. Description of crystal structures

2.4.1. $\{n\text{-Bu}_2\text{Sn}(\text{O}_2\text{CC}_4\text{H}_9\text{NOS}_2)_2\text{O}\}_2$ (**1**)

The molecular structure of complex **1** is shown in Fig. 1. Selected bond distances and angles are listed in Table 1. As is the case for other known carboxystannoxanes, the complex is a tetranuclear centrosymmetric dimer with a central Sn_2O_2 four-membered ring. The four tin atoms are linked by two bridging carboxyl groups while the remaining two act as monodentate ligands to the exocyclic tin atoms. Consideration of the axial angles $\text{O}(2)\text{--Sn}(1)\text{--O}(5)$ ($168.1(3)^\circ$) and $\text{O}(1)\#1\text{--Sn}(2)\text{--O}(3)$ ($166.1(3)^\circ$) and the $\text{Sn}\text{--O}$ distances lead to the conclusion that the two tin atoms are in different environments. Both tin atoms are coordinated by two *n*-Butyl moieties which form $\text{C}\text{--Sn}\text{--C}$ angles of $133.7(6)^\circ$ and $141.8(7)^\circ$, respectively. In the case of the exocyclic $\text{Sn}(1)$ atom, coordination is completed by $\text{O}(1)$, $\text{O}(2)$ and $\text{O}(5)$ with distances of 2.019(6), 2.241(7) and 2.147(8) Å, respectively. For the endocyclic $\text{Sn}(2)$ atom, the $\text{O}(1)$, $\text{O}(1)\#1$ and $\text{O}(3)$ atoms all coordinate at distances of 2.040(6), 2.183(6) and 2.324(9) Å, and there is a longer but significant interaction of 2.764(6) Å to $\text{O}(5)\#1$. In the case of $\text{Sn}(1)$, $\text{O}(3)$ is 3.655 Å from the tin atom. However, $\text{O}(6)$ is appreciably closer at 3.085(7) Å, but it appears that the interaction is very weak. Thus it may be concluded that the exocyclic tin atom $\text{Sn}(1)$ is best described as five-coordinate, and the endocyclic $\text{Sn}(2)$ as pseudo-six-coordinate.

Furthermore, intermolecular non-bonded $\text{S}\cdots\text{O}$ weak interactions were recognized in the crystallographic analysis of **1**, which help the construction of

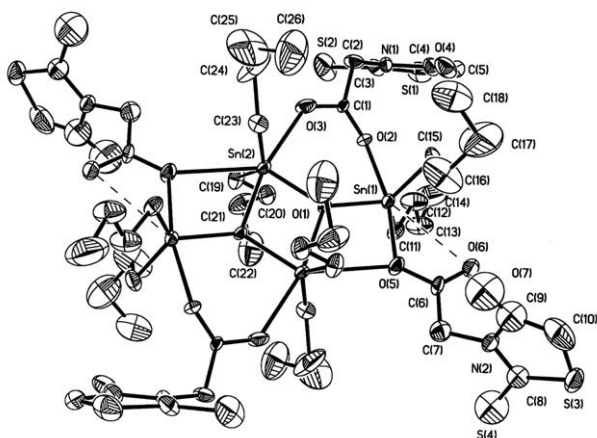


Fig. 1. Molecular structure of complex **1**.

