

Priority communication

On the reaction of $[\text{Ph}_2(\text{OH})\text{Si}]_2\text{O}$ with $t\text{-Bu}_2\text{SnCl}_2$: synthesis and characterization of the first well defined polystannasiloxane $[(t\text{-Bu}_2\text{SnO})(\text{Ph}_2\text{SiO})_2]_n$

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Abstract

The high yield synthesis of $[(t\text{-Bu}_2\text{SnO})(\text{Ph}_2\text{SiO})_2]$, **1** is reported. Compound **1** is a linear polymer in the solid state but a six-membered ring in solution. © 1997 Elsevier Science S.A.

Keywords: X-ray diffraction; Silicon; Tin; Synthesis; Polymer

1. Introduction

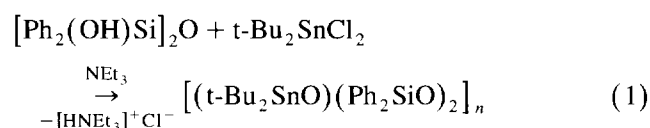
Metallasiloxanes containing Si–O–M linkages (M = main group elements as well as transition metals) are known for a long time [1,2] and have been reviewed recently [3,4]. Cyclic derivatives have received special attention as they might serve as precursors for well defined polyheterosiloxanes [5,6]. The interest in stannasiloxanes has grown in the last years [7–16] but we are aware of only two reports tentatively describing the synthesis of a polystannasiloxane [17,18].

Recently we have shown that di-tert. butyltin oxide $(t\text{-Bu}_2\text{SnO})_3$ reacts with di-tert. butyldichlorosilane $t\text{-Bu}_2\text{SiCl}_2$ and tert. butyltrifluorosilane $t\text{-BuSiF}_3$, respectively, to give cyclic six- and eight-membered stannasiloxanes (**A**) and (**B**) (Scheme 1) [19]. A six-membered ring of type (**C**) (R = *t*-Bu) which is of interest for comparison with (**A**) and $(t\text{-Bu}_2\text{SnO})_3$ was not observed along this reaction.

In an attempt to prepare a representative of a (**C**)-type structure with R = Ph by reacting easily available $[\text{Ph}_2(\text{OH})\text{Si}]_2\text{O}$ [20] with $t\text{-Bu}_2\text{SnCl}_2$ we surprisingly obtained the title compound as the first well defined polystannasiloxane.

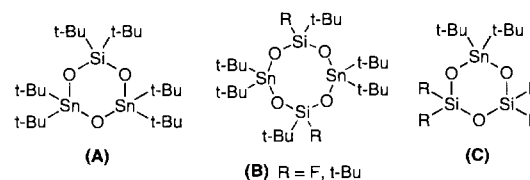
2. Results and discussion

Compound **1** is obtained in high yield according to Eq. (1). It represents a sharp-melting crystalline solid which is well soluble in common organic solvents such as chloroform, toluene or ethanol.



The molecular structure of **1** is shown in Fig. 1, selected bond lengths and bond angles are listed in Table 1.

Crystal data and structure solution of **1**: $\text{C}_{32}\text{H}_{38}\text{O}_3\text{Si}_2\text{Sn}$, $M = 645.49$, triclinic, *P*-1, $a = 11.140(2)$, $b = 12.549(2)$, $c = 13.040(2)$ Å, $\alpha = 101.319(8)^\circ$, $\beta = 106.038(8)^\circ$, $\gamma = 105.351(8)^\circ$, $V = 1616.5(5)$ Å³, $Z = 2$, $D_c = 1.326$ g cm^{–3}, $D_m = 1.322(3)$



Scheme 1.

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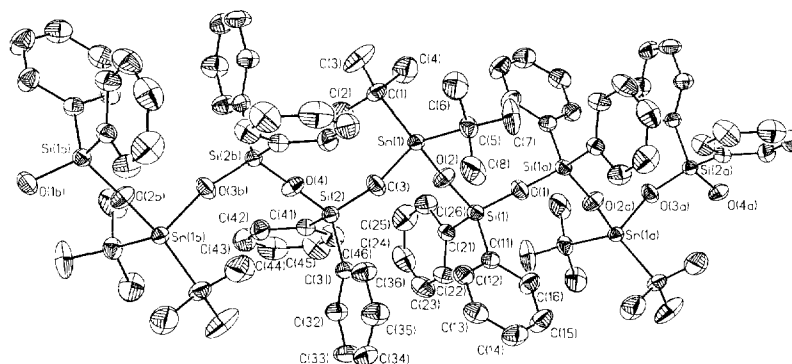


Fig. 1. View of a part of the polymeric chain of (**1**) showing 30% probability displacement ellipsoids and the atom numbering (SHELXTL-PLUS) [33]. (Symmetry transformations used to generate equivalent atoms: $a = -x, -y + 1, -z + 1$; $b = -x, -y, -z$).

