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Crystal structure of the tetrabutylbis(3-benzoylpropionato)distannoxane dimer, $[[(C_4H_9)_2SnO_2CCH_2CH_2C(O)C_6H_5]_2O]_2$

Seik Weng Ng [a], Chen Wei [b] and V.G. Kumar Das [b]

[a] *Institute of Advanced Studies and* [b] *Department of Chemistry, University of Malaya, 59100 Kuala Lumpur (Malaysia)*

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Abstract

Tetrabutylbis(3-benzoylpropionato)distannoxane crystallizes as a centrosymmetric dimer in which the intradimer Sn–O bond length is 2.047(6) Å.

Introduction

Distannoxanes can be obtained by incomplete hydrolysis of R_2SnX_2 diorganotin compounds. Originally formulated as monomeric $[(R_2XSn)_2O]$ compounds, they now appear to be essentially dimeric in the solid state. The evidence is especially compelling for the carboxylato distannoxanes, several of which have been crystallographically studied; they include the tetramethyl- [1–4], tetravinyl- [5], tetrabutyl- [6–10] and tetraphenyl- [11] distannoxanes, where X is an acetato [1], chloroacetato [2], trichloroacetato [3,6,11], trifluoroacetato [5,6], 2-aminobenzoato [7], 2-methoxybenzoato [8], 2-pyridylcarboxylato [9], or 2-thienylcarboxylato [10] ligand. Except for tetramethyldiacetatodistannoxane (which belongs to the chiral *Pa* space group) and one of the two crystallographic modifications of tetraphenylbis(trichloroacetato)distannoxane, the carboxylato-distannoxanes are centrosymmetric dimers containing a characteristic central $Sn^AO^ASn^{A'}O^{A'}$ rhombus flanked on its opposite sides by the four-membered rings, $Sn^AO^ASn^BO^B$ and $Sn^{A'}O^{A'}Sn^{B'}O^{B'}$.

The title compound was the unexpected product when dibutyltin oxide was treated with two molar equivalents of 3-benzoylpropionic acid in ethanol; when this reaction was carried out in acetone the product was dibutyltin bis(3-benzoylpropionate) [12].

Experimental

Dibutyltin oxide (2.50 g, 10 mmol) and 3-benzoylpropionic acid (3.60 g, 20 mmol) were heated together in a small volume of ethanol until a clear solution was formed. A white solid separated when the solution was cooled slowly. The solid was

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recrystallized from ethanol to give crystals of the distannoxane, $[[(C_4H_9)_2SnO_2CCH_2CH_2C(O)C_6H_5]_2O]_2$, m.p. 102–103°C. In the infrared, the compound displayed a strong band at 688 cm^{-1} that was assigned to the Sn–O–Sn stretch. The

Table 1

Positional and isotropic equivalent displacement parameters for $[[(C_4H_9)_2SnO_2CCH_2CH_2C(O)C_6H_5]_2O]_2$

