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Synthesis and characterization of triphenyl-, tri-*n*-butyl and di-*n*-butyltin derivatives of 4-carboxybenzo-18-crown-6 and -15-crown-5

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Abstract

^{1}H-, ^{13}C- and ^{117}Sn-NMR as well as ^{119m}Sn Mössbauer spectroscopy, electrospray mass spectrometry and elemental analysis of novel trioganotin and di-*n*-butyltin derivatives of 4-carboxybenzo-18-crown-6 and -15-crown-5 are reported. The X-ray crystal structure of aquatriphenyltin-4,7,10,13,16-pentaoxadicyclo[13.4.0]nonadeca-1,3(17),18-trienecarboxylate hydrate consists of trigonal bipyramidal tin with a C_3 trigonal plane and the axial positions occupied by an oxygen atom, derived from a monodentate carboxylate ligand, and a water molecule. In the lattice, the crown ether portions of the molecules are capped on either side, via hydrogen bonding interactions, by the coordinated and uncoordinated water molecules. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Triphenyltin derivative; Tri-*n*-butylin derivative; Di-*n*-butylin derivative; 4-Carboxybenzo-18-crown-6; 4-Carboxybenzo-15-crown-5

1. Introduction

After Pedersen's discovery in 1967 of the first crown ethers and their properties to bind alkali metal cations [1,2], cation–macrocycle interactions have been studied intensively [3,4]. Although adducts between organotin (IV), inorganic tin (IV) and inorganic tin (II) and crown ethers are the subject of current interest [5–12], organotin compounds with crown ether moieties bound directly via covalent bonds to tin remain rare [13].

The synthesis of new triphenyltin, tri-*n*-butyltin and di-*n*-butyltin carboxylates with carboxylate ligands containing an 18-crown-6 or a 15-crown-5 moiety are reported herein. All compounds were characterized by elemental analysis, ^{1}H-, ^{13}C- and ^{117}Sn-NMR as well as ^{119m}Sn Mössbauer spectroscopy and electrospray mass spectrometry [14–17]. Crystallographic studies have shown that organotin carboxylates show a great structural diversity in the solid state [18,19] and hence, the crystal structure of one derivative, i.e. aquatriphenyltin 4-carboxybenzo-15-crown-5 (**5**), has also been determined. It was found to incorporate a water molecule in the coordination sphere, a feature which remains relatively unusual in organotin chemistry [20–23]. In vitro antitumour activities [24–26] of these new compounds against seven human tumour cell lines were reported previously in a comparative screening with organotin polyoxaalcanecarboxylates [27].

2. Results and discussion

2.1. Synthesis

The compounds synthesised are depicted in Fig. 1.

Triphenyl and tri-*n*-butyltin carboxylates were obtained by the reaction of triphenyltin hydroxide or

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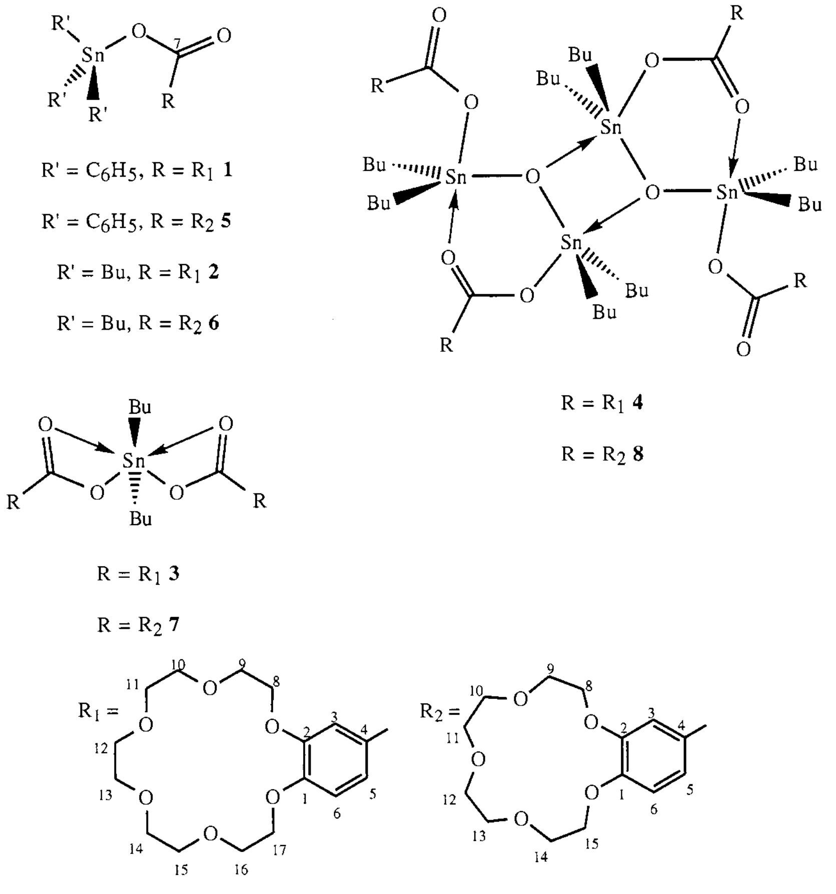

