CRYSTAL STRUCTURE OF TRIPHENYLTIN (IV) FORMATE POLYMER, $(HCO_2SnPh_3)_n$

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Abstract: The title polymer $[HCO_2Sn(C_6H_5)_3]_n$ was isolated by serendipitous from reaction in ethanol 96 % between bis-(monocyclohexyl ammonium) 2-carboxyethyl hydrogen phosphonate, $\{(CyNH_3)_2[CO_2CH_2CH_2PO_2(OH)]\}$ and triphenyltin chloride, $SnPh_3Cl$. The polymer crystallizes in the monoclinic space group $P2_1/n$ with $Z = 4$, $a = 14.7091\ (18)$ Å, $b = 15.4133\ (19)$ Å, $c = 14.7639\ (18)$ Å, $\beta = 94.242\ (2)°$ and $V = 3338.0\ (7)$ Å^3. The structure consists of an infinite chain propagating along the crystallographic a-axis direction with bidentate formate anions. The O_2SnC_3 core is organized into a *trans*-trigonal bipyramidal like-arrangement.

Keywords: infinite chain, *trans*-trigonal bipyramidal, bidentate formate anions, triphenyltin

1. INTRODUCTION

Numerous compounds belonging to the organotin (IV) family have been to be subject of applications in several fields: their industrial as well as their biocidal properties [1-3], their biological properties against bacteria, fungi and cancer cell lines [4-5] have been reported. Triphenyltin (IV) or trimethyltin (IV) derivatives or complexes exist as monomers with a four or five coordinated tin (IV) atom or polymers with a five coordinated tin (IV) atom. Many papers dealing with organotin (IV) chemistry and the coordinating ability of formate ions have been reported so far [6-11]. The crystal structure of HCO_2SnPh_3 has been determined by Molloy and coworkers in the monoclinic space group $P2_1/c$ with two independent molecules in the asymmetric unit [12].

Our group has yet published some papers dealing with $SnMe_3$ and $SnPh_3$ residues containing derivatives and complexes [13-16].

As continuation of this work, we have initiated here the study of the interactions between bis-(monocyclohexyl ammonium) 2-carboxyethyl hydrogen phosphonate, $\{(CyNH_3)_2[CO_2CH_2CH_2PO_2(OH)]\}$ and triphenyltin chloride, $SnPh_3Cl$ which afforded serendipitously crystals of the polymeric chain $[HCO_2SnPh_3]_n$ whose crystal structure is reported herein (Figure 1).

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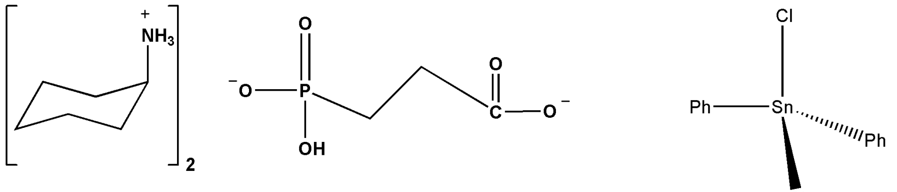
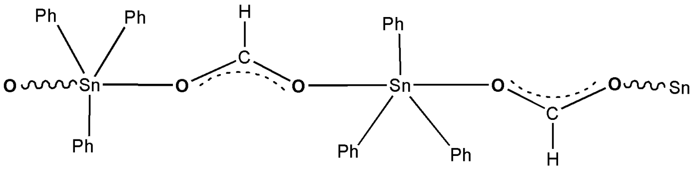


bis-(monocyclohexyl ammonium) 2-carboxyethyl hydrogen phosphonate

triphenyltin chloride



Triphenyltin formate polymer

Fig. 1. Molecular representations of bis-(monocyclohexyl ammonium) 2-carboxyethyl hydrogen phosphonate, triphenyltin chloride reagents and poly[triphenyl formate] related to this study.

