metal-organic compounds

[5-Bromo-*N*-(2-carboxylatophenyl)-salicylideniminato]dimethyltin(IV)

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The structure of the title dimethyltin(IV) complex, [2-(5-bromo-2-oxidobenzylideneamino)benzoato-$\kappa^3 O,N,O'$]-dimethyltin(IV), [Sn(CH$_3$)$_2$(C$_{14}$H$_8$BrNO$_3$)], features centrosymmetric dimers disposed about a central Sn$_2$O$_2$ core. Each Sn centre has seven-coordinate pentagonal–bipyramidal geometry, taking into account two moderately long Sn—O contacts about an inversion centre [2.679 (4) and 2.981 (4) Å]. The methyl groups are in an axial orientation.

Comment

Studies on the coordination chemistry of amino-acid-based Schiff bases with diorganotin(IV) centres show that the Sn coordination number is readily expanded (Pellerito & Nagy, 2002). Several compounds, such as the title compound, (I), form dimeric structures with an Sn$_2$O$_2$ core (Dey, Saha, Gielen *et al.*, 1999; Huber *et al.*, 1989; Gielen *et al.*, 1998). There is a short intermolecular distance between atoms O2 and O2^i in (I) [2.613 (6) Å; symmetry code: (i) $-x$, $2-y$, $2-z$], yet there is no evidence in the difference Fourier map of an H atom bound to O2 forming a hydrogen bond with O2^i.

Dimer of (I)
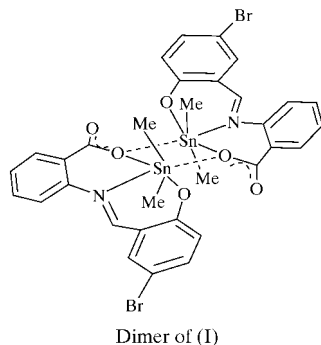
In (I), the central Sn atom adopts approximate pentagonal–bipyramidal geometry, with the two methyl groups in the axial positions. The Sn environment is seven-coordinate, involving two long Sn$\cdots$O contacts of 2.679 (4) and 2.981 (4) Å

(Table 1). The deviation of Sn from the equatorial NO$_4$ coordination plane is 0.047 (2) Å (mean deviation 0.054 Å). The O—Sn—O angle in the Sn$_2$O$_2$ core is 63.80 (15)° in (I), close to the values in similar compounds of 64.9 (2) (Dey, Saha, Gielen *et al.*, 1999) and 65.6 (2)° (Gielen *et al.*, 1998).

In (I), the two longer Sn$\cdots$O distances are shorter than those in the unbrominated complex, (II) [2.69 (1) and 3.03 (1) Å; Dey, Saha, Gielen *et al.*, 1999], despite the data being measured at the same temperature. This difference in the bond lengths between the two compounds is reversed for the other Sn—N/O bonds in the equatorial coordination plane, where for the brominated compound, (I), the bond lengths are consistently longer [Sn1—O1 2.158 (3) *cf.* 2.135 (4) Å in (II), Sn1—O2 2.206 (4) *cf.* 2.187 (4) Å in (II), and Sn1—N1 2.251 (4) *cf.* 2.230 (5) Å in (II)].

The C—Sn—C angle of 156.9 (3)° is close to that found in (II) [155.1 (3)°; Dey, Saha, Gielen *et al.*, 1999], but rather small in comparison with the value found in the diorganotin pyridine-2-phosphonate-6-dicarboxylate [168.2 (3)°; Gielen *et al.*, 1998]. The latter angle is closer to the ideal value of 180° found in regular pentagonal–bipyramidal structures, yet much larger than the ideal value of 120° for a regular trigonal–bipyramidal structure. The *N*-(2-hydroxyacetophenoneglycinate) organotin structures (Gielen *et al.*, 1998) are much closer to the latter geometry [C—Sn—C 126.0 (2)–137.4 (3)°]. Thus, the structure of (I) lies between a dimeric pentagonal–bipyramidal structure and a monomeric trigonal–bipyramidal structure, as is the case for (II) (Dey, Saha, Gielen *et al.*, 1999). Other distortions from regular geometry are seen in the deviation from 180° of the O1—Sn1—O2 [157.21 (15)°] and C101—Sn1—C102 [156.9 (3)°] angles, and from 90° of C101—Sn1—N1 [101.2 (2)°], C102—Sn1—N1 [101.8 (2)°], O1—Sn1—N1 [80.70 (14)°] and O2—Sn1—N1 [76.81 (14)°]. The last two bite angles are comparable with other *ONO*-chelated organotin(IV) complexes (Smith *et al.*, 1992; Dakternieks *et al.*, 1998; Dey, Saha, Geilen *et al.*, 1999). None of the aforementioned six-membered chelate rings is planar; their conformations are closest to a half chair.

