

Note

# [2,6-(*t*-BuOCH<sub>2</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>Sn(OH)]<sub>2</sub>O: A rare example of a monomeric tetraorganodistannoxane stabilized by intramolecular hydrogen bridges <sup>☆</sup>

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## Abstract

The synthesis and molecular structure of [2,6-(*t*-BuOCH<sub>2</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>Sn(OH)]<sub>2</sub>O (**2**), the only second example of a monomeric tetraorganodistannoxane, is reported. Compound **2** crystallizes in two polymorphic modifications (**2a**, monoclinic; **2b**, triclinic). The two modifications especially differ in their intramolecular Sn···O distances which fall in the range between 2.789(3) and 3.194(5) Å. It appears, that both the latter and intramolecular O···H–O bridges (2.882(4)–2.907(6) Å) contribute to the stability of the monomeric structures.  
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Tetraorganodistannoxanes R<sub>2</sub>XSnOSnYR<sub>2</sub> (R = alkyl, aryl; X, Y = halogen, OH, OR, OSiMe<sub>3</sub>, OCOR, OP(S)(OR)<sub>2</sub>, NO<sub>3</sub>, N<sub>3</sub>, NCS, OReO<sub>3</sub>) (Chart 1) are a well-established class of organotin compounds and have been investigated comprehensively over many years [1–3].

The reason for this ongoing interest are (i) the structural particularities such as dimerization in both solution and solid state leading to so-called ladder-type arrangements with five- and/or six-coordinate tin atoms and (ii) the application of these compounds as catalysts for a variety of organic reactions [4].

Noteworthy, among the many structurally characterized tetraorganodistannoxanes [2] there is, to the best of our knowledge, only one example of such a compound that is

monomeric in solution and in the solid state, namely [(Me<sub>3</sub>Si)<sub>2</sub>CH]<sub>2</sub>(OH)Sn]<sub>2</sub>O, hereafter referred to as compound **1** [5]. This is of some interest as it, in addition to other arguments, supports the idea that the catalytic activity of tetraorganodistannoxanes might indeed be associated with monomeric rather than dimeric species [6].

Compound **1** was obtained by hydrolysis of the related diorganotin oxide [(Me<sub>3</sub>Si)<sub>2</sub>CH]<sub>2</sub>SnO<sub>2</sub>, which in turn was obtained by oxidation with Me<sub>3</sub>NO of the diorganostannylene [(Me<sub>3</sub>Si)<sub>2</sub>CH]<sub>2</sub>Sn [5].

In course of ongoing studies on intramolecularly O,C,O-coordinated organoelement compounds [7,8] including heavy carbene analogues [9] we reacted the organolithium derivative 2,6-(*t*-BuOCH<sub>2</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>Li with SnCl<sub>2</sub> (Scheme 1).

From the crude reaction mixture which had been exposed to open atmosphere followed by addition of water the tetraorganodistannoxane [(2,6-(*t*-BuOCH<sub>2</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)<sub>2</sub>Sn(OH)]<sub>2</sub>O, **2**, was isolated as colorless crystalline material that is readily soluble in common organic solvents such as chloroform, benzene and thf [10]. Upon crystallization from different solvents, two polymorphic forms of compound **2**

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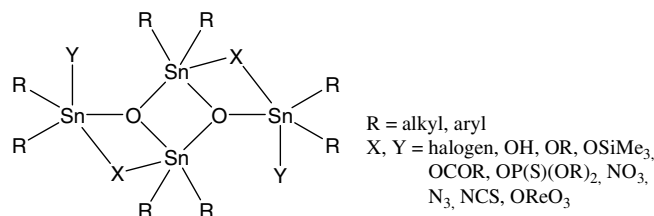
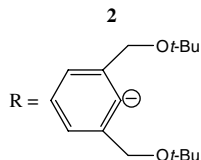
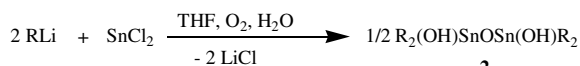


Chart 1.

Scheme 1. Synthesis of the intramolecularly coordinated tetraorganodistannoxane **2**.

were obtained, that are **2a** (monoclinic space group  $P2_1/c$ , single crystals were grown from benzene solution of **2**) and **2b** (triclinic space group  $P\bar{1}$ , obtained from hexane solution of **2**) [11] (see Table 1).

The molecular structures of **2a** and **2b** are shown in Figs. 1 and 2, respectively, and selected geometrical parameters are collected in Table 2.

