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Synthesis and structures of intramolecularly hexacoordinated organotin chlorides containing the (3-(2-methoxy) ethoxy) propyl moiety

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Abstract

Two water-soluble organotin compounds, (3-(2-methoxy)ethoxy)propyltin trichloride, **1**, and bis (3-(2-methoxy)ethoxy)propyltin dichloride, **2**, were synthesized and characterized by ^{1}H, ^{13}C and ^{119}Sn NMR spectroscopy and by X-ray diffraction. In both cases, the geometry at the tin atom is that of a distorted *cis*-octahedron, which is preserved for both compounds in $CDCl_3$ solution. A detailed solution structure is proposed for **1** from 1D ^{1}H–^{119}Sn HMQC NMR experiments. © 1997 Elsevier Science S.A.

Keywords: Tin; *Cis*-octahedral crystal structures; Hydrosolubility; HMQC NMR

1. Introduction

In addition to those of the platinum group [1,2], a variety of other metal complexes have been shown to be antitumour agents [3], among which are some organotin compounds of the type $R_2SnCl_2 \cdot L_2$, where L_2 is a chelating ligand. It has been suggested that the active species might be formed by dissociation of the ligand and replacement of at least one chlorine atom by a coordination site on DNA [4,5].

Many other organotin compounds have been shown to exhibit antitumoural properties in vitro against a wide panel of tumoural cell lines of human origin [6–9], as well as in vitro trypanocidal activity [10]. A correct evaluation of the biological merits of organotin derivatives in this context remains hampered by their low solubility in water [11]. Therefore, we are interested in the synthesis of organotin compounds with higher water solubility by introducing hydrophilic groups into the molecule. Recently, Light and Breslow [12] described tris(3-(2-methoxy)ethoxy)propyltin hydride as a water soluble tin reagent. Accordingly, the present work was initiated from the reasonable assumption that organotin chlorides containing the same dioxaalkyl moiety could likewise be water-soluble. This report deals with the preparation and the structural characterization, both in solution and solid state, of (3-(2-methoxy)ethoxy)propyltin chlorides.

2. Experimental

2.1. Preparation of compounds

To 2.35 g of tetrakis (3-(2-methoxy)ethoxy)propyltin (4 mmol) was added 1.13 g of tin tetrachloride (4.35 mmol). The mixture was left at room temperature for 15 min and then heated to 240°C for 3 h.

Compound **1**, (3-(2-methoxy)ethoxy)propyl tin trichloride, was directly distilled from the reaction mixture under reduced pressure (bp = 138–142°C/0.3 mm Hg) to yield 0.24 g of the desired compound (17.5%). It was crystallized from a dichloromethane/hexane (3/7) mixture. MS m/z (%): 343 (100); 307 (39). Basic NMR data are given in Table 1.

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Compound **2**, bis (3-(2-methoxy)ethoxy)propyltin dichloride was found pure in the reaction residue after distillation of the first derivative, (3.24 g, yield = 82.5%). Single crystals were obtained by slow evaporation of a solution of the compound in a dichloromethane/hexane (3/7) mixture. MS *m/z* (%): 389 (100); 237 (20). Basic NMR data are likewise given in Table 1.

2.2. Spectroscopic measurements

Mass spectra were recorded on a Finnigan Mat TSQ 70 triple quadrupole mass spectrometer in the fast atom bombardment (FAB) mode. The ^{1}H, ^{13}C and ^{119}Sn NMR spectra were obtained with a Bruker AC-200 spectrometer operating at 200.13, 50.32 and 74.54 MHz, respectively, and a Bruker AMX-500 spectrometer operating at 500.13, 125.77 and 186.50 MHz, respectively.

The gradient-assisted 1D ^{1}H–^{119}Sn HMQC spectra were recorded as explained elsewhere on the Bruker AMX-500 instrument [13,14].