Table 1

Selected bond lengths (Å) and bond angles ($^\circ$) for complex **1**

| | |
|--------------------|-----------|
| Sn(1)–O(1) | 2.019(6) |
| Sn(1)–C(11) | 2.117(13) |
| Sn(1)–C(15) | 2.131(17) |
| Sn(1)–O(5) | 2.147(8) |
| Sn(1)–O(2) | 2.241(7) |
| Sn(2)–O(1) | 2.040(6) |
| Sn(2)–C(23) | 2.068(19) |
| Sn(2)–C(19) | 2.128(13) |
| Sn(2)–O(1)#1 | 2.183(6) |
| Sn(2)–O(3) | 2.324(9) |
| O(2)–C(1) | 1.195(11) |
| O(3)–C(1) | 1.365(13) |
| O(4)–C(4) | 1.07(2) |
| O(5)–C(6) | 1.284(13) |
| O(6)–C(6) | 1.223(13) |
| O(7)–C(9) | 1.202(10) |
| S(1)–C(3) | 1.739(13) |
| S(1)–C(5) | 1.780(16) |
| S(2)–C(3) | 1.698(13) |
| S(3)–C(8) | 1.735(15) |
| S(3)–C(10) | 1.809(18) |
| S(4)–C(8) | 1.716(15) |
| O(1)–Sn(1)–C(11) | 117.1(5) |
| O(1)–Sn(1)–C(15) | 109.0(5) |
| C(11)–Sn(1)–C(15) | 133.7(6) |
| O(1)–Sn(1)–O(5) | 79.8(3) |
| C(11)–Sn(1)–O(5) | 94.4(5) |
| C(15)–Sn(1)–O(5) | 97.9(5) |
| O(1)–Sn(1)–O(2) | 89.2(3) |
| C(11)–Sn(1)–O(2) | 86.5(4) |
| C(15)–Sn(1)–O(2) | 90.0(5) |
| O(5)–Sn(1)–O(2) | 168.1(3) |
| O(1)–Sn(2)–C(23) | 109.3(6) |
| O(1)–Sn(2)–C(19) | 108.0(5) |
| C(23)–Sn(2)–C(19) | 141.8(7) |
| O(1)–Sn(2)–O(1)#1 | 76.8(3) |
| C(23)–Sn(2)–O(1)#1 | 96.1(6) |
| C(19)–Sn(2)–O(1)#1 | 99.8(5) |
| O(1)–Sn(2)–O(3) | 90.1(3) |
| C(23)–Sn(2)–O(3) | 83.6(6) |
| C(19)–Sn(2)–O(3) | 88.6(6) |
| O(1)#1–Sn(2)–O(3) | 166.1(3) |

the one-dimensional chain (Fig. 2). The non-bonded $\text{S}\cdots\text{O}$ distances (3.344 Å) are longer than that reported in the literature [12], similar to the sum of the van der Waals radii (S and O) (3.25 Å) [13].

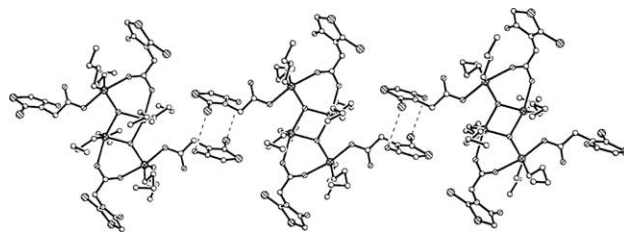


Fig. 2. Perspective view showing the one-dimensional chain of complex **1**.

2.4.2. *n*-Bu₂Sn(O₂CC₄H₄NOS₂)₂ (**2**)

The molecular structure of complex **2** is shown in Fig. 3. Selected bond distances and angles are listed in Table 2. The crystal structure is seen to be comprised of discrete molecules of **2** with the tin atom hexa-coordinated. The C–Sn–C angle of 150.3(2)° lies in the range of C–Sn–C angles of 122.6–156.9° found for diorganotin chelates in which the organo substituents do not adopt *cis*- or *trans*-geometries about the tin atom [14]. The carboxylate groups coordinate in asymmetric mode forming both short bonds (Sn(1)–O(1) 2.117(4) and Sn(1)–O(4) 2.143(4) Å) and long bonds (Sn(1)–O(2) 2.673(4) and Sn(1)–O(5) 2.445(4) Å). The anisobidentate mode of coordination of the two carboxylate structures is re-

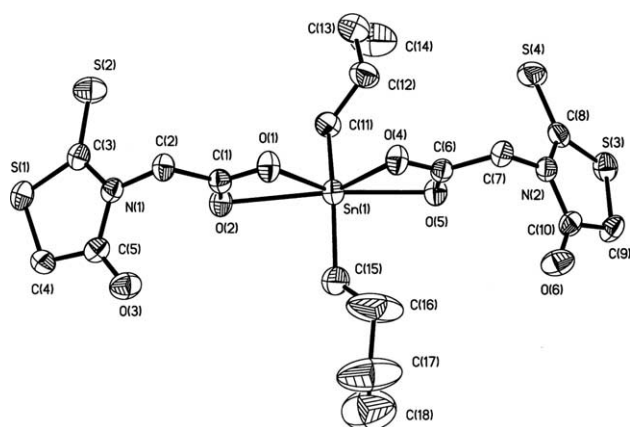


Fig. 3. Molecular structure of complex **2**.

