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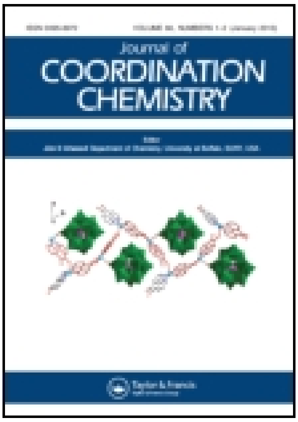

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gcoo20

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Accepted author version posted online: 25 Sep 2013.Published online: 06 Nov 2013.

To cite this article: Dain Thorpe, Andrei Callejas, Dmitry Royzman, Robert D. Pike, George Eng & Xueqing Song (2013) Synthesis and crystal structures of ionic triphenyltin complexes with oxalic and malonic acid, Journal of Coordination Chemistry, 66:20, 3647-3659, DOI: 10.1080/00958972.2013.848275

To link to this article: http://dx.doi.org/10.1080/00958972.2013.848275

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Journal of Coordination Chemistry, 2013
Vol. 66, No. 20, 3647–3659, http://dx.doi.org/10.1080/00958972.2013.848275

Synthesis and crystal structures of ionic triphenyltin complexes with oxalic and malonic acid

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(*Received 6 June 2013; accepted 5 September 2013*)

Two ionic triphenyltin complexes (**1** and **2**) were obtained *via* condensation of triphenyltin hydroxide with oxalic and malonic acids in the presence of di-*iso*butylamine. Their structures have been characterized by IR and multinuclear (^{1}H, ^{13}C, and ^{119}Sn) NMR spectroscopies. The coordinations of tin in the two triphenyltin complexes are confirmed by X-ray crystallographic studies. In the solid state, oxalate complex **1** consists of a di-*iso*butylammonium cation and an oxalatotriphenylstannate anion. Tin is five-coordinate with a *cis*-trigonal-bipyramid (TBP) geometry, as the oxalate is a chelating bidentate ligand. Complex **1** is a 1-D polymer *via* hydrogen bonding between carboxylate oxygen and ammonium nitrogen. The crystallographic studies reveal that **2** is a trinuclear triphenyltin complex formed with the molar ratio of tin, acid, and amine being 3 : 2 : 1. A negative charge is delocalized among the three tins in the complex; all tins have *trans*-TBP geometry with three phenyls in the equatorial plane and two O in axial positions. The malonates in **2** are bridging tridentate with the free carbonyl hydrogen bonded to di-*iso*butylammonium through an ethanol. This coordination and significant inter- and intramolecular hydrogen bonds between ammonium and malonate result in a 3-D polymeric structure for **2**.

Keywords: Ionic; Triphenyltin; Hydrogen bonding; X-ray

1. Introduction

Organotin(IV) derivatives have been extensively studied with respect to their biological properties against bacterial, fungus, and cancer cell lines [1–5]. However, applications of the organotin derivatives were limited by their poor water solubility. Thus, solubility is a problem for biological use of organotin(IV) complexes [6]. Increasing the aqueous solubility for a series of diphenyltin complexes has been shown to increase their effectiveness. For example, the *in vitro* anti-tumor activities (ID_{50}) of ionic diphenyltin complexes of thiosalicylate, when compared to the non-ionic diphenyltin derivative, increase from 585 to 256 ng cm^{-3} against *MCF-7* cell lines and from 15,800 to 831 ng cm^{-3} against the *wiDr* cell lines [7].

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Organotin carboxylates are well-known for their structural diversity [8–11]. The properties of organotin carboxylates are influenced by the structure of ligands and coordination number of tin. Although a large number of structural studies have been carried out on triorganotin esters of monocarboxylic acids, relatively limited work has been undertaken on organotin esters of dicarboxylic acids [12]. Recently, multidentate coordination of dicarboxylic acids has attracted chemists to focus on structural studies of triorganotin dicarboxylates [13–16].

Ongoing research in our laboratory has been directed toward design and synthesis of ionic triorganotin complexes to increase their solubilities. Condensation of triphenyltin hydroxide and a diprotic acid in the presence of an amine has proven to be effective for synthesizing ionic triphenyltin complexes [17, 18]. Previously, we reported the synthesis and crystal structure of ionic triphenyltin complexes of two diprotic thiocarboxylic acids, mercaptoacetic acid, and thiolactic acid [17, 18]. In this article, we report the synthesis and X-ray crystal structures of ionic triphenyltin complexes with oxalic and malonic acids.

2. Experimental

2.1. *Materials and measurements*

Triphenyltin hydroxide was obtained from *Alfa Aesar* and purified through recrystallization in ethanol. The two dicarboxylic acids (oxalic and malonic acid) and di-*iso*butylamine were obtained from *Sigma Aldrich* and used as received.

IR spectra from 4000 to 400 cm^{-1} were recorded as KBr pellets on a Varian 3100 FTIR fitted with the Pike Technologies *Gladi* ATR attachment. The solid samples were placed directly on the diamond window for analysis. Multinuclear (^1H, ^{13}C, and ^{119}Sn) NMR studies were performed on a Bruker 400 MHz NMR spectrometer. Sample and instrument temperatures were 298 K. Proton decoupled ^{13}C and ^{119}Sn spectra were acquired with a WALTZ decoupling sequence. ^1H and ^{13}C chemical shifts were referenced to internal TMS, while ^{119}Sn chemical shifts were referenced to tetramethyltin, externally. Elemental analyzes (C, H, and Sn) were performed by Galbraith Laboratories, Inc., Knoxville, TN, USA.

