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Crystallographic report

Triorganotin 2-(*p*-chlorophenyl)-3-methylbutyrates

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The crystal structures of two triorganotin butyrates were determined. Tricyclohexyltin 2-(*p*-chlorophenyl)-3-methylbutyrate was determined to have a distorted tetrahedral geometry. Trimethyltin 2-(*p*-chlorophenyl)-3-methylbutyrate, on the other hand, was found to be polymeric in nature with a trigonal bipyramidal configuration. The three methyl groups are located in the equatorial positions with the axial positions occupied by oxygen atoms from two different carboxylate groups. Copyright © 2003 John Wiley & Sons, Ltd.

KEYWORDS: carboxylate; crystal structures; pyrethroid; tricyclohexyltin; trimethyltin; triorganotin

COMMENT

Malaria and yellow fever are two of the most serious diseases known to man. Both are transmitted by various species of mosquito. Various triorganotins[1–3] and pyrethroids[4] have been shown to be effective against mosquito larvae and adult mosquitoes. Triorganotin pyrethroids may have an increased activity due to a synergistic effect; thus, a series of these compounds was synthesized and the crystal structures for two are reported herein.

The crystal structure analysis for tricyclohexyltin 2-(*p*-chlorophenyl)-3-methylbutyrate (**I**) is shown in Fig. 1 and reveals a monomeric structure with two significantly different Sn–O distances. The carboxylate group is coordinated to the tin atom *via* one of the carboxylate oxygen atoms forming an Sn–O(2) bond of 2.072(2) Å. The second Sn–O(1) distance is 2.862(3) Å. The second Sn–O interaction is considerably less than the van der Waals value, which would be an indication of a weak bond. In addition, the Sn–O(1) separation of 2.862(3) Å is not indicative of a significant interaction between these atoms. However, the O(2) atom exerts a steric influence and contributes to the distortion of the geometry around the tin atom. Thus, the tin atom environment is a distorted tetrahedron. These observed values are similar to those found for other tricyclohexyltin carboxylates, such as tricyclohexyltin indole-3-acetate,[5] *N*–methylindole-3-acetate,[6] 4-hydroxybenzoate[7] and 2-[(*E*)-2-(2-hydroxy-5-methylphenyl)-1-diazenyl]benzoate.[8]

The trimethyltin 2-(*p*-chlorophenyl)-3-methylbutyrate (**II**) is shown in Fig. 2 and exists in the solid state as a polymer. The geometry around the tin atom is essentially trigonal bipyramid with the three methyl groups occupying the equatorial positions. One axial position is occupied by one of the ester oxygen atoms, O(1), and the other site is occupied by an oxygen atom from another molecule. The sum of the equatorial angles was found to be 359.1° and the O(1)–Sn–O(2) angle was 170.5(1)°. These values are close to the ideal values for a trigonal bipyramidal structure of 360° and 180° respectively. There is a difference of 0.268(3) Å between the inter- and intra-molecular axial Sn–O bonds. This is similar to the reported differences for 2-furacarboxylate[9] (0.239 Å), trifluoroacetate[10] (0.28 Å) and 2-[(*E*)-2-(2-hydroxy-5-methylphenyl)-1-diazenyl]benzoate[8] (0.323 Å).

EXPERIMENTAL

Synthesis

Tricyclohexyltin or trimethyltin hydroxide (5 mmol) was added, with stirring, to 50 ml of toluene. To this solution was added 2-(*p*-chlorophenyl)-3-methylbutyric acid (5 mmol). The mixture was then refluxed for 1 h and a Dean–Stark trap was used to remove the water. The toluene was then evaporated under vacuum and a clear oil was obtained. A white solid formed after refrigerating

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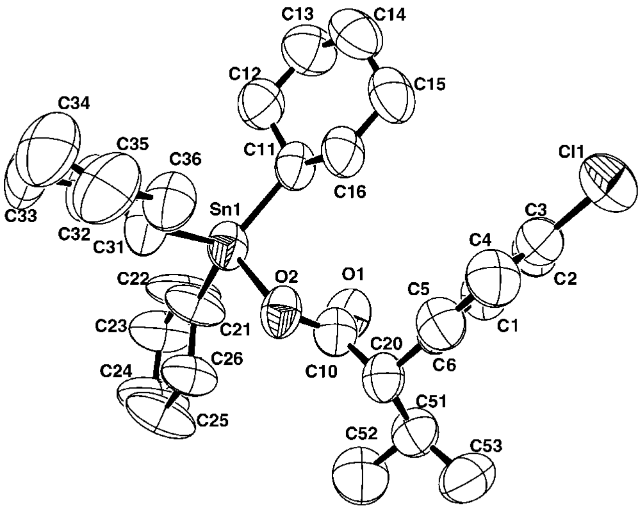