g cm^{-3} , $\lambda(\text{Cu K}\alpha) = 1.54178 \text{ \AA}$, $F(000) = 664$, $T = 296(1) \text{ K}$. Three-dimensional data were collected to a maximum θ of 74° with Cu radiation and a CAD4 diffractometer. The structure was solved by direct methods SIR92 [21] and refined by full-matrix least squares calculations using all measured F^2 data and SHELXL93 [22]. All non-H-atoms were refined anisotropically. The H atoms were placed in geometrically calculated positions and refined with the common isotropic tempera-

ture factor [$\text{C-H}_{\text{aryl}} 0.93 \text{ \AA}$, $\text{C-H}_{\text{alkyl}} 0.96 \text{ \AA}$, $U_{\text{iso}} 0.102(3) \text{ \AA}^3$]. $R_1 = 0.0390$ for 5893 ($I > 2\sigma(I)$) and $wR_2 = 0.1160$ for 6649 independent reflections. The maximum and minimum residual electron densities were 0.828 and $-1.049 \text{ e \AA}^{-3}$. Full details have been deposited with the Cambridge Crystallographic Data Centre and are also available in CIF format from the author.

In the solid state compound **1** is a linear polymer rather than the expected six-membered ring of type (C,

Table 1
Selected bond lengths (\AA), angles ($^\circ$) and torsion angles ($^\circ$) for **1**

Sn(1)–O(2)	1.952(2)	Sn(1)–O(3)	1.958(3)
Sn(1)–C(1)	2.174(3)	Sn(1)–C(5)	2.177(3)
Si(1)–O(2)	1.594(3)	Si(1)–O(1)	1.611(9)
Si(1)–C(11)	1.861(3)	Si(1)–C(21)	1.864(3)
Si(2)–O(3)	1.589(3)	Si(2)–O(4)	1.6089(9)
Si(2)–C(31)	1.866(3)	Si(2)–C(41)	1.870(3)
O(1)–Si(1a)	1.611(9)	O(4)–Si(2b)	1.6089(9)
O(2)–Sn(1)–O(3)	102.17(13)	O(2)–Sn(1)–C(1)	106.26(13)
O(3)–Sn(1)–C(1)	109.01(14)	O(2)–Sn(1)–C(5)	107.26(14)
O(3)–Sn(1)–C(5)	104.52(14)	C(1)–Sn(1)–C(5)	125.3(2)
O(2)–Si(1)–O(1)	110.89(12)	O(2)–Si(1)–C(11)	112.6(2)
O(1)–Si(1)–C(11)	107.83(13)	O(2)–Si(1)–C(21)	106.7(2)
O(1)–Si(1)–C(21)	108.77(12)	C(11)–Si(1)–C(21)	109.97(14)
O(3)–Si(2)–O(4)	110.01(12)	O(3)–Si(2)–C(31)	108.3(2)
O(4)–Si(2)–C(31)	108.37(12)	O(3)–Si(2)–C(41)	112.0(2)
O(4)–Si(2)–C(41)	108.90(13)	C(31)–Si(2)–C(41)	109.20(14)
Si(1)–O(1)–Si(1a)	180.0	Si(1)–O(2)–Sn(1)	158.6(2)
Si(2)–O(3)–Sn(1)	156.2(2)	Si(2)–O(4)–Si(2b)	180.0
O(2)–Si(1)–O(1)–Si(1a)	–62(1)	C(11)–Si(1)–O(1)–Si(1a)	61(1)
C(21)–Si(1)–O(1)–Si(1a)	–179(1)	O(1)–Si(1)–O(2)–Sn(1)	90.8(5)
C(11)–Si(1)–O(2)–Sn(1)	–30.1(6)	C(21)–Si(1)–O(2)–Sn(1)	–150.9(5)
O(3)–Sn(1)–O(2)–Si(1)	75.8(6)	C(1)–Sn(1)–O(2)–Si(1)	–170.0(5)
C(5)–Sn(1)–O(2)–Si(1)	–33.8(6)	O(4)–Si(2)–O(3)–Sn(1)	88.6(5)
C(31)–Si(2)–O(3)–Sn(1)	–153.1(5)	C(41)–Si(2)–O(3)–Sn(1)	–32.7(5)
O(2)–Sn(1)–O(3)–Si(2)	84.5(5)	C(1)–Sn(1)–O(3)–Si(2)	–27.7(5)
C(5)–Sn(1)–O(3)–Si(2)	–163.8(5)	O(3)–Si(2)–O(4)–Si(2b)	–140(2)
C(31)–Si(2)–O(4)–Si(2b)	102(2)	C(41)–Si(2)–O(4)–Si(2b)	–17(2)

