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Note

Crystal and molecular structure of dimeric bis[dibutyl(2-hydroxyphenylmethylimino-β-alaninato)tin] oxide

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Introduction

Several dicarboxylate tetraorganodistannoxanes, $[(R_2SnOCOR')_2O)_2]$, where $R = CH_3$, $n\text{-}C_4H_9$ and $R' = CH_3$, CCl_3 and CF_3 have been reported (Harrison *et al.*, 1987). Recently Tiekink (1991) studied a series of distannoxanes where a donor atom like N, S, or O resides on the carboxylate group R'. However, no study has been reported for the case when R' contains an unreacted labile functional group (Tiekink, 1991). This is because a bischelating tridentate ligand like 2,6-pyridinedicarboxylic acid reacts with diorganotin oxide to give a bicyclodicarboxylate derivative, $R_2Sn(OCOC_5H_3NCOO)$ (Gielen *et al.*, 1987). This mode of chelation was also adopted for unsymmetrical ligands; for example, the bifunctional Schiff-base ligands were reported to react with diorganotin oxides to give bicyclodiorganotin compounds like $R_2Sn[OC_6H_4CH{=}N(CH_2)_xO]$ ($R{=}CH_3$, $n\text{-}C_4H_9$, $x = 1, 2, 3$) (Tiwari *et al.*, 1986) and $R_2Sn(OC_6H_4{-}CH{=}NCH_2COO)$ ($R{=}CH_3$, $n\text{-}C_4H_9$) (Smith *et al.*).

In this paper, we report that the unsymmetric bifunctional N-salicylidene-β-alanine ligand reacts with dibutyltin oxide to give a dicarboxylate tetraorganodistannoxane whereas the labile phenolic group remains intact. This conclusion was confirmed by an X-ray structural determination for the dimer of bis[dibutyl (2-hydroxyphenylmethylimino-β-alaninato)tin] oxide, $\{[Bu_2Sn(OCOCH_2CH_2{-}N{=}CHC_6H_4OH)]_2O\}_2$.

Experimental

Preparation of N-salicylidene-β-alanine

A mixture of β-alanine (5.4 g, 60 mmol) and salicylaldehyde (8.4 g, 70 mmol) in 100 ml absolute ethanol and 20 ml methanol were refluxed for 3–4 hr. The unreacted β-alanine was filtered off and the filtrate cooled in a refrigerator. The precipitate (9.0 g, 78%) was collected, dried, and recrystallized in methanol to give pure N-salicylidene-β-alanine, m.p. 138–139°C.

Preparation of bis[dibutyl(2-hydroxyphenylmethylimino-β-alaninato)tin] oxide

An equimolar amount of N-salicylidene-β-alanine (20 mmol) and dibutyltin oxide were added to 150 ml toluene. The mixture was refluxed and the water formed removed azeotropically using a Dean-Stark apparatus (ca. 4 hr). The solvent was then removed using a rotatory evaporator and ca. 20 ml pet ether (60–80°C) was added on cooling; the precipitate (7.6 g, 44%) was collected, dried, and recrystallized from 100 ml pet ether to give a yellow solid, m.p. 93–94°C. Elemental analysis yielded C 49.94; H 6.49; N 3.21%. $C_{72}H_{112}N_4O_{14}Sn_4$ requires C 49.92; H 6.52; N 3.23%.

Crystals of suitable quality for a subsequent X-ray diffraction study were obtained as yellow prisms by slow evaporation of a solution of the title compound in benzene and pet ether.

Crystal data: $\{[Bu_2Sn(OCOCH_2N{=}CHC_6H_4OH)]_2O\}_2$, $Fw = 1732.47$, space group $P\bar{1}$ (No. 2), $a = 12.124(2)$, $b = 13.125(3)$, $c = 14.892(3)$ Å, $\alpha = 114.81(2)$, $\beta = 91.50(2)$, $\gamma = 103.88(1)°$, $V = 2066.6(7)$ Å^3, $Z = 1$, $D_c = 1.36$ g

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cm^{-3}, $F(000) = 880$, Mo $K\alpha$ radiation ($\lambda = 0.71073$ Å), μ(Mo $K\alpha$) $= 12.49\ cm^{-1}$.

