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Synthesis, spectroscopic studies and X-ray crystal structures of triorganotin(IV) derivatives containing 3,5-dinitrobenzoate, *N*-methylanthranilate and dicyclohexylacetate ligands

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The synthesis and spectroscopic characterization (infrared, ^{1}H, ^{13}C, ^{119}Sn NMR and ^{119}Sn Mössbauer) of three organotin derivatives incorporating carboxylate ligands, with general formulae $(C_6H_{11})_2CHCOOSnPh_3$ (1), $(CH_3NH)C_6H_4COOSnPh_3$ (2) and 3,5-$(NO_2)_2C_6H_4CO_2SnMe_3$ (3) are reported together with their X-ray crystal structures. The compounds were obtained by the condensation, in ethanol, of the appropriate carboxylic acid with triphenyltin hydroxyde (1, 2) or trimethyltin hydroxide (3). In the case of triphenyltin(IV) derivatives, 1 and 2, the values of the Mössbauer quadrupole splitting and the infrared data [$\Delta\nu = (\nu_{as}(O{-}C{=}O) - \nu_s(O{-}C{=}O)) > 230\ cm^{-1}$] are consistent with the presence of monomeric species in the solid state. X-ray crystallographic analysis confirms their structures as consisting of monomeric species, featuring distorted tetrahedral environments around the tin atoms. In both structures, one CSnC angle is relatively opened compared with the two others, which may be linked to the relatively close approach of the non-bonding oxygen of the carboxylate ligand to the tin center (Sn(1)–O(2) = 2.659(1) Å and 2.773(1) Å in 1 and 2 respectively). NMR data show the presence of monomeric species in solution, as found in the solid state. A significant intramolecular hydrogen bond is noticed between the hydrogen atom of the *N*-methylanthranilate ion and the non-coordinating oxygen atom in 2 (H(1A)–O(2) = 2.06 Å, N(1)–H(1A)–O(2) = 132°). Infrared and Mössbauer spectroscopy and X-ray diffraction have shown that 3 has an infinite chain structure in which the central tin atom adopts a distorted trigonal bipyramidal coordination with two oxygen atoms in axial positions, the three carbon atoms of the methyl group occupying equatorial sites. The 3,5-dinitrobenzoate anions act as bidentate bridging ligands and the SnC_3 moieties are asymmetrically trans-coordinated (Sn–O(1) and Sn–O(2): 2.181(1) and 2.501(2)). ^{13}C and ^{119}Sn NMR data reveal a cleavage of the infinite chain structure of 3 in solution; the ^{119}Sn chemical shift value (124.0 ppm), in conjunction with the magnitude of the coupling constant [$^2J(^{119}Sn{-}C{-}H) = 58.8$ Hz; $^1J(^{119}Sn{-}C) = 393.6$Hz], is consistent with a tetrahedral environment around the tin center.

KEYWORDS: infrared; Mössbauer; NMR; X-ray; trimethyltin; triphenyltin derivatives; carboxylate ligands

INTRODUCTION

For triorganotin carboxylates, it is reasonable to assume that compounds of empirical formula [$R_3Sn(O_2CR')$] (R = alkyl or aryl; R′ = alkyl or aryl) may adopt one of the four basic motifs, as defined by Willem *et al.*[1] Organotin carboxylates are widely studied, and most of them contain *trans*-O_2SnC_3

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moieties in a polymeric arrangement in the crystalline state. However, sterically demanding groups and electron-rich and chelating ligands apparently favor a monomeric structure. It has also been demonstrated that the electronegativity of the R′ groups plays an important role in the coordination mode of the carboxylate anion.[1–3] In the scope of our research work on organotin derivatives we have an interest in isolating triorganotin derivatives containing a tetrahedral tin center owing to their biological activities and their possibility to facilitate the synthesis of new adducts, when reacting with Lewis bases. Organotin carboxylates exhibit a variety of biocidal activities depending on their structure; the structure–activity relationship suggests that triorganotin derivatives, including those with tetrahedral tin centers or *trans*-O_2SnC_3 moieties, are characterized by a greater biocidal activity than those containing *cis*-O_2SnC_3.[4–6] These derivatives are cytotoxic.[7–9] We have synthesized triphenyltin *N*-methylanthranilate, triphenyltin dicyclohexylacetate and trimethyltin 3,5-dinitrobenzoate derivatives in order to study their structural behavior. In this paper we describe, in addition to the crystallographic studies, the synthetic procedures for the isolation of the compounds and their spectroscopic (infrared, Mössbauer and NMR) properties.

