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The First Examples of a Crown Ether Intramolecularly Encapsulating Mono- and Diorganotin Dications: Synthesis and Structures of $[PhSnCH_2([16]crown\text{-}5)][ClO_4]_2$ and $[HOSnCH_2([16]crown\text{-}5)][Y]_2$ ($Y = ClO_4$, CF_3SO_3)

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Dedicated to Professor Hubert Schmidbaur on the occasion of his 75th birthday

Abstract: The reaction of silver perchlorate with $[PhI_2SnCH_2([16]crown\text{-}5)]$ (**1**) and $[I_3SnCH_2([16]crown\text{-}5)]$ (**2**) gave the organotin(IV)-substituted crown ether complexes $[PhSnCH_2([16]crown\text{-}5)][ClO_4]_2$ (**3**) and $[HOSnCH_2([16]crown\text{-}5)][Y]_2$ (**4**: $Y = ClO_4$, **5**: $Y = CF_3SO_3$), respectively. All compounds have been isolated as air-stable materials and characterised by ^1H, ^{13}C, ^{119}Sn and ^{119}Sn MAS (**5**) NMR spectroscopy, ESIMS spectrometry, elemental analysis and by single-crystal X-ray diffraction analysis. The molecular structures of **3**–**5** show that the tin(IV) cation fits perfectly into the crown ether cavity and is coordinated by the five oxygen atoms of the ring to give a pentagonal bipyramidal configuration about the central metal cation. Notably, compounds **4** and **5** contain the first monomeric monoorganotin dication. Moreover, there are $^3J(^1H,^{119}Sn)$ coupling constants to the CH_2CH proton of 377 (**3**) and 470 Hz (**4**, **5**) that are, to the best of our knowledge, the biggest such couplings ever reported.

Keywords: crown compounds · host–guest systems · NMR spectroscopy · tin · X-ray diffraction

Introduction

The pioneering work of Pedersen, Lehn and Cram has set the ground for the design and development of synthetic macrocyclic compounds capable of molecular recognition of ionic and neutral substrates.[1–3] Cyclic polyethers, so called crown ethers, have been of particular interest due to their unique complexation properties.[4,5] Their ability to bind selectively cations of different charge and size has led to the synthesis of a plethora of Group I and II alkali and alkaline earth as well as transition-metal complexes of crown ethers.[6–28] Moreover, crown ethers were also employed for the separation of lanthanides, the compounds of which are of interest due to their electronic, magnetic and optical properties.[29–36] Group III–V element compounds have also attracted considerable attention with respect to their behaviour towards crown ethers. Mainly to study the stereochemical effect of the lone pair at metal atoms, complexes formed between crown ethers and the cations Tl^+,[37] In^+,[38,39] Pb^{2+},[40,41] $[SnCl]^+$,[42] $[SnI]^+$,[43] Sn^{2+},[44] $[SbCl]^{2+}$[45] and $[BiCl]^{2+}$,[45] and with the salts $PbCl_2$,[46] $PbBr_2{\cdot}H_2O$,[47] PbI_2,[48] $Pb(SCN)_2$[49] and $Pb(NO_3)_2$[50,51] have been reported. Only recently, Baines and co-workers produced the first example of a Ge^{2+} cation encapsulated by [2,2,2]cryptand as well as a series of cationic crown ether complexes of germanium(II) compounds,[52,53] whereas Cheng et al. reported germanium dications stabilised by azamacrocycles and crown ethers.[54] In most cases, the cation lies inside the cavity of the crown ether or is sandwich-like bridged between two rings. Among the numerous reports dealing with the complexation of inorganic metal cations by cyclic polyethers,

