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Synthesis and structural characterization of (4,7-dioxaoctyl)phenyldichlorostannane and triphenyltin compounds containing various polyoxaalkyl moieties

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Abstract

The synthesis and characterization of (4,7-dioxaoctyl)triphenyltin (**1**), (4,7,10-trioxaundecyl)triphenyltin (**2**), (4,7,10,13-tetraoxatetradecyl)triphenyltin (**3**), and (4,7-dioxaoctyl)phenyldichlorostannane (**4**) are reported. Investigatons using ^{1}H-, ^{13}C-, and ^{119}Sn-NMR, gradient assisted 2D ^{1}H–^{13}C HMBC and HMQC NMR, 1D ^{1}H–^{119}Sn HMQC NMR demonstrate that **1**–**3** are essentially tetracoordinated. By contrast, the structure of compound **4**, determined by X-ray diffraction methods, reveals a hexacoordinated, distorted octahedral geometry, in which the 4,7-dioxaoctyl ligand is tridentate, with a facial arrangement of the C, O, O atoms with respect to tin. NMR investigations reveal that this structure exists in solution, but is labilized by a double ring opening–closing mechanism. © 2001 Published by Elsevier Science B.V.

Keywords: Polyoxaalkylstannanes; NMR; X-ray diffraction

1. Introduction

In the solid state, diorganotin dihalides show a strong tendency to undergo polymeric associations of the type Sn–X···Sn by intermolecular coordination [1,2]. They can also expand the valence shell at tin by additional intramolecular coordination of electronegative substituents containing an O or N atom linked to carbon chains themselves bound to tin. Thus, a number of octahedral L_2SnX_2 complexes, where L_2 is a chelating ligand forming one Sn–C covalent bond and a O→Sn or N→Sn coordinative bond, have been reported [3–7]. The following compounds, $(RCOCH_2CH_2)_2SnCl_2$ (R = OCH_3 or NH_2) [8], $(EtOOCCH_2CHRCH_2)_2SnBr_2$ (R = COOEt) [9,10], $(CH_3OCH_2CH_2OCH_2CH_2CH_2)_2SnCl_2$ [11], $[(CH_3)_2NCH_2CH_2C(CH_3)_2]_2SnCl_2$ [12] and $[(CH_3)_2NCH_2CH_2CH_2]_2SnF_2$ [13] all feature a hexacoordinated tin atom because of two additional intramolecular O→Sn or N→Sn interactions.

Related to these studies, the coordination behavior of different alkyl substituted monoorganotin trichlorides has also been investigated for $CH_3COO(CH_2)_nSnCl_3$ ($n = 3–5$) [14], $HO(CH_2)_nSnCl_3$ ($n = 3–5$) [15] and $CH_3OCH_2CH_2OCH_2CH_2CH_2SnCl_3$ [11] which display intra- and/or inter-molecular associations in solution and/or solid state.

This report describes the synthesis and characterization of (4,7-dioxaoctyl)triphenyltin (**1**), (4,7,10-trioxaundecyl)triphenyltin (**2**), (4,7,10,13-tetraoxatetradecyl)triphenyltin (**3**), and (4,7-dioxaoctyl)phenyldichlorostannane (**4**) (Fig. 1). They each possess at least two potential additional donor sites. Our main investigative tools are ^{1}H-, ^{13}C-, and ^{119}Sn-NMR, gradient assisted 2D ^{1}H–^{13}C HMBC and HMQC NMR, 1D ^{1}H–^{119}Sn HMQC NMR, as well as electrospray mass