2.3. Determination of the crystal structures

2.3.1. Crystal structure determination for 1

Data for a crystal of **1** (approximate size 0.2 × 0.2 × 0.4 mm) were collected on a four-circle X-ray diffractometer. Crystal data and details about data collection and refinement are given in Table 2. The cell parame-

Table 1
NMR spectroscopic data for **1** and **2** in $CDCl_3$ solutions

$(\overset{6}{CH_3}-O-\overset{5}{CH_2}-\overset{4}{CH_2}-O-\overset{3}{CH_2}-\overset{2}{CH_2}-\overset{1}{CH_2})_nSnCl_{4-n}$

	$n=1$	$n=2$
	Compound **1**	Compound **2**
δ H-1	2.05 (m)	1.8 (t)
δ H-2	2.15 (m)	2.05 (m)
δ H-3, H-4, H-5	3.6–3.9 (m)	3.5–3.8 (m)
δ H-6	3.35 (s)	3.30 (s)
δ C-1	27.6	26.8
δ C-2	24.0	24.8
δ C-3	69.3	71.7
δ C-4, C-5	69.9, 71.4	70.4, 71.5
δ C-6	58.9	58.7
$^{1}J(^{13}C-^{119}Sn)$	871	674
$^{2}J(^{13}C-^{119}Sn)$	69	40
$^{3}J(^{13}C-^{119}Sn)$	78	31
$\delta\,^{119}Sn$	−157.4	−80.1

^{1}H and ^{13}C chemical shifts are expressed in ppm (reference = TMS). ^{119}Sn chemical shifts are expressed in ppm with tetramethyltin as reference.
The $^{n}J(^{13}C-^{119}Sn)$ coupling constants are expressed in Hz.
Concentrations: ca. 100 mg/0.5 ml.
Abbreviations: s (singlet), m (complex pattern), t (triplet).

Table 2
Experimental data for the crystal structure determination of **1**

Crystal data	
Formula	$C_6H_{13}Cl_3O_2Sn\cdot 2H_2O$
Formula weight	378.2 g mol^{-1}
Absorption coefficient	$\mu = 2.419$ mm^{-1}
Crystal system	triclinic
Space group	$P\bar{1}$, $Z=2$
Lattice constants	$a = 7.378(5)$ Å
(MoK α)	$b = 8.641(5)$ Å
	$c = 11.356(4)$ Å
	$\alpha = 98.61(4)°$
	$\beta = 101.57(4)°$
	$\gamma = 97.38(5)°$
Temperature	293 K
Density	$D_m = 1.816$ g cm^{-3}
Data collection	
Diffractometer	Four-circle CAD4 (Enraf-Nonius)
Radiation	MoK α; graphite monochromator
Scan type	ω scans
Scan width	$(1.80+0.35\tan\theta)°$
Measuring angles	
θ 2–25°	
hkl	h, $-8\rightarrow 8$; k, $0\rightarrow 10$; l, $-13\rightarrow 13$
Reflections	2625 total
	2237 independent
	2142 with $I > 3\sigma(I)$
Computing	
Programs	MITHRYL [35]
Atomic scattering factors for neutral atoms	$\Delta f', \Delta f''$ [36]
Refinement	Diagonal matrix least-squares on F
Residuals	$R_w = 0.035$
	$R = 0.028$
$\Delta\rho_{max}$; $\Delta\rho_{min}$	0.25; −0.23 e Å^{-3}
Goodness of fit	$S = 4.30$
Number of parameters refined	195

Table 3
Fractional coordinates and equivalent isotropic temperature factors for **1**

Atom	x	y	z	B_{eq}
Sn(1)	0.1143(1)	0.8972(0)	0.2277(0)	2.9(0)
Cl(2)	−0.1625(2)	0.7123(2)	0.1166(1)	5.0(1)
Cl(3)	0.0940(2)	0.8073(2)	0.4108(1)	4.3(1)
Cl(4)	−0.0332(2)	1.1247(2)	0.2711(1)	4.6(1)
C(5)	0.2282(8)	0.9429(7)	0.0761(5)	3.6(2)
C(6)	0.3960(8)	0.8495(7)	0.0649(5)	4.1(2)
C(7)	0.3354(9)	0.6782(7)	0.0766(5)	4.1(2)
O(8)	0.2910(5)	0.6802(8)	0.1952(3)	3.1(1)
C(9)	0.2402(8)	0.5218(7)	0.2194(6)	4.1(2)
C(10)	0.4051(9)	0.4382(7)	0.2441(6)	4.8(3)
O(11)	0.5397(6)	0.5261(5)	0.3443(4)	5.2(2)
C(12)	0.6953(11)	0.4500(10)	0.3788(9)	7.8(4)
O(13)	0.6417(5)	0.8494(5)	0.4182(4)	4.6(2)
O(14)	0.3909(6)	1.0392(5)	0.3469(4)	4.6(2)