2. EXPERIMENTAL SETUP

Synthesis of $(HCO_2SnPh_3)_n$

All chemicals were purchased and used as received, without any further purification. The isolation of the polymer follows two steps. The salt bis-(monocyclohexyl ammonium) 2-carboxyethyl hydrogen phosphonate, $\{(CyNH_3)_2[CO_2CH_2CH_2PO_2(OH)]\}$ was preliminary synthesized by partially neutralizing 2-carboxyethyl phosphonic acid with monocyclohexylamine in a 1:2 molar stoichiometry. The poly[triphenyl formate] was then prepared from the reaction of $\{(CyNH_3)_2[CO_2CH_2CH_2PO_2(OH)]\}$ (0.100 g, 0.199 mmol) with $SnPh_3Cl$ (0.070 g, 0.199 mmol) in 20 mL of ethanol 96%. The proposed chemical reaction is as follow (equation (1)):

$$\left\{\left(C_yNH_3\right)_2[CO_2CH_2CH_2PO_2(OH)]\right\} + SnPh_3Cl + 2H_2O \rightarrow HCO_2SnPh_3 + Cy_2NH_2Cl + \\ +(OH)CH_2CH_2PO(OH)_2 + Cy_2NH_2OH \qquad (1)$$

After some days of a slow solvent evaporation at room temperature 298 K, colorless crystals suitable for X-ray diffraction analysis were obtained.

X-ray crystallography of $(HCO_2SnPh_3)_n$

A crystal of approximate dimensions 0.200 × 0.120 × 0.100 mm was used for data collection. The X-ray crystallographic data were collected using a Bruker *SMART* CCD area detector diffractometer, at $T = 100$ K. Data were measured using ω scans using Mo*K*α radiation (λ = 0.71073 Å) using a collection strategy to obtain a hemisphere of unique data determined by Bruker *SMART* [17]. Cell parameters were determined and refined using the Bruker *SAINT* program [18]. Data were corrected for absorption by multi-scan absorption correction using *SADABS* [19]. The structure was solved using *SHELXS* [20] and the structure refined using least-squares minimization *SHELXL2013* [21].

Program used for the representation of the molecular representations: *Olex2* [22]. The Crystallographic data and experimental details for structural analyses are summarized in Table 1. Selected bond lengths and angles are listed in Tables 2.

CCDC 2001247 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif, or by e-mailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK.

Table 1. Crystal data and structure refinement for **$(HCO_2SnPh_3)_n$**.

Parameters	**Compound**
Empirical formula	$C_{38}H_{32}O_4Sn_2$
Formula weight	790.01
Temperature	100 (2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$P2_1/n$
Unit cell dimensions	a = 14.7091 (18) Å
	α = 90°
	b = 15.4133 (19) Å
	β = 94.242 (2)°
	c = 14.7639 (18)Å
	γ = 90°
Volume	3338.0 (7) $Å^3$
Z	4
Calculated density	1.572 g cm^{-3}
Absorption coefficient	1.535 mm^{-1}
F(000)	1568
Crystal size	0.200 × 0.120 × 0.100 mm^3
Theta range for data collection	2.42–30.68°
Limiting indices	$-20 \leq h \leq 20$, $-22 \leq k \leq 22$, $-20 \leq l \leq 20$
Reflections collected/unique	37913/9784
R_{int}	0.0555
Absorption correction	Multi-scan
Max. and min. transmission	0.746 and 0.641
Refinement method	Least-squares matrix: full
Data/restraints/parameters	9784/0/398
Goodness-of-fit on F^2	1.088
Final R indices ($I > 2\sigma(I)$)	R_1 = 0.0451, wR_2 = 0.1185
R indices (all data)	R_1 = 0.0504, wR_2 = 0.1143
Largest diff. peak and hole	1.702 and -2.345 e $Å^{-3}$

$w = 1/[\sigma^2(F_o^2) + (0.0602P)^2 + 5.0135P]$ where $P = (F_o^2 + 2F_c^2)/3$

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

Bonds		**Angles**	
Atom-Atom	Bond length	Atom-atom-atom	Angle value
Sn1—C1	2.115 (5)	C1—Sn1—C13	119.11 (18)
Sn1—C7	2.126 (4)	C7—Sn1—C13	121.77 (17)
Sn1—C13	2.129 (5)	C1—Sn1—O1	87.37 (15)
Sn1—O1	2.231 (3)	C7—Sn1—O1	91.63 (15)
Sn1—O3	2.306 (3)	C13—Sn1—O1	96.80 (16)
Sn2—$O2^i$	2.289 (3)	C1—Sn1—O3	86.39 (15)
Sn2—O4	2.225 (4)	C7—Sn1—O3	87.78 (15)
O2—$Sn2^{ii}$	2.289 (3)	C13—Sn1—O3	89.82 (15)
Sn2—C31	2.121 (5)	O1—Sn1—O3	172.54 (13)
Sn2—C19	2.136 (5)	C25—Sn2—O4	96.14 (16)
Sn2—C25	2.141 (4)	C31—Sn2—$O2^i$	85.68 (15)
C35—C36	1.391 (7)	C19—Sn2—$O2^i$	87.00 (16)
O1—C37	1.255 (6)	C25—Sn2—$O2^i$	90.55 (15)
O2—C37	1.244 (6)	O4—Sn2—$O2^i$	172.93 (13)

3. RESULTS AND DISCUSSION

The structure of triphenyltin formate crystallizes as colourless block-like crystals in the monoclinic space group $P2_1/n$. The asymmetric unit of the title compound consists of two formate anions and two $SnPh_3$ moieties coordinated by oxygen formate anions (Figure 2).