Fig. 1. Structures proposed for compounds **1** to **8**.

tri-*n*-butyltin acetate with 4-carboxybenzo-18-crown-6 or 4-carboxybenzo-15-crown-5, respectively (Eqs. (1) and (2)).

$$(C_6H_5)_3SnOH + RCOOH \rightarrow (C_6H_5)_3SnOCOR + H_2O \tag{1}$$

$$Bu_3SnOCOCH_3 + RCOOH \rightarrow Bu_3SnOCOR + CH_3COOH \tag{2}$$

The starting material for di-*n*-butyltin carboxylates was di-*n*-butyltin oxide [28], which yields two different compounds depending on the molar ratio acid/tin engaged in the reaction: bis[di-*n*-butyl(carboxylato)tin]oxide for a 1/1 ratio and di-*n*-butyltin di(carboxylate) for a 2/1 ratio (Eqs. (3) and (4)).

$$4Bu_2SnO + 4RCOOH \rightarrow \{[Bu_2Sn(OCOR)]_2O\}_2 + 2H_2O \tag{3}$$

$$Bu_2SnO + 2RCOOH \rightarrow Bu_2Sn(OCOR)_2 + 2H_2O \tag{4}$$

2.2. X-ray structure of **5**

Triorganotin carboxylates, R_3SnO_2CR', are known to adopt a variety of motifs in the solid state [18,19,29]. For derivatives in which the organic residue does not contain an additional potential donor atom, the majority of the structures adopt one of two basic motifs as shown in Fig. 2. In the extreme, motif B is monomeric and contains four-coordinate tin and motif C is polymeric with five-coordinate tin. Five-coordinate, trigonal bipyramidal tin is also found in a small number of structures where an additional neutral ligand, normally water, is incorporated in the coordination geometry, i.e. in $R_3Sn(O_2CR')L$, shown as motif A in Fig. 2. The structures that are known to adopt this motif are

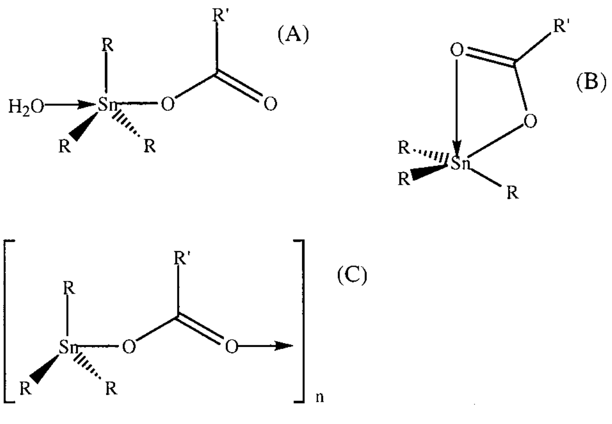

Fig. 2. Possible structures for triorganotin carboxylates [18,19].