2.2. *Synthesis of di-isobutylammonium* κ^2*-oxalatotriphenylstannate*

Complex **1** was prepared from reaction of the mono-ammonium salt of oxalic acid with triphenyltin hydroxide. The ammonium salt was prepared as a solution by addition, with stirring, of 2 mmoles of di-*iso*butylamine to 30 mL of acetone containing 2 mmoles of oxalic acid. To this ammonium salt solution was added, dropwise, 2 mmoles of tripehnyltin hydroxide in 20 mL acetone. A cloudy solution was formed immediately and became clear after the reaction mixture was refluxed for 2 h. Slow evaporation of the resultant solution gave crystals suitable for X-ray diffraction analyzes. Yield 59%, mp 108–109 °C. Anal. Calcd for $C_{28}H_{35}NO_4Sn$ (%): C, 59.18; H, 6.21; Sn, 20.89. Found: C, 59.47; H, 6.12; Sn, 20.64. IR (cm^{-1}): 2574, 2688, 1609 (νCOO_{as}), 1388 (νCOO_{sym}), 458 (ν_{Sn-O}). ^1H NMR ($CDCl_3$ solution): δ 0.95 ppm [12H, $NCH_2CH(C\boldsymbol{H}_3)_2$, doublet, J(HH) 6.7 Hz]; δ 1.94 ppm [2H, $NCH_2C\boldsymbol{H}(CH_3)_2$, multiplet, J(HH) 6.8 Hz]; 2.57 ppm [4H, $NC\boldsymbol{H}_2CH(CH_3)_2$, doublet, J(HH) 7.0 Hz]; 7.40–7.42 [9H, Sn–C_6H_5-*meta* + *para*]; 7.64–7.67 [6H, Sn-C_6H_5-*ortho*]. ^{13}C NMR ($CDCl_3$ solution): δ 20.2 ppm [$NCH_2CH(\boldsymbol{C}H_3)_2$]; 25.5 ppm [$NCH_2\boldsymbol{C}H(CH_3)_2$];

55.7 ppm [N$\boldsymbol{C}$H$_2$CH(CH$_3$)$_2$]; 128.3, 129.2, 136.2, 137.0 [Sn-C$_6$H$_5$]. ^{119}Sn NMR (CDCl$_3$ solution): δ −45.5 ppm.

2.3. *Synthesis of di-isobutylammonium μ^2-malonatotriphenylstannate*

Two millinoles of triphenyltin hydroxide was dissolved in a 125 mL round bottom flask with 30 mL of hot ethanol. The resultant solution was mixed with malonic acid (2 millinoles) followed by addition of an equal molar amount of di-*iso*butyl amine. The reaction mixture was refluxed for 2 h and then allowed to cool to room temperature. Fine crystals suitable for X-ray analysis were obtained overnight. Yield 64%, mp 177–179 °C. Anal. Calcd for $C_{70}H_{75}NO_9Sn_3$ (%): C, 58.77; H, 5.28; Sn, 24.89. Found: C, 58.62; H, 5.18; Sn, 24.80. IR (cm^{-1}): 3158, 2694, 2582, 1660, 1591 (νCOO_{as}), 1420 (νCOO_{sym}), 462 (ν_{Sn-O}). ^{1}H NMR (CDCl$_3$ solution): δ 0.95 ppm [12H, NCH$_2$CH(C$\boldsymbol{H}_3$)$_2$, doublet, *J*(HH) 6.7 Hz]; 1.94 ppm [2H, NCH$_2$C$\boldsymbol{H}$(CH$_3$)$_2$, nonet, *J*(HH) 6.8 Hz]; 2.57 ppm [4H, NC$\boldsymbol{H}_2$CH(CH$_3$)$_2$, doublet, *J*(HH) 7.0 Hz]; 3.46 ppm [4H, COC$\boldsymbol{H}_2$CO, singlet], 7.40–7.42 [9H, Sn-C$_6$H$_5$-*meta* + *para*]; 7.64–7.67 [6H, Sn–C$_6$H$_5$-*ortho*]. ^{13}C NMR (CDCl$_3$ solution): δ 20.4 ppm [NCH$_2$CH($\boldsymbol{C}$H$_3$)$_2$]; 26.1 ppm [NCH$_2$$\boldsymbol{C}$H(CH$_3$)$_2$]; 55.8 ppm [N$\boldsymbol{C}H_2$CH(CH$_3$)$_2$]; 41.6 ppm [CO$\boldsymbol{C}H_2$CO]; 128.9 [Sn-C$_m$, $J(^{119}Sn{-}^{13}C) = 13.3$ Hz]; 130.1 [Sn–C$_p$, $J(^{119}Sn{-}^{13}C) = 63.9$ Hz]; 136.8 [Sn–C$_o$, $J(^{119}Sn{-}^{13}C) = 48.5$ Hz]; 138.0 [Sn–C$_i$, $J(^{117/119}Sn{-}^{13}C) = 617.8/647.4$ Hz]; 173.4 [COO]. ^{119}Sn NMR (CDCl$_3$ solution): δ −103.9 ppm.

2.4. *X-ray crystallography*

Colorless needle like crystals of **1** and **2** were mounted on a sealed tube and used for data collection. Crystal structure data were collected using a Bruker SMART Apex II X-ray diffractometer with an Oxford Cryostream low-temperature device using graphite-monochromated Cu Kα radiation. The data were corrected for Lorentz and polarization effects. The structure was solved by direct methods (SHELXS97) [19] and refined by full-matrix least-squares on all F^2 data (SHELXL97) [19]. Non-hydrogen atoms were refined with anisotropic thermal parameters, and hydrogens included from the geometry of the molecules were refined isotropically. A summary of the crystal data, experimental details, and refinement results are listed in table 1.

