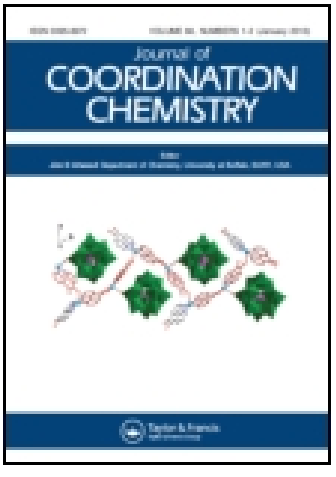

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Synthesis and structural characterization of monomeric and polymeric supramolecular organotin(IV) 4-chlorophenylethanoates

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Synthesis and structural characterization of monomeric and polymeric supramolecular organotin(IV) 4-chlorophenylethanoates

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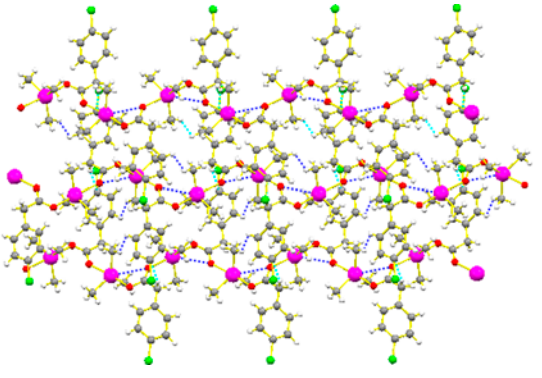

Four monomeric and three polymeric organotin(IV) carboxylates have been synthesized and characterized by elemental analysis, FT-IR, multinuclear NMR (^{1}H, ^{13}C, and ^{119}Sn), and X-ray single-crystal analysis. The latter technique revealed the monomeric 2-D supramolecular structure for Et_2Sn(IV) derivative and polmeric nature which form layer-by-layer supramolecular structure in case of Me_3Sn (IV) derivative.

Four monomeric [*n*-Bu_2SnL_2 (**1**), Et_2SnL_2 (**2**), Me_2SnL_2 (**3**), and *n*-Oct_2SnL_2 (**7**)] and three polymeric {[*n*-$Bu_3SnL]_n$ (**4**), $[Me_3SnL]_n$ (**5**), and $[Ph_3SnL]_n$ (**6**)} organotin(IV) carboxylates, where L = 4-chlorophenylethanoate, were synthesized and characterized by elemental analysis, FT-IR, and multinuclear NMR (^{1}H, ^{13}C, and ^{119}Sn). Compounds **2** and **5** were also analyzed by X-ray single-crystal analysis showing monomeric and zigzag structures, respectively. Two types of O…H (2.641 Å) and Cl…H (2.943 Å) non-covalent interactions generate a 2-D supramolecular structure for **2**. Layer-by-layer supramolecular structure was observed for **5** in which polymeric chains are

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connected via non-covalent interactions {Cl…H (2.869 Å), H…π (2.899 Å)}, and unconventional dihydrogen {H…H (2.381 Å)} interactions.

Keywords: Organotin; Monomeric; Polymeric; 2-D Supramolecular; Layer-by-layer arrangement

1. Introduction

Supramolecular systems can be used for molecular recognition, host–guest chemistry, and as catalysts [1]. Organotin(IV) carboxylates have drawn attention for their easy one-pot synthesis, fine-tuning of structural and functional features, and stable tin–carbon as well as carboxylic oxygen bonds. A large number of supramolecular organotin(IV) carboxylates have been prepared and structurally characterized [1, 2]. Structural types such as monomers, dimers, tetramers, oligomers, and polymers have been reported [3–7]. The diverse structural motifs found in this family of complexes have been attributed to the nature of carboxylic acid, tin-bound *R* groups, and metal–ligand molar ratio [8, 9]. Intermolecular bonds and interactions (hydrogen bonds, van der Waals forces, and $\pi\ldots\pi$ interactions) play key roles in generation of a variety of stable supramolecular infrastructures [1]. Preference of a particular tin carboxylate to adopt a given structure stems from a combination of steric and electronic factors [9]. The various structures play an important role in bioactivity of organotin (IV) carboxylates [10–13]. Thus, synthesis of new supramolecular organotin(IV) complexes is important in the development of pharmaceutical and industrial organotins. The 4-chlorophenyl ethanoic acid containing a semi-rigid CH_2COO and polar chloro that can adopt a variety of spatial orientations is an ideal ligand for creation of fascinating supramolecular structures [14]. Continuing our interest in the structural chemistry of organotin(IV) carboxylates and their applications, we report synthesis, spectral characterization, and single-crystal analysis of organotin(IV) derivatives of 4-chlorophenyl ethanoic acid; molecular modeling shows these to be candidates for formation of supramolecular structures that may impact biological and other applications.