Table 4
Selected bond lengths (Å) and angles (°) for **1**

Bond lengths			
Sn(1)–Cl(2)	2.416(2)	C(6)–C(7)	1.51(1)
Sn(1)–Cl(3)	2.351(2)	C(7)–O(8)	1.447(8)
Sn(1)–Cl(4)	2.402(2)	O(8)–C(9)	1.453(8)
Sn(1)–C(5)	2.127(7)	C(9)–C(10)	1.49(1)
Sn(1)–O(8)	2.442(4)	C(10)–O(11)	1.397(9)
Sn(1)–O(14)	2.292(5)	O(11)–C(12)	1.41(1)
C(5)–C(6)	1.51(1)	O(11)–H(113)	1.90(7)
Interatomic angles			
Cl(2)–Sn(1)–Cl(3)	91.48(6)	C(5)–Sn(1)–O(8)	76.9(2)
Cl(2)–Sn(1)–Cl(4)	98.24(6)	C(5)–Sn(1)–O(14)	85.9(2)
Cl(2)–Sn(1)–C(5)	98.2(2)	O(8)–Sn(1)–O(14)	86.0(2)
Cl(2)–Sn(1)–O(8)	87.0(1)	Sn(1)–C(5)–C(6)	110.5(5)
Cl(2)–Sn(1)–O(14)	170.9(1)	C(5)–C(6)–C(7)	112.4(6)
Cl(3)–Sn(1)–Cl(4)	95.04(6)	C(6)–C(7)–O(8)	106.5(5)
Cl(3)–Sn(1)–C(5)	158.3(2)	Sn(1)–O(8)–C(7)	107.0(4)
Cl(3)–Sn(1)–O(8)	84.3(1)	Sn(1)–O(8)–C(9)	124.6(4)
Cl(3)–Sn(1)–O(14)	82.0(1)	C(7)–O(8)–C(9)	112.6(5)
Cl(4)–Sn(1)–C(5)	102.7(2)	O(8)–C(9)–C(10)	112.5(6)
Cl(4)–Sn(1)–O(8)	174.7(1)	C(9)–C(10)–O(11)	109.9(6)
Cl(4)–Sn(1)–O(14)	88.8(1)	C(10)–O(11)–C(12)	113.5(6)

ters were determined by least-squares from setting angles for 25 reflections. In the collection of intensities, the $\theta/2\theta$ scan method was used, and 2237 independent reflections were collected in the region $\theta < 25°$.

Correction was made for Lorentz and polarisation effects. 2142 reflections with $I > 3\sigma(I)$ were considered, observed and were used in the subsequent calculations. A semi-empirical method of absorption correction was applied [15].

The structure was solved by Patterson and Fourier techniques. All the H atoms were located from a difference Fourier map. Diagonal-matrix least-squares refinement of atomic coordinates and anisotropic thermal parameters for non-hydrogen atoms, isotropic for H atoms, gave a final $R = 0.028$ ($R_w = 0.035$, $S = 4.30$) for 2142 independent significant reflections and 195 parameters. The resulting atomic coordinates are listed in Table 3; the bond lengths and bond angles, in Table 4. The structure of **1**, together with the atomic numbering scheme, is depicted in Fig. 1.

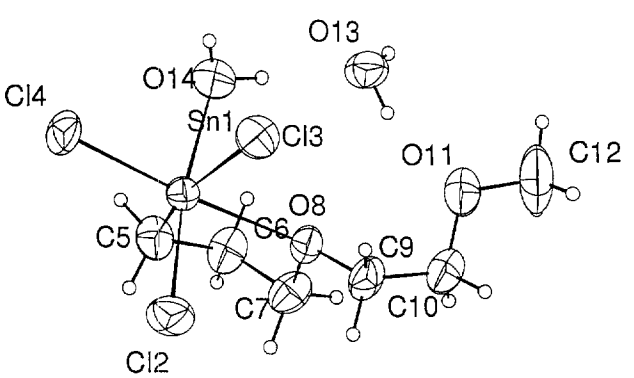

Fig. 1. Structure and atomic numbering scheme for compound **1**.