Symmetry transformations used to generate equivalent atoms: $a = -x, -y + 1, -z + 1$; $b = -x, -y, -z$

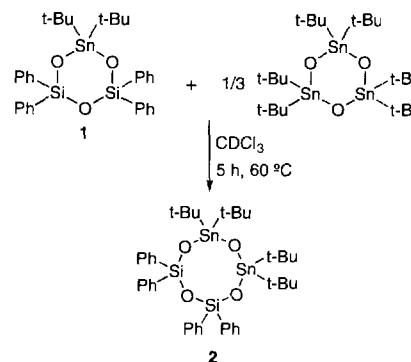
R = Ph) (Scheme 1). To the best of our knowledge **1** represents the first structurally characterized polymeric stannasiloxane.

The polymer consists of linear O(1)–Si(1)–O(2)–Sn(1)–O(3)–Si(2)–O(4) units in which both the silicon and tin atoms show tetrahedral configurations (mean angles around Si(1) 109.46°, Si(2) 109.46°, Sn(1) 109.09°). However, as a result of the *t*-butyl groups the geometry around Sn(1) is more distorted as expressed by the large C(1)–Sn(1)–C(5) angle of 125.3(2)°. The Si(1)–O(2)–Sn(1) and Si(2)–O(3)–Sn(1) angles of 158.6(2)° and 156.2(2)°, respectively, are bigger in comparison with the Si–O–Sn angle of 140.0(8)° found for (Ph₃SnOSiPh₂)₂O [8]. This might be attributed to the different substituent pattern at the tin atoms in these two compounds. The Si(1)–O(1)–Si(1a) angle amounts to 180° which is again larger than the Si–O–Si angle of 165.4(10)° determined for (Ph₃SnOSiPh₂)₂O [8]. Si–O–Si angles of 180° have previously been observed for other siloxanes [23–26]. The Si–O (average: 1.600 Å), Sn–O (average: 1.955 Å) and Sn–C (average: 2.175 Å) distances are as expected and comparable to related compounds [8].

In contrast to its polymeric solid state structure **1** is a six-membered ring of type (C, R = Ph) in solution. The Field Desorption mass spectrum of a solution of **1** in chloroform exclusively shows a single peak at *m/e* 646 with the correct isotopic distribution calculated for [(*t*-Bu₂SnO)(Ph₂SiO)₂]. This structure is also confirmed by an osmometric molecular weight determination (20 mg in 2 ml CHCl₃ at 58°C). The ¹¹⁹Sn NMR (CDCl₃) displays a single resonance at –119.5 ppm with ²J(¹¹⁹Sn–O–²⁹Si) 34 Hz and ¹J(¹¹⁹Sn–¹³C) 467 Hz which is considerably high frequency shifted in comparison with its ¹¹⁹Sn MAS resonance at –167.1 ppm indicating different structures in solution and in the solid state. The ²⁹Si NMR spectrum shows a single resonance at –35.9 ppm with unresolved ²J(^{117/119}Sn–O–²⁹Si) of 34 Hz. The chemical shift is in line with those reported for [(PhBO)(Ph₂SiO)₂] (δ –30.8 ppm) [5] and (Ph₂SiO)₃ (δ –33.0 ppm) [5] for which six-membered ring structures are confirmed by X-ray analysis [5,27]. The six-membered ring structure of **1** is further supported by the small ²J(¹¹⁹Sn–O–²⁹Si) coupling of 34 Hz which indicates a small Sn–O–Si angle. Geminal ²J(¹¹⁹Sn–X) couplings are known to be very sensitive to changes of the bond angle [28,29].

As was pointed out for [(PhBO)(Ph₂SiO)₂] [5] by Manners et al. a considerable ring strain is also to be expected for **1** in solution. The thermodynamic driving force for the polymerization of **1** upon crystallization might be the relief of this strain. It is also the reason for the almost quantitative formation of [(*t*-Bu₂SnO)₂(Ph₂SiO)₂] **2** upon reaction of **1** with (*t*-Bu₂SnO)₃ (Scheme 2).

Although **2** has not been isolated yet its structure in



Scheme 2.

solution follows unambiguously from ²⁹Si (δ –45.3 ppm, ²J(¹¹⁹Sn–O–²⁹Si) 66 Hz) and ¹¹⁹Sn (δ –125.7 ppm, ²J(¹¹⁹Sn–O–¹¹⁷Sn) 685 Hz, ²J(¹¹⁹Sn–O–²⁹Si) 67 Hz, ¹J(¹¹⁹Sn–¹³C) 506 Hz) NMR spectroscopy. Especially the ²J(¹¹⁹Sn–O–²⁹Si) coupling is very close to the value of 65 Hz found for related [(*t*-Bu₂SnOSiPh₂O)₂] for which a (B)-type structure has been confirmed for both solution and solid state [29].