EXPERIMENTAL

Materials and methods

$SnMe_3Cl$, KOH, Ph_3SnOH and the acids $(C_6H_{11})_2CHCOOH$, $CH_3NHC_6H_4COOH$ and 3,5-$(NO_2)_2C_6H_4CO_2H$ were purchased from Aldrich Chemicals and used without further purification. $SnMe_3OH$ is obtained by reacting $SnMe_3Cl$ with KOH in methanol and filtering the precipitate of KCl.

Spectroscopic characterization

Details of the infrared and Mössbauer spectrophotometers used and data collection procedures are reported elsewhere.[10,11] NMR spectra for **1**, **2** and **3** were recorded as saturated $CDCl_3$ solutions at room temperature, using a Bruker 300 MHz spectrometer. The ^{1}H, ^{13}C and ^{119}Sn NMR were measured at 300.13 MHz, 75.47 MHz and 111.92 MHz respectively. ^{1}H and ^{13}C NMR chemical shifts and $\delta(^{119}Sn)$ NMR are given in parts per million and are referred respectively to tetramethylsilane and $SnMe_4$, all set to 0.00 ppm; the coupling constants are given in hertz. Elemental analyses of **1**, **2** and **3** were performed using an Exeter Analytical CE 440 analyzer. Infrared data are given in wavenumbers. Abbreviations: vs = very strong, s = strong, m = medium, w = weak. Mössbauer parameters are given in millimeters per second; QS: quadrupole splitting; IS: isomer shift; Γ: (full width at half-height FWHH).

Synthesis of 1–3

Each compound was obtained by the condensation, in ethanol, of the appropriate carboxylic acid with triphenyltin hydroxyde (**1**, **2**) or trimethyltin hydroxide (**3**) in a 1 : 1 ratio. The mixtures were stirred for several hours at room temperature and a slow solvent evaporation gave crystals suitable for X-ray analysis. Colorless crystals were obtained in the case of **1** (yield 72%; m.p. 73 °C) and **2** (yield 68%; m.p. 98 °C), whereas in the case of **3** yellow crystals are obtained (yield 67%, m.p. 148 °C).

$(C_6H_{11})_2CHCOOSnPh_3$ (**1**). Elemental analysis [Found (%) (calc. (%) for $C_{32}H_{38}O_2Sn$)]: C, 67.20 (66.96); H, 4.62 (4.53). Infrared (cm^{-1}): 1619 s $\nu_{as}CO_2$, 1396 s ν_sCO_2; 820 m, 802 m δCO_2; 562 m νSnO; 269 vs $\nu_{as}SnC_3$; 238 vs $\delta_{as}SnC_3$; 218 m ν_sSnC_3. Mössbauer ($mm\,s^{-1}$): IS = 1.45, QS = 2.45, $\Gamma = 0.87$. NMR [$CDCl_3$; δ (ppm); ^nJ (Hz)]: ^{1}H NMR: $\delta(C_6H_{11} + CH)$: [2.2–0, m, 23H]; δ(phenyl proton): [7.8–7.2, m, 15H]. ^{13}C NMR: 36.6 CHCOO, δ(carbon atoms of the cyclohexyl rings): 31.4 (CH–C), 29.8 (C_β), 26.7 (C_γ), 26.5 (C_δ). δ(carbon of the phenyl): 139.0 [C_i, $^1J(^{119}Sn{-}^{13}C) = 567.4$], 137.1 [$C_o$, $^2J(^{119}Sn{-}^{13}C) = 48.2$], 130.1 ($C_p$), 128.9 [$C_m$, $^3J(^{119}Sn{-}^{13}C) = 62.76$], 159.9 (CO). ^{119}Sn NMR: $\delta(^{119}Sn) = -120.0$.