2. Experimental setup

The organotin(IV) precursors were purchased from Aldrich and used without purification. The solvents were dried according to the reported procedures [15]. The melting points were recorded on an electrothermal melting point apparatus; model MP-D mitamura Riken Kogyo (Japan). Microanalysis was done using a Leco CHNS 932 apparatus. IR spectra were recorded with KBr pellets from 4000 to 400 cm^{-1} using a Bio-Rad Excaliber FT-IR, model FTS 300 MX spectrometer (USA). ^{1}H and ^{13}C NMR were recorded at room temperature on a Bruker Avance Digital 300 MHz NMR spectrometer (Switzerland) using $CDCl_3$ as an internal reference [δ ^{1}H ($CDCl_3$) = 7.28 and δ ^{13}C ($CDCl_3$) = 77.0]. ^{119}Sn NMR spectra were obtained with Me_4Sn as an external reference [δ (^{119}Sn) = 37.290665]. Chemical shifts (δ) are given in ppm.

2.1. *Di-n-butyltin(IV) bis[4-chlorophenylethanoate] (1)*

The sodium salt R′COONa (0.693 g, 5 mM) was refluxed for 10 h with dibutyltin(IV) dichloride (0.760 g, 2.5 mM) in dry toluene contained in a 250-mL two-necked

round-bottom flask. The turbid solution was left overnight at room temperature. The sodium chloride formed was filtered off and the filtrate was rotary evaporated. The resultant solid was recrystallized from chloroform and *n*-hexane (4 : 1) mixture. (Yield: 81%). M.p. 95–98 °C. Anal. Calcd (Found) for $C_{24}H_{30}Cl_2O_4Sn$: C, 50.35 (50.33); H, 5.24 (5.26) %. IR (cm^{-1}): 1586 $\nu(OCO)_{asym}$, 1444 $\nu(OCO)_{sym}$, 142 $\Delta\nu$, 527 ν(Sn–C), 482 ν(Sn–O). ^{1}H NMR ($CDCl_3$, ppm): 3.66 (s, H_2, 4H), 7.25 (d, $H_{4,4'}$, 4H), 7.31 (d, $H_{5,5'}$, 4H), 1.63–1.50 (m, $H_{\alpha,\beta}$, 8H), 1.33–1.28 (m, H_γ, 4H), 0.84 (t, H_δ, 6H). ^{13}C NMR ($CDCl_3$, ppm): 181.4 (C-1), 40.5 (C-2), 132.9 (C-3), 130.6 (C-4,4′), 128.7 (C-5,5′), 133.0 (C-6), 25.1 [C-α, $^1J(^{119}Sn–^{13}C)$ = 807 Hz], 26.5 [C-β, $^2J(^{119}Sn–^{13}C)$ = 38 Hz], 26.2 [C-γ, $^3J(^{119}Sn–^{13}C)$ = 82 Hz], 13.5 (C-δ). ^{119}Sn NMR ($CDCl_3$, ppm): −237.1.

2.2. *Diethyltin(IV) bis[4-chlorophenylethanoate] (2)*

Compound **2** was prepared and recrystallized in the same way as **1** (R′COONa: 0.963 g, 5 mM, diethytin(IV) dichloride: 0.619 g, 2.5 mM, Yield: 86%). M.p. 107–108 °C. Anal. Calcd (Found) for $C_{20}H_{22}Cl_2O_4Sn$: C, 46.51 (46.47); H, 4.26 (4.30) %. IR (cm^{-1}): 1601 $\nu(OCO)_{asym}$, 1492 $\nu(OCO)_{sym}$, 109 $\Delta\nu$, 541 ν(Sn–C), 488 ν(Sn–O). ^{1}H NMR ($CDCl_3$, ppm): 3.67 (s, H_2, 4H), 7.25 (d, $H_{4,4'}$, 4H), 7.31 (d, $H_{5,5'}$, 4 H), 1.62 (q, H_α, 4H), 1.21 (t, H_β, 6H). ^{13}C NMR ($CDCl_3$, ppm): 181.6 (C-1), 40.3 (C-2), 132.8 (C-3), 130.6 (C-4,4′), 128.8 (C-5,5′), 133.0 (C-6), 17.4 [C-α, $^1J(^{119}Sn–^{13}C)$ = 588 Hz], 8.8 [C-β, $^2J(^{119}Sn–^{13}C)$ = 43 Hz]. ^{119}Sn NMR ($CDCl_3$, ppm): −155.4.

