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Di-*n*-butylbis(2′,4′-difluoro-4-hydroxybiphenyl-3-carboxylato-*O*,*O*′)tin(IV)

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Key indicators

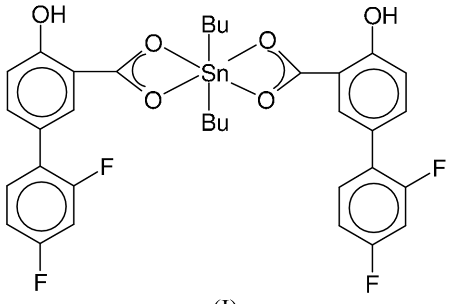
Single-crystal X-ray study
T = 170 K
Mean σ(C–C) = 0.007 Å
Disorder in main residue
R factor = 0.050
wR factor = 0.148
Data-to-parameter ratio = 16.3

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

The crystal structure of the title compound, $[Sn(C_4H_9)_2(C_{13}H_7F_2O_3)_2]$, contains discrete molecules in which the central Sn atoms are asymmetrically coordinated to two carboxylates and by two C atoms of two *n*-butyl groups. The Sn—C distances are identical within 3σ limits [mean Sn—C 2.118 (2) Å]. The Sn—O distances are significantly different from each other, with the mean value for the shorter distances being 2.098 (3) Å, while the longer Sn—O distances are 2.570 (3) and 2.686 (3) Å. The geometry around the Sn atom is highly distorted octahedral, that may be best described as one based on skew-trapezoidal planar geometry. The hydroxyl groups and the carboxylate O atoms are hydrogen bonded, forming six-membered rings and exhibit an *S*(6) pattern of hydrogen bonding.

Comment

Studies on the structure–activity relationships of organotin compounds have led to numerous reports in recent years (Vatsa *et al.*, 1991; Gielen *et al.*, 1994; McManus *et al.*, 1994; Ahmad *et al.*, 2002). Moreover, organotin compounds with a coordination number higher than four have been found to possess high biological activity, enhanced reactivity and stereochemical non-rigidity (Mehring *et al.*, 1998). In continuation of our efforts in the synthesis and structural characterization of organotin derivatives of donor ligands containing chalcogens, with special reference to their biological applications (Badshah *et al.*, 1994; Danish *et al.*, 1995; Ali *et al.*, 1993; Choudhary *et al.*, 2001; Bhatti *et al.*, 2000; Parvez, Ali, Mazhar, Bhatti & Choudhary, 1999; Parvez, Ali, Mazhar, Bhatti & Khokhar, 1999; Parvez, Bhatti *et al.*, 2000), we have prepared di-*n*-butylbis(2′,4′-difluoro-4-hydroxybiphenyl-3-carboxylato-*O*,*O*′)tin(IV), (I), the crystal structure of which is reported in this paper.



(I)

The structure of (I) is composed of discrete monomeric molecules (Fig. 1), in which hexacoordinated Sn atoms are surrounded by four O atoms of the carboxylate ligands and

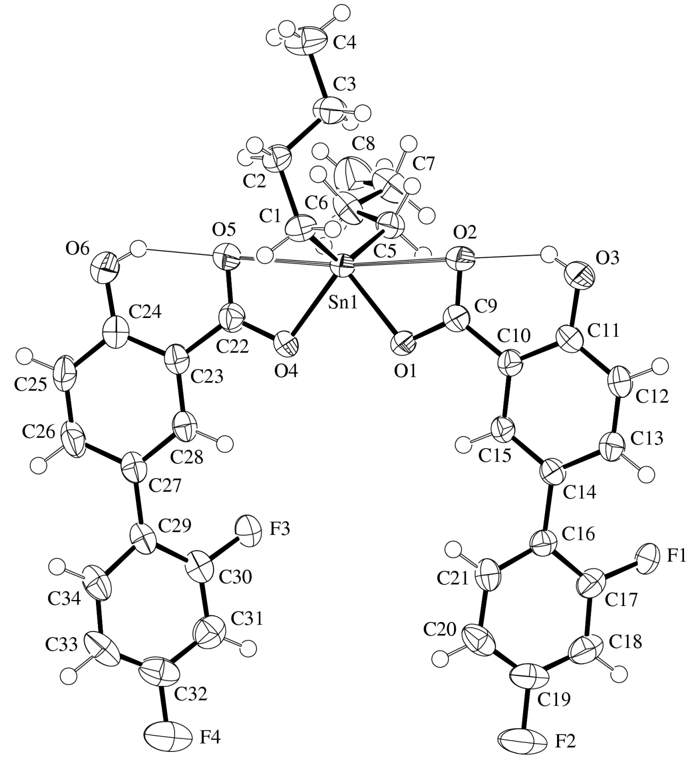


Figure 1
*ORTEP*II (Johnson, 1976) drawing of (I), with displacement ellipsoids plotted at the 50% probability level.