2.3.2. Crystal structure determination for 2

A crystal (approximate size $0.2 \times 0.3 \times 0.5$ mm), mechanically fragile, was sealed in a Lindemann glass capillary, and data were collected on a four-circle X-ray diffractometer. They were corrected for Lorentz and polarisation effects. It was considered necessary to correct for absorption [15]. Crystal data and details about data collection and refinement are given in Table 5.

3357 reflections were measured ($\theta_{max} = 25°$). 2566 were independent, of which 2267 had $I > 3\sigma(I)$. After reduction to Fo values, a Wilson plot was calculated from which starting values were obtained for the scale parameter and the overall isotropic parameter B. The positions of the non-hydrogen atoms were found from the three-dimensional Patterson and Fourier syntheses. Block-diagonal least-squares refinement with isotropic

Table 5
Experimental data for the crystal structure determination of **2**

Crystal data	
Formula	$C_{12}H_{26}Cl_2O_4Sn$
Formula weight	423.9 g mol^{-1}
Absorption coefficient	$\mu = 1.756$ mm^{-1}
Crystal system	monoclinic
Space group	$P2_1/n$, $Z = 4$
Lattice constants	$a = 9.298(3)$ Å
(MoKα)	$b = 10.463(8)$ Å
	$c = 18.324(7)$ Å
	$\beta = 96.36(3)°$
Temperature	293 K
Density	$D_m = 1.589$ g cm^{-3}
Data collection	
Diffractometer	Four-circle CAD4 (Enraf-Nonius)
Radiation	MoKα; graphite monochromator
Scan type	ω scans
Scan width	$(2 + 0.35 \tan\theta)°$
Measuring angles	
θ	2–25°
hkl	h, $0 \rightarrow 11$; k, $0 \rightarrow 12$; l, $-21 \rightarrow 21$
Reflections	3557 total
	2566 unique
	2267 with $I > 3\sigma(I)$
Computing	
Programs	MITHRYL [35]
Atomic scattering factors for neutral atoms	$\Delta f'$, $\Delta f''$ [36]
Refinement	Diagonal matrix least-squares on F
Residuals	$R_w = 0.092$
	$R = 0.099$
$\Delta\rho_{max}$; $\Delta\rho_{min}$	0.6; -0.6 e Å^{-3}
Goodness of fit	$S = 8.60$
Number of parameters refined	276

Table 6
Fractional coordinates and equivalent isotropic temperature factors for **2**

Atom	x	y	z	B_{eq}
Sn(1)	0.4830(1)	−0.0138(1)	0.2387(1)	3.1(0)
Cl(2)	0.5913(5)	0.1316(5)	0.3302(3)	4.8(2)
Cl(3)	0.5350(6)	0.1105(5)	0.1329(3)	5.2(2)
C(5)	0.6456(17)	−0.1596(17)	0.2416(9)	3.4(7)
C(6)	0.5980(19)	−0.2789(17)	0.2753(10)	4.0(8)
C(7)	0.5673(22)	−0.2582(18)	0.3529(10)	4.5(9)
O(8)	0.4532(12)	−0.1672(12)	0.3512(6)	3.6(5)
C(9)	0.4276(23)	−0.1212(19)	0.4218(10)	4.7(9)
C(10)	0.3245(21)	−0.2105(18)	0.4604(10)	4.4(9)
O(11)	0.4039(14)	−0.3155(13)	0.4866(7)	4.9(7)
C(12)	0.3249(25)	−0.3970(22)	0.5295(11)	5.5(11)
C(13)	0.2574(21)	0.0272(22)	0.2431(11)	4.9(9)
C(14)	0.1615(20)	−0.0842(20)	0.2160(10)	4.5(9)
C(15)	0.1887(23)	−0.1283(24)	0.1409(11)	5.7(11)
O(16)	0.3359(13)	−0.1670(14)	0.1408(6)	4.6(6)
C(17)	0.3635(30)	−0.2074(27)	0.0690(12)	7.4(15)
C(18)	0.4549(53)	−0.3004(27)	0.0664(19)	15.3(28)
O(19)	0.4009(19)	−0.4166(15)	0.0905(9)	7.1(9)
C(20)	0.5237(33)	−0.4986(32)	0.1063(17)	10.1(21)

temperature factors gave $R = 0.11$, which decreased to 0.10 when anisotropic temperatures were applied. The H atoms were introduced in the calculations from a difference Fourier map. Final atomic coordinates are listed in Table 6; the bond lengths and bond angles in Table 7. The structure of **2**, together with the atomic numbering scheme, is depicted in Fig. 2. [2]