$(CH_3NH)C_6H_4COOSnPh_3$ (**2**). Elemental analysis [Found (%) (calc. (%) for $C_{10}H_{12}N_2O_6Sn$)]: C, 62.86 (62.37); H, 4.52 (4.59); N, 2.90 (2.79). Infrared (cm^{-1}) 1622 s $\nu_{as}CO_2$; 1431 s ν_sCO_2; 860 s, 802 s δCO_2; 558 w νSnO; 269 s $\nu_{as}SnC_3$; 238 s $\delta_{as}SnC_3$; 217 s ν_sSnC_3. Mössbauer ($mm\,s^{-1}$): IS = 1.52, QS = 2.52, $\Gamma = 0.91$. NMR [$CDCl_3$; δ (ppm); ^nJ (Hz)]: $\delta(CH_3)$ [2.8 s, 3H]: $\delta(NH)$ [6.5 q, 1H], δ(phenyl proton): [7.8–7.1, m, 15H]. ^{13}C NMR, δ(carbon of the phenyl): 138.9 [C_i, $^1J(^{119}Sn{-}^{13}C) = 543.1$], 137.0 [$C_o$, $^2J(^{119}Sn{-}^{13}C) = 47.1$], 130.2 ($C_p$), 129.0 [$C_m$, $^3J(^{119}Sn{-}^{13}C) = 63.4$]. δ(carbon of the *N*-methylanthralinate anion, ortho, meta and para are defined with respect to the COOH group): 134.9 ($C{-}CO_2$), 133.7 ($C{-}N$), 114.4 (C_o), 110.6 (C_m), 30.0 (CH_3); 152.2 (CO). ^{119}Sn NMR: $\delta(^{119}Sn) = -118.0$.

3,5-$(NO_2)_2C_6H_4CO_2SnMe_3$ (**3**). Elemental analysis: [Found (calc. (%) for $C_{10}H_{12}N_2O_6Sn$)]: C, 32.46 (32.03); H, 3.20 (3.44); N 7.36 (7.86). Infrared (cm^{-1}): 1622 vs, 1581 s, 1538 vs, 1374 vs, 1339 vs ($\nu CO_2 + \nu NO_2$); 792 s, 777 s δCO_2; 560 s $\nu_{as}SnC_3$; 554 s νSnO. Mössbauer ($mm\,s^{-1}$): IS = 1.31, QS = 3.65, $\Gamma = 0.91$. NMR [$CDCl_3$; δ (ppm); ^nJ (Hz)]: ^{1}H NMR 0.71 [s, 9H, $Sn(CH_3)_3$, $^2J(^{119,117}Sn{-}C{-}H) = 58.8, 56.1$], 7.12–7.89 [m, phenyl protons, 3H]; ^{13}C NMR (ipso, ortho, meta and para are defined with respect to the COOH group): 21.9 [s, $Sn(CH_3)_3$; $^1J(^{119,117}SnC) = 393.6, 376.1$], 136.4 [$C_i$, d, $J = 33.1$], 121.9 [C_o, d, $J = 33.1$], 148.4 [C_m (CNO_2), s], 130.0 [C_p, s], 168.7 [CO]. ^{119}Sn NMR: $\delta(^{119}Sn) = 124.0$.

X-ray data collection

General crystal and experimental details are reported in Table 1. Data collections for **1**, **2** and **3** were carried out at 170(2) K (**1**) and 150(2) K (**2**, **3**) on a Nonius Kappa CCD diffractometer equipped with an Oxford Cryostream crystal cooling apparatus. The data were corrected for Lorentz and polarization effects and for absorption (except **1**). The structures were solved using direct methods (SHELXS-86[12]) and each refined by a full-matrix least-squares procedure based on F^2 using SHELXL-97[13] with anisotropic displacement parameters for all non-hydrogen atoms.

Table 1. Crystal data for $(C_6H_{11})_2CHCOOSnPh_3$ (**1**), $(CH_3NH)C_6H_4COOSnPh_3$ (**2**) and 3,5-$(NO_2)_2C_6H_4CO_2SnMe_3$ (**3**)