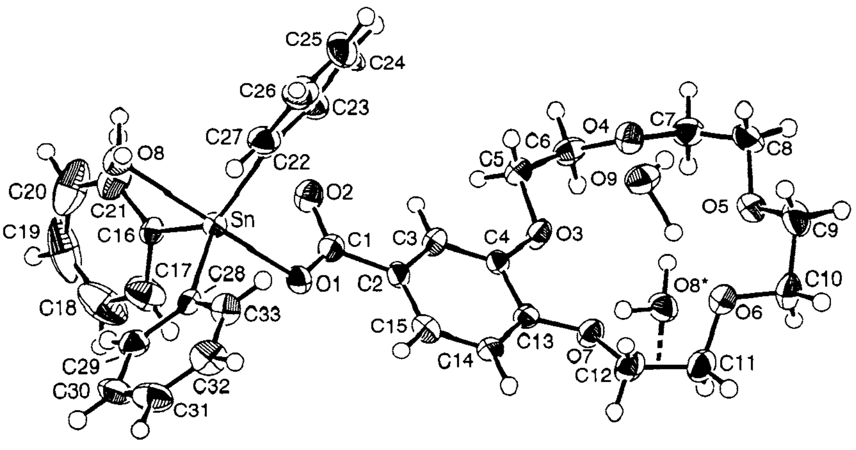

Fig. 3. Molecular structure and crystallographic numbering scheme employed for **5**.

[$Me_3Sn(O_2C_5H_4N$-2)OH_2] [30], [*n*-Bu_3Sn(*N*-phthaloylglycinate)OH_2] [31], {$Ph_3Sn[O_2CC_6H_4(N{=}N(C_6H_3$-4-OH-5-CHO))-*o*]$OH_2$} [32] and [$Ph_3Sn(O_2CCl_3)MeOH$] [33]. The structure of **5** also adopts this motif as shown in Fig. 3; selected interatomic parameters are collected in Table 1.

The tin atom lies 0.2569(6) Å out of the trigonal plane defined by the three ipso carbon atoms of the phenyl rings, in the direction of the O(1) atom. The Sn–O(1) bond distance of 2.120(6) Å is significantly shorter than the Sn–O(2) separation of 2.937(6) Å. Further, there are no intermolecular contacts < 4.0 Å formed between the tin and O(2) atoms leading to the conclusion that the carboxylate ligand coordinates in the monodentate mode. As expected the Sn–O(8) distance of 2.471(6) Å, i.e. involving the water molecule, is significantly longer than the Sn–O(1) distance. In addition to the presence of coordinated water, there is solvent water in the lattice which participates in hydrogen bonding.

The coordinated water molecule forms three close contacts in the lattice. These are O(8)–H(81)...O(3)^i 2.35 Å [O(8)...O(3)^i 3.099(8) Å, O(8)–H(81)...O(3)^i 135°], O(8)–H(81)...O(7)^i 2.12 Å [2.919(8) Å, 141°] and O(8)–H(82)...O(5)^i 2.32 Å [2.777(8) Å, 109°]; symmetry operation i: $0.5 + x$, $0.5 - y$, $-0.5 + z$. Similarly, the solvent water molecule forms three close contacts: O(9)–H(91)...O(4) 2.76 Å [3.022(9) Å, 109°], O(9)–H(91)...O(5) 2.92 Å [3.277(9) Å, 121°] and O(9)–H(92)...O(6) 1.65 Å [2.896(8) Å, 173°]. This arrangement implies that all ether oxygen atoms participate in intermolecular hydrogen bonding. In the lattice the crown ether moieties are aligned parallel to the *a*-axis. They do not form channels as the distance between successive crown ethers corresponds to the *a*-distance of 10.217(5) Å. Indeed, each crown ether is 'capped' on one side by the coordinated water molecule and on the other by the solvent water molecule as per the hydrogen bonding scheme described above. Formally it can be formulated that motif A is realized simply from motif B by *trans*-substitution of the carbonyl oxygen for a water ligand, accompanied by a change of configuration of tin from *cis* to *trans*.