Both tin atoms exhibit a distorted trigonal bipyramidal configuration with C(1), C(21), O(1) (at Sn1) and C(41), C(61), O(2) (at Sn2) occupying the equatorial, and O(3), O(31) (at Sn1) and O(3), O(71) (at Sn2) occupying the axial positions. For **2a** and **2b**, the intramolecular Sn(1)···O(31) distances of 2.789(3) and 2.795(4) Å, respectively, are almost identical whereas the Sn(2)···O(71) distances of 2.839(3) and 3.194(5) Å are longer and differ considerably. The three former distances are similar to the Sn–O distances found for {2,6-(*t*-BuOCH<sub>2</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>}Ph<sub>2</sub>Sn(mimt) (mimt = 1-methylimidazole-2-thiolate, Sn–O 2.7875(16) Å) [12] and (Z)-3,4,4-trimethyl-1-(triphenylstannyl)-1-penten-3-ol, Ph<sub>3</sub>SnCH=CHC(OH)(Me)(*t*-Bu), Sn–O 2.772(5) Å [13] whereas the latter is even longer than the Sn–O distance found in {2,6-(MeOCH<sub>2</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>}Ph<sub>3</sub>Sn (Sn–O 2.966(1) Å) [14]. The Sn(1)–O(1)/Sn(2)–O(2) distances fall in the range between 1.949(4) (**2b**) and 1.983(5) Å (**2b**) which is shorter than the corresponding Sn–O distance in the parent compound [ {(Me<sub>3</sub>Si)<sub>2</sub>CH}<sub>2</sub>(OH)Sn]<sub>2</sub>O (**1**) (2.032(7) Å) [5] and the Sn–O distance to the terminal hydroxy-group in [ {(Me<sub>3</sub>SiCH<sub>2</sub>)<sub>2</sub>(OH)Sn]<sub>2</sub>O<sub>2</sub> (2.032(4) Å) [15]. The Sn(1)–O(3)/Sn(2)–O(3) distances fall in the narrow range between 1.979(4) (**2b**) and 1.953(4) Å (**2b**) which is close to the corresponding distance in [ {(Me<sub>3</sub>Si)<sub>2</sub>CH}<sub>2</sub>(OH)Sn]<sub>2</sub>O (**1**) (1.956(4) Å). The Sn(1)–O(3)–Sn(2) angles of 134.42(14)/134.4(2)° are much bigger than the corresponding angle in compound **1** (125.0(5) [5]. Most remarkably, there are intramolecular O(1)···O(2) distances

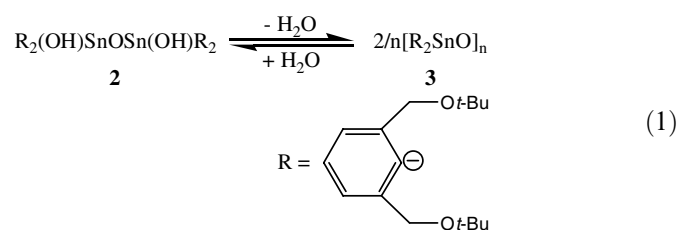
Table 1

Crystal data and the structure refinement details for compounds **2a** and **2b**