X-ray data collection, structure solution and refinement

Raw intensities (7454 unique reflections) collected to $2\theta_{max} = 55°$ on a Nicolet R3m/V diffractometer were processed with the profile-fitting procedure of Diamond (1969) and corrected for absorption using ψ-scan data (Kopfmann and Huber, 1968), of which 4940 with $I > 3\sigma(I)$ were considered as observed and used in the structure analysis. The structure was solved by the direct method. The terminal methyl group of each of the two butyl ligands bonded to Sn(1) exhibited two-fold positional disorder and was represented by two C atoms of half site occupancy. Except for the C atoms of these two butyl groups, all other non-hydrogen atoms were refined with anisotropic temperature factors. The hydroxy H atom was located from a difference map and the other H atoms (except those in the butyl groups containing the disordered C atoms) were generated geometrically (C—H bonds fixed at 0.96 Å). The hydrogen atoms were assigned appropriate isotropic temperature factors and included in structure factor calculations. Final R and R_w are 0.043 and 0.060, respectively, with $w = [\sigma^2(F_o) + 0.0004|F_o|^2]^{-1}$. Computations were performed using the SHELXL-PLUS program package (Sheldrick, 1985) on a DEC MicroVAX-II computer. Analytic expressions of neutral-atom scattering factors were used, and anomalous dispersion corrections were incorporated (*International Tables for X-Ray Crystallography*, Vol. IV, 1974).

Results and discussion

Bifunctional tridentate ligands usually react with diorganotin oxides to give bicyclo derivatives (Gielen *et al.*, 1987; Tiwari, *et al.*, 1986, Smith, *et al.*), and it was anticipated that the ligand $HOC_6H_4CH{=}NCH_2CH_2COOH$ would behave likewise. However, our X-ray structural investigation of $\{[Bu_2Sn(OCOCH_2CH_2N{=}CHC_6H_4OH)]_2O\}_2$ confirmed the dicarboxylato-tetraorganostannoxane formulation.

The molecular structure of the dimer is illustrated in Fig. 1 which shows the numbering scheme employed. The fractional atomic coordinates with equivalent isotropic thermal parameter are listed in Table 1, and the bond lengths and bond angles are given in Table 2. The structure consists of discrete molecules of $\{[Bu_2Sn(OCOCH_2CH_2{-}N{=}CHC_6H_4OH)]_2O\}_2$, there being no significant intra- and intermolecular contacts between Sn and the phenolic O and imino N atoms.

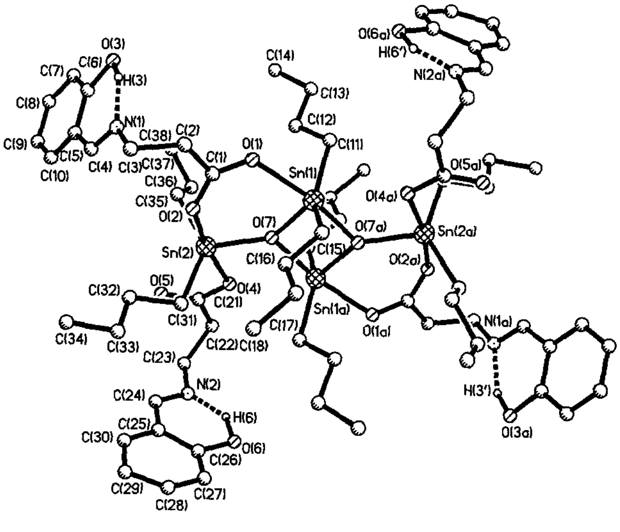

Fig. 1. Perspective view showing the molecular structure of $\{[Bu_2Sn(OCOCH_2CH_2N{=}CHC_6H_4OH)]_2O\}_2$.

As observed for the related compounds (Mokal *et al.*, 1991), the core geometry of the molecule consists of a centrosymmetric planar four-membered Sn_2O_2 ring with two exocyclic R_2Sn entities connected to the bridging O(7,7a) atoms. The two pairs of exo- and endocyclic Sn atoms are each linked by a bidentate bridging carboxylato ligand, and the two remaining carboxylato ligands coordinate the exocyclic Sn atom in the monodentate mode with a Sn(2) · · · O(5) separation of 2.924(6) Å. The short C(21)—O(5) bond distance of 1.20(1) Å is consistent with a similar C—O bond length of 1.225(9) Å reported for a corresponding nonbridging carbonyl group in the compound $\{[Bu_2Sn(OCOCH_2SPh)]_2O\}_2$ (Mokal *et al.*, 1991). Thus both Sn atoms in these two related structures are five-coordinate and exist in trigonal bipyramidal geometries. The axial positions about the Sn(2) atom are defined by two carboxylate O atoms, i.e., O(2) and O(4), and the Sn atom lies 0.11 Å out of the trigonal plane in the direction of the O(4) atom. Similarly for the Sn(1) atom, the carboxylate O(1) and the bridging O(7a) atoms occupy axial positions with the Sn atom lying 0.07 Å out of the trigonal plane in the direction of the O(7a) atom.