3. Results and discussion

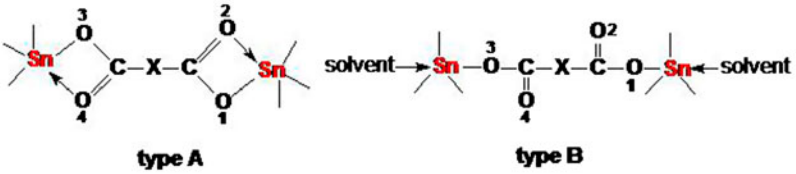
3.1. *Crystal structures of 1 and 2*

The majority of the studied triphenyltin aliphatic carboxylates in the solid state form linear polymers [8, 9]. Carbonyl groups in carboxylates have strong coordination ability either intramolecularly to form a monomeric structure with *cis*-trigonal bipyramidal (TBP) geometry around tin, or intermolecularly to form a polymeric chain with *trans*-TBP geometry around tin.

In the case of dicarboxylates, six different bonding modes have been reported for triorganotin dicarboxylates [20–26]. Triorganotin esters of tetradentate dicarboxylates can be either monomeric (scheme 1) or polymeric chains (scheme 2) depending on the coordination of carboxylate.

Table 1. Crystallographic data and structure refinement parameters for **1** and **2**.

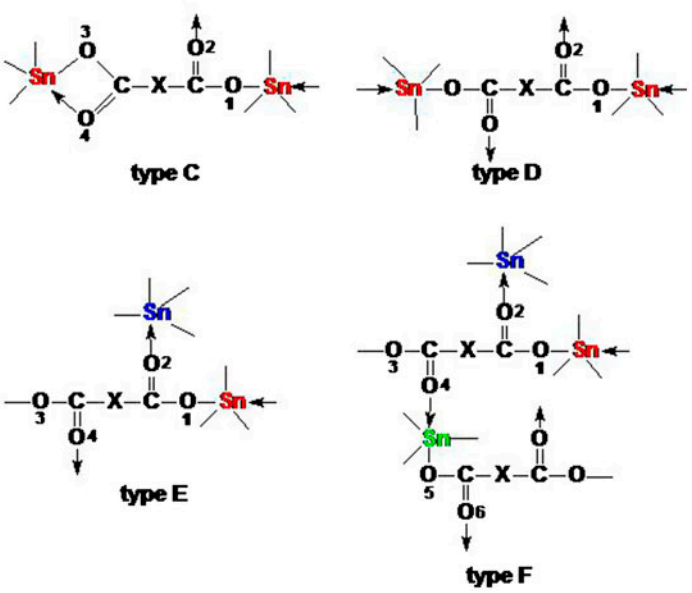
Complex **1**	Complex **2**
$C_{28}H_{35}NO_4Sn$	$C_{35}H_{37.50}N_{0.50}O_{4.50}Sn_{1.50}$
$M_r = 1136.52$	$M_r = 715.19$
Triclinic, $P1$	Orthorhombic, $Pna2_1$
$a = 9.0036(1)$ Å	$a = 23.1910(3)$ Å
$b = 17.9448(3)$ Å	$b = 19.9363(3)$ Å
$c = 18.1028(3)$ Å	$c = 14.1171(2)$ Å
$\alpha = 103.419(1)°$	$\alpha = 90°$
$\beta = 91.074(1)°$	$\beta = 90°$
$\gamma = 96.502(1)°$	$\gamma = 90°$
$V = 2823.61(7)$ Å^3	$V = 6526.94(16)$ Å^3
$Z = 2$	$Z = 8$
$F\,(000) = 1168$	$F\,(000) = 2896$
Cu $K\alpha$ radiation, $\lambda = 1.54178$ Å	Cu $K\alpha$ radiation, $\lambda = 1.54178$ Å
$\mu = 7.441$ mm^{-1}	$\mu = 9.50$ mm^{-1}
$T_{min} = 0.1042$, $T_{max} = 0.7967$	$T_{min} = 0.169$, $T_{max} = 0.702$
47,708 measured reflections	11,710 measured reflections
9785 independent reflections	10,780 independent reflections
8087 reflections with $I > 2\sigma(I)$	71,478 reflections with $I > 2\sigma(I)$
$R_{int} = 0.0485$	$R_{int} = 0.060$
$R[F^2 > 2\sigma(F^2)] = 0.029$	$R[F^2 > 2\sigma(F^2)] = 0.037$
$wR(F^2) = 0.077$	$wR(F^2) = 0.104$
$S = 1.02$	$S = 1.03$



Scheme 1. Possible bonding modes in monomeric triorganotin dicarboxylates.

Monomeric *bis*(triorganotin) dicarboxylates will be formed if the carbonyl is prevented from approaching a tin in a neighboring molecule due to steric hindrance. The carboxylate in this bonding type (A) is reported as chelating bidentate and the geometry around tin is *cis*-TBP [20]. Interesting coordination competition between carbonyl and solvent has been observed [21]. The coordination of carbonyl groups to tin can be interrupted by a solvent with coordination ability. The competition will favor solvent if there is compensation for the carbonyl to form hydrogen bonding. For example, binuclear monomeric structure (type B) has been reported for *bis*(triorganotin) dicarboxylate complexes when the coordination of the carbonyl groups is replaced by a solvent molecule such as water in *bis*(triphenyltin) succinate [21].