2.3. NMR spectroscopy

All compounds were characterized by ^1H-, ^{13}C- and ^{117}Sn-NMR in $CDCl_3$. The ^1H-NMR data are reported in Table 2. For compounds **1** and **5**, the ^1H chemical shift ranges of the triphenyltin moiety were deduced from signal intensities and from estimated $^3J(^1H-^{117/119}Sn)$ coupling constants. The assignment of the butyltin moiety for compounds **2** to **4**, **6** and **7** is based on $^nJ(^1H-^1H)$ coupling constants, multiplicities, signal integration, $^1H-^{13}C$ HMQC and $^1H-^{13}C$ HMBC experiments. Signal overlapping precluded the determination of the $^2J(^1H-^{119/117}Sn)$ and $^3J(^1H-^{119/117}Sn)$ coupling constants for compounds **2**–**4** and **6**–**8**. The proton chemical shifts of H(3), H(5) and H(6) were assigned on the basis of $^nJ(^1H-^1H)$ coupling constants and were further confirmed by $^1H-^{13}C$ HMQC and $^1H-^{13}C$ HMBC experiments. The methylenic ^1H chemical shifts of the crown ether moieties were assigned at least in part

Table 1
Selected bond lengths (Å) and angles (°) for **5**

Sn–O(1)	2.120(6)	Sn–O(8)	2.471(6)
Sn–C(16)	2.120(8)	Sn–C(22)	2.134(7)
Sn–C(28)	2.145(7)	C(1)–O(1)	1.905(10)
C(1)–O(2)	1.234(9)		
O(1)–Sn–O(8)	177.4(2)	O(1)–Sn–C(16)	99.7(3)
O(1)–Sn–C(22)	97.0(2)	O(1)–Sn–C(28)	92.9(3)
O(8)–Sn–C(16)	82.7(2)	O(8)–Sn–C(22)	80.4(2)
O(8)–Sn–C(28)	87.3(2)	C(16)–Sn–C(22)	135.4(3)
C(16)–Sn–C(28)	111.2(3)	C(22)–Sn–C(28)	108.9(3)
Sn–O(1)–C(1)	112.6(5)		

Table 2
^{1}H-NMR data in $CDCl_3$ of compounds **1** to **8** [a]

	1	**2**	**3**	**4**	**5**	**6**	**7**	**8** [b]
CH(o)	7.7–7.8 m [60]	–	–	–	7.7–7.8 m [60]	–	–	–
CH(m)(p)	7.4–7.5 m	–	–	–	7.4–7.5 m	–	–	–
CH(3)	7.62 d (2)	7.54 d (2)	7.58 s	7.49 s	7.60 d (2)	7.54 d (2)	7.59 d (2)	7.54 s
CH(5)	7.7–7.8 m	7.63 dd (8, 2)	7.73 d (8)	7.54 d (8)	7.7–7.8 m	7.63 dd (8, 2)	7.74 dd (8, 2)	7.60 m, u
CH(6)	6.91 d (9)	6.82 d (8)	6.86 d (8)	6.84 d (8)	6.82 d (8)	6.82 d (8)	6.86 d (8)	6.89 d (8)
CH_2(8)(17)	4.1–4.3 m	4.1–4.3 m	4.1–4.3 m	4.1–4.3 m	–	–	–	–
CH_2(9)(16)	3.8–4.0 m	3.8–4.0 m	3.8–4.0 m	3.8–4.0 m	–	–	–	–
CH_2(10)(11)(14)(15)	3.6–3.8 m	3.6–3.8 m	3.6–3.8 m	3.6–3.8 m	–	–	–	–
CH_2(12)(13)	3.67 Ψs	3.65 Ψs	3.65 Ψs	3.62 Ψs	–	–	–	–
CH_2(8)(15)	–	–	–	–	4.1–4.2 m	4.1–4.2 m	4.1–4.2 m	4.1–4.3 m
CH_2(9)(14)	–	–	–	–	3.8–3.9 m	3.8–3.9 m	3.8–4.0 m	3.9–4.0 m
CH_2(10)(11)(12)(13)	–	–	–	–	3.73 Ψs	3.73 Ψs	3.75 Ψs	3.77 Ψs
HOH	–	~2.0 bs	–	–	~2.0 b	~2.0 b	–	–
$CH_2(\alpha)$	–	1.2–1.3 m	1.7–1.8 m	1.4–1.6 m	–	1.2–1.4 m	1.7–1.8 m	1.5–1.7 m
$CH_2(\beta)$	–	1.6–1.7 m	1.7–1.8 m	1.6–1.8 m	–	1.6–1.7 m	1.7–1.8 m	1.6–1.8 m
$CH_2(\gamma)$	–	1.2–1.3 m	1.37 tq (7, 7)	1.1–1.4 m	–	1.2–1.4 m	1.38 tq (7, 7)	1.2–1.5 m
$CH_3(\delta)$	–	0.89 t (7)	0.86 t (7)	0.7–0.9 m	–	0.89 t (7)	0.86 t (7)	0.7–0.9 m

[a] Chemical shifts in ppm with respect to TMS; coupling constants in Hz, $^nJ(^1H–^1H)$ in parentheses, $^nJ(^1H–^{117/119}Sn)$ between square brackets. Abbreviations: s = singlet; Ψs = pseudo singlet; d = doublet, dd = doublet of doublets; m = complex pattern; b = broad; t = triplet; tq = triplet of quartets.