The *cis* configuration adopted by both carboxylato ligands, as indicated by the torsion angles N(1)—C(4)—C(5)—C(6) (−0.4°) and N(2)—C(24)—C(25)—C(26) (4.4°), is conductive to the formation of intramolecular hydrogen bonds [N(1) · · · O(3) = 2.59(2) Å and N(2) · · · O(6) = 2.52(2) Å], which compare well

Table 1. Atomic coordinates ($\times 10^5$ for Sn; $\times 10^4$ for other atoms) and equivalent isotropic temperature factors[a] ($Å^2 \times 10^4$ for Sn; $\times 10^3$ for others)

Atom	x	y	z	U_{eq}	Atom	x	y	z	U_{eq}
Sn(1)	39174(3)	53296(4)	−4279(3)	671(2)	C(15)	4413(7)	7151(7)	−32(6)	102(2)
Sn(2)	38695(4)	52116(4)	20396(3)	773(3)	C(16)	4622(10)	7953(9)	1057(7)	167(4)
O(1)	2218(3)	5485(4)	151(3)	84(2)	C(17)	5083(12)	9251(12)	1202(11)	220(6)
O(2)	2613(4)	6121(4)	1782(4)	93(3)	C(18)	5174(30)	10080(18)	2283(14)	271(16)
O(3)	−1399(5)	3375(6)	1216(5)	132(4)	C(18′)	4191(30)	9403(26)	581(24)	354(23)
O(4)	5269(3)	4462(4)	2098(3)	85(3)	C(21)	5347(6)	4294(7)	2887(6)	87(4)
O(5)	4692(4)	4500(5)	3489(4)	106(3)	C(22)	6346(7)	3817(8)	2982(6)	108(5)
O(6)	8777(7)	7177(8)	4139(6)	188(6)	C(23)	6890(9)	4328(9)	4048(8)	131(7)
O(7)	4435(3)	5041(4)	736(3)	72(2)	C(24)	7061(7)	6301(11)	5073(7)	111(6)
N(1)	−23(5)	5466(6)	2071(5)	89(3)	C(25)	7513(8)	7529(11)	5407(7)	117(6)
N(2)	7438(6)	5553(9)	4381(6)	114(5)	C(26)	8383(10)	7952(12)	4895(9)	150(8)
C(1)	2024(5)	5982(6)	1009(6)	76(4)	C(27)	8758(15)	9131(16)	5241(13)	254(13)
C(2)	1014(6)	6491(7)	1150(6)	95(4)	C(28)	8327(19)	9869(16)	6029(15)	239(13)
C(3)	502(6)	6607(7)	2130(6)	101(5)	C(29)	7506(17)	9565(25)	6449(15)	245(17)
C(4)	216(6)	5237(9)	2812(6)	96(5)	C(30)	7143(12)	8328(15)	6164(10)	178(9)
C(5)	−238(7)	4183(9)	2853(7)	103(6)	C(31)	4677(7)	6888(7)	3265(5)	116(5)
C(6)	−1056(8)	3229(10)	2029(8)	115(6)	C(32)	3850(9)	7247(11)	4077(8)	183(9)
C(7)	−1531(10)	2182(10)	2110(10)	146(8)	C(33)	4358(13)	8472(11)	4804(11)	269(13)
C(8)	−1203(14)	2044(15)	2889(13)	170(12)	C(34)	3514(16)	8670(13)	5543(12)	323(17)
C(9)	−411(15)	2920(19)	3664(12)	180(14)	C(35)	2440(6)	3788(7)	1811(7)	110(5)
C(10)	96(9)	3992(12)	3643(8)	137(8)	C(36)	2618(6)	2594(7)	1395(7)	120(6)
C(11)	2910(6)	3755(6)	−1608(5)	82(2)	C(37)	1527(8)	1681(9)	1310(10)	167(8)
C(12)	2255(7)	2854(6)	−1257(6)	109(2)	C(38)	1728(11)	478(10)	907(12)	242(13)
C(13)	1629(8)	1665(8)	−2133(7)	137(3)	H(3)	−1028	4251	1375	200
C(14)	817(12)	900(11)	−1768(11)	105(5)	H(6)	8370	6095	3999	200
C(14′)	2441(22)	1132(25)	−2794(21)	309(20)					

[a] U_{eq} defined as one third of the trace of the orthogonalized U tensor. The atoms C(14), C(14′), C(18) and C(18′) have the same site occupancy factor of 1/2.