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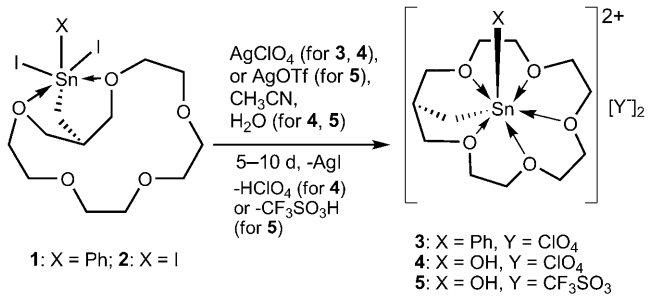
those relating to the interaction with cationic organometallic compounds are very rare, even though the stabilisation of such species and their isolation as air-stable materials are of fundamental interest, notably due to their potential in organic synthesis. Reported are the complexes $[MeMg([15]crown-5)]^{+}$[55] and $[AlMe_2([15]crown-5)]^{+}$[56] in which the magnesium and the aluminium atoms lie within the macrocycle and are coordinated by all crown ether oxygen atoms. In the specific case of organotin(IV) cation, only one report of complexes with crown ethers, namely, $[SnLPh_2]^{2+}$ (L = [12]crown-4, [15]crown-5, [18]crown-6), is known, which, on the basis of IR and ^1H NMR spectra, suggests the tin atom is inside the cavity and coordinated by four oxygen atoms of the ring.[57] However, there is no crystal structure yet to support this suggestion. More efforts have been devoted to the isolation of complexes involving neutral diorganotin(IV) compounds, such as $[SnR_2X_2]$ (R = alkyl, aryl; X = halogen), or tin(IV) halides, where they act as second-sphere ligands and interact with the crown ether through a water molecule by hydrogen bonds[58–61] or where they are coordinated outside the ring by the oxygen atoms of the crown.[62,63] Owing to the affinity of crown ethers for metal cation, careful size selection should enable encapsulation of cationic organotin(IV) compounds and their isolation in the solid state.

In the context of our systematic studies on organotin-substituted crown ethers[64–68] and our general interest in intramolecularly coordinated organotin cations,[69–71] we report herein the first examples of structurally characterised cationic mono- and diorganotin(IV) complexes of crown ethers, namely, $[PhSnCH_2([16]crown-5)]^{2+}(ClO_4^-)_2$ (**3**) and $[HOSnCH_2([16]crown-5)]^{2+}(Y^-)_2$ (**4**, Y = ClO_4; **5**, Y = CF_3SO_3). Notably, compounds **4** and **5** are the only second examples of a monoorganotin(IV) cation and the first ones that are monomeric.

Results and Discussion

Synthetic aspects: The reaction of diiodo(1,4,7,10,13-pentaoxacyclohexadec-15-metlyl)phenylstannane (**1**)[65] with $AgClO_4$, (2 mol equiv) in acetonitrile in the dark afforded the corresponding diorganotin dication as its perchlorate salt **3** in moderate yield (Scheme 1). In a similar manner, the reaction of the triiodo(1, 4, 7, 10, 13-pentaoxacyclohexadec-15-methyl)stannane (**2**)[72] with $AgClO_4$ or AgOTf (3 mol equiv) gave, after recrystallisation from CH_3CN/diethyl ether in the presence of air moisture or upon the addition of water, the crown ether substituted monoorganotin hydroxide dication as its perchlorate or triflate salts **4** and **5**, respectively (Scheme 1).



Scheme 1. Synthesis of compounds **3**–**5**.

It is likely that the initially formed organotin trication that we failed to isolate even when the perchlorate counteranions were replaced by triflate reacts with water to give the compounds **4** and **5**, respectively.

The compounds **3**–**5** are colourless and air-stable crystalline materials that are soluble in organic solvents such as DMSO, CH_3OH, CH_3CN.

Molecular structures: The molecular structures of compounds **3** and **4** are represented in Figure 1. That of compound **5** is given in the Supporting Information. Selected geometrical data of **3**–**5** are collected in Tables 1 and 2.

Table 1. Selected bond lengths [Å] for compounds **3**-**5**.

	3		**4**	**5**
Sn(1)–C(1)	2.1016(18)	Sn(1)–C(1)	2.106(5)	2.099(3)
Sn(1)–C(21)	2.1071(18)	Sn(2)–C(21)	2.115(4)	
Sn(1)–O(1)	2.2933(14)	Sn(1)–O(1)	2.271(4)	2.267(2)
Sn(1)–O(2)	2.3203(14)	Sn(2)–O(11)	2.278(3)	
Sn(1)–O(3)	2.2612(14)	Sn(1)–O(2)	2.252(3)	2.251(2)
Sn(1)–O(4)	2.3561(14)	Sn(2)–O(12)	2.255(3)	
Sn(1)–O(5)	2.3336(14)	Sn(1)–O(3)	2.258(3)	2.242(2)
C(21)–C(22)	1.534(3)	Sn(2)–O(13)	2.262(3)	
		Sn(1)–O(4)	2.279(3)	2.268(2)
		Sn(2)–O(14)	2.280(3)	
		Sn(1)–O(5)	2.280(3)	2.273(2)
		Sn(2)–O(15)	2.2300(3)	
		Sn(1)–O(6)	1.930(3)	1.917(2)
		Sn(2)–O(16)	1.936(4)	