The Sn1—O2(carboxyl) bond length [2.206 (4) Å] is longer than that for Sn1—O1 [2.158 (3) Å]. Such a difference in bond length has been found in similar complexes: 2.151 (8) and 2.078 (10) Å (Smith *et al.*, 1992), 2.188 (3) and 2.068 (4) Å (Khoo *et al.*, 1997), and 2.187 (4) and 2.135 (4) Å (Dey, Saha, Gielen *et al.*, 1999). These Sn—O distances are slightly longer in (I) than in the compounds described above.

The Sn1—N1 bond length of 2.251 (4) Å in (I) is comparable with the values observed for Ph$_2$Sn(OC$_6$H$_4$-CH=NC$_6$H$_4$O) [2.241 (3) Å; Preut *et al.*, 1976] and [Vin$_2$Sn{2-OC$_6$H$_4$C(CH$_3$)=NCH$_2$COO}OH$_2$] [Vin is vinyl; 2.254 (4) Å; Dakternieks *et al.*, 1998]. However, this bond is longer in (I) than in other organotin(IV) complexes derived from *ONO*-donor tridentate Schiff bases [2.158 (8) Å (Smith *et al.*, 1992) and 2.174 (6)–2.198 (5) Å (Dakternieks *et al.*, 1998)], and shorter than in the six-coordinate complexes R_2Sn(Vanophen) [R is Ph, ^{n}Bu or Me; Vanophen is *N,N′*-bis(3-methoxysalicylaldehyde)-1,2-phenylenediiminate; 2.266 (2)–2.280 (2) Å; Dey, Saha, Das *et al.*, 1999].
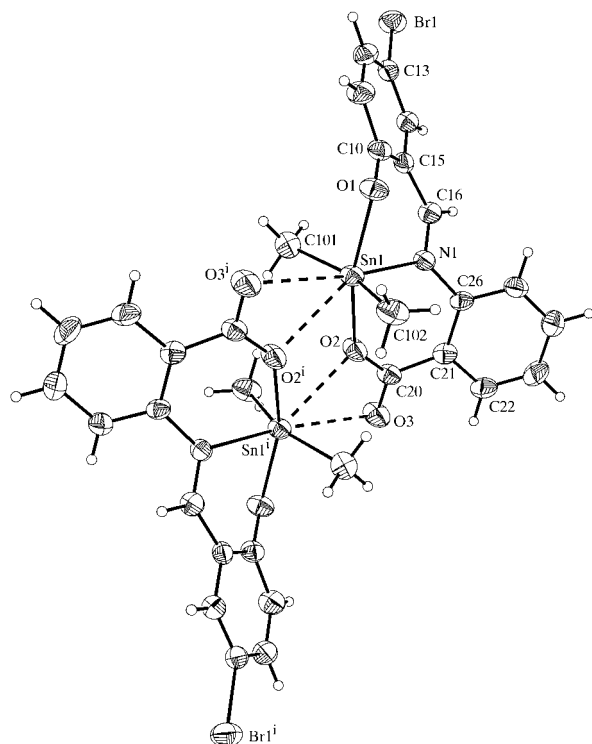
Figure 1
A perspective view of the dimer in (I), with displacement ellipsoids at the 50% probability level. H atoms are shown as small circles with an arbitrary radius of 0.2 Å [symmetry code: (i) $-x, 2 - y, 2 - z$].