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

| | |
|-------------------|------------|
| Sn(1)–C(15) | 2.095(6) |
| Sn(1)–C(16) | 2.106(5) |
| Sn(1)–O(1) | 2.117(4) |
| Sn(1)–O(4) | 2.143(4) |
| Sn(1)–O(2) | 2.673(4) |
| Sn(1)–O(5) | 2.445(4) |
| C(1)–O(1) | 1.287(5) |
| C(1)–O(2) | 1.215(5) |
| C(6)–O(4) | 1.279(5) |
| C(6)–O(5) | 1.225(5) |
| C(15)–Sn(1)–C(16) | 150.3(2) |
| C(15)–Sn(1)–O(1) | 100.4(2) |
| C(16)–Sn(1)–O(1) | 99.38(18) |
| C(15)–Sn(1)–O(4) | 102.21(19) |
| C(16)–Sn(1)–O(4) | 101.34(19) |
| O(1)–Sn(1)–O(4) | 85.24(13) |
| C(15)–Sn(1)–O(5) | 89.77(19) |
| C(16)–Sn(1)–O(5) | 88.36(17) |
| O(1)–Sn(1)–O(5) | 141.59(13) |
| O(4)–Sn(1)–O(5) | 56.36(11) |
| C(15)–Sn(1)–C(6) | 96.66(19) |
| C(16)–Sn(1)–C(6) | 95.29(19) |
| O(1)–Sn(1)–C(6) | 114.00(16) |
| O(4)–Sn(1)–C(6) | 28.77(13) |
| O(5)–Sn(1)–C(6) | 27.59(11) |

flected in the disparity of the associated C–O bonds: the C–O bond distances for the weakly coordinating oxygen atoms of 1.215(5) and 1.225(5) Å is shorter than the C–O bond distances associated with the strongly bound oxygen atoms of 1.287(5) and 1.279(5) Å. Nevertheless, the longer Sn–O bond distances are significantly below the sum of the van der Waals radii for these atoms (3.68 Å [15]), and therefore these oxygen atoms must be considered as bonding. The geometry found about the tin atom in **2** is best described as a skew-trapezoidal bipyramid geometry and closely resembles those found for the structures of *n*-Bu₂Sn(O₂CCH₂SC₆H₅)₂ [16], *n*-Bu₂Sn[O₂CC₅H₃N(SMe-2)]₂ [17] and *n*-Bu₂Sn[O₂CC₆H₃(OH)₂-2,4]₂ [8].

The most interesting aspect of the structure concerns the intermolecular weak Sn···O interactions and non-bonded S···S and S···O interactions, which help the construction of the dimer (Fig. 4). The two weak Sn···O bond lengths are equal, 2.927(4) Å, which is less than the sum of the van der Waals radii (3.58 Å [15]). The non-bonded S···O distances (3.288 Å) are similar to that revealed in complex **1**. As for the non-bonded S···S interactions, the value (3.588 Å) is longer than those reported in the literatures [18,19] but is shorter than the sum of the van der Waals radii (S and S) (3.70 Å) [13]. Moreover, the dimers are connected to a one-dimensional polymer (Fig. 5) through non-bonded S···S interactions (3.400 Å).

2.4.3. [PhSn(O)O₂CC₄H₄NOS₂]₆ · 3H₂O (**3**)

The complex **3** is hexameric and adopts the drum-shaped structure. The sides are constructed from Sn₂O₂ stannoxane rings and faces from Sn₃O₃ planes. An S₆ axis passes through the center of the faces of the molecule. For each hexamer in the unit cell there are three water molecules of solvation. The molecule structure is shown in Fig. 6 and selected bond lengths and bond angles are listed in Table 3.