2.3. *Dimethyltin(IV) bis[4-chlorophenylethanoate] (3)*

Compound **3** was prepared and recrystallized in the same way as **1** (R′COONa: 0.963 g, 5 mM, dimethytin(IV) dichloride 0.549 g, 2.5 mM, Yield: 65%). M.p. 128 °C. Anal. Calcd (Found) for $C_{18}H_{18}Cl_2O_4Sn$: C, 44.26 (42.23); H, 3.69 (3.70) %. IR (cm^{-1}): 1558 $\nu(OCO)_{asym}$, 1410 $\nu(OCO)_{sym}$, 148 $\Delta\nu$, 510 ν(Sn–C), 481 ν(Sn–O). ^{1}H NMR ($CDCl_3$, ppm): 3.65 (s, H_2, 4H), 7.23 (d, $H_{4,4'}$, 4H), 7.31 (d, $H_{5,5'}$, 4H), 0.97 [s, H_α, 6H, $^2J(^{119/117}Sn–^1H)$ = 82/79 Hz]. ^{13}C NMR ($CDCl_3$, ppm): 181.0 (C-1), 40.3 (C-2), 132.6 (C-3), 130.6 (C-4,4′), 128.7 (C-5,5′), 133.0 (C-6), 4.4 [C-α, $^1J(^{119/117}Sn–^{13}C)$ = 638/611 Hz]. ^{119}Sn NMR ($CDCl_3$, ppm): −231.8.

2.4. *Tri-n-butyltin(IV) 4-chlorophenylethanoate (4)*

Compound **4** was prepared in the same way as **1**, using equimolar molar amounts (R′CO-ONa: 0.963 g, 5 mM, tributyltin(IV) chloride: 1.627 g, 5 mM, Yield: 78%). M.p. gel. Anal. Calcd (Found) for $C_{20}H_{33}ClO_2Sn$: C, 52.17 (52.19); H, 7.17 (7.15) %. IR (cm^{-1}): 1595 $\nu(OCO)_{asym}$, 1387 $\nu(OCO)_{sym}$, 208 $\Delta\nu$, 525 ν(Sn–C), 487 ν(Sn–O). ^{1}H NMR ($CDCl_3$, ppm): 3.59 (s, H_2, 2H), 7.23 (d, $H_{4,4'}$, 2H), 7.28 (d, $H_{5,5'}$, 2H), 1.65–1.55 (m, H_α, 6H), 1.39–1.24 (m, $H_{\beta,\gamma}$, 12H), 0.91 (t, H_δ, 9H). ^{13}C NMR ($CDCl_3$, ppm): 176.5 (C-1), 41.8 (C-2), 132.5 (C-3), 130.6 (C-4,4′), 128.4 (C-5,5′), 134.2 (C-6), 16.8 [C-α, $^1J(^{119}Sn–^{13}C)$ = 350 Hz], 27.8 [C-β, $^2J(^{119}Sn–^{13}C)$ = 21 Hz], 26.9 [C-γ, $^3J(^{119/117}Sn–^{13}C)$ = 64/62 Hz], 13.6 (C-δ). ^{119}Sn NMR ($CDCl_3$, ppm): 109.3.

2.5. *Trimethyltin(IV) 4-chlorophenylethanoate (5)*

Compound **5** was prepared in the same way as **1**, using equimolar molar amounts (R′CO-ONa: 0.963 g, 5 mM, trimethyltin(IV) chloride: 0.996 g, 5 mM, Yield: 77%). M.p. 97 °C.

Anal. Calcd (Found) for $C_{11}H_{15}ClO_2Sn$: C, 39.52 (39.49); H, 4.49 (4.48) %. IR (cm^{-1}): 1578 $\nu(OCO)_{asym}$, 1390 $\nu(OCO)_{sym}$, 188 $\Delta\nu$, 550 ν(Sn–C), 470 ν(Sn–O). ^{1}H NMR ($CDCl_3$, ppm): 3.59 (s, H2, 2H), 7.23 (d, $H_{4,4'}$, 2H), 7.29 (d, $H_{5,5'}$, 2H), 0.56 [s, H_α, 9H, $^2J(^{119/117}Sn–^1H) = 58/56$ Hz]. ^{13}C NMR ($CDCl_3$, ppm): 176.5 (C-1), 41.3 (C-2), 132.5 (C-3), 131.8 (C-4,4′), 128.5 (C-5,5′), 134.1 (C-6), −2.3 [C-α, $^1J(^{119/117}Sn–^{13}C) = 397/380$ Hz]. ^{119}Sn NMR ($CDCl_3$, ppm): 138.1.