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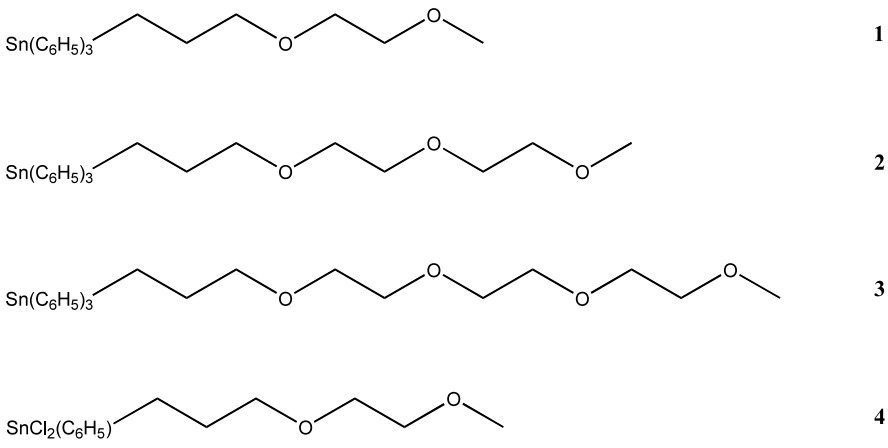

Fig. 1. Structures of compounds **1**–**4**.

spectrometry and ^{119m}Sn Mössbauer spectroscopy. The crystal structure of compound **4** has been determined by X-ray diffraction methods.

2. Experimental

2.1. Spectroscopic measurements

NMR spectra for basic compound characterization were recorded at 303 K on a Bruker Avance DRX250 instrument equipped with a Quattro probe tuned to 250.13, 62.93 and 89.15 MHz for ^{1}H, ^{13}C and ^{117}Sn nuclei, respectively. Other NMR data were acquired on a Bruker AMX500 spectrometer at 500.13 and 186.50 MHz for ^{1}H and ^{119}Sn nuclei, respectively. ^{1}H and ^{13}C chemical shifts were referenced to the appropriate solvent peak with the usual values calibrated against Me_4Si. The ^{117}Sn and ^{119}Sn reference frequencies were calculated from the absolute references $\Xi(^{117}\text{Sn}) = 35.632295$ MHz and $\Xi(^{119}\text{Sn}) = 37.290655$ MHz [16]. 2D ^{1}H–^{13}C HMQC [17] and HMBC [18] as well as ^{1}H–^{119}Sn HMQC correlation spectra were acquired using the pulse sequences of the Bruker program library, adapted to include gradient pulses [19–22] as described previously [23,24].

Chemical shifts are in ppm, coupling constants in Hz, $^{n}J(^{1}\text{H}-^{1}\text{H})$ in parentheses, and $^{n}J(^{119}\text{Sn}-^{1}\text{H})$ and $^{n}J(^{119}\text{Sn}-^{13}\text{C})$ between square brackets; abbreviations: s = singlet; t = triplet, tt = triplet of triplets; m = complex multiplet.

The Mössbauer spectra were recorded as described elsewhere [25].

The electrospray mass spectra [26,27] were recorded in the cationic mode on a Micromass Quattro II instrument coupled to a Masslynx system (ionization in an electric field of 3.5 kV; source temperature: 80 °C; source pressure 1 atm; analyzer pressure 10^{-5} mbar). The monoisotopic fragment-ions (^{1}H, ^{12}C, ^{14}N, ^{16}O, ^{23}Na, ^{35}Cl, ^{39}K, ^{120}Sn), were observed in the cationic mode, in MeOH solution.

2.2. Crystal structure determination

Intensity data for colorless **4** were measured at 173 K on a Rigaku AFC7R diffractometer employing Mo–K_α radiation and the ω–2θ scan technique such that θ_{max} was 27.5°. Corrections were made for Lorentz and polarization effects [28] and for absorption employing an empirical procedure [29]. Crystallographic data are summarized in Table 1.