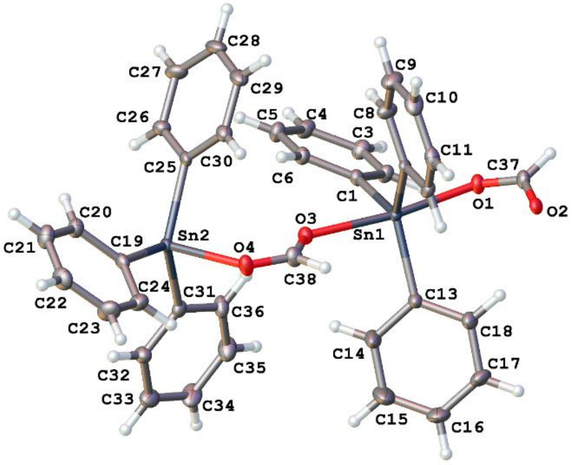


Fig. 2. The molecular structure of $(HCO_2SnPh_3)_n$ showing the atom labelling. Displacement ellipsoids are drawn at the 50% probability level.

In the structure of the polymer, each Sn atom is five-coordinated by three phenyl groups and two oxygen atoms. Thus, the O_2SnC_3 core adopts a *trans*-trigonal bipyramidal arrangement with phenyl groups at the basal plane and O formate atoms occupying the trans-positions. These are two different tin centres Sn (1) and Sn (2) chemically identical. The C—O bonds within the formate ion show a π delocalization and are in the range of the reported lengths [12, 23-26]. The O—Sn—O bond angles of 172.54 (13) and 172.93 (13) deviate strongly from the ideal value evidencing a great distortion, while the two sums of the equatorial angles at both tin centres of 359.64° and 359.52° very close to 360, indicate an almost planarity of the SnC_3 frame. The Sn-O distances Sn(1)—O(1) = 2.231 (3), Sn(1)—O(3) = 2.306 (3), Sn2—O2i = 2.289 (3) and Sn2—O(4) = 2.225 (4) Å] are different indicating a dissymmetric *trans*-coordination at tin atoms similarly to the triphenyltin formate polymer crystal structure determined by Molloy and coworkers. In the crystal of compound $(HCO_2SnPh_3)_n$. The formate anions bridge the tin centres leading to a polymeric chain structure within the lattice (Figure 3). The chains interact through van der Waals forces.

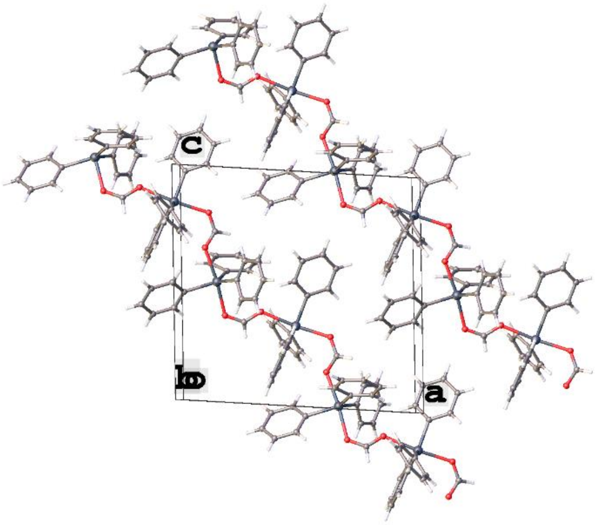


Fig. 3. The partial packing diagram showing the polymeric chain structure of compound $(HCO_2SnPh_3)_n$. Displacement ellipsoids are drawn at the 50% probability level.

4. CONCLUSIONS

The studied polymer exhibits an infinite chain within the lattice. The formate ions behave as bridging bidentate ligands connecting the $SnPh_3$ moieties in which each Sn atom lies at the centre of a *trans*-trigonal bipyramidal. However, a significant distortion is present about the coordinating, fashion of the formate ions towards tin atoms. Further investigation on formic acid and especially interactions between bis-(monocyclohexyl ammonium) 2-carboxyethyl hydrogen phosphonate and other organotin (IV) compounds are in progress.

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