2.6. *Triphenyltin(IV) 4-chlorophenylethanoate (6)*

Compound **6** was prepared in the same way as **1**, using equimolar molar amounts (R′CO-ONa: 0.963 g, 5 mM, triphenyltin(IV) chloride: 1.627 g, 5 mM, Yield: 79%). M.p. 133 °C. Anal. Calcd (Found) for $C_{26}H_{21}ClO_2Sn$: C, 60.00 (59.96); H, 4.04 (4.08) %. IR (cm^{-1}): 1573 $\nu(OCO)_{asym}$, 1392 $\nu(OCO)_{sym}$, 181 $\Delta\nu$, 456 ν(Sn–O). ^{1}H NMR ($CDCl_3$, ppm): 3.73 (s, H_2, 2H), 7.30–7.20 (m, $H_{4,4'}$, 2H), 7.30–7.20 (m, $H_{5,5'}$, 2H), 7.55–7.40 (m, $H_{\beta,\gamma,\delta}$, 15H). ^{13}C NMR ($CDCl_3$, ppm): 177.7 (C-1), 40.6 (C-2), 132.7 (C-3), 130.7 (C-4,4′), 128.6 (C-5,5′), 133.53 (C-6), 137.91 [C-α, $^1J(^{119}Sn–13C) = 647$ Hz], 136.8 [C-β, $^2J(^{119}Sn–^{13}C) = 48$ Hz], 128.9 [C-γ, $^3J(^{119}Sn–^{13}C) = 64$ Hz], 130.3 [C-δ, $^4J(^{119}Sn–13C) = 13.5$ Hz]. ^{119}Sn NMR ($CDCl_3$, ppm): −107.2.

2.7. *Di-n-octyltin(IV) bis[4-chlorophenylethanoate] (7)*

R′COOH (0.853 g, 5 mM) and dioctyltin(IV) oxide (0.903 g, 2.5 mM) were suspended in dry toluene (100 mL) in a single-necked round-bottom flask (250 mL) equipped with a Dean–Stark apparatus. The mixture was refluxed for 10 h and water formed during the condensation reaction was removed after regular intervals. A clear solution thus obtained was cooled to room temperature and solvent was removed under reduced pressure. The solid obtained was recrystallized from chloroform and *n*-hexane (4 : 1) mixture (Yield: 78%). M.p. 78–80 °C. Anal. Calcd (Found) for $C_{32}H_{46}Cl_2O_4Sn$: C, 56.14 (56.10); H, 6.72 (6.76) %. IR (cm^{-1}): 1597 $\nu(OCO)_{asym}$, 1450 $\nu(OCO)_{sym}$, 147 $\Delta\nu$, 539 ν(Sn–C), 466 ν(Sn–O). ^{1}H NMR ($CDCl_3$, ppm): 3.65 (s, H_2, 4H), 7.25 (d, $H_{4,4'}$, 4H), 7.31 (d, $H_{5,5'}$, 4H), 1.64–1.51 (bs, $H_{\alpha,\beta}$, 8H), 1.31–1.22 (bs, $H_{\gamma,\gamma'}$, 20H), 0.90 (t, $H_{\delta'}$, 6H]. ^{13}C NMR ($CDCl_3$, ppm): 181.4 (C-1), 40.8 (C-2), 132.8 (C-3), 130.6 (C-4,4′), 128.7 (C-5,5′), 133.0 (C-6), 25.4 (C-α), 24.4 (C-β), 33.2 [C-γ, $^3J(^{119}Sn–^{13}C) = 91$ Hz], 31.8 (C-δ), 29.1 (C-α′), 29.0 (C-β′), 22.7 (C-γ′), 14.1 (C-δ′). ^{119}Sn NMR ($CDCl_3$, ppm): −147.2.

2.8. *X-ray crystallographic studies*

A crystal fragment, cut to size to fit in the homogeneous part of the X-ray beam, was mounted on a glass fiber and aligned on a Bruker SMART APEX CCD diffractometer (Platform with full three-circle goniometer). The crystal was cooled to 100(1) K using the Bruker KRYOFLEX low-temperature device. Intensity measurements were performed using graphite-monochromated Mo-Kα radiation from a sealed ceramic diffraction tube (SIEMENS). Data integration and global cell refinement were performed with SAINT [16] and SAINTPLUS was used for space group determination (XPREP) [16]. The structure was solved by Patterson method; extension of the model was accomplished by direct methods and applied to difference-structure factors using the program DIRDIF [17]. All refinement calculations and graphics were performed with SHELXL, PLUTO, and PLATON.

3. Results and discussion

3.1. *Synthesis of 1–7*

Reaction of R_3SnCl/R_2SnCl_2 with NaL in 1 : 1/1 : 2 molar ratios and R_2SnO with HL in 1 : 2 molar ratio led to complexes according to equations (1)–(3), scheme 1. The resulting complexes were obtained in good yield (65–86%). All complexes were white solids, stable in air, and soluble in $CHCl_3$ and DMSO.