The structure was solved by heavy-atom methods [30] and refined by a full-matrix least-squares procedure based on F [28]. All non-hydrogen atoms were refined with anisotropic displacement parameters and hydrogen atoms were included in the model in their idealized positions. After the inclusion of a weighting scheme of the form $w = 1/[\sigma^2(F) + 0.00001|F|^2]$, the refinement

Table 1
Crystallographic parameters for compound **4**

Formula	$C_{12}H_{18}Cl_2O_2Sn$
Formula weight	383.9
Crystal size (mm)	$0.13 \times 0.24 \times 0.27$
Crystal system	Monoclinic
Space group	$P2_1/c$
a (Å)	13.373(5)
b (Å)	7.464(2)
c (Å)	14.602(2)
β (°)	97.31(2)
V (Å^3)	1445.6(7)
Z	4
D_{calc} (cm^{-3})	1.764
$F(000)$	760
μ (cm^{-1})	21.24
Unique data	3573
Data with $I \geq 3\sigma(I)$	2589
R	0.022
R_w	0.025
ρ (e Å^{-3})	0.56

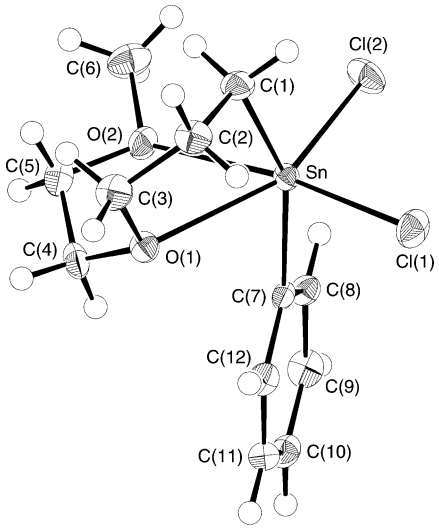

Fig. 2. Molecular structure and crystallographic numbering scheme employed for compound **4**.

was continued until convergence. Final refinement details are given in Table 1 and the crystallographic numbering scheme is shown in Fig. 2, which was drawn at the 50% probability level [31].

2.3. Synthesis

2.3.1. (4,7-Dioxaoctyl)triphenyltin

4,7-Dioxaoctene was obtained as described previously [32]. Compound **1** (4,7-dioxaoctyl)triphenyltin, was prepared by hydrostannation of the 4,7-dioxaoctene (500 mg, 4.30 mmol) with triphenyltin hydride (750 mg, 2.14 mmol) in the presence of AIBN (45 mg, 0.27 mmol) [33]. The reaction was carried out under nitrogen at 70 °C over 24 h. The resulting mixture was extracted with petroleum ether and only the filtrate was evaporated in vacuo. Purification was achieved by column chromatography (silica/1: CH_2Cl_2; 2: $CHCl_3$) and gave 1.6 g (3.42 mmol) of **1** as a colorless oil (62%).

Anal. Calc. for $C_{24}H_{28}O_2Sn$: C, 61.70; H, 6.05. Found: C, 61.9; H, 5.9%.

^{1}H-NMR ($CDCl_3$): $\delta = 7.50–7.57$ m, 6H [$^2J(^{119}Sn–^1H) = 46$], H(o); $\delta = 7.30–7.38$ m, 9H, H(m) and H(p); $\delta = 1.46–1.55$ m, 2H [$^2J(^{119}Sn–^1H) = 57$], H(1); $\delta = 1.95–2.08$ m, 2H [$^3J(^{119}Sn–^1H) = 57$], H(2); $\delta = 3.46$ t (7), 2H, H(3); $\delta = 3.40–3.44$ m, 4H, H(5) and H(6); $\delta = 3.32$ s, 3H, H(8).