	1	2	3
Empirical formula	$C_{32}H_{38}O_2Sn$	$C_{26}H_{23}NO_2Sn$	$C_{10}H_{12}N_2O_6Sn$
Formula weight	573.31	500.14	374.91
Crystal size (mm^3)	0.20 × 0.20 × 0.25	0.15 × 0.25 × 0.25	0.15 × 0.15 × 0.20
Wavelength (Å)	0.710 73	0.710 69	0.710 73
Crystal system	Monoclinic	Triclinic	Monoclinic
Space group	$P2_1/n$	$P\bar{1}$	$P2_1/a$
Unit cell dimensions			
a (Å)	13.1670(2)	10.7165(1), $\alpha = 99.3620(5)$	17.8710(3)
b (Å)	15.2330(2)	11.3984(2)	7.0880(1)
c (Å)	14.0430(2)	11.7209(2), $\gamma = 117.0000(9)$	22.7860(3)
β (°)	95.3150(7)	110.1970(6)	112.855(1)
V (Å^3)	2804.54(7)	1106.45(3)	2659.69(7)
Z	4	2	8
Absorption coefficient (mm^{-1})	0.937	1.176	1.945
θ range (°)	3.4–30.1	3.5–30.1	3.7–27.5
Reflections collected	58 811	21 834	32 447
Independent reflections	8216	6442	6067
Reflections observed $I > 2\sigma(I)$	6285	6051	4945
Data/restraints/parameters	8216/0/317	6442/1/277	6067/0/350
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.035, wR_2 = 0.102$	$R_1 = 0.024, wR_2 = 0.058$	$R_1 = 0.028, wR_2 = 0.063$
R indices (all data)	$R_1 = 0.056, wR_2 = 0.120$	$R_1 = 0.026, wR_2 = 0.059$	$R_1 = 0.043, wR_2 = 0.069$
Largest diff. peak and hole (e^- Å^{-3})	1.03 and −1.12	0.85 and −0.87	1.39 and −0.65
Deposition number	CCDC 231421	CCDC 231422	CCDC 231420

RESULTS AND DISCUSSION

Spectroscopic characterization

Mössbauer spectroscopy

The Mössbauer spectra of compounds **1**–**3** exhibit a simple quadrupole split doublet typical of triorganotin(IV) derivatives, with FWHH values that support the presence of a single well-defined tin site. The IS values, 1.45–1.52 mm s^{-1}, are typical of a tetravalent tin in organometallic derivatives. The measured QS values, 2.45 (**1**), 2.52 (**2**) and 3.65 mm s^{-1} (**3**), are consistent with a tetrahedral environment around the tin center in **1** and **2** and a *trans*-O_2SnC_3 stereochemistry about the tin in (**3**).[14,15]

Infrared spectroscopy

The most prominent absorptions are reported in the Experimental section. Infrared O–C=O stretching frequencies have been used to distinguish coordinated from non-coordinated carboxyl groups, and also to determine the nature of bonding of the carboxylate, viz. monodentate, bidentate or bridging. The infrared spectra indicate that ν_{as} (O–C=O) values shown by the triphenyltin(IV), derivatives **1** and **2**, get shifted to lower frequencies, 1622 cm^{-1} and 1619 cm^{-1} respectively, in comparison with those of the free acids, i.e. $(C_6H_{11})_2CHCOOH$ (1699 cm^{-1}) and $(CH_3NH)C_6H_4COOH$ (1680 cm^{-1}). In addition, the values of $\Delta\nu$ (>230 cm^{-1}) for both triphenyltin(IV) derivatives have been found comparable to those obtained for monocordinated triorganotin compounds, indicating that the carboxylate group acts as a monodentate ligand.[16–19] Further spectroscopic evidence of the presence of monomeric species in the triphenyltin(IV) derivatives is the presence of a strong bands at 218 and 217 cm^{-1} due to ν_sSnC_3 in the infrared spectra of **1** and **2**. The presence of this band is an indication of C_{3v} symmetry for SnC_3 moieties (this band disappears or appears as a weak band in the case of planar SnC_3 moieties). In the case of the trimethyl(IV) derivative it is difficult to assign with certainty the νCO_2 frequencies owing to the presence of the NO_2 groups. The appearance of $\nu_{as}SnC_3$ as a strong band and the absence of ν_sSnC_3 in the 510–515 cm^{-1} region allowed us to infer the presence of planar or almost planar SnC_3 moieties.

The Mössbauer and the infrared spectroscopic data infer the presence of a tetrahedral environment around the tin centers in **1** and **2** and trigonal bipyramidal environment in those of **3**.

NMR spectroscopy

In the case of the triphenyltin(IV) derivatives, the cyclohexyl and the phenyl protons appear as complex patterns in the 0–2.2 and 7–8 ppm regions, respectively. The ^{119}Sn spectra of **1** and **2** exhibit a resonance at −120 and −118 ppm; these values, along with the coupling constants [$^1J(^{119}Sn–^{13}C)$ = 567.4 Hz (**1**) and 543.1 Hz (**2**)], are consistent with a tetrahedral environment around the tin center in solution.[20–23]