Compound **3** consists of the distinct dication $[PhSnCH_2([16]crown-5)]^{2+}$ and two perchlorate anions with the closest interionic Sn(1)···O(12) distance of 4.762(4) Å. This distance is beyond the sum of the van der Waals radii of both atoms and reveals noncoordination. However, there are intermolecular H(32)···O(7) and H(27 B)···O(14) distances of 2.47 and 2.48 Å that are below the sum of the van der Waals radii[73] of hydrogen (1.20–1.45 Å) and oxygen (1.50 Å). The most important feature of the structure of compound **3** is the intramolecular complexation of the Sn(1) cation by the five crown ether oxygen atoms, resulting in a distorted pentagonal bipyramidal configuration of Sn(1). The O(1)–O(5) atoms occupy the equatorial positions and the C(1) and C(21) atoms occupy the axial positions of the pentagonal bipyramid. The distortion from the ideal geometry is especially manifested by the C(1)-Sn(1)-C(21) angle of 165.57(8) instead of 180° and the consecutive O-Sn-O angles ranging from 69.72(5) (O(2)-Sn(1)-O(3)) to 76.37(5)° (O(1)-Sn(1)-O(5)), but with the average angle of 72.12° being almost identical to the ideal one of 72.00°. The oxygen

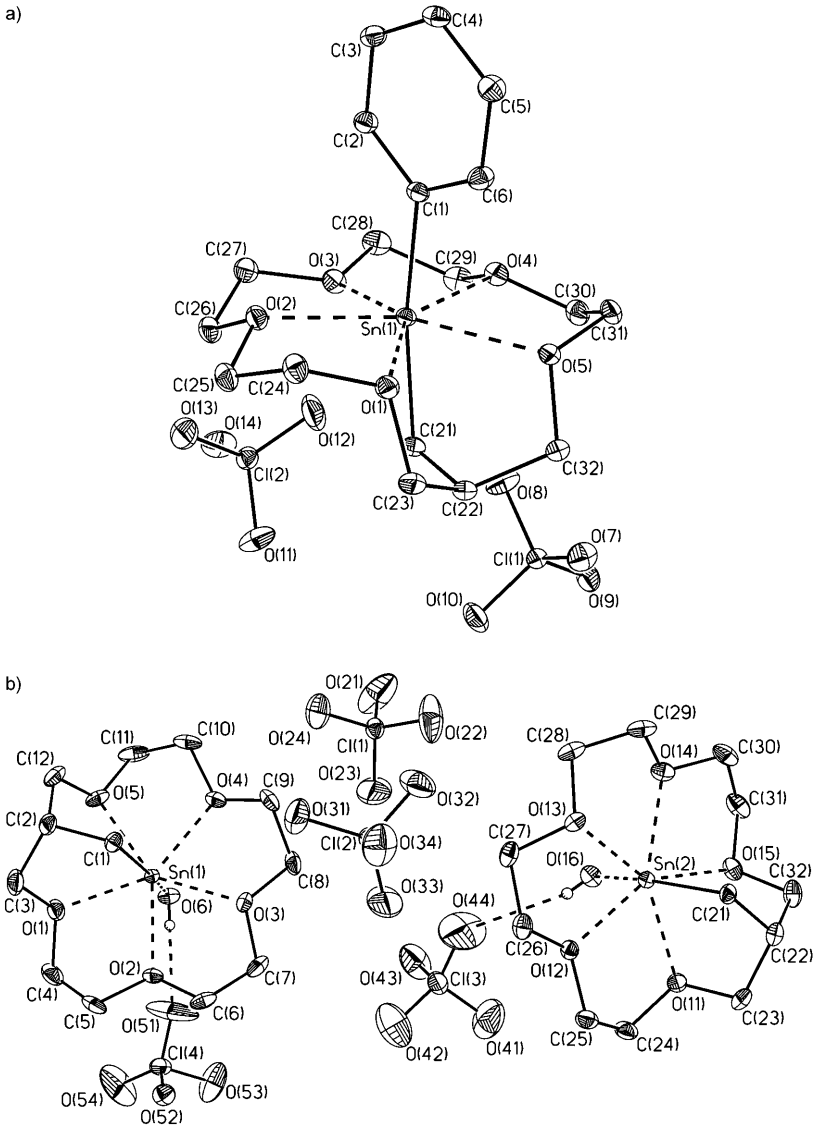


Figure 1. Molecular structure of a) **3** and b) **4** showing 30% probability displacement ellipsoids and the crystallographic numbering scheme.