^{13}C-NMR: $\delta = 139.6$ [$^1J(^{119}Sn–^{13}C) = 489$], C(i); $\delta = 137.6$ [$^2J(^{119}Sn–^{13}C) = 35$], C(o); $\delta = 129.0$ [$^3J(^{119}Sn–^{13}C) = 48$], C(m); $\delta = 129.4$ [$^4J(^{119}Sn–^{13}C) = 11$], C(p); $\delta = 7.7$ [$^1J(^{119}Sn–^{13}C) = 399$], C(1); $\delta = 27.1$ [$^2J(^{119}Sn–^{13}C) = 21$], C(2); $\delta = 74.8$ [$^3J(^{119}Sn–^{13}C) = 67$], C(3); $\delta = 70.6$, C(5); $\delta = 72.5$, C(6); $\delta = 59.6$, C(8).

^{117}Sn-NMR: $\delta = -100.3$.

ESMS: $M + Na^+$, 491; $M + K^+$, 507.

Mössbauer: QS, 0.71 mm s^{-1}; IS, 1.29 mm s^{-1}.

2.3.2. (4,7,10-Trioxaundecyl)triphenyltin

The same procedure was used as described for **1** in the synthesis of (4,7,10-trioxaundecyl)triphenyltin, compound **2**, except for the column chromatography [silica/1: CH_2Cl_2; 2: CH_2Cl_2–CH_3CH_2OH (1:1)] (65%).

Anal. Calc. for $C_{26}H_{32}O_3Sn$: C, 61.08; H, 6.31. Found: C, 60.6; H, 6.4%.

^{1}H-NMR ($CDCl_3$): $\delta = 7.50–7.55$ m, 6H [$^2J(^{119}Sn–^1H) = 47$], H(o); $\delta = 7.31–7.38$ m, 9H, H(m) and H(p); $\delta = 1.46–1.52$ m, 2H [$^2J(^{119}Sn–^1H) = 57$], H(1); $\delta = 1.95–2.02$ m, 2H [$^3J(^{119}Sn–^1H) = 55$], H(2); $\delta = 3.42–3.47$ m, 4H, H(3) and H(5); $\delta = 3.48–3.53$ m, 4H, H(6) and H(9); $\delta = 3.55–3.59$ m, 2H, H(8); $\delta = 3.35$ s, 3H, H(11).

^{13}C-NMR: $\delta = 139.7$ [$^1J(^{119}Sn–^{13}C) = 489$], C(i); $\delta = 137.2$ [$^2J(^{119}Sn–^{13}C) = 35$], C(o); $\delta = 129.1$ [$^3J(^{119}Sn–^{13}C) = 47$], C(m); $\delta = 129.4$ [$^4J(^{119}Sn–^{13}C) = 11$], C(p); $\delta = 7.7$ [$^1J(^{119}Sn–^{13}C) = 400$], C(1); $\delta = 27.2$ [$^2J(^{119}Sn–^{13}C) = 21$], C(2); $\delta = 74.7$ [$^3J(^{119}Sn–^{13}C) = 64$], C(3); $\delta = 70.7$, C(5); $\delta = 71.13$, $\delta = 71.15$, C(6) and C(8); $\delta = 72.6$, C(9); $\delta = 59.6$, C(11).

^{117}Sn-NMR: $\delta = -100.3$.

ESMS: $M + Na^+$, 535; $M + K^+$, 551.

Mössbauer: QS, 0.90 mm s^{-1}; IS, 1.33 mm s^{-1}.

2.3.3. (4,7,10,13-Tetraoxatetradecyl)triphenyltin

The synthesis and purification of (4,7,10,13-tetraoxatetradecyl)triphenyltin (**3**), are as described for compound **2** (60%).

Anal. Calc. for $C_{28}H_{36}O_4Sn$: C, 60.56; H, 6.54. Found: C, 59.8; H, 6.8%.

^{1}H-NMR ($CDCl_3$): $\delta = 7.49–7.57$ m, 6H [$^2J(^{119}Sn–^1H) = 43$], H(o); $\delta = 7.29–7.39$ m, 9H, H(m) and H(p); $\delta = 1.46–1.55$ m, 2H [$^2J(^{119}Sn–^1H) = 57$], H(1); $\delta = 1.93–2.07$ m, 2H [$^3J(^{119}Sn–^1H) = 58$], H(2); $\delta = 3.40–3.75$ m, 14H, H(3), H(5), H(6), H(8), H(9), H(11) and H(12); $\delta = 3.34$ s, 3H, H(14).