Table 2. Bond lengths (Å) and bond angles (°)[a]

Sn(1)−O(1)	2.275(4)	Sn(1)−O(7)	2.037(5)
Sn(1)−C(11)	2.117(5)	Sn(1)−C(15)	2.130(8)
Sn(1)−O(7a)	2.182(4)	Sn(2)−O(2)	2.262(6)
Sn(2)−O(4)	2.172(5)	Sn(2)−O(7)	2.017(4)
Sn(2)−C(31)	2.152(6)	Sn(2)−C(35)	2.119(7)
O(1)−C(1)	1.226(9)	O(2)−C(1)	1.26(1)
O(3)−C(6)	1.37(2)	O(4)−C(21)	1.29(1)
O(5)−C(21)	1.20(1)	O(6)−C(26)	1.35(1)
O(7)−Sn(1a)	2.182(4)		
N(1)−C(3)	1.44(1)	N(1)−C(4)	1.30(1)
N(2)−C(23)	1.44(1)	N(2)−C(24)	1.28(1)
C(1)−C(2)	1.51(1)	C(2)−C(3)	1.56(1)
C(4)−C(5)	1.39(2)	C(5)−C(6)	1.45(1)
C(5)−C(10)	1.37(2)	C(6)−C(7)	1.41(2)
C(7)−C(8)	1.31(3)	C(8)−C(9)	1.37(2)
C(9)−C(10)	1.41(3)	C(11)−C(12)	1.55(1)
C(12)−C(13)	1.544(9)	C(13)−C(14)	1.51(2)
C(13)−C(14′)	1.49(3)	C(15)−C(16)	1.49(1)
C(16)−C(17)	1.57(2)	C(17)−C(18)	1.50(2)
C(17)−C(18′)	1.51(4)	C(21)−C(22)	1.52(1)