Polymeric structures can also be formed through intermolecular Sn-O-C=O→Sn bonds for dicarboxylates [22]. When carboxylates are bridging bidentate, two types of polymeric structures are reported [23–25]. Zigzag polymeric chains (type C) have been reported as the propagation of the polymer chain *via* one carboxylate was terminated due to steric hindrance. In this bonding mode, one carboxylate is chelating bidentate while the other is bridging bidentate. Therefore, one tin is *cis*-TBP while the other adopts *trans*-TBP geometry with the three R-groups in the equatorial plane and two O in axial positions [23]. A macrocyclic structure will be obtained if there is no steric hindrance or solvent to



Scheme 2. Possible bonding modes in polymeric triorganotin dicarboxylates.

interrupt the coordination of both carboxylates [24, 25]. Bridging tetradentate dicarboxylates are reported to have either type D or E [24, 25] (scheme 2), or type F [26], a trinuclear complex which is a combination of type D and E. In these cases, tins adopt *trans*-TBP geometry. The crystal structures for **1** and **2** show new types of coordination in the chemistry of triorganotin dicarboxylates.

The single-crystal X-ray data for **1** and **2** are summarized in table 1 and bond distances and angles in tables 2 and 3. ORTEP views of the two complexes are shown in figures 1 and 2, respectively.

The X-ray studies revealed clearly that **1** is a new type of pseudo-polymeric structure for triorganotin dicarboxylate in which a cyclic ring is formed as both of the carboxylates coordinate to the same tin. Both carboxylates are monodentate coordinating to Ph_3Sn, while the two free carbonyls are hydrogen bonded to di-*iso*butylammonium anions (figure 3). **1** consists of a di-*iso*butylammonium cation and an oxalatotriphenylstannate. The anionic tin complex has a distorted *cis*-trigonal bipyramid geometry with two carbons and one oxygen occupying equatorial positions, and O and phenyl occupying the axial positions, similar to the di-*cyclo*hexylammonium thiolactatotriphenylstannate reported [18]. The Sn–C bond lengths for the two equatorial phenyl groups (2.135(3) and 2.142(3) Å) are slightly shorter than for the axial phenyl (2.161(3) Å). The axial skeleton is slightly bent with the C3–Sn1–O1 angle of 160.84(9)°. The O7–Sn1–O1 angle was significantly reduced (72.72(8)°) due to steric and electronic effects in the oxalatotriphenylstannate. Complex **1** crystallizes as two polymorphs, 1a and 1b (figure 1). The two polymorphs have interaction through intermolecular hydrogen bonding between ammonium and carboxylate to form a loose pseudo-1-D polymer chain along axis *a* (figure 4). Important hydrogen bonding parameters for **1** are listed in table 4. There are two significant hydrogen bonds between the cation and anion, the N on ammonium hydrogen bonded to carbonyl O on carboxylate and to the carboxyl O from an adjacent triphenylstannate (figure 3).

Table 2. Selected bond lengths and angles (Å, °) for **1**.

Sn(1)–O(1)	2.087(2)	O(1)–Sn(1)–C(15)	114.41(11)
Sn(1)–C(15)	2.135(3)	O(1)–Sn(1)–C(9)	118.78(11)
Sn(1)–C(9)	2.142(3)	C(15)–Sn(1)–C(9)	119.19(11)
Sn(1)–C(3)	2.161(3)	O(1)–Sn(1)–C(3)	88.14(10)
Sn(1)–O(3)	2.320(2)	C(15)–Sn(1)–C(3)	105.58(12)
Sn(2)–O(5)	2.131(2)	C(9)–Sn(1)–C(3)	103.46(12)
Sn(2)–C(31)	2.142(3)	O(1)–Sn(1)–O(3)	72.69(8)
Sn(2)–C(43)	2.147(3)	C(15)–Sn(1)–O(3)	82.75(10)
Sn(2)–C(37)	2.171(3)	C(9)–Sn(1)–O(3)	86.62(10)
Sn(2)–O(7)	2.230(2)	C(3)–Sn(1)–O(3)	160.83(9)
O(1)–C(2)	1.295(4)	O(5)–Sn(2)–C(31)	112.87(12)
O(2)–C(2)	1.202(4)	O(5)–Sn(2)–C(43)	125.44(12)
O(3)–C(1)	1.259(4)	C(31)–Sn(2)–C(43)	117.06(11)
O(4)–C(1)	1.233(4)	O(5)–Sn(2)–C(37)	82.89(10)
O(5)–C(30)	1.284(4)	C(31)–Sn(2)–C(37)	104.60(11)
O(6)–C(30)	1.222(4)	C(43)–Sn(2)–C(37)	103.96(12)
O(7)–C(29)	1.266(4)	O(5)–Sn(2)–O(7)	72.50(8)
O(8)–C(29)	1.215(4)	C(31)–Sn(2)–O(7)	89.58(10)
		C(43)–Sn(2)–O(7)	87.06(11)
		C(37)–Sn(2)–O(7)	154.95(10)