[b] Product **8** contains **7**; u = undefined because of signal overlapping of **7** and **8**.

from signal integration and from $^1H–^{13}C$ HMQC and $^1H–^{13}C$ HMBC spectra in areas where overlapping is limited.

The ^{13}C-NMR data are shown in Table 3. $^nJ(^{13}C–^{117/119}Sn)$ satellites and signal intensities were used to assign the ^{13}C chemical shifts of the triphenyltin, tri-*n*-butyltin and di-*n*-butyltin moieties [34,35]. No $^1J(^{13}C–^{117/119}Sn)$ were observed for the C(ipso) signals, due to low intensities. Compounds **4** and **8** showed broader ^{13}C resonances therefore precluding the observation of any $^nJ(^{13}C–^{117/119}C)$ coupling constants. The aromatic ^{13}C signals of the carboxylate moiety were assigned on the basis of $^1H–^{13}C$ HMQC and $^1H–^{13}C$ HMBC, and ^{13}C DEPT-135 experiments, the former spectra being needed for the crown ether moiety. The assignment could not be achieved further than the γ-position of the crown ether, with respect to the aromatic ring, owing to their signals being unresolved in the ^1H spectra.

The ^{117}Sn-NMR data are given in Table 4. All compounds except **4** and **8** exhibit a single resonance. The two resonances of equal intensities for **4** and **8** result from their dimeric structure characterized by *endo*- and *exo*-cyclic tin atoms (see Fig. 1) [28]. The ^{117}Sn chemical shifts of compounds **1**, **2**, **4** and **5** are characteristic for four-coordination in solution [36,37]. Those of compounds **3** and **7** confirm the proposed structure.

2.4. *Mössbauer spectroscopy*

The Mössbauer parameters are listed in Table 5. The quadrupole splittings QS are found in the range of 3.28–3.41 mm s^{-1}, except for triphenyltin carboxylates having values of 2.33 for compound **1** and 2.77 for compound **5**. The latter are values excluding polymeric pentacoordinate structures of type C (see Fig. 2) [36–

Table 3
^{13}C-NMR data in $CDCl_3$ of compounds **1** to **8** [a]

	1	**2**	**3**	**4**	**5**	**6**	**7**	**8** [b]
C(i)	138.5	–	–	–	138.7	–	–	–
C(o)	137.0 [47/49]	–	–	–	136.9 [47/49]	–	–	–
C(m)	129.0 [61/63]	–	–	–	128.9 [61/65]	–	–	–
C(p)	130.2 [13]	–	–	–	130.1 [13]	–	–	–
C(7)	172.7	171.4	175.7	172.6	172.8	171.4	175.8	172.6
C(1)	152.9	152.2	153.3	152.5	153.1	152.5	153.5	152.6
C(2)	148.0	148.1	148.3	148.3	148.3	148.4	148.5	148.4
CH(3)	114.9	115.0	115.3	115.3	115.7	115.5	115.4	115.4
C(4)	122.8	125.0	122.7	126.3	123.3	125.1	122.9	126.3
CH(5)	125.1	124.2	124.9	124.0	125.2	124.4	125.0	124.1
CH(6)	111.7	112.1	112.3	112.4	112.1	112.3	112.2	112.3
CH_2(10)(11)(12)(13)(14)(15)	70.80	70.96	70.9	70.8	–	–	–	–
	70.77	70.84	70.9	70.8				
	70.71	70.77	70.81	70.7				
	70.66	70.73	70.76	70.6				
	70.53	70.66	70.73	70.6				
	70.51	70.61	70.67	70.5				
CH_2(9)(16)	69.4	69.5	69.5	69.42	–	–	–	–
	69.2	69.4	69.4	69.35				
CH_2(8)(17)	68.8	68.9	69.2	69.1	–	–	–	–
	68.6	68.8	69.0	68.9				
CH_2(10)(11)(12)(13)	–	–	–	–	70.95	71.2	71.11	71.11
					70.92	71.2	71.09	71.09
					70.31	70.57	70.39	70.42
					70.23	70.52	70.31	70.34
CH_2(9)(14)	–	–	–	–	69.3	69.59	69.4	69.4
					69.2	69.49	69.2	69.3
CH_2(8)(15)	–	–	–	–	68.9	69.1	69.0	69.0
					68.5	68.9	68.6	68.7
CH_2(α)	–	16.6	25.4	29.5	–	16.6	25.5	29.7
		[341/358]	[569/596]	[n.o.] [c]		[350/362]	[561/588]	[n.o.]
				28.3				28.6
				[n.o.]				[n.o.]
CH_2(β)	–	27.9	26.7	26.7	–	27.9	26.7	27.7
		[20]	[33]	26.6		[20]	[34]	27.4
CH_2(γ)	–	27.0	26.3	27.6	–	27.0	26.4	26.7
		[62/65]	[95]	27.4		[62/65]	[103]	26.6
CH_3(δ)	–	13.7	13.5	13.5	–	13.6	13.6	13.68
				13.4				13.61

