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The tin(IV) coordination environment in di-*n*-butyltin di-*p*-bromobenzoate, a monomeric diorganotin ester

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
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Abstract

Di-*n*-butyltin di-*p*-bromobenzoate is an air-stable compound which crystallizes in the monoclinic space group $C2/c$ with a 21.346(4), b 6.962(4), c 17.174(6) Å, β 107.81(2)°; $Z = 4$. The refinement of the structure from 1561 $I > 3\sigma(I)$ Mo- K_α reflections converged at $R = 0.033$. The monomeric molecule lies on a two-fold rotation axis passing through the tin atom. The coordination geometry is best described as a skew-trapezoidal bipyramid, in which the carboxylate (bite angle 54.0(1)°) oxygen atoms comprise the trapezoidal plane (Sn-O^I 2.075(3), Sn-O^{II} 2.635(4) Å), with the α -carbon (Sn-C 2.114(5) Å, C-Sn-C' 130.6(2)°) atoms tilting over the longest edge (O^{II}-Sn-O^{II'} 171.1(1)°) of this plane.

Introduction

Accumulated spectral evidence on diorganotin dicarboxylates points to a six-coordinated tin whose geometry is *trans*-C₂SnO₄ octahedral [1]. Owing to its small bite angle * (ca. 55°), the C(=O)O group does not chelate the metal atom, and the carboxylate ligand in diorganotin dicarboxylates is generally believed to adopt a bridging mode. This expectation is not, however, confirmed by recent X-ray diffraction studies. For example, the geometry of the tin atom in dimethyltin

* The bite angle for a flat Sn  ring can be calculated trigonometrically; if typical bond dimensions are assumed, e.g., Sn-O 2.25 Å, C-O 1.25 Å and O-C-O 120°, then $\theta = 2 \sin^{-1}((1.25 \sin 60)/2.25)$, i.e. ca. 55°.

diacetate, a discrete chelated molecule whose methyl–tin–methyl angle is $135.9(2)^\circ$, is regarded as being severely distorted from the *trans*- O_h geometry [2]. In polymeric dimethyltin dipicolinate [3], both carboxylate groups bridge successive atoms, but an intramolecular tin–nitrogen bond raises the coordination number to seven. The tin atom in the dimeric diphenyltin bis(trichloroacetate) moiety in the tetranuclear $[(C_6H_5)_2Sn(OCOCCL_3)_2 \cdot [(C_6H_5)_2Sn(OCOCCL_3)(OH)]]_2$ [4] compound is six-coordinate, but the phenyl groups are in a *cis* disposition. Carboxylate bridges in divinyltin bistrifluoroacetate, if present, are disrupted when the compound complexes with the bidentate base 2,2'-bipyridyl [5], and unidentate carboxylate groups result. On the other hand, diorganotin mono-esters [6,7] are carboxylate-bridged, as are most triorganotin carboxylates [8].

The stereochemistry of the C_2Sn skeleton of some di-*n*-butyltin carboxylates has been studied by solution carbon-13 NMR spectroscopy. The resonances of the butyl group in the dibenzoate esters can be easily assigned since the aromatic and aliphatic signals are widely separated; diagnostic of the C_2Sn skeletal geometry is the magnitude of the one-bond coupling constant, $^1J(^{13}C-^{119}Sn)$. This has a value of 586 Hz for di-*n*-butyltin di-*p*-ethoxybenzoate [9,10] and of 590 Hz for di-*n*-butyltin dibenzoate [11]; the former compound is claimed to be a five-coordinate dimer with bridging and chelating carboxyl groups, whereas the latter compound is suggested to be a six-coordinate monomer with skew-trapezoidal bipyramidal geometry at tin.

The solid state structures of diorganotin esters have been less well investigated than those of the triorganotin carboxylates, which have been well-studied because of the biocidal properties associated with the triorganostannyl group. As a contribution to the more definitive description of diorganotin esters, and in resolution of the above question concerning the nature of the benzoate esters, we report here the crystal structure of di-*n*-butyltin di-*p*-bromobenzoate.