Compound	<b>2a</b>	<b>2b</b>
Empirical formula	C <sub>64</sub> H <sub>102</sub> O <sub>11</sub> Sn <sub>2</sub>	C <sub>64</sub> H <sub>102</sub> O <sub>11</sub> Sn <sub>2</sub>
Formula weight	1284.84	1284.84
Temperature (K)	173(1)	173(1)
Wavelength (Å)	0.71073	0.71073
Crystal system, space group	Monoclinic, $P2_1/c$	Triclinic, $P\bar{1}$
Unit cell dimensions		
<i>a</i> (Å)	13.2748(7)	13.427(4)
<i>b</i> (Å)	20.625(2)	14.481(5)
<i>c</i> (Å)	25.062(2)	18.141(7)
$\alpha$		82.90(1)
$\beta$ (°)	104.810(4)	70.38(3)
$\gamma$		88.50(2)
Volume (Å <sup>3</sup> )	6633.9(8)	3297(2)
<i>Z</i>	4	2
Density (calculated) (Mg/m <sup>3</sup> )	1.286	1.294
Absorption coefficient (mm <sup>-1</sup> )	0.807	0.812
<i>F</i> (000)	2696	1398
Crystal size (mm)	0.15 × 0.15 × 0.13	0.10 × 0.10 × 0.10
Theta range for data collection (°)	3.08 to 25.35	2.92 to 25.28.
Index ranges	–15 ≤ <i>h</i> ≤ 15, –24 ≤ <i>h</i> ≤ 24, –30 ≤ <i>h</i> ≤ 29	–16 ≤ <i>h</i> ≤ 16, –17 ≤ <i>k</i> ≤ 17, –19 ≤ <i>l</i> ≤ 21
	58 345/11 919	32 493/11 209
	[ <i>R</i> <sub>int</sub> = 0.082]	[ <i>R</i> <sub>int</sub> = 0.076]
	4476	3873
Completeness to $2\theta = 27.48$	98.1%	93.6%
Absorption correction	None	None
Refinement method	Full-matrix least-squares on <i>F</i> <sup>2</sup>	Full-matrix least-squares on <i>F</i> <sup>2</sup>
	11 919/0/723	11 209/0/699
Goodness-of-fit on <i>F</i> <sup>2</sup>	0.524	0.775
Final <i>R</i> indices [ <i>I</i> > 2σ( <i>I</i> )]	<i>R</i> <sub>1</sub> = 0.0366, <i>wR</i> <sub>2</sub> = 0.0555	<i>R</i> <sub>1</sub> = 0.053, <i>wR</i> <sub>2</sub> = 0.086
<i>R</i> indices (all data)	<i>R</i> <sub>1</sub> = 0.1408, <i>wR</i> <sub>2</sub> = 0.0679	<i>R</i> <sub>1</sub> = 0.1757, <i>wR</i> <sub>2</sub> = 0.0968
Maximum shift/esd	0.001	0.001
Largest differences in peak and hole (e Å <sup>-3</sup> )	0.456 and –0.357	0.633 and –0.488

of 2.882(4) (**2a**) and 2.891(6) Å (**2b**), and O(1)···O(11) (**2a**) and O(2)···O(51) (**2b**) distances of 2.891(4) and 2.907(6) Å which hint at weak O–H···O hydrogen bridges.

In solution, compound **2** undergoes the equilibrium that is shown in the following equation:



Thus, the <sup>119</sup>Sn NMR spectrum of a solution of compound **2** in C<sub>6</sub>D<sub>6</sub> showed two resonances at δ –152 (signal *a*, integral 4) and δ –174 (signal *b*, integral 1). Signal *a* is tentatively assigned to the molecular diorganotin oxide **3** with *n* being likely 2 or 3 whereas signal *b* belongs to compound **2**. This interpretation is supported by the observation that

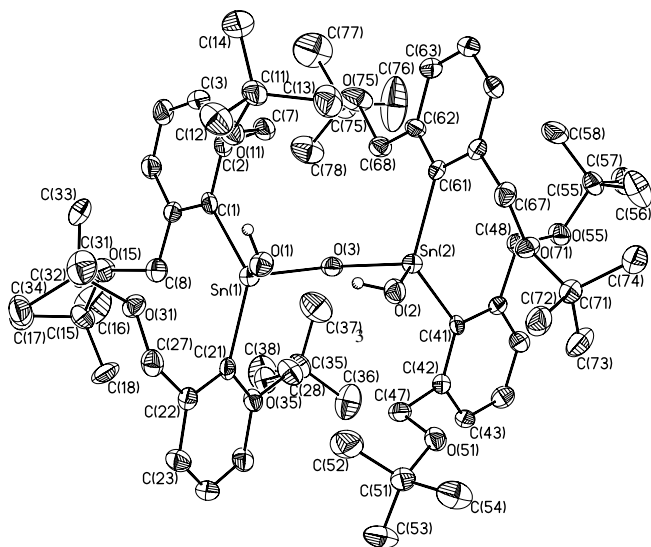


Fig. 1. General view (SHELXTL) of **2a** showing 30% displacement ellipsoids and the atom numbering scheme. The hydrogen atoms (except OH) are omitted for clarity.