[a] Chemical shifts in ppm with respect to TMS; $^nJ(^{13}C–^{117/119}Sn)$ coupling constants between square brackets.

[b] Sample contains **7**.

[c] n.o. = not observed.

Table 4
^{117}Sn-NMR data in $CDCl_3$ of compounds **1** to **8** [a]

1	**2**	**3**	**4**	**5**	**6**	**7**	**8**
−115.7	108.2	−156.2	−213.0	−116.3	107.4	−156.8	−212.5
			−217.3				−216.9

[a] Chemical shifts in ppm with respect to $(CH_3)_4Sn$.

38]. The difference of 0.44 mm s^{-1} between the QS values of the triphenyltin compounds **1** and **5** is higher than for tributyltin carboxylates (0.12 mm s^{-1}) or dibutyltin dicarboxylates (0.11 mm s^{-1}). This is consistent with **1** and **5** having necessarily a slightly different tin-atom geometry in solid state, since **5** is found hydrated while **1** is not, the X-ray analysis for **5** revealing an unusual type-A structure as shown in Fig. 2. A type-B structure can be proposed for compound **1** although it cannot be inferred whether there is a co-

Table 5
^{119m}Sn Mössbauer parameters: QS (mm s^{-1}) quadrupole splitting, IS (mm s^{-1}) isomer shift relative to Ca^{119}SnO$_3$, Γ_1 and Γ_2 (mm s^{-1}) line width

	QS	IS	Γ_1	Γ_2
1	2.33	1.24	0.76	0.81
2	3.41	1.44	0.94	0.94
3	3.40	1.39	0.72	0.85
4	3.36	1.27	0.96	0.99
5	2.77	1.23	0.99	0.94
6	3.29	1.45	0.94	0.88
7	3.28	1.41	0.92	0.93
8	3.38	1.33	0.98	0.95

Table 6
Characteristic electrospray fragment-ions for compounds **1**–**7** [a]

Fragment	**1**	**5**
$M+Na^+$	729	685
$M+K^+$	745	701
	2	**6**
$M+H^+$	647	
$M+H_2O+H^+$	665	
$M+NH_4^+$		620
$M+Na^+$	669	625
	3	**7**
$M+Na^+$	967	879
$M+K^+$		895
	4	**8**
$M/2+Na^+$	1217	1129
$M/2+K^+$	1233	1145

[a] Only fragments from M are listed.

