Bis(1,1,3,3-tetramethyl-1,3-dibenzoato-distannoxane)

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In centrosymmetric octamethyl-$1\kappa^2C,2\kappa^2C,3\kappa^2C,4\kappa^2C$-tetra-kis-$\mu$-benzoato-$1{:}2\kappa^2O,O';2{:}3\kappa^2O;3{:}4\kappa^2O,O';1{:}4\kappa^2O$-bis-$\mu_3$-oxo-$1{:}2{:}3k^3O;1{:}3{:}4k^3O$-tetratin, $[[(CH_3)_2SnO_2CC_6H_5]_2O]_2$; the exocyclic Sn atom is five-coordinated and has a *trans*–C_3SnO_2 trigonal bipyramidal geometry [C—Sn—C = 139.4 (2)°] and the endocyclic Sn atom is six-coordinated and has a severely distorted *trans*-C_2SnO_4 octahedral geometry [C—Sn—C = 145.6 (2)°].

Comment

In the supramolecular self-assembled structures of dimeric 1,1,3,3-tetraorgano-1,3-dicarboxylatodistannoxanes, the monomeric $R_2(R'CO_2)Sn—O—Sn(O_2CR')R_2$ moieties are linked by two dative Sn←O interactions involving their distannoxanyl O atoms. The dative bond is unusually short in such organotin compounds, these being typically as short as the covalent Sn—O bond, so that the covalent and dative bonds are not readily distinguished (Ng *et al.*, 1991; Haiduc & Edelmann, 1999). The most common of the four types of such tetranuclear aggregates has two bridging and two mono-dentate carboxylate groups, and one Sn atom is five-coordinated, whereas the other is six-coordinated.

(I)
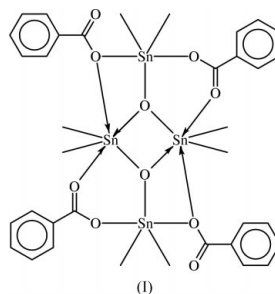
The benzoate derivative, bis(1,1,3,3-tetramethyl-1,3-dibenzoatodistannoxane), (I), adopts this centrosymmetric configuration (Fig. 1). The five-coordinated Sn atom has a bent C_2Sn skeleton [C—Sn—C = 139.4 (2) Å], as does the six-coordinated Sn atom [C—Sn—C = 145.6 (2)°]. The five-coordinated Sn atom is bonded to a monodentate benzoate group, whose —CO_2 unit displays single and double C—O bonds. The singly bonded atom O1 acts as a bridging atom, forming a relatively short bond with the five-coordinated Sn atom [Sn1—O1 = 2.165 (3) Å] and a very long bond with the six-coordinated Sn atom [O1—Sn2ⁱ 2.800 (3) Å; symmetry code: (i) $1 - x, 1 - y, 1 - z$]. The doubly bonded atom O2 is engaged in a weak C—H$_{Ar}$···O$_{CO}$ interaction [C15···O2ⁱⁱ = 3.450 (6) Å and C—H···Oⁱⁱ = 165°; symmetry code: (ii) $-\frac{1}{2} + x, \frac{3}{2} - y, \frac{1}{2} + z$], which links adjacent molecules into a layer structure (Fig. 2).

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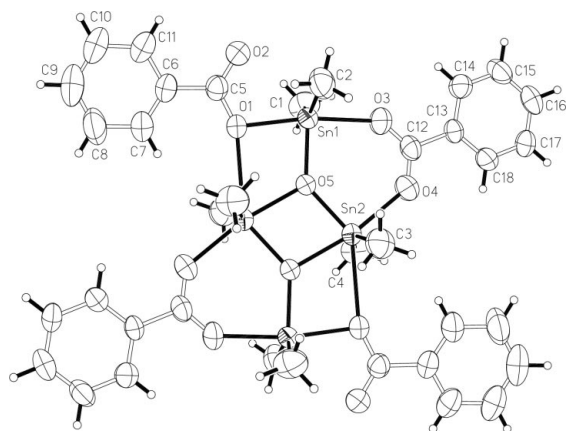
Figure 1
*ORTEP*II (Johnson, 1976) plot of the centrosymmetric 1,1,3,3-tetra-methyl-1,3-dibenzoatodistannoxane dimer, with displacement ellipsoids drawn at the 50% probability level. H atoms are shown as spheres of arbitrary radii.
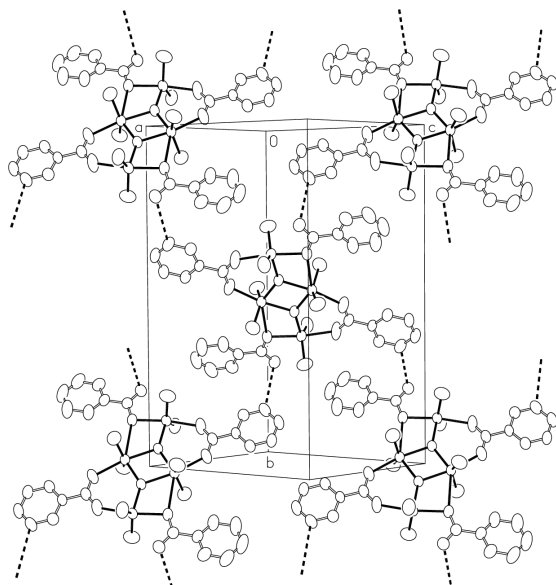

Figure 2
*ORTEP*II (Johnson, 1976) plot of the supramolecular C—H···O interactions in bis(1,1,3,3-tetramethyl-1,3-dibenzoatodistannoxane). H atoms have been omitted.