Complex **2** has an unusual stoichiometric ratio of 3 : 2 : 1 for triphenyltin, malonate, and di-*iso*butylammonium. All tins have *trans*-TBP geometry with three phenyls occupying the equatorial position and two O from bridging bidentate carboxylates occupying the axial positions (O1–Sn1–O3 171.20(15)°, O1–Sn2–O3 174.00(11)° and O1–Sn3–O3 171.47 (16)°). Short and slightly longer tin–oxygen distances are observed for Sn1 (2.152(5), 2.344 (4) Å), and Sn3 (2.203(5), 2.324(4) Å) as reported in literature for polymeric triorganotin carboxylates in which the longer Sn–O is considered as a dative bond and the shorter one is considered as a covalent bond; nearly identical Sn–O lengths are observed for Sn2 (2.235 (4), 2.249(4) Å), which is an indication of both Sn–O bonds being covalent. However, there is no significant difference between dative and covalent Sn–O bonds, suggesting the observed negative charge on Sn2 is dispersed on all three tins. Two different carboxylates are observed for the malonates, with one carboxylate having two nearly identical C–O bonds (C3–O: 1.264(7), 1.262(7); C4–O: 1.268(7), 1.253(7) Å) while the other one has two slightly different C–O bond lengths (C1–O: 1.213(7), 1.289(7); C6–O: 1.236(7), 1.282(7) Å), indicating a bridging tridentate mode for malonate in which one carboxylate is bidentate while the other one is monodentate as depicted in scheme 3. This type of coordination allows propagation of the polymer *via* coordination of carbonyl-O4 and O6 to give a 2-D polymer layer (figure 4). This bonding pattern makes enough spaces in the lattice to include ethanol molecules in the unit cell as shown in the crystal structure (figure 2). O2 and O8 of the carbonyls are free of coordination to tin; the lack of coordination is apparently caused by availability of hydrogen bonding to di-*iso*butylammonium or ethanol (figure 5), linking each polymeric layer into a 3-D polymer network (scheme 3). Important hydrogen bond parameters for **2** are listed in table 5.

3.2. *IR spectroscopy*

The absence of broad bands around 2500–2800 cm^{-1} in infrared spectra of both complexes, due to OH absorption of COOH, supports coordination of carboxylate to tin. Sharp bands were observed in both complexes at 460 cm^{-1}, indicating formation of Sn–O bonds [27].

Table 3. Selected bond lengths and angles (Å, °) for **2**.

Sn1–C7	2.112(5)	C7–Sn1–C19	116.7(2)
Sn1–C19	2.119(6)	C7–Sn1–C13	118.1(2)
Sn1–C13	2.134(6)	C19–Sn1–C13	124.0(2)
Sn1–O1	2.152(5)	C7–Sn1–O1	88.6(2)
Sn1–O4^{i}	2.344(4)	C19–Sn1–O1	92.4(2)
Sn2–C25	2.138(6)	C13–Sn1–O1	99.4(2)
Sn2–C31	2.143(6)	C7–Sn1–O4^{i}	86.84(19)
Sn2–C37	2.155(4)	C19–Sn1–O4^{i}	82.93(18)
Sn2–O3	2.235(4)	C13–Sn1–O4^{i}	89.4(2)
Sn2–O5	2.249(4)	O1–Sn1–O4^{i}	171.20(15)
Sn3–C43	2.124(6)	C25–Sn2–C31	110.33(18)
Sn3–C49	2.132(6)	C25–Sn2–C37	125.3(3)
Sn3–C55	2.134(5)	C31–Sn2–C37	124.3(3)
Sn3–O7	2.203(5)	C25–Sn2–O3	84.89(19)
Sn3–O6	2.324(4)	C31–Sn2–O3	93.3(2)
O1–C1	1.289(7)	C37–Sn2–O3	92.9(3)
O2–C1	1.213(7)	C25–Sn2–O5	90.34(19)
O3–C3	1.264(7)	C31–Sn2–O5	84.9(2)
O4–C3	1.262(7)	C37–Sn2–O5	92.9(3)
O4–Sn1^{ii}	2.344(4)	O3–Sn2–O5	174.00(11)
O5–C4	1.268(7)	C43–Sn3–C49	125.5(2)
O6–C4	1.253(7)	C43–Sn3–C55	116.9(2)
O7–C6	1.282(7)	C49–Sn3–C55	117.0(2)
O8–C6	1.236(7)	C43–Sn3–O7	91.5(2)
C1–C2	1.541(9)	C49–Sn3–O7	98.0(2)
C2–C3	1.515(8)	C55–Sn3–O7	87.9(2)
C4–C5^{iii}	1.511(8)	C43–Sn3–O6	83.03(19)
C5–C4^{iv}	1.511(8)	C49–Sn3–O6	90.6(2)
C5–C6	1.516(9)	C55–Sn3–O6	88.73(19)
C7–C12	1.389(8)	O7–Sn3–O6	171.47(16)
C7–C8	1.412(8)	C1–O1–Sn1	115.2(4)
C8–C9	1.404(8)	C3–O3–Sn2	122.5(4)
C9–C10	1.393(9)	C3–O4–Sn1^{ii}	135.3(4)
C10–C11	1.367(9)	C4–O5–Sn2	121.6(4)
C11–C12	1.410(8)	C4–O6–Sn3	135.4(3)
		C6–O7–Sn3	111.9(4)
		O2–C1–O1	124.7(6)
		O4–C3–O3	122.7(5)
		O6–C4–O5	123.3(5)
		O6–C4–C5^{iii}	120.5(5)
		O5–C4–C5^{iii}	116.2(5)
		C4^{iv}–C5–C6	115.3(5)

Symmetry codes: (i) $-x$, $-y$, $z-1/2$; (ii) $-x$, $-y$, $z+½$; (iii) $-x$, $-y+1$, $z+1/2$; (iv) $-x$, $-y+1$, $z-1/2$.