(a)

$$R_2SnCl_2 + 2NaL \rightarrow R_2SnL_2 + 2NaCl \quad (1)$$

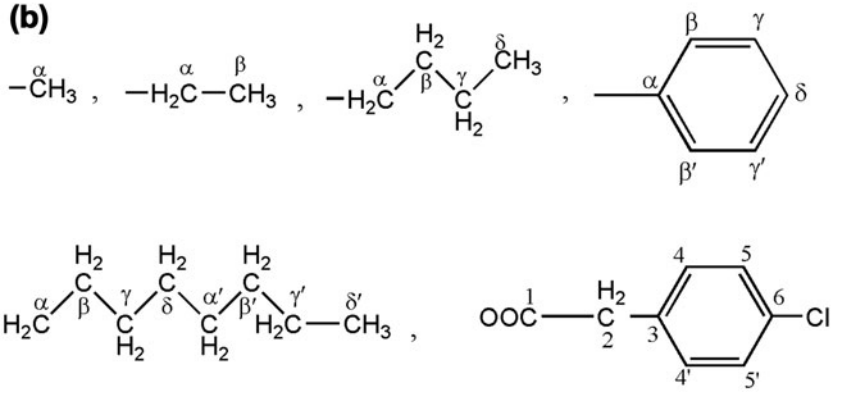
R = *n*-Butyl (**1**), Ethyl (**2**), Methyl (**3**)

$$R_3SnCl + NaL \rightarrow R_3SnL + NaCl \quad (2)$$

R = *n*-Butyl (**4**), Methyl (**5**) Phenyl (**6**)

$$n\text{-}Oct_2SnO + 2HL \rightarrow n\text{-}Oct_2SnL_2 + H_2O \quad (3)$$

(b)



Scheme 1. (a) Synthesis of **1–7** and (b) numbering scheme of ligand and Sn attached organic groups.

3.2. *IR spectra*

IR spectra are useful for analyzing bonding in organotin carboxylates [18]. The most important stretching frequencies are those associated with Sn–O and COO. The strong absorptions at 488–456 cm^{-1}, absent in spectra of the free acid, are due to Sn–O stretching vibrations [19]. Complexes **1–7** showed $\nu(COO)_{asym}$ and $\nu(COO)_{sym}$ at 1601–1558 cm^{-1} and 1492–1387 cm^{-1}, respectively. The magnitude of $\Delta\nu = [\nu(COO)_{asym} - \nu(COO)_{sym}]$ can be used to identify the coordination of carboxylate with monodentate ($\Delta\nu > 250\ cm^{-1}$), bridging bidentate ($150 < \Delta\nu < 250\ cm^{-1}$) or chelating bidentate ($\Delta\nu < 150\ cm^{-1}$) fashion [20]. Our results show a chelating bidentate behavior in **1–3** and **7,** and a bridging bidentate

bonding in **4–6** in the solid state. The conclusions from IR data are consistent with the X-ray crystallographic data for **2** and **5**.

3.3. *NMR spectra*

^{1}H NMR data of **1–7** given in Section 2 show the expected integration and peak multiplicities. The disappearance of resonance at 11.67 ppm in the spectra of **1–7** show deprotonation of the acid. ^{1}H NMR spectra exhibit three sets of signals due to ligand of the complexes, a singlet in the aliphatic region due to CH_2, and two doublets downfield with integration values of 1 : 1, arising from the aromatic protons of the benzene ring. The protons of the alkyl groups attached to Sn are in the upfield regions of the spectra [20]. For **6**, a multiplet in the aromatic region (7.55–7.40 ppm) is ascribed to phenyl protons bonded to Sn. The values of [^{2}J($^{119/117}$Sn–^{1}H)] coupling constants for **3** and **5** are 82/79 Hz and 58/56 Hz, respectively, confirming six- and four-coordinate Sn in **3** and **5**, respectively, in solution [21]. Complexes **1**, **4**, and **7** give a complex pattern for attached alkyl groups except the clear terminal methyl groups (0.84–0.91), while **2** shows a quartet and a triplet due to methylene and methyl groups in the expected region.

The ^{13}C NMR spectra of diorganotin derivatives show a downfield shift, while triorganotin derivatives show an upfield shift for carboxylic carbon compared with the free ligand acid (178.1 ppm). The downfield shift in diorganotin(IV) derivatives is due to bidentate behavior and a subsequent electron density transfer from the ligand to the tin atom. For triorganotin(IV) derivatives, an upfield shift indicates localization of carbonyl group and a monodentate behavior of the ligand that results in a low coordination number for tin. The presence of four resonances at 128.4–134.2 ppm and a single resonance at 40.3–41.8 ppm in ^{13}C NMR spectra of the complexes are from benzene and methylene carbon of the ligand, respectively. The coordination number of the complexes is further confirmed by ^{1}J which shows five or higher coordination for diorganotin(IV) and four for triorganotin(IV) derivatives. The alkyl carbons attached to tin are assigned according to the literature values for analogous compounds [20]. Generally, the ^{1}H and ^{13}C NMR spectra of the complexes exhibit no additional resonance, reflecting the purity of the complexes. The coordination number of the complexes assigned on the basis of ^{1}H and ^{13}C is further confirmed by δ(^{119}Sn) values. For **1** and **3** δ(^{119}Sn), values are −210 to −400 ppm [22] showing six-coordinate tin, while **2** and **7** have ^{119}Sn signal at −90 to −190 ppm for five-coordinate tin. Triorganotin(IV) carboxylates show a tetrahedral geometry as their ^{119}Sn signals are typical for four-coordinate tin [20].