Atom	*x*	*y*	*z*	*B* (Å^2) [a]
Sn1	1.26367(5)	0.45255(6)	1.03175(5)	3.47(2)
Sn2	0.94787(5)	0.36517(5)	0.98468(5)	3.43(2)
O	1.1017(5)	0.4778(5)	1.0118(5)	3.4(1)
O21	1.1954(5)	0.2834(5)	1.0129(5)	4.0(2)
O22	1.3779(5)	0.2688(6)	1.0457(6)	5.0(2)
O23	1.2374(7)	0.0639(8)	0.8206(6)	7.4(2)
O31	0.7639(5)	0.3445(5)	0.9634(5)	4.3(2)
O32	0.7677(6)	0.1617(5)	0.9468(7)	6.0(2)
O33	0.580(1)	0.1527(9)	0.7366(8)	10.5(4)
C1	1.3348(9)	0.4537(9)	0.9013(8)	4.5(3)
C2	1.287(1)	0.354(1)	0.8150(8)	6.0(3)
C3	1.339(1)	0.354(1)	0.7238(9)	6.9(4)
C4	1.289(2)	0.254(1)	0.638(1)	10.0(5)
C5	1.3444(9)	0.5037(9)	1.1848(8)	4.6(3)
C6	1.295(1)	0.441(1)	1.2551(9)	6.5(4)
C7	1.360(1)	0.487(1)	1.364(1)	8.1(4)
C8	1.308(2)	0.430(2)	1.436(1)	11.2(6)
C9	0.973(1)	0.319(1)	1.1259(8)	5.5(3)
C10	0.915(2)	0.377(2)	1.200(1)	11.9(6)
C11	0.936(2)	0.351(2)	1.3011(1)	12.1(6)
C12	0.890(3)	0.416(3)	1.372(2)	22(1)
C13	0.9655(9)	0.285(1)	0.8380(9)	5.7(3)
C14	0.874(1)	0.282(1)	0.756(1)	8.8(4)
C15	0.900(1)	0.233(1)	0.625(1)	9.2(4)
C16	0.803(2)	0.217(2)	0.572(2)	15.8(8)
C21	1.2825(9)	0.2251(8)	1.0276(7)	4.3(3)
C22	1.251(1)	0.1007(8)	1.0244(8)	5.0(3)
C23	1.1409(9)	0.0472(8)	0.9537(8)	4.3(3)
C24	1.1501(9)	0.0348(8)	0.8454(8)	5.1(3)
C25	1.050(1)	−0.0161(8)	0.7669(8)	4.8(3)
C26	1.067(1)	−0.042(1)	0.6676(9)	7.0(4)
C27	0.973(1)	−0.088(1)	0.592(1)	8.4(5)
C28	0.866(1)	−0.105(1)	0.617(1)	8.7(5)
C29	0.851(1)	−0.079(1)	0.715(1)	8.5(4)
C30	0.945(1)	−0.034(1)	0.793(1)	6.5(3)
C31	0.7122(9)	0.2414(8)	0.9473(8)	4.5(3)
C32	0.5860(8)	0.2352(9)	0.934(1)	5.6(3)
C33	0.5315(9)	0.1151(9)	0.8870(9)	5.3(3)
C34	0.544(1)	0.086(1)	0.782(1)	7.1(4)
C35	0.509(1)	−0.034(1)	0.724(1)	8.7(4)
C36	0.469(2)	−0.112(1)	0.774(1)	11.7(6)
C37	0.436(2)	−0.230(2)	0.714(2)	18.3(9)
C38	0.446(2)	−0.245(2)	0.613(2)	17.8(9)
C39	0.489(2)	−0.167(2)	0.562(2)	17.6(9)
C40	0.520(2)	−0.055(2)	0.622(1)	13.9(7)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $B = 4/3[a^2B_{1,1} + b^2B_{2,2} + c^2B_{3,3} + ab(\cos\alpha)B_{1,2} + ac(\cos\beta)B_{1,3} + bc(\cos\gamma)B_{2,3}]$.

carbonyl stretching bands were located at 1626, 1658, 1687 cm^{-1} (asymmetric) and 1310, 1358 cm^{-1} (symmetric).

An Enraf–Nonius CAD4 diffractometer was used for the crystal structure determination. Unit-cell parameters were fixed from 25 strong reflections in the $17 \leqslant \theta \leqslant 19°$ thin shell [13]. Intensity data were collected at room temperature up to a $2\theta_{max}$ of 44°. Direct phase determination using 3190 $|F_o| \geqslant 2.5\sigma|F_o|$ out of 3886 unique Mo-K_α reflections revealed only two Sn atoms, but the C and O atoms were derived from successive difference-Fourier syntheses. All the non-H atoms were refined anisotropically; H-atoms were included at fixed calculated positions. Refinement based on F converged at $R_1 = 0.039$, $R_2 = 0.046$; unit weights were used. Computations were performed using the MOLEN structure determination program [14] on a DEC MicroVax II minicomputer. The atomic coordinates are listed in Table 1, and the dimer is shown in Fig. 1. Other crystallographic details, including thermal displacement parameters and lists of observed and calculated structure factors, are available from the authors.