Table 7
Selected bond lengths (Å) and angles (°) for **2**

Bond lengths			
Sn(1)–Cl(2)	2.402(5)	O(11)–C(12)	1.42(3)
Sn(1)–Cl(3)	2.426(6)	C(13)–C(14)	1.51(3)
Sn(1)–C(5)	2.15(2)	C(14)–C(15)	1.50(3)
Sn(1)–C(13)	2.15(2)	C(15)–O(16)	1.43(3)
C(5)–C(6)	1.48(3)	O(16)–C(17)	1.43(3)
C(6)–C(7)	1.51(3)	C(17)–C(18)	1.29(5)
C(7)–O(8)	1.42(2)	C(18)–O(19)	1.41(4)
O(8)–C(9)	1.43(2)	O(19)–C(20)	1.43(4)
C(9)–C(10)	1.56(3)	Sn(1)–O(8)	2.65(1)
C(10)–O(11)	1.38(2)	Sn(1)–O(16)	2.67(1)
Interatomic angles			
Cl(2)–Sn(1)–Cl(3)	96.5(2)	C(13)–C(14)–C(15)	113(2)
Cl(2)–Sn(1)–C(5)	101.1(5)	C(14)–C(15)–O(16)	110(2)
Cl(2)–Sn(1)–C(13)	100.6(6)	C(15)–O(16)–C(17)	111(2)
Cl(3)–Sn(1)–C(5)	101.5(5)	O(16)–C(17)–C(18)	116(3)
Cl(3)–Sn(1)–C(13)	101.8(6)	C(17)–C(18)–O(19)	112(3)
C(5)–Sn(1)–C(13)	145.9(7)	C(18)–O(19)–C(20)	106(2)
Sn(1)–C(5)–C(6)	111(1)	O(8)–Sn(1)–Cl(2)	84.9(3)
C(5)–C(6)–C(7)	112(2)	O(8)–Sn(1)–C(5)	71.6(5)
C(6)–C(7)–O(8)	107(2)	O(8)–Sn(1)–Cl(3)	173.1(3)
C(7)–O(8)–C(9)	114(1)	O(8)–Sn(1)–C(13)	84.5(6)
O(8)–C(9)–C(10)	112(2)	O(16)–Sn(1)–Cl(2)	174.0(3)
C(9)–C(10)–O(11)	107(2)	O(16)–Sn(1)–C(5)	84.1(5)
C(10)–O(11)–C(12)	113(2)	O(16)–Sn(1)–Cl(3)	85.3(3)
Sn(1)–C(13)–C(14)	112(1)	O(16)–Sn(1)–C(13)	73.4(6)

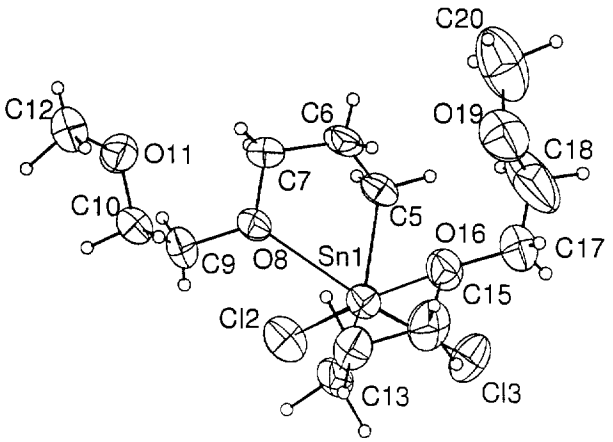

Fig. 2. Structure and atomic numbering scheme for compound **2**.

3. Results and discussion

3.1. Synthetic aspects

The starting material, tetrakis(3-(2-methoxy)ethoxy)propyl tin, was obtained as described by Light and Breslow [12]. It was submitted to a redistribution reaction with tin tetrachloride. It has been previously shown that this kind of reaction occurs rapidly at room temperature [16]. However, tetrakis-(3-(2-methoxy)ethoxy)propyltin does not react with $SnCl_4$ at room temperature; therefore, we used more drastic conditions (240°C, 3 h) [17,18]. This disproportionation reaction is known to proceed in different steps. A mixture of the trialkyltin chloride and the alkyltin trichloride is formed simply upon mixing the tetraalkyl tin and tin tetrachloride at room temperature. Subsequently, heating this mixture to 240°C yields a further redistribution providing the dialkyltin dichloride. It is known that using an excess of tin tetrachloride causes a small amount of monoalkyltin trichloride to remain unreacted in the reaction mixture [19].