Due to the presence of strong intramolecular hydrogen bonding, the stretching vibration of amino N–H in both complexes is lowered and broadened, and the weak broad bands observed at 2400–2700 cm^{-1} in both IR spectra are attributed to these restricted vibrations, an indication of ammonium in the complex. A broad absorption at 3300 cm^{-1} for **2**, assignable to ν(OH), was observed, suggesting presence of ethanol intermolecularly H-bonded.

The mode of coordination of carboxylate to metals including tin has been deduced using the differences between the asymmetric and symmetric stretch of the OCO group [28]. The magnitude of $\Delta\nu = \nu_{asym}$ (OCO) − ν_{sym} (OCO) of 250 cm^{-1} or over would indicate that carboxylate is monodentate, while Δν of 150 cm^{-1} or less would indicate that carboxylate is bidentate. A difference of 150–200 cm^{-1} is indicative of bidentate carboxylate with a

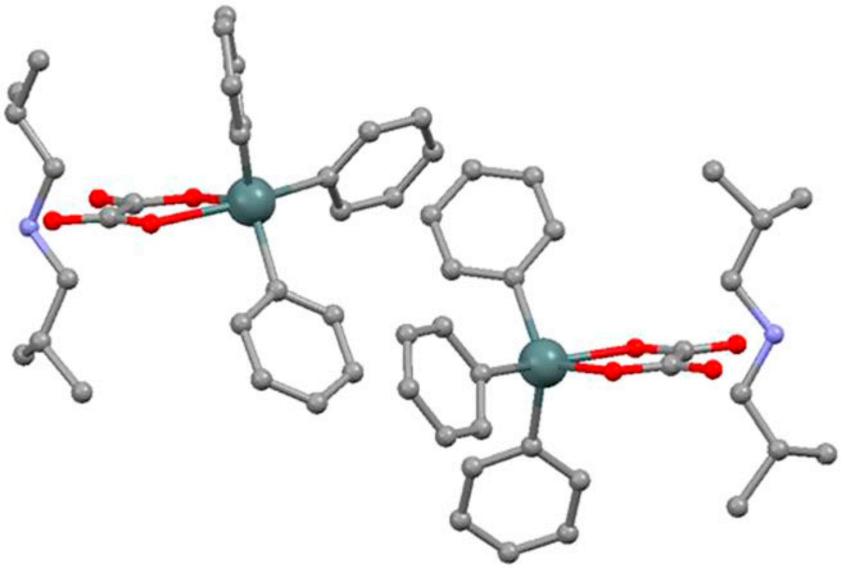


Figure 1. Molecular structure of **1** showing the atom labeling scheme. Ellipsoids are drawn at the 35% probability level. Hydrogens are omitted for clarity.

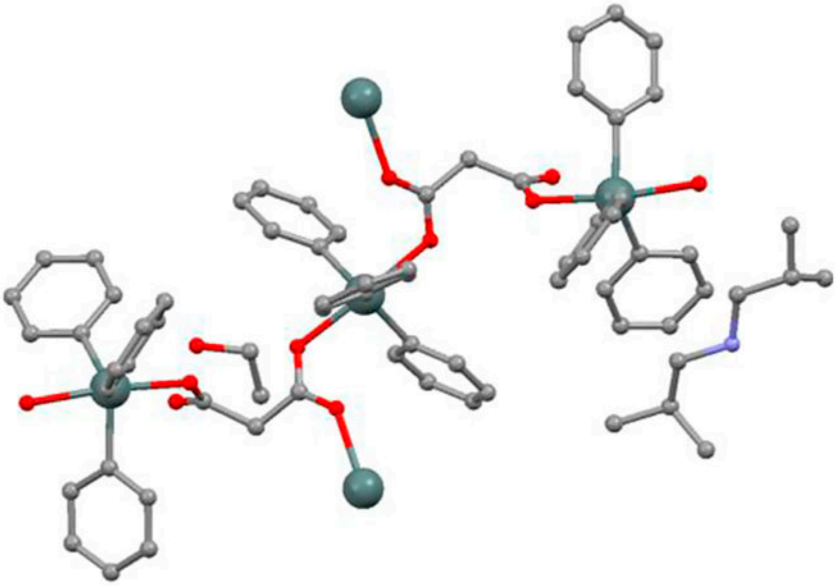


Figure 2. Molecular structure of **1** showing the atom labeling scheme. Ellipsoids are drawn at the 35% probability level. Hydrogens are omitted for clarity.

bridging configuration [29, 30]. However, in solid state hydrogen bonding for C=O could cause ambiguity of the assignment. Both complexes have multi bands for OCO because the two carboxylates have different coordination as shown in crystal structures. In **1**, the