3. Experimental

(Ph₂SiOH)₂O, (*t*-Bu₂SnO)₃ and *t*-Bu₂SnCl₂ were synthesized by literature methods [20,30–32]. The solvents were dried by standard procedures and freshly distilled prior to use. All operations were carried out under an atmosphere of nitrogen.

NMR spectra were recorded in CDCl₃ on a Bruker DRX 400 spectrometer at 400.13 MHz (¹H), 100.62 MHz (¹³C), 79.49 MHz (²⁹Si) and 149.21 MHz (¹¹⁹Sn) using Me₄Si and Me₄Sn, respectively, as external references. The ¹¹⁹Sn MAS NMR spectrum was recorded on a Bruker MSL 400 spectrometer by using cross polarization (recycle delay 8.0 s, 90°C pulse 5.0 μs, contact time 3.5 ms) at spinning frequencies of 10 and 14 kHz, respectively. The mass spectra were obtained on a Finnigan MAT 8230 spectrometer. FD method: dipping the emission wire into a solution of some single crystals of **1** in chloroform. EI activation: evaporation of one single crystal at 201°C, ionization potential 70 eV. The IR spectrum was recorded on a Bruker FTIR IFS 113v spectrometer and the Raman spectrum was obtained on a Jobin Yvon T64000 spectrometer (Ar laser, ν_E 514.5 nm). The molecular weight measurement was performed on a Knauer osmometer.

3.1. Synthesis of [(*t*-Bu₂SnO)(Ph₂SiO)₂]_n (**1**)

A solution of Bu₂SnCl₂ (1.52 g, 5.00 mmol) in 30 ml of acetone was added dropwise to a magnetically stirred solution of (Ph₂SiOH)₂O (2.07 g, 5.00 mmol) and triethylamine (1.01 g, 10.0 mmol) in 30 ml of

acetone. A white precipitate of $[\text{HNEt}_3]^+\text{Cl}^-$ is formed immediately. The precipitate was filtered off and the solvent was evaporated in vacuo. The solid residue was recrystallized from toluene affording 2.71 g (4.19 mmol, 84%) of $[(t\text{-Bu}_2\text{SnO})(\text{Ph}_2\text{SiO})_2]$, **1** as colourless crystalline solid, mp 238°C.

Crystals suitable for X-ray analysis were obtained by slow evaporation of a dichloromethane/hexane solution of **1**.

^1H NMR: δ 1.26 ppm, $^3\text{J}({}^{119}\text{Sn}-{}^1\text{H})$ 103.2 Hz (s, 18 H, Bu^t), 7.7–7.2 ppm (m, 20 H, Ph). ^{13}C NMR: δ 29.4 ppm (CMe₃), 40.7 ppm, $^1\text{J}({}^{119}\text{Sn}-{}^{13}\text{C})$ 465 Hz (CMe₃), C_m 127.4, C_p 129.4, C_o 134.3, C_i 137.6 ppm. ^{29}Si NMR: δ –35.9 ppm, $^2\text{J}({}^{119/117}\text{Sn}-\text{O}-{}^{29}\text{Si})$ 34.3 Hz. ^{119}Sn NMR: δ –119.5 ppm, $^2\text{J}({}^{119}\text{Sn}-\text{O}-{}^{29}\text{Si})$ 34.3 Hz, $^1\text{J}({}^{119}\text{Sn}-{}^{13}\text{C})$ 567 Hz (CMe₃). ^{119}Sn MAS NMR (149.21 MHz): δ –167.1 ppm. MS (m/e): 533 (M–2 Bu^t, 63%), 455 (M–2 Bu^t, –Ph, 100%), 377 (M–2 Bu^t, –2 Ph, 21%), 57 (Bu^t, 59%). IR(Nujol): 2962, 2920, 1463, 1378, 1118, 1031, 970, 699, 519, 483 cm^{–1}, Raman: 3049, 2855, 1593, 1172, 1001, 806, 504 cm^{–1}.

Anal. Found: C, 59.7; H, 6.1. Calc. for C₃₂H₃₈O₃Si₂Sn (MW 645.6): C, 59.7; H, 5.9.

3.2. NMR scale synthesis of $[(t\text{-Bu}_2\text{SnO})_2(\text{Ph}_2\text{SiO})_2]$ (**2**)

1 (64.6 mg, 0.1 mmol) and (t-Bu₂SnO)₃ (24.9 mg, 0.1 mmol) in 300 μl CDCl₃ were heated to 60°C for 5 h to give a clear solution. Both ^{119}Sn and ^{29}Si NMR spectroscopy shows formation of **2** in 95% yield. In addition there are also traces of the starting compounds left as shown by ^{119}Sn signals at –83.6 ((t-Bu₂SnO)₃) and –120.3 ppm (**1**). [33]

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