In the case of the trimethyltin(IV) derivative **3**, the phenyl protons of the carboxylate appear as a complex pattern in the 7–8 ppm region. The ^{119}Sn NMR spectrum exhibits a resonance at 124.0 ppm; this value is similar to those reported for tetrahedral trimethyltin heterocycles.[1,24] The ^{119}Sn NMR chemical shift value, in conjunction with the magnitude of the coupling constants [$^2J(^{119}\text{Sn–C–H}) = 58.8$ Hz; $^1J(^{119}\text{Sn–C}) = 393.5$ Hz], is consistent with a tetrahedral environment around the tin center in solution. In addition, the calculated C–Sn–C angles, using equations developed by Lockhart and co-workers[25,26] are 111.5° (with $\theta = 0.161[^2J]^2 - 1.32[^2J] + 133.4$) and 111.3° (using $[^1J] = 11.4\theta - 875$). These values of θ imply a cleavage of the infinite chain structure in solution, leading to the presence of monomeric species. The infinite chain structure apparent in the solid state (see below) is lost upon dissolution, as previously reported for other triorganotin derivatives, including carboxylates.[1,8,27,28]

Crystallography

The structures of **1** and **2** are shown in Figs 1 and 2 respectively, together with selected interatomic parameters. The structures consist of discrete molecules, with no significant interaction between the tin centers and the non-bonding oxygen (O(2)), in **1** and **2** respectively, (Sn(1)–O(2) = 2.659(1) Å and 2.773(1) Å for **1** and **2** respectively); the molecules adopt a C-type structure in the classification of Tiekink.[29] The tin atoms in both molecules are linked to three phenyl groups and one oxygen atom, leading to a distorted tetrahedral geometry. The tetrahedral angle ranges are 92.33(8)–121.52(9)° in **1** and 95.14(5)–117.60(6)° in **2**. However, but if the angles C(13)–Sn(1)–C(1) in **1** and C(7)–Sn–C(13) in **2** are not considered, there the ranges become smaller. The opening of the C(13)–Sn(1)–C(1) in **1** and C(7)–Sn–C(13) in **2** can be attributed to the relatively close approach of the O(2) atom of the carboxylic group to the tin centres, shown as dotted lines in Figs 1

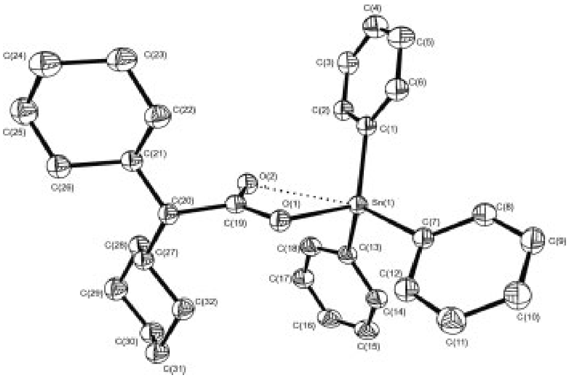

Figure 1. Molecular structure of $(C_6H_{11})_2CHCOOSnPh_3$ (**1**) showing the labeling scheme (the hydrogen atoms have been omitted for clarity). Selected bonds distances (Å) and angles (°): O1–Sn 2.084(1), O(2)–Sn 2.659(1), Sn–C(1) 2.131(2), Sn–C(7) 2.141(2), Sn–C(13) 2.133(2), C(19)–O(2) 1.226(3), C(19)–O(1) 1.307(3) Å; O(1)–Sn–C(1) 110.94(8), O(1)–Sn–C(7) 92.33(8), O(1)–Sn–C(13) 121.52(8), C(1)–Sn–C(7) 115.14(9), C(1)–Sn–C(13) 121.52(9), C(7)–Sn–C(13) 109.27(9)°.