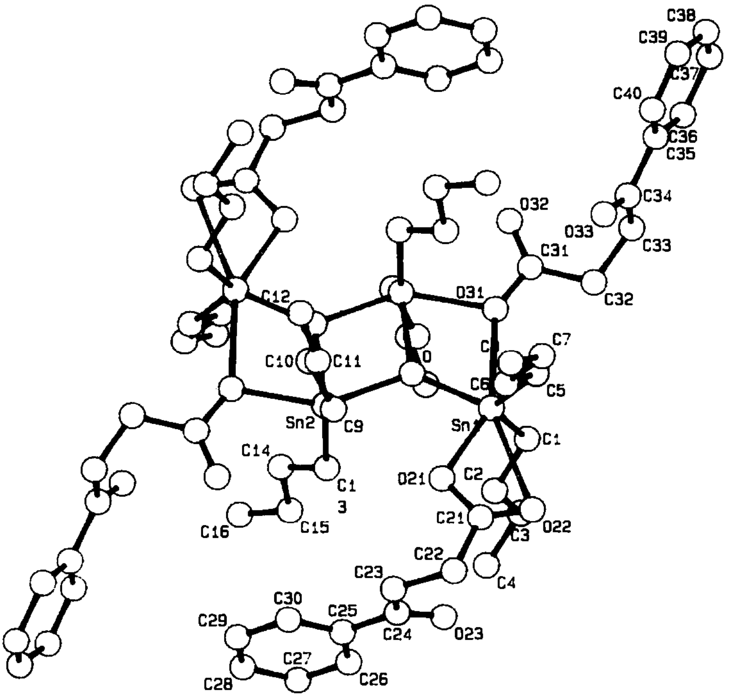


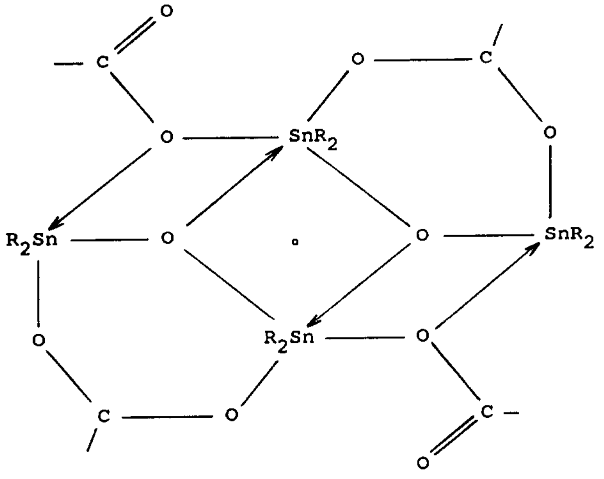
Fig. 1. PLUTO plot of tetrabutylbis(3-benzoylpropionato) distannoxane. Selected bond distances (Å) and angles (°): Sn1–O 1.993(6), Sn1–O21 2.121(6), Sn1–O22 2.746(7), Sn1–O31′ 2.517(7), Sn1–C1 2.13(1), Sn1–C5 2.14(1), Sn2–O 2.171(6), Sn2–O′ 2.047(6), Sn2–O31 2.191(6), Sn2–C9 2.12(1), Sn2–C13 2.13(1) Å; O–Sn1–O21 82.3(2), O–Sn1–O22 134.4(2), O–Sn1–O31′ 67.7(2), O–Sn1–C1 112.8(4), O–Sn1–C5 106.1(4), O21–Sn1–O22 52.3(2), O21–Sn1–O31′ 150.0(2), O21–Sn1–C1 103.7(3), O21–Sn1–C5 106.1(4), O22–Sn1–O31′ 157.8(2), O22–Sn1–C1 84.6(3), O22–Sn–C5 81.7(3), O31′–Sn1–C1 87.5(3), O31′–Sn1–C5 87.0(3), C1–Sn1–C5 128.3(4), O–Sn2–O′ 74.3(2), O–Sn2–O31 148.1(2), O–Sn2–C9 96.6(4), O–Sn2–C13 94.8(4), O′–Sn2–O31 73.9(2), O′–Sn2–C9 114.1(4), O′–Sn2–C13 111.9(4), O31–Sn2–C9 95.0(4), O31–Sn2–C13 98.3(4), C9–Sn2–C13 134.0(5), Sn1–O21–C21 106.1(6), Sn2–O31–C31 118.1(6), Sn1–O–Sn2 132.7(3), Sn1–O31′–Sn2′ 96.8(2), Sn2–O–Sn2′ 105.7(2)°. Symmetry transformation: (′) $2-x$, $1-y$, $2-z$.