3.4. *Crystal structures of 2 and 5*

X-ray structure of **2** is shown in figure 1; crystal data, selected bond distances, and angles are summarized in tables 1 and 2. The crystal structure shows that Sn exists in a distorted octahedral or skew trapezoidal geometry defined by two axial ethyls and four oxygens of two carboxyl groups at basal positions. The major departure from ideal octahedral geometry is found in the angles of H_5C_2–Sn–C_2H_5 {132.8 (8)°} and O1–Sn–O1_a {169.4(5)°}. The C–Sn–C angle of 132.8(8)° 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 tin [23]. The two ethyls are bent towards the O1_a–Sn–O1 plane, resulting in an increased interelectronic repulsion and a larger

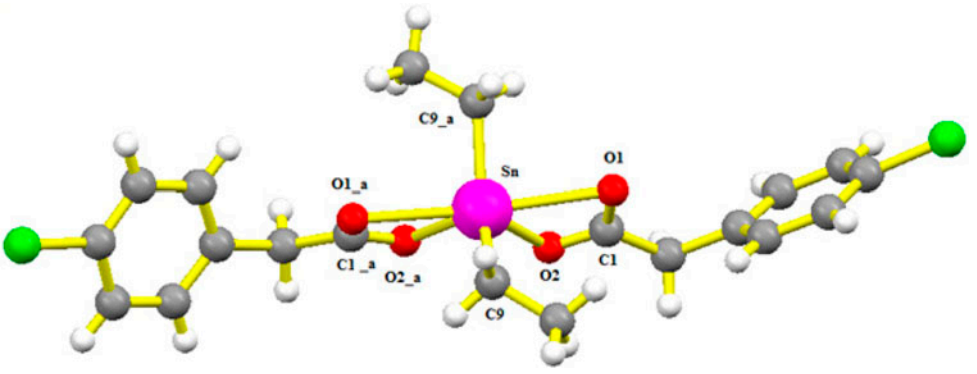


Figure 1. Ball and stick diagram of the asymmetric unit of **2**.

Table 1. Crystal data and structure refinement parameters for **2** and **5**.

	2	**5**
Moiety formula	$C_{20}H_{22}Cl_2O_4Sn$	$C_{11}H_{15}ClO_2Sn$
Formula weight	516.0	333.40
Crystal system	Monoclinic	Monoclinic
Space group	*C2*	$P2_1/c$
a (Å)	24.10(4)	11.3026(14)
b (Å)	5.340(9)	9.6549(12)
c (Å)	9.135(16)	13.2073(17)
β (°)	111.66(2)	113.5197(14)
V (Å^3)	1093(3)	1321.5(3)
T	–	0.82
θ ranges for data collection (°)	3.51–25.02	2.70–27.50
Z	4	4
ρ_{Calcd}, g cm^{-3}	1.568	1.676
F (0 0 0)	516	656
Crystal size (mm)	0.51 × 0.12 × 0.06	0.51 × 0.47 × 0.39
Temperature (K)	100(1)	100(1)
Index ranges	*h*: −28→28; *k*: −6→6; *l*: −10→10	*h*: −13→14; *k*: −12→12; *l*: −17→17
Total data	3341	10,890
Unique data [R_{int}]	1832[0.0891]	3033[0.0262]
Final *R* indices [$I > 4\sigma(I)$]	$R1 = 0.1291$, $wR2 = 0.2970$	$R1 = 0.0258$, $wR2 = 0.0653$

Table 2. Selected bond lengths (Å) and angles (°) of **2**.