A number of the distannoxanes have been isolated as the products either from the condensation of a diorganotin oxide with two molar equivalents of the carboxylic acid, or from the metathetical reaction of a diorganotin dihalide with a metal carboxylate (Tiekink, 1991a, 1994). The dicarboxylate that is initially formed is unstable with respect to hydrolysis to the distannoxane. An example is shown by dimethyltin diacetate, an air-sensitive compound (Lockhart *et al.*, 1987) that can hydrolyze to the distannoxane (Lockhart *et al.*, 1986). On the other hand, dimethyltin dibenzoate represents an exception, as it is air-stable; the monomeric compound adopts a skew-trapezoidal bipyramidal geometry [C—Sn—C = 147.2 (7)°] (Tiekink, 1991b).

Experimental

Dimethylphenyltin iodide was obtained by the cleavage of the tin–phenyl bond of dimethyldiphenyltin by elemental iodine (Davison & Rakita, 1970; Amini *et al.*, 1989). In an attempt to synthesize di-methylphenyltin benzoate, equimolar quantities of dimethylphenyltin iodide (0.35 g, 1 mmol) and silver benzoate (0.23 g, 1 mmol) were dissolved in ethanol to give a precipitate that was presumed to be silver iodide. The precipitate was removed and the solvent evaporated off to furnish a white material. Crystals (m.p. 514–515 K) were grown from a methanol–toluene solvent system. In the ^{1}H NMR spectrum in CDCl$_3$, the tin–methyl coupling constant was 90 Hz.

Crystal data

$[Sn_4O_2(CH_3)_8(C_7H_5O_2)_4]$
$M_r = 1111.47$
Monoclinic, $P2_1/n$
$a = 9.4001 (6)$ Å
$b = 20.952 (1)$ Å
$c = 11.2920 (7)$ Å
$\beta = 110.671 (2)°$
$V = 2080.8 (2)$ Å^3
$Z = 2$

$D_x = 1.774$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 3680 reflections
$\theta = 1.9$–$27.5°$
$\mu = 2.42$ mm^{-1}
$T = 293 (2)$ K
Prism, colorless
$0.15 \times 0.05 \times 0.03$ mm

Data collection

Bruker CCD area-detector diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.713$, $T_{max} = 0.931$
20323 measured reflections

4785 independent reflections
3723 reflections with $I > 2\sigma(I)$'
$R_{int} = 0.041$
$\theta_{max} = 27.5°$
$h = -12 \rightarrow 12$
$k = -27 \rightarrow 27$
$l = -14 \rightarrow 14$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.034$
$wR(F^2) = 0.080$
$S = 1.01$
4785 reflections
230 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o{}^2) + (0.0227P)^2 + 0.958P]$
where $P = (F_o{}^2 + 2F_c{}^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.69$ e Å^{-3}
$\Delta\rho_{min} = -0.32$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Sn1—C1	2.096 (5)	Sn2—C4	2.089 (5)
Sn1—C2	2.103 (5)	Sn2—O1^i	2.800 (3)
Sn1—O1	2.165 (3)	Sn2—O4	2.226 (3)
Sn1—O3	2.232 (3)	Sn2—O5	2.035 (2)
Sn1—O5	2.015 (2)	Sn2—O5^i	2.153 (2)
Sn2—C3	2.099 (5)		
C1—Sn1—C2	139.4 (2)	C3—Sn2—O5^i	96.3 (2)
C1—Sn1—O1	96.7 (2)	C4—Sn2—O1^i	78.3 (2)
C1—Sn1—O3	86.3 (2)	C4—Sn2—O4	85.8 (2)
C1—Sn1—O5	109.2 (2)	C4—Sn2—O5	107.4 (2)
C2—Sn1—O1	97.0 (2)	C4—Sn2—O5^i	96.6 (2)
C2—Sn1—O3	86.0 (2)	O1^i—Sn2—O4	125.5 (1)
C2—Sn1—O5	110.7 (2)	O1^i—Sn2—O5	141.3 (1)
O1—Sn1—O3	171.0 (1)	O1^i—Sn2—O5^i	64.7 (1)
O1—Sn1—O5	80.6 (1)	O4—Sn2—O5	93.2 (1)
O3—Sn1—O5	90.4 (1)	O4—Sn2—O5^i	169.8 (1)
C3—Sn2—C4	145.6 (2)	O5—Sn2—O5^i	76.6 (1)
C3—Sn2—O1^i	78.8 (2)	Sn1—O5—Sn2	135.2 (1)
C3—Sn2—O4	87.0 (2)	Sn1—O5—Sn2^i	121.4 (1)
C3—Sn2—O5	106.6 (2)	Sn2—O5—Sn2^i	103.4 (1)

Symmetry code: (i) $1 - x, 1 - y, 1 - z$.

H atoms were positioned geometrically and were allowed to ride on their parent C atoms, with $U_{iso}(H) = 1.2U_{eq}(C)$ for the aromatic C atoms and $U_{iso}(H) = 1.5U_{eq}(C)$ for the methyl C atoms.

Data collection: *SMART* (Bruker, 1997); cell refinement: *SAINT* (Bruker, 1997); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*II (Johnson, 1976); software used to prepare material for publication: *SHELXL*97.

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