We were able to synthesize (3-(2-methoxy)ethoxy)propyltin trichloride (**1**) and bis (3-(2-methoxy)ethoxy)propyltin dichloride (**2**) via a one-pot reaction (Fig. 3). The two derivatives were separated subsequently by distillation under reduced pressure.

3.2. Description of the crystal state structures

Both compounds contain a six-coordinate tin atom. For **2**, one oxygen atom of each of the polyoxaalkyl

[2] Nota bene: there is no atom 4; this choice was made so that the first dioxaalkyl chain has the same numbering as for compound 1.

Table 8
Comparison of some bond distances of compounds **1** and **2**, and related *cis* and *trans* adducts, respectively $Me_2SnCl_2 \cdot Me_2NCH[(OEt)_2PO]_2$ [20] and $Me_2SnCl_2 \cdot$ Ph-CH[$(OEt)_2$PO]-NH-$(CH_2)_2$-NH-CH[$(OEt)_2$PO]Ph [21]

	1, this work	**2**, this work	*cis* adduct, [20]	*trans* adduct, [21]
Sn–Cl	2.416(2)	2.402(5)	2.48(2)	2.578(1)
	2.351(2)	2.426(6)	2.46(3)	2.578(1)
	2.402(2)			
Sn–O	2.442(4)	2.65(1)	2.38(7)	2.250(3)
	2.292(5)	2.67(1)	2.64(7)	2.250(3)
Sn–C	2.127(7)	2.15(2)	2.12(9)	2.108(4)
		2.15(2)	2.11(8)	2.108(4)

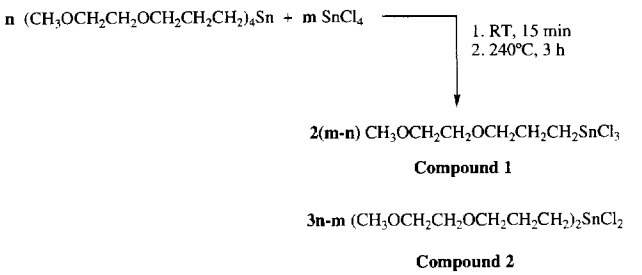

Fig. 3. Synthesis of compounds **1** and **2** using redistribution reactions between tetrakis(3-(2-methoxy)ethoxypropyl)tin and tin tetrachloride, with $m > n$.

substituents is coordinated to tin with the two oxygens displaying a *cis* configuration. For **1**, where only a single polyoxaalkyl substituent is present, the second oxygen atom used to reach the same coordination state is that of an exogenous water molecule. In both cases, the two chlorine atoms are in mutual *cis* position. The remaining atoms linked to tin (one carbon and one chlorine for **1**, two carbons for **2**) are in mutual *trans* position.

The Sn–O, Sn–Cl and Sn–C bond distances (and the main bond angles) in the distorted octahedral geometry of compounds **1** and **2** are similar to those of other *cis* complexes of comparable type, as shown by an example in Table 8 [20,21]. The Sn–O bonds in the *cis* adducts are significantly longer than those in the *trans* complexes, while the Sn–Cl bond distances are shorter, with the Sn–C bonds being approximately equal. These differences can arise from a redistribution of electron density in O–Sn–Cl fragments in *cis* complexes compared with O–Sn–O and Cl–Sn–Cl in *trans* adducts.

3.3. Characteristics in solution

Compounds **1** and **2** were characterized in $CDCl_3$ solution by ^1H, ^{13}C and ^{119}Sn NMR spectroscopy (Table 1) [22,23].