Experimental

A mixture of di-*n*-butyltin oxide and *p*-bromobenzoic acid in 1/2 molar ratio was heated in the minimum volume of toluene. Hexane was added, and the solution then dried over molecular sieves and allowed to evaporate in the air to yield clear, colorless crystals, m.p. $148^\circ C$. Anal.: Found: C, 41.70; H, 4.13. $C_{22}H_{26}Br_2O_4Sn$ calcd.: C, 41.74; H, 4.11%. The carbonyl stretching bands of the compound in the infrared (Nujol) are found at ca. 1600 cm^{-1} . The carbon-13 NMR (chemical shift in ppm (coupling constant in Hz)) values for $(H_3C^4H_2C^3H_2C^2H_2C^1)_2Sn[OC(O)C_6H_4-p-Br]_2$ in $CDCl_3$ are C^1 25.6 (583.2), C^2 26.6 (35.2), C^3 26.3 (99.7), C^4 13.5 (–), $C(O)O$ 175.1, C_6H_4 128.3, 129.0, 131.6, 131.9.

Intensity data were recorded at 295 K on a $0.25 \times 0.50 \times 0.15$ mm crystal on a CAD4 four-circle diffractometer using a $2\theta/\theta$ scan mode to $2\theta_{max}$ 50° (monochromatic Mo- K_α radiation, λ 0.71069 Å). The 1561 observed reflections with $I > 3\sigma(I)$ were used in the full matrix least-squares refinement after Gaussian absorption correction and solution of the structure by the heavy-atom method. Non-H atom parameters were refined anisotropically, with H atom parameters constrained at estimated positions. The XTAL program system on a Perkin–Elmer 3240 computer [12] was used in the calculations. The atomic coordinates are listed in Table 1, and the molecular structure is illustrated in Fig. 1.

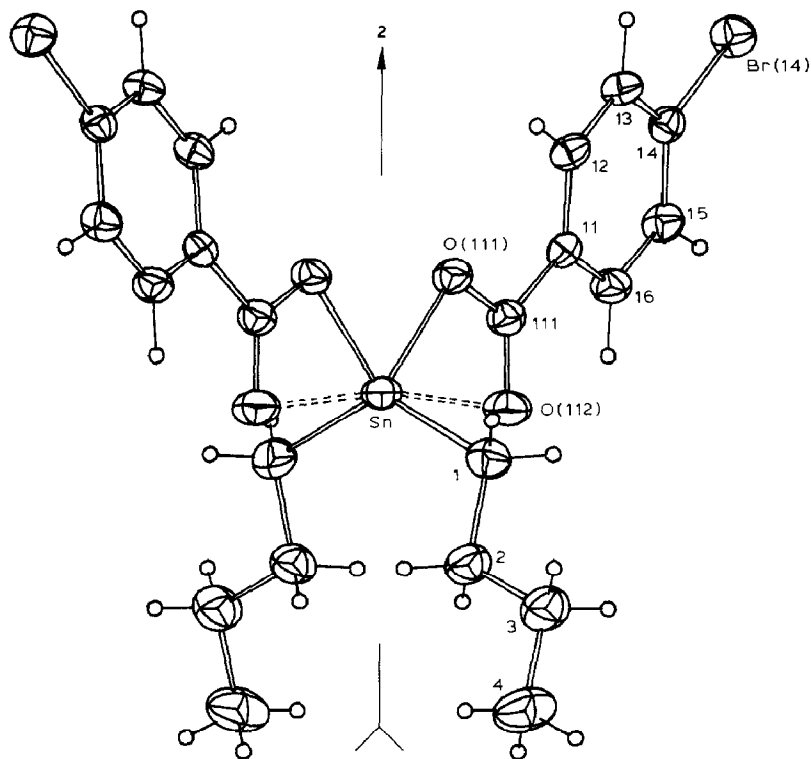


Fig. 1. Selected bond distances and angles in di-*n*-butyltin di-*p*-bromobenzoate: Sn–C(1) 2.114(5), Sn–O(111) 2.075(3), Sn–O(112) 2.635(4) Å; C(1)–Sn–C(1)′ 130.6(2), C(1)–Sn–O(111) 111.0(2), C(1)–Sn–O(112) 87.3(2), C(1)–Sn–O(111)′ 106.1(2), C(1)–Sn–O(112)′ 89.0(2), O(111)–Sn–O(112) 54.0(1), O(111)–Sn–O(111)′ 81.1(1), O(111)–Sn–O(112)′ 134.8(1), O(112)–Sn–O(112)′ 171.1(1)°. Symmetry transformation (′): $\bar{x}, y, 0.5 - z$. Thermal ellipsoids are of 20% probability amplitude for the non-hydrogen atoms for which labeling is also shown; hydrogen atoms have arbitrary radii of 0.1 Å.