^{13}C-NMR: $\delta = 139.7$ [$^1J(^{119}Sn–^{13}C) = 489$], C(i); $\delta = 137.7$ [$^2J(^{119}Sn–^{13}C) = 35$], C(o); $\delta = 129.1$ [$^3J(^{119}Sn–^{13}C) = 47$], C(m); $\delta = 129.4$ [$^4J(^{119}Sn–^{13}C) = 11$], C(p); $\delta = 7.8$ [$^1J(^{119}Sn–^{13}C) = 397$], C(1); $\delta = 27.2$ [$^2J(^{119}Sn–^{13}C) = 20$], C(2); $\delta = 74.7$ [$^3J(^{119}Sn–^{13}C) = 64$], C(3); $\delta = 70.7$, C(5); $\delta = 71.11$, $\delta = 71.14$, $\delta = 71.20$, $\delta = 71.25$, C(6), C(8), C(10) and C(11); $\delta = 72.6$, C(12); $\delta = 59.6$, C(14).

^{117}Sn-NMR: $\delta = -100.4$.

ESMS: $M + NH_4^+$, 574; $M + Na^+$, 579; $M + K^+$, 594.

Mössbauer: QS, 0.00 mm s^{-1}; IS, 1.53 mm s^{-1}.

2.3.4. (4,7-Dioxaoctyl)phenyldichlorostannane

(4,7-Dioxaoctyl)phenyldichlorostannane (**4**), was obtained after treatment of **1** with anhydrous HCl at

−78 °C in methylene chloride (95%). Crystals suitable for X-ray analysis were grown in petroleum ether at −10 °C (m.p. 49–50 °C).

Anal. Calc. for $C_{12}H_{18}Cl_2O_2Sn$: C, 37.55; H, 4.73. Found: C, 37.4; H, 4.7%.

^{1}H-NMR ($CDCl_3$): $\delta = 7.76–7.82$ m, 6H [$^2J(^{119}Sn–^1H) = 85$], H(o); $\delta = 7.43–7.52$ m, 9H, H(m) and H(p); $\delta = 1.99$ t (7), 2H [$^2J(^{119}Sn–^1H) = 181$], H(1); $\delta = 2.23$ tt (6, 7), 2H [$^3J(^{119}Sn–^1H) = 83$], H(2); $\delta = 3.76$ t (6), 2H, H(3); $\delta = 3.64$ t (5), 2H, H(5); $\delta = 3.30$ t (6), 2H, H(6); $\delta = 3.14$ s, 3H, H(8).

^{13}C-NMR: $\delta = 141.6$ [$^1J(^{119}Sn–^{13}C) =$ not visible], C(i); $\delta = 135.1$ [$^2J(^{119}Sn–^{13}C) = 68$], C(o); $\delta = 129.0$ [$^3J(^{119}Sn–^{13}C) = 87$], C(m); $\delta = 130.7$ [$^4J(^{119}Sn–^{13}C) = 18$], C(p); $\delta = 22.6$ [$^1J(^{119}Sn–^{13}C) = 629$], C(1); $\delta = 25.3$ [$^2J(^{119}Sn–^{13}C) = 40$], C(2); $\delta = 70.8$ [$^3J(^{119}Sn–^{13}C) = 20$], C(3); $\delta = 70.4$, C(5); $\delta = 71.1$, C(6); $\delta = 58.6$, C(8).

^{117}Sn-NMR: $\delta = -73.6$.

ESMS: $(C_6H_5)ClSnR^+$, 349.

Mössbauer: QS, 3.78 mm s^{-1}; IS, 1.53 mm s^{-1}.