The Sn—C$_{methyl}$ bond lengths in (I) [2.098 (6) and 2.100 (5) Å] are very similar to those found in (II) [2.102 (7) and 2.103 (6) Å; Dey, Saha, Gielen *et al.*, 1999] and in a related dimethyl species [2.091 (14) and 2.142 (14) Å; Smith *et al.*, 1992].

Experimental

Compound (I) was prepared by the reaction of N-(2-carboxyphenyl)-5'-bromosalicylidenimine (1.5 g, 4.68 mmol) and Me$_2$SnCl$_2$ (1.03 g, 4.68 mmol) in dry methanol (25 ml) at room temperature. Suitable single crystals of (I) were obtained overnight (yield: 1.75 g, 80%; m.p. > 517 K). Analysis found: C 40.88, H 3.08, N 2.95, Sn 25.01%; calculated for (I): C 41.16, H 3.02, N 3.0, Sn 25.42%; IR (KBr disc): ν(COO) 1634 cm^{-1}.

Crystal data

[Sn(CH$_3$)$_2$(C$_{14}$H$_8$BrNO$_3$)]	$D_x = 1.892$ Mg m^{-3}
$M_r = 466.89$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/n$	Cell parameters from 29
$a = 8.8719$ (17) Å	reflections
$b = 12.0961$ (17) Å	$\theta = 5.2$–12.5°
$c = 15.323$ (4) Å	$\mu = 4.01$ mm^{-1}
$\beta = 94.702$ (16)°	$T = 293$ (2) K
$V = 1638.9$ (6) Å^3	Rectangular block, yellow
$Z = 4$	$0.96 \times 0.56 \times 0.28$ mm

Data collection

Bruker $P4$ diffractometer	$R_{int} = 0.039$
ω scans	$\theta_{max} = 25$°
Absorption correction: ψ scan	$h = -10 \rightarrow 1$
(North *et al.*, 1968)	$k = -1 \rightarrow 14$
$T_{min} = 0.081$, $T_{max} = 0.326$	$l = -18 \rightarrow 18$
3818 measured reflections	3 standard reflections
2875 independent reflections	every 97 reflections
2411 reflections with $I > 2\sigma(I)$	intensity decay: none

Refinement

Refinement on F^2	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.042$	$w = 1/[\sigma^2(F_o^2) + (0.0679P)^2]$
$wR(F^2) = 0.109$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.04$	$(\Delta/\sigma)_{max} < 0.001$
2875 reflections	$\Delta\rho_{max} = 1.55$ e Å^{-3}
199 parameters	$\Delta\rho_{min} = -1.34$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Sn1—C101	2.098 (6)	Sn1—O2^i	2.679 (4)
Sn1—C102	2.100 (5)	Sn1—O3^i	2.981 (4)
Sn1—O1	2.158 (3)	Sn1—N1	2.251 (4)
Sn1—O2	2.206 (4)		
C101—Sn1—C102	156.9 (3)	O1—Sn1—O2	157.21 (15)
C101—Sn1—O1	90.71 (19)	C101—Sn1—N1	101.2 (2)
C102—Sn1—O1	90.65 (18)	C102—Sn1—N1	101.8 (2)
C101—Sn1—O2	90.0 (2)	O1—Sn1—N1	80.70 (14)
C102—Sn1—O2	97.5 (2)	O2—Sn1—N1	76.81 (14)

Symmetry code: (i) $-x, 2 - y, 2 - z$.

H-atom positions were calculated and constrained to the idealized geometries used by *SHELXL*97 (Sheldrick, 1997), with C—H = 0.93 Å for Csp^2 H atoms and 0.96 Å for methyl H atoms. The H-atom displacement parameters were treated as riding, with U_{iso}(H) = 1.2U_{eq}(C$_{Ph}$) or 1.5U_{eq}(C$_{Me}$).

Data collection: *XSCANS* (Siemens, 1996); cell refinement: *XSCANS*; data reduction: *SHELXTL* (Bruker, 1997); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL*.

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