Crystal data

$C_{72}H_{108}O_{14}Sn_4$; FW 1672.42; triclinic, $P\bar{1}$, a 12.1302(5), b 12.2237(5), c 13.8691(5) Å, α 101.185(3), β 99.436(3), γ 94.196(3)°, V 1978.3(1) Å^3, $D_{\text{X-ray}}$ 1.404 g cm^{-3}, μ 13.06 cm^{-1} for $Z = 1$.

Results and discussion

The centrosymmetric dicarboxylatodistannoxanes whose crystal structures have been determined adopt various conformations. In the most common [2–8,10,11] conformation, one carboxylato group is coordinated to two tin atoms through its two oxygens and the other carboxylato group is attached unidentately to one of the tin atoms. The two monomers from a dimer thorough coordinate bonds, as shown in



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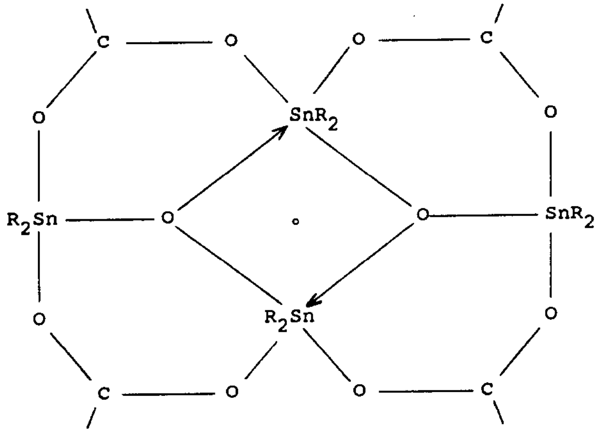
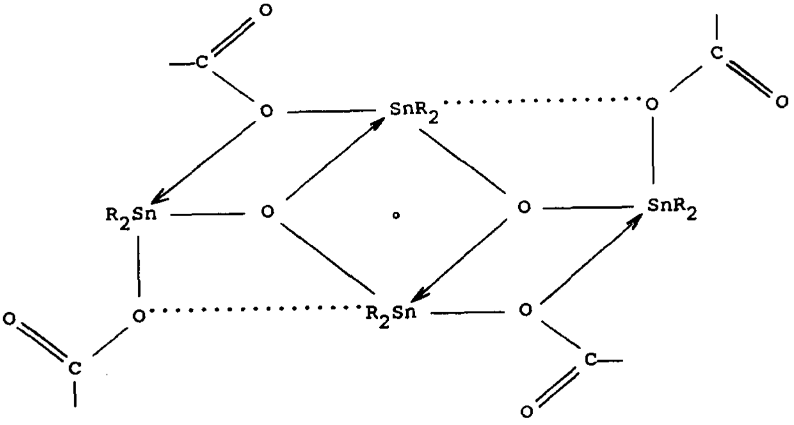


II

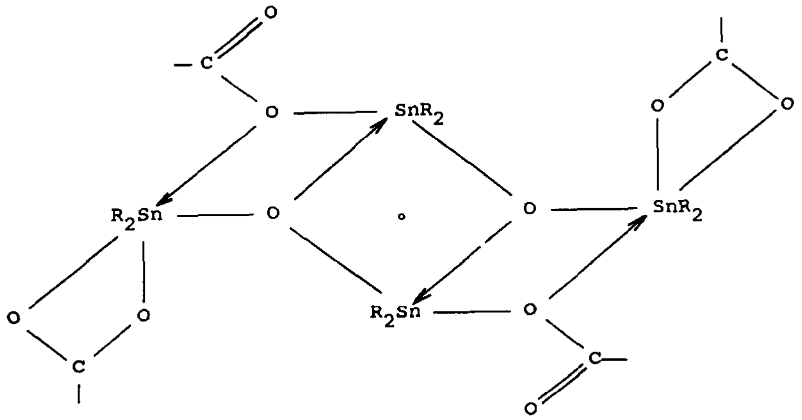
I. The two tin atoms belonging to the central Sn_2O_2 ring, and which are related by the center of inversion, exist in an unambiguous six-coordinate environment. On the other hand, the two tin atoms of the outer Sn_2O_2 rings are essentially five-coordinate. In the tetramethyl-, but not in the tetrabutyl-distannoxane derivatives, additional intermolecular Sn · · · O links (e.g., 3.09 Å in both the the monochloro- [2] and the trichloro- [3] acetatodistannoxanes) give rise to an overall chain crystal structure.