The six tin atoms are chemically equivalent, as are the six trivalent oxygen atoms. The Sn–O framework of the molecule can be described as a drum with top and bottom faces each being comprised of a six-membered Sn₃O₃ tristanoxane ring. The drum faces are joined

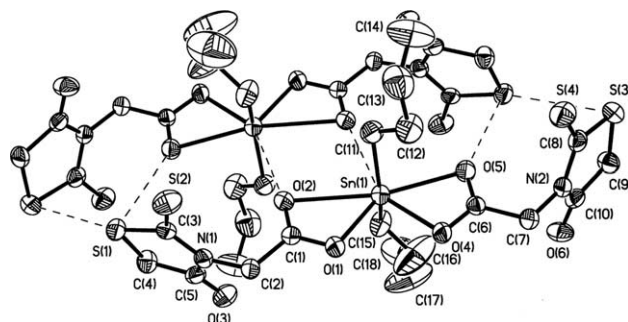


Fig. 4. The dimeric structure of complex **2**.

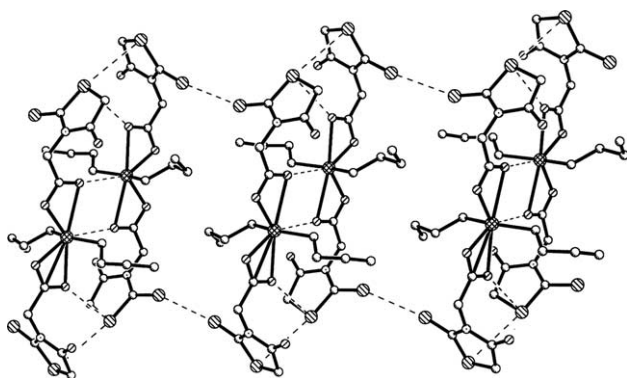


Fig. 5. Perspective view showing the one-dimensional polymer of complex 2.

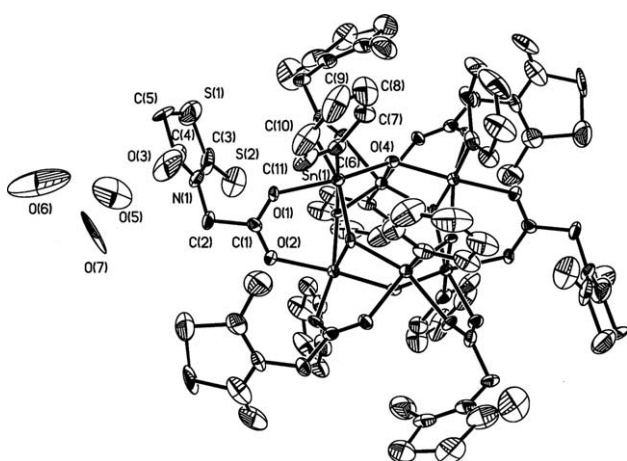


Fig. 6. Molecular structure of complex 3.

together by six Sn–O bonds containing tricoordinated oxygen atoms. 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 tin atoms. Concomitant with the equivalence of the Sn–O bonds to a particular carboxylate group is the corresponding equivalence of the pairs of C–O carboxylate bond lengths. The hexamer provides the first example of tin atoms symmetrically bridged by a carboxylate group.

The distannoxane ring units of the sides of the drum are not planar but are folded along the Sn–Sn vectors so that the oxygen atoms are directed toward the interior of the cavity. Similarly, the tristannoxane ring faces of the drum are not planar but have the oxygen atoms 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 oxygen atoms, in a trigonal-antiprismatic arrangement, and the entrance to the cavity is defined by three oxygen atoms arranged as an approximate equilateral triangle.

The coordination geometry about each Sn atom is completed by a C atom of the phenyl group which