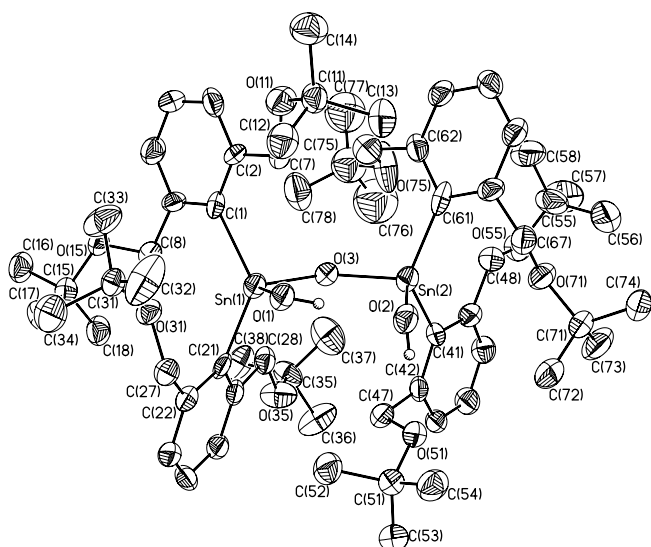


Fig. 2. General view (SHELXTL) of **2b** showing 30% displacement ellipsoids and the atom numbering scheme. The hydrogen atoms (except OH) are omitted for clarity.

addition of a droplet of water to the solution shifted the equilibrium to the left, i.e. the integral of signal *b* increased. Attempts at isolating compound **3** failed.

In conclusion, it appears that not only kinetic stabilization by bulky substituents such as in compound **1** but also intramolecular hydrogen bridges between SnOH-functions and donor atoms such as oxygen being part of the organic substituent *R* allows isolation of monomeric tetraorgano-distannoxanes, like the title compound. This concept was already exploited for the synthesis of the diorganotin dihydroxide  $\text{Fc}_2\text{Sn}(\text{OH})_2$  ( $\text{Fc} = \text{CpFeC}_5\text{H}_3\text{CH}_2\text{NMe}_2$ ) [16] and might even work for the stabilization of an organotin trihydroxide.

Table 2

Selected bond distances (Å) and bond angles (°) for compounds **2a** and **2b**

	<b>2a</b> ( <i>P2</i> (1)/ <i>c</i> )	<b>2b</b> ( <i>P1</i> )
Sn(1)–O(1)	1.976(3)	1.949(4)
Sn(1)–O(3)	1.963(3)	1.979(4)
Sn(1)–O(31)	2.789(3)	2.795(4)
Sn(1)–C(1)	2.144(4)	2.127(7)
Sn(1)–C(21)	2.151(4)	2.123(7)
Sn(2)–O(2)	1.954(3)	1.983(5)
Sn(2)–O(3)	1.974(3)	1.953(4)
Sn(2)–O(71)	2.839(3)	3.194(5)
Sn(2)–C(41)	2.146(4)	2.145(7)
Sn(2)–C(61)	2.150(4)	2.082(8)
O(1) ... O(2)	2.882(4)	2.891(6)
O(1) ... O(11)	2.891(4)	
O(2) ... O(51)		2.907(6)
C(1)–Sn(1)–C(21)	127.3(2)	126.0(3)
C(1)–Sn(1)–O(1)	114.2(2)	113.8(3)
C(1)–Sn(1)–O(3)	100.4(1)	99.5(2)
C(1)–Sn(1)–O(31)	88.7(1)	84.5(2)
C(21)–Sn(1)–O(1)	105.1(2)	105.2(3)
C(21)–Sn(1)–O(3)	106.8(1)	107.5(2)
C(21)–Sn(1)–O(31)	67.3(1)	69.0(2)
O(3)–Sn(1)–O(31)	170.9(1)	175.9(2)
Sn(1)–O(3)–Sn(2)	134.4(1)	134.4(2)
C(41)–Sn(2)–C(61)	122.9(2)	126.2(3)
C(41)–Sn(2)–O(2)	116.1(2)	110.8(3)
C(41)–Sn(2)–O(3)	100.7(1)	103.5(2)
C(41)–Sn(2)–O(71)	87.3(1)	83.3(2)
C(61)–Sn(2)–O(2)	106.8(2)	103.4(3)
C(61)–Sn(2)–O(3)	106.7(1)	110.7(3)
C(61)–Sn(2)–O(71)	68.7(1)	64.1(2)
O(3)–Sn(2)–O(71)	172.0(1)	173.2(1)