two C atoms of two *n*-butyl groups. The Sn atom lies in the same plane as the four O atoms coordinated to it and the two butyl groups lie above and below this plane. The C1—Sn1—C5 angle in (I) is 135.04 (18)°, which is comparable to the corresponding angle in similar structures (Gibson *et al.*, 1997; Parvez *et al.*, 1997). The Sn—C distances are identical within 3σ limits [mean Sn—C 2.118 (2) Å]. On the other hand, the carboxylates are asymmetrically coordinated to Sn, with Sn—O distances significantly different from each other, with the mean value for the shorter distances being 2.098 (3) Å, while the longer Sn—O distances are 2.570 (3) and 2.686 (3) Å, for the two ligands, indicating that the former bonds are covalent and the latter are coordinate. The geometry around the Sn atom is highly distorted octahedral, that may be best described as one based on a skew-trapezoidal planar geometry. Several structures exhibiting similar geometry around Sn and an anisobidentate mode of coordination of the carboxylate ligands as found in (I), have been reported previously, *e.g.* $Me_2Sn(OAc)_2$ (Lockhart *et al.*, 1987), $Bu_2Sn(O_2CCH_2SC_6H_5)_2$ (Sandhu *et al.*, 1989), $Bu_2Sn[O_2C(CH_2Ph)C(H)N(H)C(O)CH_2Cl]_2$ (Sandhu *et al.*, 1991), $Me_2Sn(O_2CPh)_2$ (Tiekink, 1991), $Et_2Sn(O_2CC_5H_3NSMe)_2$ (Gielen *et al.*, 1992), $Me_2Sn[(CO_2)(NO)(CO)CpRe]_2$ (Gibson *et al.*, 1997), $Et_2Sn(O_2C_7H_5S)_2$ (Parvez *et al.*, 1997), $Me_2Sn(O_2CCH_2Cl)_2$ (Dakternieks *et al.*, 1999), and $Bu_2Sn(O_2C_7H_5S)_2$ (Yahyi *et al.*, 2001), *etc.* The bond distances and angles involving the Sn atom in (I) are in agreement with the corresponding values found for similar Sn complexes in the Cambridge Structural Database (Allen & Kennard, 1993).

The molecular dimensions in the 2′,4′-difluoro-4-hydroxybiphenyl-3-carboxylate ligand are unexceptional, with mean distances as follows: aromatic C—C 1.386 (13), Csp^2—Csp^2 1.480 (8), Csp^3—Csp^3 1.519 (5) and O—Csp^2 1.348 (2) Å. The C—O bond distances in the delocalized region of the carboxylates are significantly different from each other; these distances for the weakly coordinated O atoms are shorter [mean 1.256 (6) Å] than the C—O distances of the strongly bound O atoms [mean 1.293 (7) Å]. The C—F distances involving the disordered F atoms are slightly shorter than those involving the ordered F atoms, with mean values of 1.332 (3) and 1.358 (2) Å, respectively. It is interesting to note that both the hydroxyphenylcarboxylates and the Sn atom lie in a plane. The angles between the least-squares planes of the biphenyl rings C10—C15 and C16—C21 and the rings C23—C28 and C29—C34 are 39.1 (2) and 34.8 (2)°, respectively. The hydroxyl groups are involved in intramolecular hydrogen bonding with the O atoms coordinated to the Sn atom, forming six-membered rings with O2···H3 and O5···H6 interactions of 1.90 and 1.89 Å, and the angles O3—H3···O2 and O6—H6···O5 are 144 and 146°, respectively. In terms of graph-set representation (Bernstein *et al.*, 1994), these rings exhibit an *S*(6) pattern of hydrogen bond; *S*(6) denotes an intramolecular hydrogen-bonded six-membered ring. Hydrogen-bonded *S*(6)-type rings with similar hydrogen-bonding geometry have been reported in a number of structures, *e.g.* eupatorin (Parvez *et al.*, 2001), pefloxacinium methanesulfonate 0.10 hydrate (Parvez, Arayne *et al.*, 2000), *etc.*