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

| | |
|----------------------|-----------|
| Sn(1)–O(4) | 2.073(6) |
| Sn(1)–O(4)#1 | 2.088(7) |
| Sn(1)–O(4)#2 | 2.094(7) |
| Sn(1)–C(6) | 2.108(10) |
| Sn(1)–O(1) | 2.145(7) |
| Sn(1)–O(2)#3 | 2.151(7) |
| O(1)–C(1) | 1.264(11) |
| O(2)–C(1) | 1.254(11) |
| O(2)–Sn(1)#1 | 2.151(7) |
| O(4)–Sn(1)#3 | 2.088(7) |
| O(4)–Sn(1)#4 | 2.094(6) |
| O(4)–Sn(1)–O(4)#1 | 78.3(2) |
| O(4)–Sn(1)–O(4)#2 | 104.5(3) |
| O(4)#1–Sn(1)–O(4)#2 | 77.8(2) |
| O(4)–Sn(1)–C(6) | 105.0(3) |
| O(4)#1–Sn(1)–C(6) | 176.0(3) |
| O(4)#2–Sn(1)–C(6) | 99.0(3) |
| O(4)–Sn(1)–O(1) | 157.3(2) |
| O(4)#1–Sn(1)–O(1) | 86.0(2) |
| O(4)#2–Sn(1)–O(1) | 87.9(2) |
| C(6)–Sn(1)–O(1) | 91.4(4) |
| O(4)–Sn(1)–O(2)#3 | 85.5(2) |
| O(4)#1–Sn(1)–O(2)#3 | 89.3(2) |
| O(4)#2–Sn(1)–O(2)#3 | 161.6(2) |
| C(6)–Sn(1)–O(2)#3 | 93.2(3) |
| O(1)–Sn(1)–O(2)#3 | 77.9(3) |
| C(1)–O(1)–Sn(1) | 129.6(6) |
| C(1)–O(2)–Sn(1)#1 | 129.0(6) |
| Sn(1)–O(4)–Sn(1)#3 | 100.5(2) |
| Sn(1)–O(4)–Sn(1)#4 | 132.4(3) |
| Sn(1)#3–O(4)–Sn(1)#4 | 99.8(2) |

occupies a position *trans* to a framework O atom. Thus each Sn atom is coordinated by three framework O atoms, two carboxylate O atoms and a C atom such that the O_5C donor set defines a distorted octahedron.

3. Experimental details

3.1. Materials and measurements

Di-*n*-butyltin oxide, diphenyltin oxide and rhodamine-*N*-acetic acid were purchased from Aldrich. Analytical grade solvents were dried before use. The melting points were obtained with Kofler micro-melting point apparatus and are uncorrected. Infrared-spectra were recorded on a Nicolet-460 spectrophotometer using KBr discs and sodium chloride optics. ^1H , ^{13}C and ^{119}Sn NMR spectra were recorded on a Varian Mercury Plus 400 spectrometer operating at 400, 101 and 186.50 MHz, respectively. The TMS was used as internal standard and Me_4Sn was used as external standards. The chemical shifts were given in ppm in CDCl_3 solvent. Elemental analyses were performed with a PE-2400II apparatus.

3.2. Synthesis of complex $\{[n\text{-Bu}_2\text{Sn}(\text{O}_2\text{CC}_4\text{H}_4\text{NO}\text{-}\text{S}_2)]_2\text{O}\}_2$ (**1**)

A mixture of rhodanine-*N*-acetic acid (0.382 g, 2.00 mmol) and di-*n*-butyltin oxide (0.498 g, 2.00 mmol) in toluene (40 ml) is refluxed for 10 h using a Dean-Stark trap. After cooling to room temperature, the solvent mixture is removed under vacuum until solid product is obtained. The solid is then recrystallized from ether-petroleum and the buff crystal is obtained. m.p. 170–172 °C. Yields, 0.716 g (0.415 mmol, 83% yield). *Anal.* Calcl. for $\text{C}_{52}\text{H}_{88}\text{N}_4\text{O}_{14}\text{S}_8\text{Sn}_4$: C, 36.21; H, 5.14; N, 3.25. Found: C, 36.42; H, 5.40; N, 3.18%. IR (KBr, cm^{-1}): $\nu(\text{C}=\text{O})$ 1744s; $\nu(\text{COO})_{\text{as}}$ 1668s, 1603s; $\nu(\text{COO})_{\text{s}}$ 1463s, 1398s; $\nu(\text{C}=\text{S})$ 1190s; $\nu(\text{Sn}-\text{O}-\text{Sn})$ 636m, $\nu(\text{Sn}-\text{O})$ 484m. ^1H NMR (CDCl_3 , ppm): δ 4.88 (s, 8H, N-CH₂), 4.26 (s, 8H, ring-CH₂), 1.84–1.25 (m, 24H, Sn(CH₂)₃), 0.94 (t, 12H, CH₃). ^{13}C NMR (CDCl_3 , ppm): δ 194.5 (C=S), 177.5 (COO), 167.5 (C=O), 45.3 (N-CH₂), 39.6 (ring-CH₂), 29.4/28.5 (αCH_2 , $^1J(^{119}\text{Sn}-^{13}\text{C})$ 658 Hz, nv), 26.2/26.8 (βCH_2 , $^2J(^{119}\text{Sn}-^{13}\text{C})$ 45, 43 Hz), 27.3/26.1 (γCH_2 , $^3J(^{119}\text{Sn}-^{13}\text{C})$ 130, 128 Hz), 13.5/13.2 (CH₃). ^{119}Sn NMR (CDCl_3 , ppm): δ -205.3, -210.8.