3. Results and discussion

3.1. Crystal structure of compound 4

The molecular strucure of **4** is illustrated in Fig. 2 and selected geometric parameters are collected in Table 2. The tin atom is hexacoordinated, existing in a $C_2Cl_2O_2$ donor set. The disposition of the donor atoms is such that the oxygen atoms occupy mutually *cis* positions as do the chlorides, and the carbon atoms occupy positions approximately *trans* to each other. The *trans* angles, i.e. Cl(1)–Sn–O(2), Cl(2)–Sn–O(1) and C(1)–Sn–C(7), of 171.61(4), 154.20(5) and 155.5(1)°, respectively, indicate significant deviations from the ideal geometry.

Table 2
Geometric parameters (Å, °) for compound **4**

Bond distances			
Sn–Cl(1)	2.468(1)	Sn–Cl(2)	2.407(1)
Sn–O(1)	2.553(2)	Sn–O(2)	2.540(2)
Sn–C(1)	2.129(3)	Sn–C(7)	2.124(3)
O(1)–C(3)	1.450(4)	O(1)–C(4)	1.443(4)
O(2)–C(5)	1.440(3)	O(2)–C(6)	1.431(4)
Bond angles			
Cl(1)–Sn–Cl(2)	99.58(3)	Cl(1)–Sn–O(1)	105.76(4)
Cl(1)–Sn–O(2)	171.61(4)	Cl(1)–Sn–C(1)	93.25(8)
Cl(1)–Sn–C(7)	94.40(7)	Cl(2)–Sn–O(1)	154.20(5)
Cl(2)–Sn–O(2)	88.56(5)	Cl(2)–Sn–C(1)	101.16(7)
Cl(2)–Sn–C(7)	100.42(7)	O(1)–Sn–O(2)	66.35(6)
O(1)–Sn–C(1)	72.92(9)	O(1)–Sn–C(7)	82.63(8)
O(2)–Sn–C(1)	87.14(9)	O(2)–Sn–C(7)	82.00(8)
C(1)–Sn–C(7)	155.5(1)	Sn–O(1)–C(3)	109.4(1)
Sn–O(1)–C(4)	110.8(1)	C(3)–O(1)–C(4)	113.7(2)
Sn–O(2)–C(5)	117.8(1)	Sn–O(2)–C(6)	123.1(2)
C(5)–O(5)–C(6)	110.8(2)		

Of particular interest in the structure and relevant to the solution studies reported below is the coordination mode of the 4,7-dioxaoctyl ligand, which is tridentate, forming a covalent interaction to tin via one of the terminal carbon atoms as well as two coordinative bonds to tin involving oxygen atoms. This mode of coordination results in the formation of puckered –Sn–C–C–C–O– (the respective torsion angles for Sn–C(1)–C(2)–C(3), Sn–O(1)–C(3)–C(2) and O(1)–C(3)–C(2)–C(1) are −60.3(3), −21.4(2) and 52.1(3)°) and –Sn–O–C–C–O– five-membered rings (Sn–O(1)–C(4)–C(5), Sn–O(2)–C(5)–C(4) and O(1)–C(4)–C(5)–O(2) are −51.4(2), −28.1(3) and 52.9(3)°, respectively). It is noted that while the Sn–O bond distances of 2.553(2) and 2.540(2) Å are longer than the sum of the covalent radii of tin and oxygen (2.1 Å), they are well within the sum of their van der Waals radii (3.7 Å) and hence, these must be considered significant bonding interactions. A small disparity in the Sn–O distances is reflected in a more significant disparity in the Sn–Cl distances. Thus, the shorter Sn–O(2) bond is *trans* to the longer Sn–Cl(1) bond. There does not appear to be any inherent chemical reason for these differences and it is therefore argued that these arise as a result of intra- and inter-molecular Sn···H interactions. The importance of such interactions in organotin chemistry has been noted previously [6,34,35]. In the present case, the Cl(1) atom that forms the longer Sn–Cl bond sits in a pocket defined by four hydrogen atoms and forms a relatively close intramolecular interaction. By contrast, the Cl(2) atom forms a close intramolecular interaction with a phenyl–H and three weaker intermolecular Cl···H interactions. There is no evidence for π···π interactions in the crystal structure but there are interactions of the type C–H···π.