On the basis of the well-known correlation of the $^1J(^{13}C-^{119}Sn)$ coupling constant with the C–Sn–C angle [24], it can be reasonably proposed that the chelated distorted *cis* octahedral structure observed in the crystalline state for **2** is retained upon dissolution in $CDCl_3$. The ^{119}Sn chemical shift of **2** is fairly typical for a six-coordinate diorganotin dichloride [25] with two moderately strong coordinations, confirming the struc-

Table 9
NMR spectroscopic data for **1** at variable concentration in $CDCl_3$ solution, recorded at 500 MHz proton resonance frequency

$\overset{6}{CH_3}-O-\overset{5}{CH_2}-\overset{4}{CH_2}-O-\overset{3}{CH_2}-\overset{2}{CH_2}-\overset{1}{CH_2}-SnCl_3$

H	80 mg/0.5 ml	40 mg/0.5 ml	10 mg/0.5 ml
H-1	2.04 (t, 6.5) [97]	2.06 (t, 6.5) [97]	2.07 (t, 6.5) [97]
H-2	2.17 (tt, 6.5, 5.5) [269]	2.17 (tt, 6.5, 5.5) [264]	2.19 (tt, 6.5, 5.5) [262]
H-3	3.73 (t, 5.5) [5.5]	3.75 (t, 5.5) [5.5]	3.76 (t, 5.5) [5.5]
H-4	3.89 (t, 4.5)	3.90 (t, 4.5)	3.90 (t, 4.5)
H-5	3.61 (t, 4.5)	3.62 (t, 4.5)	3.63 (t, 4.5)
H-6	3.33 (s)	3.34 (s)	3.35 (s)
	$^1H-^{119}Sn$ HMQC correlations at all ^1H resonances	$^1H-^{119}Sn$ HMQC correlations at all ^1H resonances	$^1H-^{119}Sn$ HMQC correlations at all ^1H resonances **except** H-6
^{13}C			
C-1	27.4 [865/829]	26.9 [850/815]	27.4 [832/801]
C-2	24.0 [69]	24.0 [68]	24.0 [67]
C-3	69.3 [77]	69.4 [75]	69.5 [75]
C-4	69.9	70.0	70.1
C-5	71.4	71.6	71.8
C-6	58.8	58.8	58.8
^{119}Sn	−154.6	−143.5	−134.3

Abbreviations as in Table 1.
$^3J(^1H-^1H)$ coupling constants are given in parentheses with the multiplet structure.
$^nJ(^1H-^{119}Sn)$ as well as $^1J(^{13}C-^{119/117}Sn)$ and unresolved $^2J(^{13}C-^{119/117}Sn)$ and $^3J(^{13}C-^{119/117}Sn)$ coupling constants are given between squared brackets.

ture of **2** in $CDCl_3$ solution to be identical to that of the crystal state.

It has been shown recently [14] in CH_3CO-$O(CH_2)_nSnCl_3$ compounds [26] ($n = 3$–5), that intramolecular as well as intermolecular coordinations can occur; their relative importance is a function of concentration, at least when $n = 4$ and 5 [14]. To investigate whether comparable coordinations can exist in the very similar compound **1**, $CH_3OCH_2CH_2$-$O(CH_2)_3SnCl_3$, we performed, as for such trichlorostannylalkyl esters [14], gradient assisted [27] 1D ^1H–^{119}Sn HMQC [28] NMR experiments [29–31]. This question is of interest because the 3-(2-methoxy)ethoxy)propyl contains two potentially coordinating oxygen atoms.

The principles and applications of the HMQC technique have been extensively reviewed [29–32]. Briefly, it edits ^1H resonances of only those ^1H nuclei which are coupled to ^{119}Sn nuclei. In other terms, the result in the ^1H spectrum is specific spectral editing of the $^nJ(^1H$–$^{119}Sn)$ coupling satellites of those ^1H nuclei that exhibit such a coupling, with n going typically up to 5, all remaining noncoupled proton resonances being suppressed. The quality of suppression of the latter resonances is significantly improved by using gradient pulses rather than phase cycling only [13,14,30,32].

To investigate the possible existence of both intra- and intermolecular coordination in compound **1**, we recorded ^1H, ^{13}C and ^{119}Sn, as well as 1D ^1H–^{119}Sn HMQC spectra at three different concentrations. The results are shown in Table 9.

The full assignment of all resonances of **1** was achieved from 2D ^1H–^{13}C HMQC [28] and HMBC [33,34] spectra correlating proton resonances with ^{13}C resonances through mutual $^2J(^1H$–$^{13}C)$ and $^3J(^1H$–$^{13}C)$ couplings of the corresponding nuclei.