3.3. Synthesis of complex $n\text{-Bu}_2\text{Sn}(\text{O}_2\text{CC}_4\text{H}_4\text{NOS}_2)_2$ (**2**)

A mixture of rhodanine-*N*-acetic acid (0.764 g, 4.00 mmol) and di-*n*-butyltin oxide (0.498 g, 2.00 mmol) in toluene (40 ml) is refluxed for 10 h using a Dean-Stark trap. After cooling to room temperature, the solvent

mixture is removed under vacuum until solid product is obtained. The solid is then recrystallized from ether-petroleum and the buff crystal is obtained. M.p. 164–166 °C. Yields, 0.957 g (1.56 mmol, 78% yield). *Anal.* Calc. for $\text{C}_{18}\text{H}_{26}\text{N}_2\text{O}_6\text{S}_4\text{Sn}$: C, 35.25; H, 4.27; N, 4.57. Found: C, 35.01; H, 4.44; N, 4.27%. IR (KBr, cm^{-1}): $\nu(\text{C}=\text{O})$ 1738s; $\nu(\text{COO})_{\text{as}}$ 1602s; $\nu(\text{COO})_{\text{s}}$ 1401s; $\nu(\text{C}=\text{S})$ 1187s; $\nu(\text{Sn}-\text{O})$ 481w. ^1H NMR (CDCl_3 , ppm): δ 4.83 (s, 4H, N-CH₂), 4.32 (s, 4H, ring-CH₂), 1.88–1.30 (m, 12H, Sn(CH₂)₃), 0.91 (t, 6H, CH₃). ^{13}C NMR (CDCl_3 , ppm): δ 194.6 (C=S), 176.2 (COO), 167.8 (C=O), 45.2 (N-CH₂), 39.7 (ring-CH₂), 26.6 (αCH_2 , $^1J(^{119}\text{Sn}-^{13}\text{C})$ 591 Hz), 26.4 (βCH_2 , $^2J(^{119}\text{Sn}-^{13}\text{C})$ 40 Hz), 26.5 (γCH_2 , $^3J(^{119}\text{Sn}-^{13}\text{C})$ 113 Hz), 13.4 (CH₃). ^{119}Sn NMR (CDCl_3 , ppm): δ -141.6.

3.4. Synthesis of complex $[\text{PhSn}(\text{O})\text{O}_2\text{CC}_4\text{H}_4\text{NOS}_2]_6 \cdot 3\text{H}_2\text{O}$ (**3**)

A mixture of rhodanine-*N*-acetic acid (0.382 g, 2.00 mmol) and diphenyltin oxide (0.578 g, 2.00 mmol) in toluene (40 ml) is refluxed for 10 h using a Dean-Stark trap. After cooling to room temperature, the solvent mixture is removed under vacuum until solid product is obtained. The solid is then recrystallized from ether-petroleum and the buff crystal is obtained. M.p. >220 °C. Yields, 0.617 g (0.250 mmol, 75% yield). *Anal.* Calcl. for $\text{C}_{66}\text{H}_{60}\text{N}_6\text{O}_{27}\text{S}_{12}\text{Sn}_6$: C, 32.14; H, 2.45; N, 3.41. Found: C, 31.89; H, 2.35; N, 3.29%. IR (KBr, cm^{-1}): $\nu(\text{C}=\text{O})$ 1742s; $\nu(\text{COO})_{\text{as}}$ 1627s, 1580s; $\nu(\text{COO})_{\text{s}}$ 1434s, 1359s; $\nu(\text{C}=\text{S})$ 1188s; $\nu(\text{Sn}-\text{O}-\text{Sn})$ 624m, $\nu(\text{Sn}-\text{O})$ 435m. ^1H NMR (CDCl_3 , ppm): δ 7.53–7.29 (m, 30H,