Figure 1. Molecular structure of **I** [$Cy_3SnO_2CC(CH_3)_2C_6H_4Cl$ -4]. Key geometric parameters: Sn(1)–O(2) 2.072(2), Sn(1)–O(1) 2.862(3), Sn(1)–C(11) 2.157(4), Sn(1)–C(21) 2.156(6), Sn(1)–C(31) 2.162(4), C(10)–O(1) 1.219(4), C(10)–O(2) 1.289(4) Å; C(11)–Sn(1)–C(21) 120.9(2), C(11)–Sn(1)–C(31) 116.02(16), C(21)–Sn(1)–C(31) 111.5(3), O(2)–Sn(1)–C(11) 104.60(12), O(2)–Sn(1)–C(21) 104.4(2), O(2)–Sn(1)–C(31) 94.64(14), O(1)–Sn(1)–O(2) 49.90(8)°, H atoms omitted for clarity. Positional disorder is present in one cyclohexyl ring (C21–C26). Distances between carbon atoms were therefore fixed to reasonable values and occupancies were constrained to sum to 1.0. For clarity, only one component is shown.

overnight. The solid was then dissolved in 95% ethanol and, upon slow evaporation, crystals were obtained suitable for X-ray diffraction analyses. **I**: yield 74%, m.p. 81–83 °C. Anal. Found: C, 60.23; H, 7.95; Sn, 20.96. Calc. for $C_{29}H_{45}ClO_2Sn$: C, 60.17; H, 7.82; Sn, 20.47%. **II**: yield 82%, m.p. 162–164 °C. Anal. Found: C, 45.02; H, 5.51; Sn, 31.18. Calc. for $C_{14}H_{21}ClO_2Sn$: C, 44.79; H, 5.64; Sn, 31.63%.

Crystallography

Intensity data for **I** and **II** were collected at 273 K on a Bruker, SMART CCD diffractometer. **I**, a colorless crystal $0.3 \times 0.4 \times 0.5$ mm^3, $C_{29}H_{45}ClO_2Sn$, $M = 579.79$, triclinic, $P+1$, $a = 10.934(4)$, $b = 11.733(5)$, $c = 11.872(5)$ Å, $\alpha = 85.330(7)$, $\beta = 85.127(8)$, $\gamma = 76.801(8)$°, $V = 1474.5(10)$ Å^3, $Z = 2$, 6608 unique data ($\theta_{\max}$ 28.5°), $R = 0.071$ (all data), $\omega R = 0.126$ (all data), $\rho_{\max} = 0.684$ e Å^{-3}. **II**, a colorless crystal $0.10 \times 0.22 \times 0.44$ mm^3, $C_{14}H_{21}ClO_2Sn$, $M = 375.45$, monoclinic, $P2_1/c$, $a = 11.760(4)$, $b = 10.392(3)$, $c = 13.903(4)$ Å, $\beta = 95.123(5)$°, $V = 1692.3(9)$ Å^3, $Z = 4$, 3926 unique data ($\theta_{\max}$ 28.6°), $R = 0.043$ (all data), $\omega R = 0.077$ (all data), $\rho_{\max} = 0.553$ e Å^{-3}. Programs used: SHELXTL, SADABS, WINGX, ORTEP. CCDC deposition numbers: (**I**) 205 010; (**II**) 205 011.

Acknowledgements

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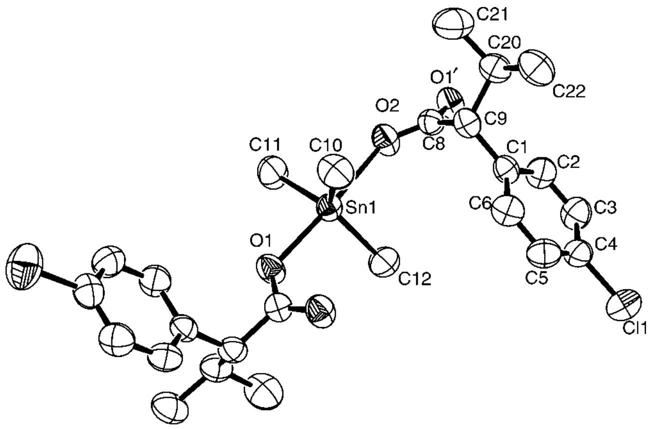

Figure 2. Molecular structure of **II** [$Me_3SnO_2CC(CH_3)_2C_6H_4Cl$ -4]. Key geometric parameters: Sn(1)–O(1) 2.1867(19), Sn(1)–O(2) 2.455(2), Sn(1)–C(10) 2.130(3), Sn(1)–C(11) 2.121(3), Sn(1)–C(12) 2.134(3), C (8)–O(1) 1.280(3), C(8)–O(2) 1.246(3) Å; C(11)–Sn(1)–C(10) 114.31(15), C(11)–Sn(1)–C(12) 121.14(15), C(10)–Sn(1)–C(12) 123.65(15), O(1)–Sn(1)–C(11) 88.80(11), O(1)–Sn(1)–C(10) 96.63(11), O(1)–Sn(1)–C(12) 93.81(11), O(2)–Sn(1)–C(11) 83.18(11), O(2)–Sn(1)–C(10) 91.38(11), O(2)–Sn(1)–C(12) 85.99(11), O(1)–Sn(1)–O(2) 44.79 (12)°. H atoms omitted for clarity. Symmetry operator for O1′ is $-x+2, y+1/2, -z+1/2$.

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