Crystal Structure of Tripropyltin 2-(*p*-Chlorophenyl)-3-Methylbutyrate

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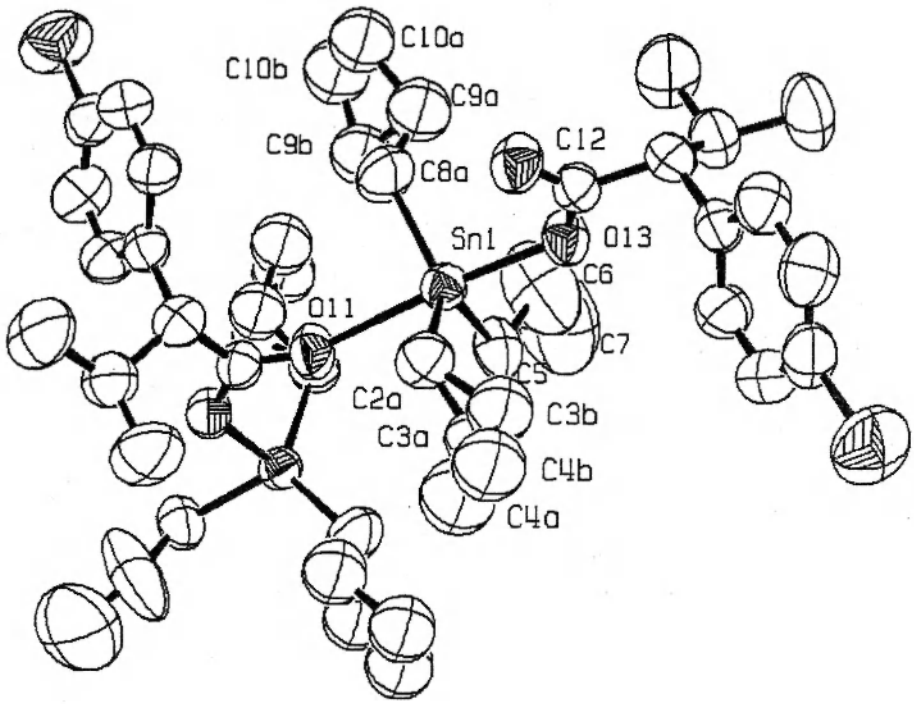

Fig. 1: Molecular structure of $[Pr_3SnO_2CCH(i\text{-}C_3H_7)C_6H_4Cl\text{-}p]$. Key geometric parameters: Sn1-O11 2.519(3), Sn1-O13 2.153(3), Sn1-C2A 2.127(6), Sn1-C8A 2.132(6), Sn1-C5 2.152(6), C12-O11 1.229(6), C12-O13 1.271(5) Å; C2A-Sn1-C8A 124.5(3), C2A-Sn1-C5 115.7(2), C8A-Sn1-C5 117.7(3), O13-Sn1-C2A 96.71(19), O13-Sn1-C8A 98.1(2), O13-Sn1-C5 88.98(18), H-atoms omitted for clarity. Symmetry code: 1-x, y-0.5, 0.5-z.

COMMENT

The structural chemistry of triorganotin carboxylates, $R_3Sn(O_2CR')$, continues to receive attention owing to their anti-tumor /1-3/ and structural possibilities /4/. When the carboxylate group acts as a monodentate ligand a tetrahedral complex /4, 5/ results whereas a pentacoordinated complex /4, 5/, either as a discrete

monomer or a bridged polymer, forms when the ligand acts as a bidentate ligand. It has been well established that triorganotin carboxylates with bulky R groups attached to the tin atom tend to favor tetrahedral monomeric structures, while sterically less demanding R groups would favor pentacoordinated bridged polymeric structures /4, 6, 7/. However, pentacoordinated structures, in general, are favored when there are electron-withdrawing R groups attached to the tin atom /4, 8}. The understanding of the relationship among various factors responsible for the preferential coordination may be important in evaluating the biochemical action of triorganotins derivatives /6, 9/. In the literature, the most frequently reported crystal structures are those for the trimethyl, triphenyl and tricyclohexyltin carboxylates /4/ while no references are found for the crystal structure of tripropyltin carboxylate.