Table 4
Crystal data and structure refinement parameters for complexes **1**, **2** and **3**

| Complexes | 1 | 2 | 3 |
|--|--|---|---|
| Empirical formula | $\text{C}_{52}\text{H}_{88}\text{N}_4\text{O}_{14}\text{S}_8\text{Sn}_4$ | $\text{C}_{18}\text{H}_{26}\text{N}_2\text{O}_6\text{S}_4\text{Sn}$ | $\text{C}_{66}\text{H}_{60}\text{N}_6\text{O}_{27}\text{S}_{12}\text{Sn}_6$ |
| Formula weight | 1724.50 | 613.34 | 2466.26 |
| Crystal system | Orthorhombic | Triclinic | Rhombohedral |
| Space group | <i>Pbca</i> | <i>P</i> $\bar{1}$ | <i>R</i> $\bar{3}$ |
| <i>Unit cell dimensions</i> | | | |
| <i>a</i> (Å) | 14.507(8) | 9.732(13) | 24.48(3) |
| <i>b</i> (Å) | 22.265(12) | 10.176(13) | 24.48(3) |
| <i>c</i> (Å) | 23.135(13) | 13.242(18) | 15.23(3) |
| α (°) | 90 | 76.861(19) | 90 |
| β (°) | 90 | 82.961(19) | 90 |
| γ (°) | 90 | 81.09(2) | 120 |
| <i>V</i> (Å ³) | 7473(7) | 1256(3) | 7906(22) |
| <i>Z</i> | 4 | 2 | 3 |
| <i>D_c</i> (mg m ⁻³) | 1.533 | 1.621 | 1.652 |
| Absorption coefficient (mm ⁻¹) | 1.600 | 1.384 | 1.713 |
| <i>F</i> (000) | 3472 | 620 | 3870 |
| Crystal size (mm) | 0.53 × 0.42 × 0.27 | 0.27 × 0.13 × 0.10 | 0.35 × 0.34 × 0.25 |
| θ range (°) | 1.76–25.03 | 1.59–25.03 | 1.65–25.03 |
| Reflections collected | 32,708 | 6467 | 11,715 |
| Independent reflections | 5909 [<i>R</i> _{int} = 0.0797] | 4369 [<i>R</i> _{int} = 0.0283] | 2767 [<i>R</i> _{int} = 0.2467] |
| Data/restraints/parameters | 5909/161/350 | 4369/10/280 | 2767/10/214 |
| Goodness-of-fit on <i>F</i> ² | 1.010 | 0.999 | 0.968 |
| Final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)] | <i>R</i> ₁ = 0.0662, <i>wR</i> ₂ = 0.1494 | <i>R</i> ₁ = 0.0414, <i>wR</i> ₂ = 0.0850 | <i>R</i> ₁ = 0.0556, <i>wR</i> ₂ = 0.0973 |
| <i>R</i> indices (all data) | <i>R</i> ₁ = 0.1619, <i>wR</i> ₂ = 0.2082 | <i>R</i> ₁ = 0.0640, <i>wR</i> ₂ = 0.0921 | <i>R</i> ₁ = 0.1379, <i>wR</i> ₂ = 0.1333 |

Sn(C₆H₅), 4.88 (s, 12H, N-CH₂), 4.26 (s, 12H, ring-CH₂), ¹³C NMR (CDCl₃, ppm): δ 194.8 (C=S), 177.3 (COO), 165.7 (C=O), 139.2 (C_i, ¹J¹⁹Sn-¹³C) 1187 Hz), 137.6 (C_p), 129.5 (C_m), 127.3 (C_o), 44.9 (N-CH₂), 40.1 (ring-CH₂). ¹¹⁹Sn NMR (CDCl₃, ppm): δ -505.9.

3.5. X-ray structures determination

All X-ray crystallographic data were collected on a Bruker SMART CCD 1000 diffractometer with graphite monochromated Mo K α radiation ($\lambda = 0.71073$ Å) at 298 K. A semi-empirical 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. The positions of hydrogen atoms were calculated, and their contributions in structural factor calculations were included. Crystal data and experimental details of the structure determinations are listed in Table 4.

4. Supplementary material

Crystallographic data (excluding structure factors) for the structures reported in this paper (**1**, **2** and **3**) have been deposited with the Cambridge Crystallographic Data Center as supplementary publication nos. CCDC-233180, 227956, 233179. Copies of the data can be obtained free of charge on application to the Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk or <http://www.ccdc.cam.ac.uk>).

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