One modification of tetraphenylbis(trichloroacetato)distannoxane [11] adopts a conformation (II) in which all four carboxylato groups are bidentate, to give four six-membered rings, a conformation that can be envisaged as being derived from the previous conformation by a rotation of the pendant carboxylato group about the C–O bond.

In conformation III, two of the four carboxylato groups are coordinated through the ester oxygen atoms to the tin atoms, whereas the other two are unidentate. The



III



IV

ester oxygen of the latter set of carboxylato groups are, however, weakly linked to the tin atoms of the central Sn_2O_2 ring. The coordination number of all tin atoms is therefore essentially five. There is only one example of a carboxylato-distannoxane crystallizing in this conformation, namely, tetrabutylbis(2-pyridylcarboxylato)distannoxane [9]; however, the assignment of geometries at tin is more complicated since Sn · · · N contacts are also present.

Figure 1 shows that tetrabutylbis(3-propionato)distannoxane adopts a conformation similar to that adopted by the 2-picolinato-distannoxane, but since the length of the Sn · · · O interaction (3.221(7) Å) in the former exceeds that (3.066(5) Å [9]) in the latter, the structure is more appropriately represented by conformation IV. The present structure determination confirms the dimeric nature of the compound. The Sn–O bonds in the monomer are 1.993(6) and 2.171(6) Å, and the intradimer Sn–O bond of 2.047(6) Å is intermediate between the two distances. This tin–oxygen bond is much shorter than the ester oxygen–tin bonds in the molecule ((2.121(6), 2.191(6) Å). The angle at the distannoxane oxygen is opened to 132.7(3)°. The central Sn2–O–Sn2′–O′ is constrained by symmetry to be perfectly flat; the outer Sn1–O–Sn2′–O31′ rings are also flat (max. deviation 0.015(6) Å).

For the constituent Sn1 atoms in the outer Sn_2O_2 ring, the primary coordination sphere about each tin site includes the C1, C5, O, O21 and O31′ atoms, which make up an approximate *cis*-C_2SnO_3 trigonal bipyramid (C1–Sn1–C5 128.3(4)°). The distortion is severe, as can be seen from the axial bond angle at Sn1 (150.0(2)°) and the sum of angles (347.2(12)°) in the equatorial plane. The acyl O22 atom is located only 2.746(7) Å away from Sn1, but if this distance is regarded as corresponding to a formal dative bond, the Sn1 atom then has a six-coordinate status. The O, O21, O22 and O31′ atoms can be seen to comprise a trapezoidal plane, which is almost perpendicular to the plane passing through C1, Sn1 and C5. The overall geometry at Sn1 may therefore be described as a skew-trapezoidal bipyramid. This 2.746(7) Å dative bond is somewhat longer than those found in the skew-trapezoidal bipyramidal dibutyltin bis-4-thiophenoxyacetate (2.559(5) Å [15]) and dibutyltin 2-bromobenzoate (2.617(5) Å); the latter structure is distorted from a skew-trapezoidal bipyramid towards a *trans*-pentagonal bipyramid since the molecules are packed in the crystal structure as weakly bridged dimers [16].

For the constituent Sn2 atoms in the central Sn_2O_2 ring, the enveloping C9, C13, O, O′ and O31 atoms define a distorted *cis*-C_2SnO_3 trigonal bipyramidal configuration (C–Sn–C 134.0(5)°). The equatorial plane is flat (sum of angles 360.0(13)°), but the axial bonds are severely bent (148.1(2)°).

Acknowledgments

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