Sn–O1	2.603(17)	Sn–C9	2.13(3)
Sn–O2	2.173(16)	Sn–C9_a	2.13(3)
Sn–O1_a	2.603(17)	O1–C1	1.33(3)
Sn–O2_a	2.173(16)	O2–C1	1.26(3)
C9–Sn–C9_a	132.8(8)	C9_a–Sn–O2_a	111.4(8)
C9–Sn–O1	84.3(8)	O1–Sn–O2	55.1(5)
C9–Sn–O2	111.4(8)	O1–Sn–O1_a	169.4(5)
C9–Sn–O1_a	91.5(8)	O1–Sn–O2_a	135.4(5)
C9–Sn–O2_a	104.0(8)	O2–Sn–O1_a	135.4(5)
C9_a–Sn–O1	91.5(8)	O2–Sn–O2_a	81.7(6)
C9_a–Sn–O2	104.0(8)	C1_a–Sn–O2_a	26.6(7)
C9_a–Sn–O1_a	84.3(8)	O1_a Sn–O2_a	55.1(5)

Table 3. Selected bond lengths (Å) and angles (°) of **5**.

Sn–O1	2.212(2)	Sn–O2_b	2.324(2)
Sn–C9	2.125(3)	O1–C1	1.263(3)
Sn–C10	2.131(3)	O2–C1	1.258(3)
Sn–C11	2.129(3)		
O1–Sn–C9	88.92(10)	C9–Sn–C11	117.34(10)
O1–Sn–C10	94.35(10)	C9–Sn–O2_b	85.25(10)
O1–Sn–C11	95.23(10)	C10–Sn–C11	124.20(12)
O1–Sn–O2_b	173.32(7)	C10–Sn–O2_b	85.52(10)
C9–Sn–C10	117.68(11)	C11–Sn–O2_b	90.34(10)

O1_a–Sn–O1 angle (169.4(5)°). The enhanced steric effect is reflected in a reduced *trans* angle, O2_a–Sn–O2 (81.7°). This distortion is uniform on either side of Sn in the basal plane as shown by equivalent O1–Sn–O2 and O1_a–Sn–O2_a angles, 55.1°. Carboxylates coordinate anisobidentate forming a short bond (Sn–O2 and Sn–O2_a 2.173(16) Å) and a long bond (Sn–O1 and Sn–O1_a 2.603(17) Å). The longer Sn–O bond distances are significantly below the sum of the van der Waals radii of these atoms (3.68 Å) [24], and therefore these Sn–O interactions can be considered as bonds. Two types of O…H (2.641 Å) and Cl…H (2.943 Å) non-covalent interactions generate the 2-D supramolecular structure for **2** (figure 2).

The crystal structure of **5** exhibits the familiar structural motif of a polymeric chain [20], propagating in a zigzag fashion along the crystallographic [0 1 0] direction (figure 3). A single deprotonated 4-chlorophenylethanoate bridges adjacent *trans*-R_3Sn center via the carboxylate. As a result of the bidentate coordination of the ligand, each Sn has a coordination number of five. The three methyl groups on tin occupy equatorial positions, while the axial positions are occupied by two oxygens from the two carboxylates. The tin(IV) has a distorted trigonal bipyramidal coordination. The index of trigonality τ {square pyramidal ($\tau = 0$) and trigonal bipyramidal ($\tau = 1$)}, as defined by Addison et al. [25], is 0.82 for **5**, confirming a distorted trigonal bipyramidal geometry. Crystal data, selected bond lengths, and angles for **5** are listed in tables 1–3. The O–Sn–O angle in **5** {173.32(7)°} slightly deviates from ideal value {180°}. The sum of the C–Sn–C bond angles in **5** {359.22°} is close to ideal {360°}. All the Sn–O and Sn–C distances are 2.212–2.324 Å (av. 2.268 Å) and

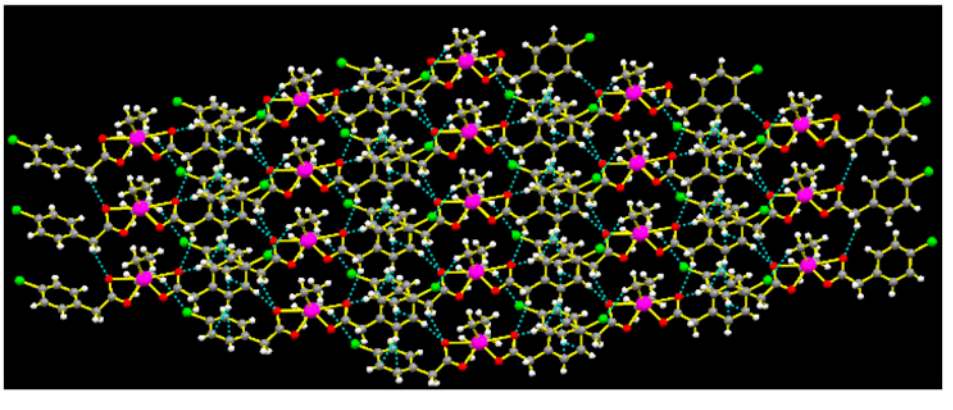


Figure 2. 2-D supramolecular structure of **2** mediated by O…H (2.641 Å) and Cl…H (2.943 Å) interactions.