Table 2. Continued

C(22)—C(23)	1.50(1)	C(24)—C(25)	1.43(2)
C(25)—C(26)	1.46(2)	C(25)—C(30)	1.35(2)
C(26)—C(27)	1.36(2)	C(27)—C(28)	1.38(3)
C(28)—C(29)	1.26(3)	C(29)—C(30)	1.44(3)
C(31)—C(32)	1.58(1)	C(32)—C(33)	1.47(1)
C(33)—C(34)	1.51(3)	C(35)—C(36)	1.50(1)
C(36)—C(37)	1.52(1)	C(37)—C(38)	1.52(2)
O(3)—H(3)	1.05	O(6)—H(6)	1.31
N(1) · · · H(3)	1.65	N(2) · · · H(6)	1.45
O(3) · · · N(1)	2.59(2)	O(6) · · · N(2)	2.52(2)
O(1)—Sn(1)—O(7)	90.3(2)	O(1)—Sn(1)—C(11)	84.7(2)
O(7)—Sn(1)—C(11)	110.7(3)	O(1)—Sn(1)—C(15)	89.9(3)
O(7)—Sn(1)—C(15)	110.2(3)	C(11)—Sn(1)—C(15)	138.8(3)
O(1)—Sn(1)—O(7a)	165.2(2)	O(7)—Sn(1)—O(7a)	75.7(2)
C(11)—Sn(1)—O(7a)	95.7(2)	C(15)—Sn(1)—O(7a)	99.3(3)
O(2)—Sn(2)—O(4)	168.7(2)	O(2)—Sn(2)—O(7)	89.7(2)
O(4)—Sn(2)—O(7)	80.0(2)	O(2)—Sn(2)—C(31)	84.3(3)
O(4)—Sn(2)—C(31)	95.1(3)	O(7)—Sn(2)—C(31)	112.9(3)
O(2)—Sn(2)—C(35)	87.7(3)	O(4)—Sn(2)—C(35)	100.4(3)
O(7)—Sn(2)—C(35)	111.0(3)	C(31)—Sn(2)—C(35)	135.3(3)
Sn(1)—O(1)—C(1)	129.7(4)	Sn(2)—O(2)—C(1)	133.1(4)
Sn(2)—O(4)—C(21)	111.7(5)	Sn(1)—O(7)—Sn(2)	134.8(2)
Sn(1)—O(7)—Sn(1a)	104.3(2)	Sn(2)—O(7)—Sn(1a)	120.4(2)
C(3)—N(1)—C(4)	119.6(6)	C(23)—N(2)—C(24)	119.2(9)
O(1)—C(1)—O(2)	125.1(7)	O(1)—C(1)—C(2)	117.3(7)
O(2)—C(1)—C(2)	117.5(7)	C(1)—C(2)—C(3)	113.5(8)
N(1)—C(3)—C(2)	110.4(6)	N(1)—C(4)—C(5)	125.2(7)
C(4)—C(5)—C(6)	120.2(11)	C(4)—C(5)—C(10)	121.8(8)
C(6)—C(5)—C(10)	118.0(12)	O(3)—C(6)—C(5)	119.9(11)
O(3)—C(6)—C(7)	121.2(8)	C(5)—C(6)—C(7)	118.7(12)
C(6)—C(7)—C(8)	121.1(11)	C(7)—C(8)—C(9)	121.2(19)
C(8)—C(9)—C(10)	121.0(20)	C(5)—C(10)—C(9)	119.7(10)
Sn(1)—C(11)—C(12)	113.7(5)	C(11)—C(12)—C(13)	113.0(7)
C(12)—C(13)—C(14)	111.1(8)	C(12)—C(13)—C(14′)	111.8(11)
C(14)—C(13)—C(14′)	117.0(16)	Sn(1)—C(15)—C(16)	116.3(8)
C(15)—C(16)—C(17)	108.8(10)	C(16)—C(17)—C(18)	109.7(15)
C(16)—C(17)—C(18′)	105.0(14)	C(18)—C(17)—C(18′)	110.1(20)
O(4)—C(21)—O(5)	122.9(9)	O(4)—C(21)—C(22)	113.5(7)
O(5)—C(21)—C(22)	123.5(9)	C(21)—C(22)—C(23)	111.5(7)
N(2)—C(23)—C(22)	108.8(10)	N(2)—C(24)—C(25)	122.7(10)
C(24)—C(25)—C(26)	119.1(10)	C(24)—C(25)—C(30)	122.9(12)
C(26)—C(25)—C(30)	117.9(13)	O(6)—C(26)—C(25)	119.5(12)
O(6)—C(26)—C(27)	124.7(14)	C(25)—C(26)—C(27)	115.8(13)
C(26)—C(27)—C(28)	121.4(18)	C(27)—C(28)—C(29)	126.2(20)
C(28)—C(29)—C(30)	114.0(20)	C(25)—C(30)—C(29)	123.8(16)
Sn(2)—C(31)—C(32)	111.0(5)	C(31)—C(32)—C(33)	108.7(10)
C(32)—C(33)—C(34)	102.7(11)	Sn(2)—C(35)—C(36)	117.7(5)
C(35)—C(36)—C(37)	111.2(7)	C(36)—C(37)—C(38)	110.5(9)
O(3)—N(3) · · · N(1)	146	O(6)—H(6) · · · N(2)	132

[a] Symmetry transformation a $(-x, -y, -z)$.

with the corresponding value [2.62(8) Å] reported for 2-bromo-N-salicylidene aniline (Burr *et al.*, 1969). Thus the labile phenol group and the imino nitrogen atom are both rendered ineffective for coordinative interaction with the tin atoms in the structure. As observed from Table 2, the O—H distances (1.05 and 1.31 Å) are shorter than the H · · · N distances (1.65 and 1.45 Å), indicating that strong intramolecular hydrogen bonding between the donor phenolic group and the acceptor imino nitrogen atom takes precedence over the formation of an intermediate zwitterion by shifting the phenolic proton to the imino nitrogen as reported previously (Kawaya *et al.*, 1985, Bullock *et al.*, 1979).

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H atom coordinates, thermal parameters and structure factor data have been deposited with British Library, Boston Spa, Wetherby, West Yorkshire, UK, as supplementary publication 63229 (30 pages).