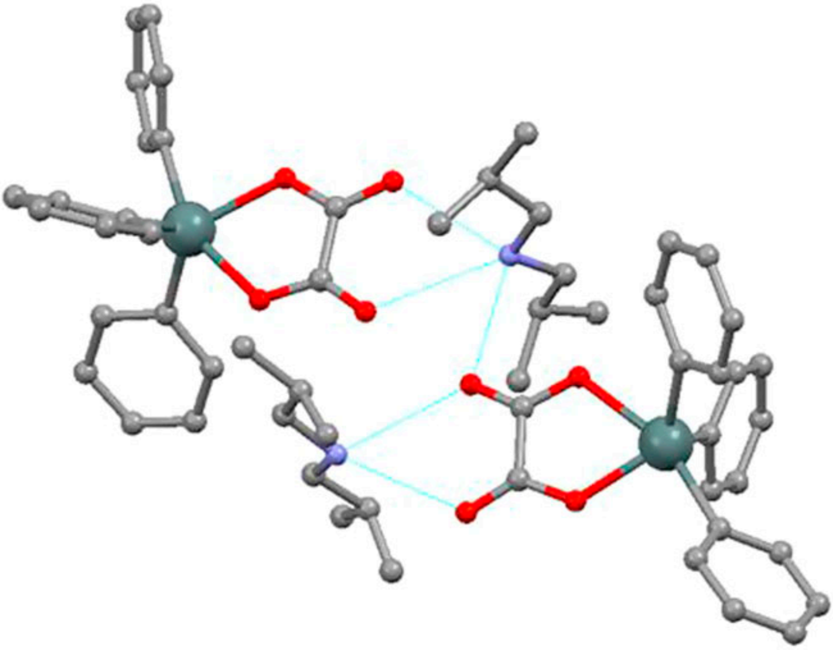


Figure 3. Intermolecular hydrogen bonding formed in **1**.

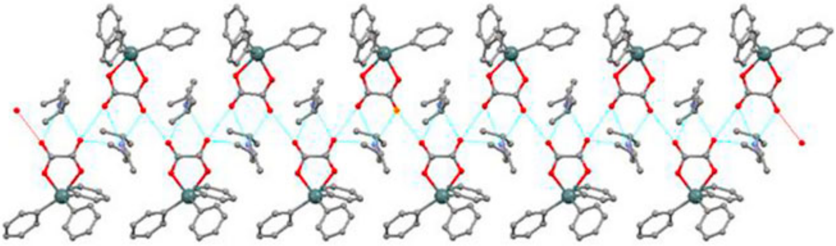
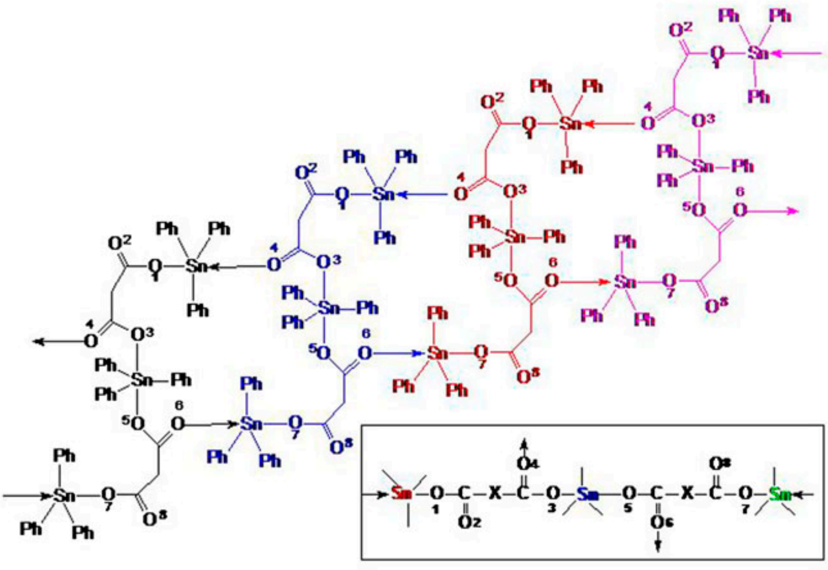


Figure 4. Perspective view of the pseudo polymer chain formed *via* hydrogen bonding in **1**.

Table 4. Hydrogen-bond geometry (Å, °) for **1**.

D–H···*A*	*D*–H	H···*A*	*D*···*A*	*D*–H···*A*
N1–H1*A*···O6^{i}	0.90	2.06	2.956(4)	175
N1–H1*B*···O8	0.90	2.08	2.960(4)	166
N1–H1*B*···O4^{i}	0.90	2.54	3.015(4)	114
N2–H2*A*···O6^{ii}	0.90	2.21	3.080(4)	162
N2–H2*A*···O2^{iii}	0.90	2.50	3.047(4)	120
N2–H2*B*···O8^{iii}	0.90	2.06	2.944(4)	168

Symmetry codes: (i) *x*, *y* − 1, *z*; (ii) *x*−1, *y*, *z*; (iii) *x*, *y* + 1, *z*.



Scheme 3. Polymeric bonding mode for **2** showing the propagation of the polymer chain in two directions.

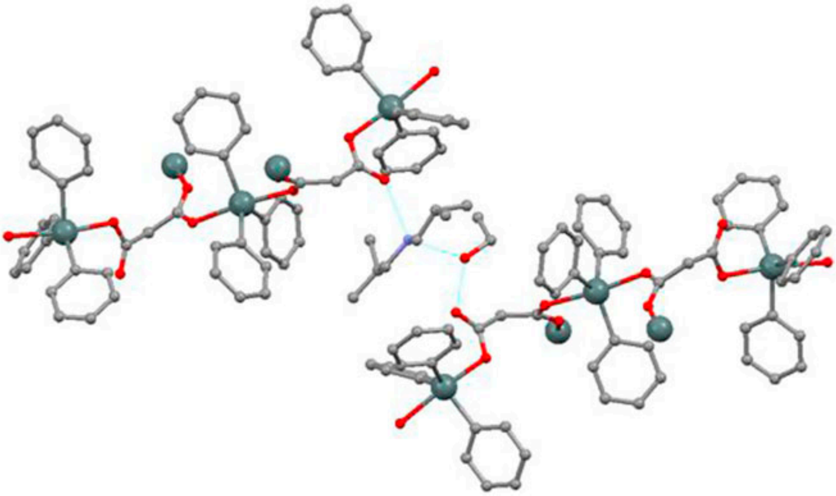


Figure 5. Hydrogen bonding formed among diisobutylammonium, ethanol and carbonyl of the carboxylate in **2**.

observed difference of 218 cm^{-1} could be ascribed to hydrogen bonding interaction between the carbonyl group and the ammonium rather than coordination of C=O to tin. The observed difference of 171 cm^{-1} for **2** would indicate that one carboxylate in malonate is a bridged ligand, suggesting that carboxylate oxygen is bonded to tin, while the carbonyl oxygen is bonded to ammonium through H-bonding. The IR data are therefore supportive of the solid-state structure as described in crystallographic studies.