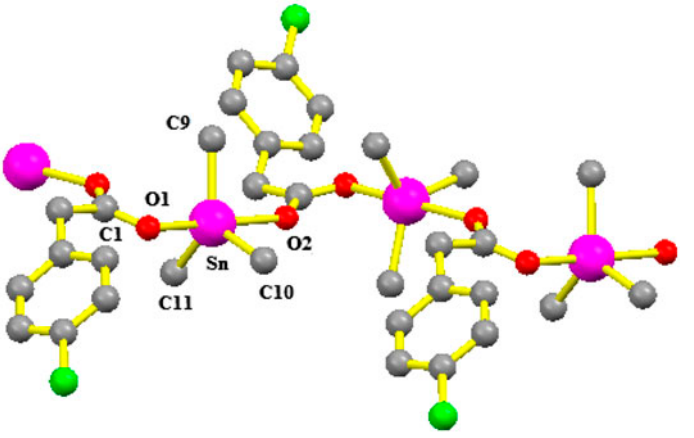


Figure 3. Ball and stick diagram of **5** showing the zigzag polymeric structure.

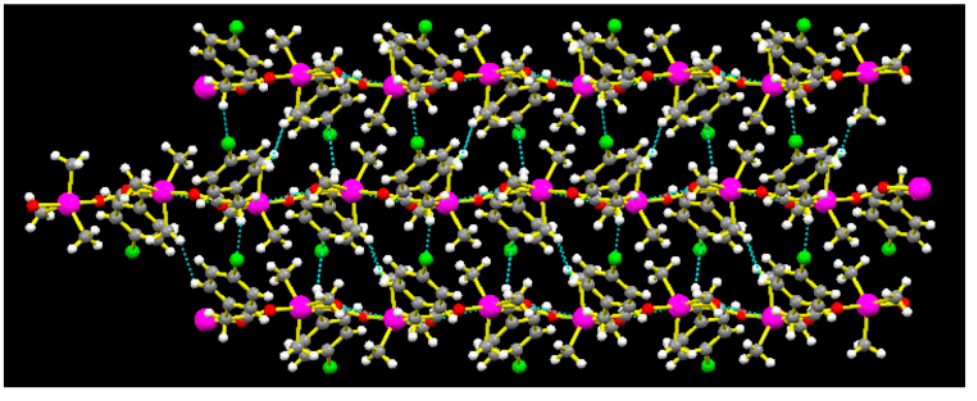


Figure 4. Layer-by-layer supramolecular structure of **5** in which polymeric chains are connected via Cl…H (2.869 Å), H…π (2.899 Å), and H…H (2.381 Å) interactions.

2.125–2.131 Å (av. 2.128 Å), consistent with those reported for other triorganotin carboxylates [20, 26].

The packing diagram offers a layer-by-layer supramolecular structure for **5** in which polymeric chains are connected via Cl…H (2.869 Å) and H…π (2.899 Å) non-covalent interactions (figure 4). Weak H…H (2.381 Å) interactions involving electron deficient methyl and electron-rich phenyl hydrogens provide further stability to the layer-by-layer structure. These unconventional dihydrogen bonds are shorter than the sum of the van der Waals radii for two hydrogens (2.4 Å); such bonds are well documented and their physical, chemical, and biological significance have been well established [27–29]. The crystal structures shown by **2** and **5** are in agreement with other organotin(IV) carboxylates reported [30–33].

4. Conclusion

Seven new organotin(IV) 4-chlorophenylethanoates were synthesized and characterized by elemental analysis, FT-IR, multinuclear NMR (^{1}H, ^{13}C, and ^{119}Sn), and X-ray single-crystal analysis. Based on the results obtained, four compounds were assigned a monomeric structure {[*n*-Bu_2SnL_2 (**1**), Et_2SnL_2 (**2**), Me_2SnL_2 (**3**), *n*-Oct_2SnL_2 (**7**)]} and three polymeric {[*n*-$Bu_3SnL]_n$ (**4**), $[Me_3SnL]_n$ (**5**), $[Ph_3SnL]_n$ (**6**)}, however, the latter three did not maintain their polymeric nature in solution as shown by multinuclear NMR. Compounds **2** and **5** were analyzed by X-ray single-crystal analysis showing monomeric and zigzag structures, respectively. Two types of O…H (2.641 Å) and Cl…H (2.943 Å) non-covalent interactions generate the 2-D supramolecular structure for **2**. A layer-by-layer supramolecular structure was observed for **5** in which polymeric chains are connected via non-covalent {Cl…H (2.869 Å), H…π (2.899 Å)} and unconventional dihydrogen {H…H (2.381 Å)} interactions.

Supplementary material

Crystallographic data for the structural analysis are available from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, UK on request, quoting the deposition number 940510 and 940511 for **2** and **5**.

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