Table 7
Elemental analysis of compounds **1** to **7** (found [calculated])

	Structure	C	H
1	$C_{35}H_{38}SnO_8$	60.2 [59.60]	5.5 [5.43]
2	$C_{29}H_{50}SnO_8 \cdot H_2O$	52.5 [52.50]	8.3 [7.90]
3	$C_{42}H_{64}SnO_{16}$	53.5 [53.46]	7.1 [6.84]
4	$C_{100}H_{164}Sn_4O_{34}$	50.0 [50.35]	7.1 [6.94]
5	$C_{33}H_{34}SnO_7 \cdot H_2O$	58.4 [58.34]	5.7 [5.35]
6	$C_{27}H_{46}SnO_7 \cdot 1/2H_2O$	53.1 [53.14]	7.8 [7.77]
7	$C_{38}H_{56}SnO_{14}$	53.9 [53.35]	6.7 [6.60]

ordination from the carbonyl oxygen to tin [36–38]. The QS values for **2** and **6** are typical for a polymeric structure of type-C with an equatorial SnR$_3$ unit and two apical carboxylates [36–38], corresponding to a five-coordinate structure in the solid state. The two different tin atoms of compound **4** could not be discriminated by Mössbauer spectroscopy since the method is less sensitive to small variations to the tin environment than ^{117}Sn NMR spectroscopy [28]. The QS values of compounds **3**, **4** and **7** are in agreement with the structure proposed in Fig. 1 [27].

2.5. Electrospray mass spectrometry

Table 6 shows the monoisotopic mass spectra (^{1}H, ^{12}C, ^{14}N, ^{16}O, ^{23}Na, ^{39}K, ^{120}Sn) in the cationic mode of water/acetonitrile solutions. Complexation by direct or hydrolyzed fragments or solvent molecules are observed frequently. The hydrolyzed species give an indication about the stability inside the spectrometer [39]. Adducts with alkali cations (Na$^+$ and K$^+$) are observed for all compounds. Complexation with alkali metal ions generates a cation which often facilitates the detection by the spectrometer [14–16]. The cations originate from the starting free acids, 4-carboxybenzo-18-crown-6 and -15-crown-5. This is not unusual since the crown ether moiety is complexed easily by alkali cations (Na$^+$ and K$^+$) and NH$_4^+$ [40]. In some cases, complexation with alkali cations gave the only evidence for the existence of the molecular mass of the basic compound M.

2.6. Elemental analyses

C and H elemental analyses have been performed for all compounds (see Table 7). Compounds **2**, **5** and **6** are found to contain water: compounds **2** and **5** (bulk powder) contain one water molecule per triorganotin carboxylate and compound **6** contains water in a (2/1) triorganotin carboxylate/water ratio. The presence of water was confirmed by ^{1}H-NMR and, for compound **5**, also by single crystal X-ray diffraction analysis.

3. Experimental

3.1. Synthesis

3.1.1. Triorganotin carboxylates

Compounds **1** and **5** are prepared typically by mixing equimolar amounts of triphenyltin hydroxide (515 mg; 1.40 mmol) and the appropriate 4-carboxybenzocrown (356 mg or 438 mg; 1.40 mmol) in 250 ml benzene in a 500 ml flask equipped with a Dean–Stark funnel. The mixture is refluxed for 4–48 h. The binary azeotrope benzene/water is distilled off up to 50% of the initial solvent volume. The remaining solution is evaporated under vacuum. The synthesis with tri-*n*-butyltin acetate yielding **2** and **6** is analog under elimination of acetic acid.

3.1.2. Diorganotin carboxylates

Di-*n*-butyltin oxide is refluxed in benzene with the appropriate amount of 4-carboxybenzocrown (1/1 molar ratio 4-carboxybenzocrown + di-*n*-butyltin oxide for **3** and **7**; 2/1 molar ratio for **4** and **8**) under the same conditions as for the triorganotin carboxylates.

Compound **8** could not be separated from **7** by chromatography on Sephadex LH-20 or recrystalliza-

Table 8
Synthesis data for compounds **1** to **8**

	M.p. (°C)	Yield (%)	Reflux time	Purification method
1	110–112	98	10	Recrystallization from diethyl ether/hexane
2	45–47	80	4	Recrystallization from hexane/chloroform
3	125–127	96	6	Recrystallization from hexane/chloroform
4	96–98	90	12	Sephadex LH–20; elution with methylene chloride/chloroform; recrystallization from hexane/chloroform
5	130–131	95	48	Recrystallization from hexane
6	Liquid	90	25	Sephadex LH-20; elution with methylene chloride/chloroform
7	130–132	98	48	Recrystallization from petroleum ether/methylene chloride
8	90–105 [a]		20	Sephadex LH-20; elution with methylene chloride/chloroform [a]

[a] Unseparable from **7**.

tion. This is probably due to a disproportionation reaction which yields **7** and di-*n*-butyltin oxide as supported by the formation of a precipitate in the NMR tube during data acquisition.