Table 5. Hydrogen-bond geometry (Å, °) for **2**.

D–H···*A*	*D*–H	H···*A*	*D*···*A*	*D*–H···*A*
O9–H9*A*···N1[i]	0.84	2.00	2.741(8)	146
N1–H1*A*···O8[ii]	0.92	1.76	2.678(6)	172
N1–H1*B*···O9[iii]	0.92	1.84	2.741(8)	164

Symmetry codes: (i) $x-1/2, -y+1/2, z-1$; (ii) $x+1, y, z+1$; (iii) $x+1/2, -y+1/2, z+1$.

3.3. *NMR spectroscopies*

The (^{1}H, ^{13}C, and ^{119}Sn) NMR spectra of the two complexes were recorded in $CDCl_3$. Assignment of the proton resonances were based on their intensity, multiplicity, and coupling constants. The proton–proton connectivity was determined from correlated spectroscopy experiments (H, H–COSY). The number of protons calculated from integration of the spectra is in agreement with those calculated for the molecule. The protons on phenyl show two groups of multiplets, one at 7.55–7.75 ppm assigned to *ortho*–H and another at 7.25–7.45 ppm assigned to *meta*, and *para*-H, with relative intensity of 2 : 3. The ^{1}H NMR spectra of **1** and **2** show downfield chemical shifts for NH_2 of di-*iso*butylammonium supporting the existence of hydrogen bonds between NH_2 and carboxylate in both complexes. ^{119}Sn chemical shifts have also been correlated with the coordination number of tin. The ^{119}Sn chemical shift's range for four-coordinate trialkyltin compounds is +200 and −60 ppm, while five-coordinate trialkyltin is −100 to −300 ppm [31, 32]. Complex **1** exhibits a single-sharp resonance at −45.5 ppm, characteristic for four-coordinate triphenyltin. This shows that the *cis*-TBP geometry around tin in **1** is not stable and will be dissociated to a more stable tetrahedral geometry. ^{119}Sn NMR spectrum of **2** shows only a singlet around −103.9 ppm, which is in contradiction with the trinuclear complex shown in the crystal structure of **2**. The explanation for this observation is that polymeric **2** is dissociated into four-coordinate triphenyltin complex in solution [31, 32]. The dissociation is also supported by observed J(^{13}C–^{119}Sn) coupling constant of 747.4 Hz, typical for four-coordinate triphenyltin compounds [31, 32].

4. Conclusions

Two ionic triphenyltin dicarboxylates were synthesized. The carboxylates show different coordination in two structurally similar dicarboxylates (oxalate and malonate), with oxalate chelating bidentate while malonate is bridging tridentate. The free carbonyl groups in **1** and **2** have interaction with ammonium cations *via* hydrogen bonding. In solid state, **1** is a *pseudo*-1-D polymeric structure linked through hydrogen bonds between carbonyl and di-*iso*butylammonium, different from the 1-D polymer formed through bidentate bridging of carboxylates for *trans*-TBP triorganotin monocarboxylates [8–11]. The *cis*-TBP geometry around tin in **1** is not common for triorganotin dicarboxylates, as dicarboxylates tend to be bridging bidentate to form *tran*s-TBP around tin. Complex **1** is unique as all tins have *cis*-TBP environment. This *cis* configuration has been reported for two dinuclear tin complexes, dicyclohexylammonium μ-oxalatotricyclohexylstannate [33], and tetramethyl ammonium μ-oxalatotriphenylstannate [34], in which one tin is *cis*-TBP while the other tin has normal *trans*-TBP geometry. Complex **2** is an interesting trinulcear ionic triphenyltin complex with all tins being *trans*-TBP as expected; two malonates are involved in intermolecular coordination and one di-*iso*butylammonium cation exists in the lattice as the counter ion. A 3-D polymeric network is formed through intermolecular coordination between tin and malonate and *via* hydrogen bonding between ammonium, free ethanol, and non-bonding carbonyls. Similar ionic triorganotin dicarboxylates have been reported in literature for *bis*(dicyclohexylammonium) *tris*malonato*tetrakis*(tributylstannate) [35] and *bis*(dicyclohexylammonium) *tris*oxalato*tetrakis*(tributylstannate) [36]. However, both complexes are dissociated into four-coordinate triphenyltin in solution.

Supplementary material

CCDC-927798 and CCDC-927797 contains crystallographic data for **1** and **2**. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Center (CCDC), 12 Union Road, Cambridge CB2 1 EZ, UK; Fax:+44(0)1223-336033; E-mail: deposit@ccdc.cam.ac.uk).

Funding

Financial supports from the National Science Foundation MRI (Grant # CHE-1040094) and UDC STEM program are gratefully acknowledged.

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