One of the C(5) methylene hydrogens is disposed so as to lie over a symmetry related phenyl group. Thus, the C(5)–*H*(10) atom is separated by 2.76 Å from the ring centroid of C(7)^i–C(12)^i and the angle subtended at H(10) by C(5) and the ring centroid is 127°; symmetry operation *i*: x, $1 + y$, z.

3.2. Solution structure of compound 4

The assignment of all ^{1}H and ^{13}C resonances was achieved by 2D ^{1}H–^{13}C HMQC and HMBC experiments in $CDCl_3$ solution. The concentration independent ^{117}Sn chemical shift of compound **4** at −73.6 ppm is rather different from a reference compound without a Lewis donor, $C_6H_5Cl_2Sn(n\text{-Bu})$ (+45 ppm), but is fairly typical for a hypervalent diorganotin dichloride [3]. Its alkyl $^1J(^{119}Sn–^{13}C)$ coupling constants of 629 Hz also reflect a stronger coordination at tin as compared to $C_6H_5Cl_2Sn(n\text{-Bu})$ (503 Hz). Compound **4** contains two oxygen atoms potentially available for coordination to tin, as demonstrated in the crystalline state. In

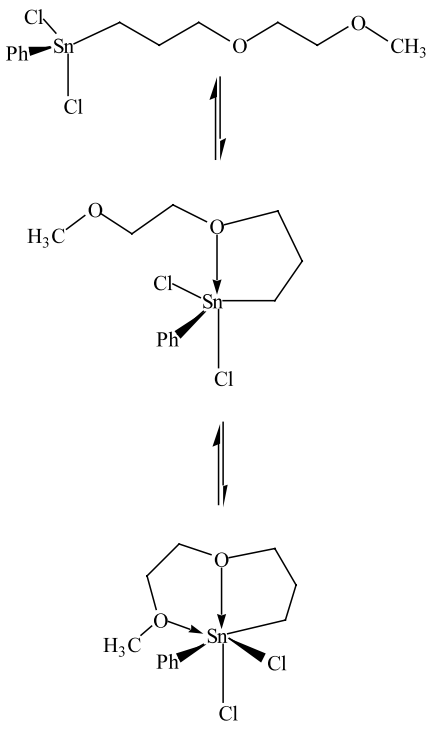

Fig. 3. Dynamic equilibrium proposed for compound **4**.

order to ascertain whether only one or both oxygen atoms are engaged in complexation to tin, we performed gradient assisted 1D $^{1}H-^{119}Sn$ HMQC NMR experiments. The ^{1}H resonances of all protons of **4** exhibit a $^{119}Sn-^{1}H$ correlation with the ^{119}Sn nucleus, including H(5), H(6) and H(8). As $^{n}J(^{119}Sn-^{1}H)$ couplings are not observed above $n = 6$ under the measurement conditions used [24], it can be deduced that $^{6}J(^{119}Sn-^{1}H)$, $^{7}J(^{119}Sn-^{1}H)$ as well as $^{9}J(^{119}Sn-^{1}H)$ coupling constants through the 4,7-dioxaoctyl group are merely to be understood as $^{3}J(^{119}Sn-^{1}H)$ and $^{4}J(^{119}Sn-^{1}H)$ coupling pathways involving coordinative O→Sn bonds. On the basis of these results it can be stressed that both oxygen atoms interact with the tin atom.