The crystal structure analysis for the titled compound reveals a polymeric structure as shown in Fig. 1. The geometry around the tin atom is essentially pentacoordinated with the three propyl groups occupying the equatorial positions with an average Sn-C length of 2.137(5) Å. One axial position is occupied by one of the ester oxygen atoms, with a Sn-O length of 2.153(3) Å. The other site is occupied by an oxygen atom from a second carboxylate group with a Sn-O length of 2.519(3) Å. The two Sn-O bond lengths are in the range 2.12(1)-2.226(1) Å and 2.246(1)-2.65(1) Å, respectively, which are similar to those observed for other carboxylate polymeric chains /4/. Compared to the previously reported crystal structure of trimethyltin 2-(*p*-chlorophenyl)-3-methylbutyrate /10/, the difference between the inter- and intra-molecular axial Sn-O bonds in the tripropyltin derivative (0.376 Å) is slightly larger than that in the trimethyltin derivative (0.268 Å), indicating a change of coordination for the carboxylate ligand from bidentate to monodentate.

EXPERIMENTAL

Tripropyltin chloride (5 mmol) was added, with stirring, to 50 mL of benzene until dissolved. To this solution was added 2,2,3,3-tetramethylcyclopropane carboxylic acid (5 mmol) and an equal molar amount of di-*iso*butylamine. The mixture was then refluxed for 1 h and the di-*iso*butylamonnium chloride formed was removed by filtration. The solvent was then removed under vacuum and a clear oil was obtained. A white solid formed after refrigeration overnight. The solid was then dissolved in 95% ethanol and, upon slow evaporation, crystals were obtained suitable for X-ray diffraction analyses. Yield 77%, mp 97-99 °C. Analysis Calculated for $C_{20}H_{33}ClO_2Sn$: C, 52.26; H, 7.24; Sn, 25.82%. Found: C, 52.38; H, 7.56; Sn, 26.00%.

A large degree of streaking was observed between Bragg peaks in all tested crystals, most likely indicative of disorder within the polymer chains. The streaking resulted in intensity being present on forbidden reflections and a few inconsistent equivalents, but on the whole only adversely affected the weakest 10% of reflections, and had a small effect on the overall refinement.

The primary challenge of this refinement was satisfactorily modeling the disordered propyl carbons in the vicinity of the tin interference fringes. Two of the chains (C2-C3-C4 and C8-C9-C10) were modeled as two distinct disordered fragments, with the innermost carbon atom refined anisotropically but fixed on a single site with a single set of thermal parameters for both fragments, and the outer carbons were refined

isotropically sitting on separate sites on the two fragments. The third chain (C5-C6-C7) had a lesser degree of disorder, and was approximated by a single fragment with larger than normal thermal parameters on the two outer carbons. All hydrogen atoms were placed using geometrical considerations and refined to ride on the nearest carbon atom. Soft restraints were used to keep the C6-C7 distance reasonable, counteracting the poorly defined locations of both atoms. Absorption corrections were done using the built-in empirical routines of the DENZO software package /11/. T*min* and T*max* were not reported by the software and were instead estimated from the crystal dimensions through SHELX.

The data collection, structure solution and refinement for the crystal were performed in the Chemistry Department at the University of Massachusetts, Amherst, MA. Crystallographic data for the structure reported in this paper have been deposited with Cambridge Crystallographic Data Center and allocated the deposition number CCDC 277460. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44 1223 336033; e-mail: **deposit@ccdc.cam.ac.uk** or www: http://www.ccdc.cam.ac.uk).

Table 1

Crystal data for Triropyltin 2-(*p*-chlorophenyl)-3-methylbutyrate

Formula	$C_{20}H_{33}ClO_2Sn$	Formula weight	459.6
Crystal system	Monoclinic	Crystal size, mm	0.50×0.40×0.30
Space group	$P2_1/c$	a, Å	10.224(5)
b, Å	9.870(5)	c, Å	23.559 (5)
β, °	100.665(5)	V	2336.3(17)
Z	4	Diffractometer	Nonius Kappa CCD
Temperature, K	293(2)	μ (Mo–Kα), mm^{-1}	1.216
F(000)	944	No. parameter	215
D_{calc}, g cm^{-3}	1.307	θ_{max} °	27.41
Reflns unique	5222	Reflns with I > 2σ(I)	3957
Weighting scheme	$1/[\sigma^2 (Fo^2)+(0.0553P)^2+2.7184/;$ $P=(Fo^2+2Fc^2)/3$	Final R [I>2σ (I)/	R(F) = 0.0484 $wR(F^2)$ = 0.136
Goodness of fit	1.069	ρ, e $Å^{-3}$	0.775
Programs used	SHELXS-97, SHELXL-97 /12/ ORTEP /13/	Deposition number	CCDC 277460

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