atoms lie below (O(1) 0.0476, O(3) 0.1741, O(5) 0.0468 Å) and above (O(2) 0.1340, O(4) 0.1344 Å) the equatorial plane with O(1) and O(5), O(2) and O(4) being practically co-planar, whereas O(3) shows the maximum deviation. The tin atom lies 0.0949 Å above the least plane in the direction of C(1). The perfect guest–host fit of the diorganotin(IV) moiety with the [16]crown-5 ether fragment is comparable with the accommodation of a sodium cation in the cavity of a [16]crown-5 ether; the latter has intramolecular diameters (d) of 1.70–2.20 Å).[3] The diameter d of Na^+ ($d=1.91$ Å)[74] and that of Sn^{IV} ($d=1.78$ Å)[74] are relatively close and both fit in this cavity.

The Sn–O bond lengths range from 2.2612(14) (Sn(1)–O(3)) to 2.3561(14) Å (Sn(1)–O(4)). They are shorter than the intramolecular Sn–O distance of 2.482(2) Å[65] found in the parent compound **1** and those found in [{($PhSn^{IV}$(μ-OH)CH_2)$_2$}([26]crown-8)][ClO_4]$_2$ (2.3759(1), 2.5367(1) Å).[75] For the crown ether complexes $[SnLCl]^+$ (L=[18]crown-5) and $[Sn_2I_3$([18]crown-6)$_2]^+$, Sn–O bond lengths in the range of 2.592(6)–2.883(7 Å)[42] and 2.612(1)–2.937(1) Å,[43] respectively, have been reported. It appears that the Sn^{IV} tin atom in compound **3** is more strongly coordinated to the [16]crown-5 than the Sn^{II} ones are bonded to [18]crown-5 and -6 ethers. The organotin cation of salt **3** has C_1-symmetry, notably induced by the crown ether ring. Such a less symmetrical arrangement of crown ethers has proved to enhance their cation-binding abilities.[76]

The unit cells of compounds **4** and **5** contain two independent molecules, the geometric parameters of which are similar. The overall structures closely resemble that of compound **3** with the difference that the axially bonded phenyl substituent in **3** is replaced by a hydroxyl group in **4** and **5**. Notable differences of the geometric parameters between **3** and **4**, **5** are 1) the consecutive O-Sn-O angles, which show smaller variations for the monorganotin hydroxide derivative **4** (70.80(12)° O(12)-Sn(2)-O(13), 74.70(13)° O(11)-Sn(2)-O(15)) than the diorganotin derivative **3** (see above); and 2) the shorter Sn–O(crown ether) bond lengths in **4** ranging from 2.230(3) (Sn(2)–O(15)) to 2.280(3) Å (Sn(2)–O(5), Sn(2)–O(14)). The latter reflect the enhanced Lewis acidity of the monoorganotin cation in **4** and **5** compared with the diorganotin cation in **3**. Moreover, there are interionic SnOH(6)···O(51) and SnOH(16)···O(44) hydrogen bonds of 2.16(6) and 2.36(6) Å, respectively, for **4**, and SnOH(6)···O(13) 1.96(3) Å for **5**.

Notably, in contrast to [{$PhSn(H_2O)_3(\mu$-OH)$\}_2$][1,5-$C_{10}H_6(SO_3)_2\}_2$], the only other monoorganotin dication,[77] compounds **4** and **5** are monomeric in the solid state. The terminal Sn(1)–O(6) and Sn(2)–O(16) bond lengths of 1.930(3) and 1.936(4) Å, respectively, are shorter than the sum of the covalent radii of Sn and O (2.10 Å).[74] The shortening might be traced to the axial position of the oxygen atoms in the pentagonal bipyramid as well as to a considerable ionic

Table 2. Selected bond angles [°] for compound **3**.