Table 8 summarises all experimental synthesis details. Compound **5** appears as a solid sample which is essentially a powder with monohydrate composition (elemental analysis). In this bulk, only a few crystals, suitable for X-ray diffraction, can be observed and selected. These crystals appear to exist as a dihydrate rather than the monohydrate of the bulk.

3.2. NMR measurements

All 2D-NMR spectra were recorded on a Bruker AMX500 spectrometer interfaced with a X32 computer and operating at 500.13 and 125.77 MHz for ^{1}H and ^{13}C nuclei, respectively. All 1D-NMR spectra were acquired on a Bruker AC250 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. ^{1}H and ^{13}C chemical shifts were referenced to the standard Me_4Si scale from respectively residual ^{1}H and $^{13}C-^{2}H$ solvent resonances of chloroform ($CHCl_3$, 7.23 and $CDCl_3$, 77.0 ppm for ^{1}H and ^{13}C nuclei, respectively). The ^{117}Sn resonance frequencies were set from the absolute reference $\Xi(^{117}Sn) + 35.632295$ MHz [41,42]. 2D gradient enhanced $^{1}H-^{13}C$ HMQC [43] and HMBC [44] correlation spectra were acquired using the pulse sequences of the Bruker program library, adapted to include gradient pulses [45–48], as described recently [49].

3.3. Mössbauer spectroscopy

The Mössbauer spectra were recorded as described in Ref. [50].

3.4. Mass spectrometry

The electrospray mass spectra were recorded in the cationic mode on a Micromass Quattro II instrument coupled with a Masslynx system (ionisation in an electric field of 3.5 kV; source temperature: 80°C; source pressure: 1 atm; analyzer pressure: 10^{-5} mbar) [51,52]. Cone voltages were 15 V for compound **2**, 30 V for compounds **3**, **7** and **8**, 50 V for compound **6**, 80 V for compound **4** and 90 V for compounds **1** and **5**.

3.5. X-ray crystallography

Intensity data for a colourless crystal of **5** were collected at 200 K on a Rigaku AFC6R diffractometer employing Mo–K_α radiation ($\lambda = 0.71073$ Å) and the ω:2θ scan technique to $2\theta_{max}$ of 50.0°. The data set was corrected for Lorentz and polarisation effects [53] as well as for absorption employing an empirical procedure [54]. Data that satisfied the $I \geq 3.0\sigma(I)$ criterion of observability were used in the subsequent analysis. Crystal data and refinement details are given in Table 9.

Table 9
Crystallographic data for **5**

Formula	$C_{33}H_{38}O_9Sn$
Formula weight	697.4
Crystal system	Monoclinic
Space group	$P2_1/n$
a (Å)	10.217(5)
b (Å)	17.388(9)
c (Å)	17.837(10)
β (°)	101.08(4)
V (Å^3)	3109(2)
Z	4
Crystal size (mm^3)	$0.10 \times 0.24 \times 0.32$
D_c (g cm^{-3})	1.489
F(000)	1432
μ (cm^{-1})	8.75
No. of data collected	5733
No. of unique data	5413
No. of reflections with $I \geq 3.0\sigma(I)$	3565
R	0.050
R_w	0.064
G.O.F.	2.47
Residual ρ_{max}/ρ_{min} (e Å^{-3})	$0.86/-1.23$

The structure was solved by direct methods [55] and refined by a full-matrix least-squares procedure based on F [53]. Non-hydrogen atoms were refined with anisotropic displacement parameters and hydrogen atoms were included in the model at their calculated positions (C–H 0.97 Å); O–H atoms were located from a difference map. The refinements were continued until convergence employing Sigma weights, i.e. $1/\sigma^2(F)$. Selected interatomic parameters are collected in Table 1 and the crystallographic numbering scheme employed is shown in Fig. 1 which was drawn with ORTEP [56] at 50% probability ellipsoids.

4. Supplementary material

Crystallographic data for the structural analysis has been deposited with the Cambridge Crystallographic Data Centre; CCDC No. 112253 for compound **5**. 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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