## 1. Supplementary material

CCDC 636263 and 636264 contain the supplementary crystallographic data for **2a** and **2b**. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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- [10] A solution of [2,6-(CH<sub>2</sub>O*t*-Bu)<sub>2</sub>-C<sub>6</sub>H<sub>4</sub>] (1.5 g, 4 mmol) in hexane (10 mL) to which had been added a solution (1.1 mL) of *n*-BuLi (1.6 M) in hexane at ambient temperature was stirred for 12 h. The solution of [2,6-(CH<sub>2</sub>O*t*-Bu)<sub>2</sub>-C<sub>6</sub>H<sub>3</sub>]Li [14] thus obtained was added dropwise to a solution of SnCl<sub>2</sub> (0.38 g, 2 mmol) in THF (20 mL) and stirred overnight. After the solvent had been removed in vacuo the residue was suspended in 40 mL of hexane and stirred for 3 h under exposure to open atmosphere followed by addition of water (3 mL) and stirring for another 30 min. The hexane layer was separated, filtered, and concentrated to a volume of 10 mL. Slow evaporation of this solution afforded compound **2b** as colorless crystals. Yield: 1.70 g (66.5%); mp 179–181°C. Anal. Calc. for C<sub>64</sub>H<sub>102</sub>O<sub>11</sub>Sn<sub>2</sub> (MW = 1284.90): C, 59.83; H, 8.00. Found: C, 59.79; H, 7.95%. MW = 1284. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 300.13 MHz): δ 1.09 (s, 72H, CH<sub>3</sub>), 4.81 (s, 16H, CH<sub>2</sub>), 7.28–7.54 (complex pattern, 12H, C<sub>6</sub>H<sub>3</sub>). <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>, 100.63 MHz): 27.6 (CH<sub>3</sub>), 65.9, 74.8 (C(CH<sub>3</sub>)<sub>3</sub>), SnC<sub>6</sub>H<sub>3</sub>, 141.2 (C(1)), 145.7, 127.0, 129.8. <sup>119</sup>Sn NMR (C<sub>6</sub>D<sub>6</sub>, 300.13 MHz): δ -174.1. MS/ESI *m/z*(%): 1268, [M - OH]<sup>+</sup>, 5%; 1194, [M - OH - (CH<sub>3</sub>)<sub>3</sub>COH]<sup>+</sup>, 7%; 676, [M/2 - O + CH<sub>3</sub>CN]<sup>+</sup>, 4%; 635, [M/2 - O]<sup>+</sup>, 4%; 561, [M/2 - O - (CH<sub>3</sub>)<sub>2</sub>COH]<sup>+</sup>, 20%; 505, [M/2 - O - (CH<sub>3</sub>)<sub>2</sub>COH - (CH<sub>3</sub>)CCH<sub>2</sub>]<sup>+</sup>, 22%; 449, [M/2 - O - (CH<sub>3</sub>)<sub>2</sub>COH - 2(CH<sub>3</sub>)CCH<sub>2</sub>]<sup>+</sup>, 20%; 391, [M/2 - O - (CH<sub>3</sub>)<sub>3</sub>COH]<sup>+</sup>, 18%. IR (KBr): ν (cm<sup>-1</sup>) 3436vbr; 3046m; 2972s; 2931m; 2874m; 1684vbr; 1574m; 1472s; 1455s; 1390s; 1363s; 1260m; 1235m, 1194s; 1094s; 1054s; 1021m; 891m; 873s; 802m, 772m, 749 br.
- [11] (a) Crystallography studies: intensity data for the colourless crystals (**2a**, **2b**) were collected on a Nonius Kappa CCD diffractometer with graphite monochromated Mo Kα radiation. The data collections covered almost the whole sphere of reciprocal space with 3 (**2a**), 4 (**2b**) sets at different κ-angles and 310 (**2a**), 366 (**2b**) frames via ω-rotation (Δ/ω = 1°) (**2a**, **2b**) at two times 30 s (**2a**), 80 s (**2b**) per frame. The crystal-to-detector distances were 3.4 cm for both molecules. Crystal decay was monitored by repeating the initial frames at the end of data collection. Analysing the duplicate reflections there was no indication for any decay. The structures were solved by direct methods SHELXS97 [11a] and successive difference Fourier syntheses. Refinement applied full-matrix least-squares methods SHELXL97 [11b]. The H atoms were placed in geometrically calculated positions using a riding model (including free rotation about Sn–O) with U<sub>iso</sub> constrained at 1.2 for non-methyl groups and 1.5 for methyl groups times U<sub>eq</sub> of the carrier atom. Atomic scattering factors for neutral atoms and real and imaginary dispersion terms were taken from *International Tables for X-ray Crystallography* [11c]. The figures were created by SHELXTL [11d]. Crystallographic data for molecules **2a** and **2a** are given in Table 1. G.M. Sheldrick, *Acta Crystallogr.* A46 (1990) 467–473;  
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