Table 1

Atomic coordinates for di-*n*-butyltin di-*p*-bromobenzoate

Atom	<i>x</i>	<i>y</i>	<i>z</i>
Sn	0	0.38134(6)	0.25
Br(14)	−0.28228(3)	1.07611(8)	0.40603(3)
O(111)	−0.0554(1)	0.6077(4)	0.2722(2)
O(112)	−0.1015(2)	0.3521(5)	0.3061(2)
C(111)	−0.0995(2)	0.5282(7)	0.2995(3)
C(11)	−0.1454(2)	0.6597(6)	0.3229(3)
C(12)	−0.1465(2)	0.8522(7)	0.3048(3)
C(13)	−0.1878(2)	0.9751(6)	0.3280(3)
C(14)	−0.2283(2)	0.9046(6)	0.3697(3)
C(15)	−0.2291(2)	0.7131(7)	0.3873(3)
C(16)	−0.1873(2)	0.5897(6)	0.3638(3)
C(1)	0.0573(3)	0.2545(8)	0.3607(3)
C(2)	0.0407(3)	0.0500(8)	0.3731(3)
C(3)	0.0820(3)	−0.037(1)	0.4499(4)
C(4)	0.0641(4)	−0.235(1)	0.4656(4)

Discussion

It was thought that the structure of di-*n*-butyltin di-*p*-bromobenzoate might differ from that of the moisture-sensitive dimethyltin diacetate since this ester is stable in the air. As depicted in Fig. 1, di-*n*-butyltin di-*p*-bromobenzoate is present as discrete molecules; there are no tin–oxygen intermolecular contacts less than 4 Å. A two-fold rotation axis passes through the tin atom, so that the molecular symmetry of the molecule is C_2 . The tin atom is essentially four-coordinate [Sn–C 2.114(5), Sn–O 2.075(3) Å], but the carbon–tin–carbon ($130.6(2)^\circ$) and oxygen–tin–oxygen ($81.1(1)^\circ$) angles exclude a strictly tetrahedral geometry since both angles differ significantly from the idealized tetrahedral value of 109.5° . Significantly, this orientation of the carboxylate group is such that the acyl oxygen atom is positioned only 2.635(4) Å away from the tin atom, well within the sum of the van der Waals radii for the two atoms. The carboxylate group therefore behaves as an anisobidentate ligand with a bite angle of $54.0(1)^\circ$.

As pointed out earlier, a bite angle of this size is not reconcilable with an O_h geometry. A small bite angle may be accommodated, however, in a skew-trapezoidal bipyramid geometry [13], and several distorted *trans*- O_h geometries have been recently re-interpreted as skew-trapezoidal bipyramidal geometries [14]. The 'six-coordinated' tin atom of dimethyltin diacetate (Sn–O 2.106(2), 2.539(2) Å; bite angle $55.14(7)^\circ$ [2]) also adopts this geometry, and its molecular symmetry is also C_2^* . Consideration of the structure of the title compound (Fig. 1) supports a similar assignment. The tin atom in the di-*p*-bromobenzoate (and the diacetate) lies in the trapezoidal plane composed of the two ester and two acyl oxygen atoms; the dihedral angle between the trapezoidal plane and the C_2 Sn plane is 90° in both structures. The Sn–O(acyl) interaction of 2.635(4) Å in the bromobenzoate is marginally longer than that found in the diacetate. Relatively long acyl tin–oxygen interactions are also found in triorganotin carboxylates, e.g., trimethyltin trifluoroacetate (2.458(15) Å [15]), trivinyltin trichloroacetate (2.49(1) Å [16]), tri-*n*-butyltin indolyl-3-acetate (2.524(3) Å [17]) and tribenzyltin acetate (2.65(2) Å [18]).

In solution, di-*n*-butyltin di-*p*-bromobenzoate yields a 1J value of 583.2 Hz. 1J values have been correlated with carbon–tin–carbon angles determined from X-ray data by the equation $^1J(^{119}\text{Sn}-^{13}\text{C}) = 9.99\theta - 746$ (θ is the carbon–tin–carbon angle) [19]. From this equation, an angle of 133° is predicted for the title compound, compared with the observed angle of $130.6(2)^\circ$.

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* *Note added in proof*: The geometry of the six-coordinate tin atom in dimethyltin di-*p*-aminobenzoate (Chandrasekhar et al., *Inorg. Chem.*, 27 (1988) 958) is also skew-trapezoidal pyramidal, but the tin atom does not lie on a two-fold crystallographic axis.

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