Experimental

To a suspension of the silver salt of 2′,4′-difluoro-4-hydroxybiphenyl-3-carboxylic acid (3.57 g, 0.01 mol) in dry chloroform (25 ml), contained in a 250 ml two-necked round-bottomed flask equipped with a water condenser and a magnetic stirring bar, di-*n*-butyltin(IV) dichloride (1.52 g, 0.005 mol) in dry chloroform (25 ml) was added dropwise with constant stirring. The reaction mixture was refluxed for 7–8 h, under an inert atmosphere and was allowed to stand overnight at room temperature. Silver chloride that had formed was filtered off and the solvent was removed under reduced pressure. The solid residue thus obtained was recrystallized from a dichloromethane/*n*-hexane (1:1) mixture to yield colourless crystals suitable for X-ray crystallographic studies.

Crystal data

$[Sn(C_4H_9)_2(C_{13}H_7F_2O_3)_2]$
M_r = 731.29
Monoclinic, $P2_1/c$
a = 10.3676 (1) Å
b = 9.2278 (1) Å
c = 33.3643 (5) Å
β = 98.0917 (6)°
V = 3160.19 (7) Å^3
Z = 4

D_x = 1.537 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 12703 reflections
θ = 1.0–27.4°
μ = 0.88 mm^{-1}
T = 170 (2) K
Block, colourless
0.15 × 0.13 × 0.09 mm

Data collection

Nonius KappaCCD diffractometer
ω and φ scans
Absorption correction: multi-scan (*SORTAV*; Blessing, 1997)
$T_{\min}$ = 0.879, $T_{\max}$ = 0.928
12703 measured reflections
6945 independent reflections

5776 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.028
$\theta_{\max}$ = 27.4°
$h = -13 \rightarrow 13$
$k = -11 \rightarrow 11$
$l = -42 \rightarrow 42$

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Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.050$
$wR(F^2) = 0.148$
$S = 1.07$
6945 reflections
426 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.075P)^2 + 5.5P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.83$ e Å^{-3}
$\Delta\rho_{\min} = -0.67$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Sn1—O1	2.095 (3)	O1—C9	1.300 (5)
Sn1—O4	2.101 (3)	O2—C9	1.250 (5)
Sn1—C5	2.116 (5)	O3—C11	1.350 (5)
Sn1—C1	2.120 (5)	O4—C22	1.285 (5)
Sn1—O5	2.570 (3)	O5—C22	1.263 (5)
Sn1—O2	2.686 (3)	O6—C24	1.346 (6)
O1—Sn1—O4	79.05 (11)	O1—Sn1—O2	53.28 (10)
O1—Sn1—C5	101.55 (15)	O4—Sn1—O2	132.33 (10)
O4—Sn1—C5	109.03 (15)	C5—Sn1—O2	83.23 (14)
O1—Sn1—C1	109.83 (17)	C1—Sn1—O2	90.36 (16)
O4—Sn1—C1	107.93 (16)	O5—Sn1—O2	172.17 (10)
C5—Sn1—C1	135.04 (18)	C9—O1—Sn1	106.5 (3)
O1—Sn1—O5	133.88 (10)	C9—O2—Sn1	80.1 (2)
O4—Sn1—O5	54.97 (11)	C22—O4—Sn1	103.5 (3)
C5—Sn1—O5	97.07 (14)	C22—O5—Sn1	82.3 (2)
C1—Sn1—O5	83.90 (16)		

Table 2
Hydrogen-bonding geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O3—H3···O2	0.84	1.90	2.626 (4)	144
O6—H6···O5	0.84	1.89	2.631 (5)	146

The *ortho*-F atoms are disordered over both *ortho* positions with equivalent site-occupancy factors. The C—F distances involving disordered F atoms were restrained using the *DFIX* command. The H atoms were located from difference Fourier syntheses and were included in the refinements at idealized positions with isotropic displacement displacement parameters 1.5 (methyl and hydroxyl) and 1.2 (the rest) times the equivalent thermal displacement parameters of the atoms to which they were bonded. The final difference map was free of any chemically significant features, with some electron density in the vicinity of the Sn atom.

Data collection: *COLLECT* (Hooft, 1998); cell refinement: *HKL DENZO* (Otwinowski & Minor, 1997); data reduction: *SCALEPACK* (Otwinowski & Minor, 1997); program(s) used to solve structure: *SAPI*91 (Fan, 1991); 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 (Sheldrick, 1997).

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