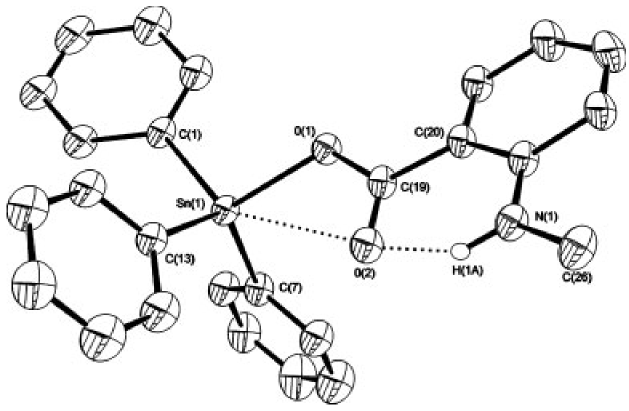

Figure 2. Molecular structure of $(CH_3NH)C_6H_4COOSnPh_3$ (**2**) showing the labeling scheme (the hydrogen atoms have been omitted for clarity). Selected bonds distances (Å) and angles (°): O(1)–Sn 2.050(1), O(2)–Sn 2.773(1), Sn–C(1) 2.128(1), Sn–C(7) 2.124(1), Sn–C(13) 2.125(1), C(19)–O(2) 1.238(1), C(19)–O(1) 1.317(1) Å, O(1)–Sn–C(1) 95.14(5), O(1)–Sn–C(7) 108,71(5), O(1)–Sn–C(13) 113.36(5), C(1)–Sn–C(7) 113.12(6), C(1)–Sn–C(13) 106.71(6), C(7)–Sn–C(13) 117.60(6)°.

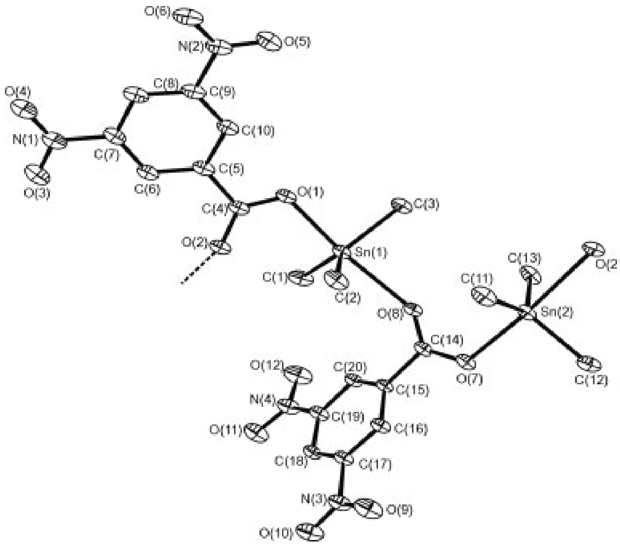

Figure 3. Molecular structure of $3,5\text{-}(NO_2)_2C_6H_4CO_2SnMe_3$ (**3**) showing the labeling scheme (the hydrogen atoms have been omitted for clarity). Selected bonds distances (Å) and angles (°): O(1)–Sn(1) 2.181(1), O(8)–Sn(1) 2.501(2), Sn(1)–C(1) 2.120(3), Sn(1)–C(3) 2.117(3), Sn(1)–C(2) 2.123(3), C(4)–O(1) 1.277(3), C(4)–O(2) 1.236(3) Å; O(1)–Sn(1)–C(1) 97.22(10), O(1)–Sn(1)–C(2) 92.70(10), O(1)–Sn(1)–C(3) 91.88(10), C(1)–Sn(1)–C(2) 123.08(13), C(1)–Sn(1)–C(3) 114.46(14), C(2)–Sn(1)–C(3) 121.06(13), O(1)–Sn(1)–O(8) 171.07(7)°.

and 2 (2.659(1) Å and 2.773(1) Å in **1** and **2** respectively). The close proximity of the O(2) atom influences the coordination geometry about the tin center. The strength of the Sn–C bond is slightly affected. The variations in the C–Sn–C angles and Sn–C bonds may be traced to the minor distortion of the tetrahedral environment. The Sn(1)–O(1) bond lengths are 2.084(1) Å and 2.050(1) Å in **1** and **2** respectively, which are on the order of those reported by Vollano *et al.*[2] for some triphenyltin(IV) esters of salicylic acid, *o*-anisic acid and *p*-methylthiobenzoic acid. The structure of **2** features strong intramolecular hydrogen bonds (H(1A)–O(2) = 2.06 Å; N(1)–H(1A)–O(2) = 132°), which may account for why Sn(1)–O(2) is longer for **2** than **1**.

A portion of the lattice structure of **3** is shown in Fig. 3. The structure is polymeric owing to the presence of bidentate bridging carboxylate ligands with disparate Sn–O(1) and Sn–O(2) distances of 2.181(1) Å and 2.501(2) Å respectively. The tin atom is thus five-coordinated, existing in a distorted trigonal bipyramidal geometry. The O(1)–Sn(1)–O(8) angle is 171.07(7)°. Similar structures are reported for other trimethyl carboxylates.[30,31]

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