The main observations from the data of Table 9 are as follows.

First, except proton 6, the ^1H resonances of all protons of **1** exhibit a ^1H–^{119}Sn HMQC correlation with the ^{119}Sn nucleus at all three concentrations, including protons 4 and 5. If it is reasonably assumed that $^6J(^1H$–$^{119}Sn)$ and $^7J(^1H$–$^{119}Sn)$ couplings through the (3-(2-methoxy)ethoxy)propyl chain are not observable, or at least cannot give rise to the significant correlation observed under the measurement conditions used (HMQC delays = 60, 200, 350 ms), it must be concluded that the observed correlations for H-4 and H-5 are due to $^3J(^1H$–$^{119}Sn)$ and $^4J(^1H$–$^{119}Sn)$ coupling pathways through a coordinative O → Sn bond. Since at very high dilution (10 mg/0.5 ml), where aggregation is not possible or at most negligible, no correlation is observed with the methoxy proton resonance, it is concluded that the coordinative O → Sn bond involved is the same as already observed in the solid state structure of **2**, namely from the first oxygen of the (3-(2-methoxy)ethoxy)propyl moiety.

Second, the very small influence of the concentration on all proton NMR parameters, including the $^3J(^1H$–$^{119}Sn)$ coupling constants, clearly indicates that the five-membered ring structure resulting from this O → Sn bond exists at all concentrations. The value of the latter coupling constant, which is very similar to that of $CH_3COO(CH_2)_3SnCl_3$ (264 Hz at 10 mg/0.5 ml) where such a 5-ring involving the alkoxy oxygen was shown to exist, confirms this [14].

Third, the existence of a single, concentration-dependent ^{119}Sn resonance shifting to low frequency by ca. 20 ppm upon eightfold concentration increase, indicates a slight but significant coordination expansion by aggregation. Since only one resonance is observed, there is an equilibrium that is fast on the ^{119}Sn NMR time scale. Because the low frequency shift of the ^{119}Sn resonance depends on concentration, this equilibrium involves an aggregated species with intermolecular O → Sn coordination, favoured at high concentration, and the five-membered ring structure proposed above, with intramolecular O → Sn coordination, favoured at low concentration. The weak coordination expansion upon concentration increase is confirmed by the concomitant increase of the $^1J(^{13}C$–$^{119/117}Sn)$ coupling constants. The appearance of a ^1H–^{119}Sn HMQC correlation between the methoxy protons (H-6) as well as the increase of the intensity of the corresponding correlation with the H-5 protons when concentration increases, clearly indicate the involvement of the second oxygen of the (3-(2-methoxy)ethoxy)propyl group in the O → Sn coordination that is responsible for this aggregation. It is proposed that, under the concentration conditions used, this aggregation is most likely to proceed by cyclodimerization, as shown in Fig. 4 where the two species involved in the fast equilibrium are displayed. Because all other NMR parameters remain fairly constant, especially the $^2J(^{13}C$–$^{119/117}Sn)$ and $^3J(^{13}C$–$^{119/117}Sn)$ as well as the $^3J(^1H$–$^{119}Sn)$ coupling constants, it seems realistic to confirm that the intramolecular coordination is retained in the aggregation.

It is stressed again [14] that the size of the ring is determinant for the strength of the O → Sn interaction. Thus, the NMR data at hand for another trichlorostannyl ether, $PhCH_2O$-$(CH_2)_5SnCl_3$, $\delta^{119}Sn = -1$ ppm and $^1J(^{13}C$–$^{119}Sn) = 665$ Hz [26], do not favour the exis-

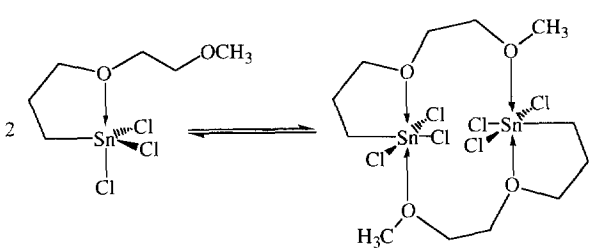

Fig. 4. Dynamic equilibrium proposed for compound **1**.

tence of any intramolecular coordination comparable to that of **2**. The higher flexibility of the 7-membered ring implying such an O → Sn interaction seems to us the most reasonable explanation.

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