In contrast to $C_6H_5Cl_2Sn(n\text{-Bu})$, $^{n}J(^{119}Sn-^{13}C)$ coupling constants do not follow the general relationship $|^{1}J(^{119}Sn-^{13}C)| \gg |^{3}J(^{119}Sn-^{13}C)| > |^{2}J(^{119}Sn-^{13}C)|$ valid for open chains [36]. Therefore, conformations of the alkyl groups must necessarily be different for both compounds.

Furthermore, the ^{119}Sn-NMR signal shifts to lower frequency upon temperature decrease ($\delta\,^{119}Sn = -104$ ppm at 183 K in CD_2Cl_2). A weak temperature dependence is observed exclusively for the ^{1}H chemical shift of H(8). These observations indicate that the interaction involving the second oxygen of the 4,7-dioxaoctyl chain is more labile and that the complexation equilibrium at the latter oxygen is more favored at lower temperatures, as might be expected.

Since our ^{119}Sn-NMR data are concentration independent, intermolecular O→Sn interactions can reasonably be excluded. The dynamic equilibrium of Fig. 3 is proposed for **4**. Our results in solution confirm the existence of intramolecular O→Sn interactions with, however, a dynamic double cycle closing/opening mechanism which is fast on the ^{1}H-, ^{13}C-, and ^{117}Sn-NMR time scales. Only at the lowest temperature accessible, 163 K, the broad ^{117}Sn resonance has started to decoalesce into a major resonance at -106.2 ppm, characteristic for five-coordination and a broader minor one around -255 ppm characteristic for six-coordination. This emphasizes that in solution, the thermal instability of the long polyoxalkyl chain favors single rather than double O→Sn complexation, unlike the crystal structure where the latter is favored.

3.3. Structure of compounds *1–3* in solution

The three compounds were characterized by ^{1}H-, ^{13}C-, and ^{117}Sn-NMR in $CDCl_3$ solution, including 2D $^{1}H-^{13}C$ HMQC and HMBC experiments. The ^{117}Sn chemical shift of **1** (-100.3 ppm) is temperature as well as concentration independent and hardly differs from the chemical shift found for $(C_6H_5)_3Sn(n\text{-Bu})$ (-97.8 ppm). The $^{n}J(^{119}Sn-^{13}C)$ coupling satellites are likewise not very different from the reference compound and display the usual open chain sequence $|^{1}J(^{119}Sn-^{13}C)| \gg |^{3}J(^{119}Sn-^{13}C)| > |^{2}J(^{119}Sn-^{13}C)|$ [36]. 1D $^{1}H-^{119}Sn$ HMQC NMR spectra reveal clear $^{119}Sn-^{1}H$ correlations between the ^{119}Sn nucleus and protons H(1), H(2) and H(3) only. The latter is not an unequivocal indicator of a coordination between O(4) and Sn, because it may result either from a $^{4}J(^{119}Sn-^{1}H)$ coupling through the organic chain, from a $^{3}J(^{119}Sn-^{1}H)$ through the coordinative O(4)–Sn bond, or from both. If it were to exist, the resulting five-coordinate species has necessarily a very low molar fraction in the equilibrium with the four-coordinate species since all other NMR parameters essentially reflect four-coordination. Moreover, this four-coordination favoring equilibrium is fast on all NMR time scales.

4. Conclusions

Hexacoordination of the tin atom in $CH_3OCH_2CH_2OCH_2CH_2CH_2SnCl_3$ in the solid state results from two ether O→Sn interactions. In solution, a dynamic equilibrium including intramolecular O→Sn interactions are observed. Even though **4** and $CH_3OCH_2CH_2OCH_2CH_2CH_2SnCl_3$ differ only by one substituent at the tin atom, their stereochemistry is dramatically different both in the solid state and in solution. Related with the lower Lewis acidity of tetraorganotins, compounds **1–3** are tetracoordinated.

5. Supplementary material

Crystallographic data for compound **4** have been deposited with the Cambridge Crystallographic Data Centre with deposition number CCDC 161858. Copies of the information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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