3				**4**			
C(1)-Sn(1)-C(21)	165.57(8)	O(3)-Sn(1)-O(4)	69.82(5)	O(6)-Sn(1)-C(1)	166.39(18)	O(2)-Sn(1)-C(1)	100.92(16)
O(1)-Sn(1)-O(2)	72.91(5)	O(3)-Sn(1)-O(5)	139.92(5)	O(16)-Sn(2)-C(21)	166.14(18)	O(12)-Sn(2)-C(21)	101.18(16)
O(1)-Sn(1)-O(3)	140.94(5)	O(3)-Sn(1)-C(1)	99.98(6)	O(1)-Sn(1)-O(2)	72.31(13)	O(3)-Sn(1)-O(4)	71.74(13)
O(1)-Sn(1)-O(4)	148.14(5)	O(3)-Sn(1)-C(21)	94.43(7)	O(11)-Sn(2)-O(12)	71.81(12)	O(13)-Sn(2)-O(14)	71.80(13)
O(1)-Sn(1)-O(5)	76.37(5)	O(4)-Sn(1)-O(5)	71.78(5)	O(1)-Sn(1)-O(3)	142.17(13)	O(3)-Sn(1)-O(5)	143.26(13)
O(1)-Sn(1)-C(1)	90.95(6)	O(4)-Sn(1)-C(1)	90.13(6)	O(11)-Sn(2)-O(13)	141.52(12)	O(13)-Sn(2)-O(15)	143.39(13)
O(1)-Sn(1)-C(21)	78.17(7)	O(4)-Sn(1)-C(21)	94.18(7)	O(1)-Sn(1)-O(4)	146.07(14)	O(3)-Sn(1)-O(6)	95.37(14)
O(2)-Sn(1)-O(3)	69.72(5)	O(5)-Sn(1)-C(1)	91.10(6)	O(11)-Sn(2)-O(14)	146.66(13)	O(13)-Sn(2)-O(16)	94.29(15)
O(2)-Sn(1)-O(4)	138.93(5)	O(5)-Sn(1)-C(21)	77.25(6)	O(1)-Sn(1)-O(5)	73.90(14)	O(3)-Sn(1)-C(1)	97.88(16)
O(2)-Sn(1)-O(5)	149.27(5)	Sn(1)-C(21)-C(22)	102.25(12)	O(11)-Sn(2)-O(15)	74.70(13)	O(13)-Sn(2)-C(21)	99.45(15)
O(2)-Sn(1)-C(1)	90.06(6)	C(23)-C(22)-C(32)	113.13(17)	O(1)-Sn(1)-O(6)	91.61(15)	O(4)-Sn(1)-O(5)	72.35(14)
O(2)-Sn(1)-C(21)	95.65(6)			O(11)-Sn(2)-O(16)	91.18(15)	O(14)-Sn(2)-O(15)	72.06(13)
				O(1)-Sn(1)-C(1)	79:83(17)	O(4)-Sn(1)-O(6)	84.06(14)
				O(11)-Sn(2)-C(21)	79.19(15)	O(14)-Sn(2)-O(16)	85.59(14)
				O(2)-Sn(1)-O(3)	71.12(13)	O(4)-Sn(1)-C(1)	97.10(17)
				O(12)-Sn(2)-O(13)	70.80(12)	O(14)-Sn(2)-C(21)	96.95(16)
				O(2)-Sn(1)-O(4)	140.45(13)	O(5)-Sn(1)-O(6)	88.39(14)
				O(12)-Sn(2)-O(14)	140.51(13)	O(15)-Sn(1)-O(16)	88.58(14)
				O(2)-Sn(1)-O(5)	145.61(14)	O(5)-Sn(1)-C(1)	79.11(16)
				O(12)-Sn(2)-O(15)	145.71(12)	O(15)-Sn(1)-C(21)	79.32(16)
				O(2)-Sn(1)-O(6)	86.32(13)	Sn(1)-C(1)-C(2)	101.1(3)
				O(12)-Sn(2)-O(16)	85.00(14)	Sn(2)-C(21)-C(22)	100.5(3)

character of these Sn−O bonds. The distances are even shorter than those reported for the monomeric diorganotin dihydroxide $(2,6\text{-}Mes_2H_3C_6)_2Sn(OH)_2$ (Sn−O 1.974(4) and 1.977(4) Å)[78] and the monoorganotin acid $\{(Me_3Si)_3CSn(OH)O\}_3$ (Sn−O 1.968–1.977 Å).[79]

Many organotin(IV) hydroxides readily condense or dimerise to afford hydroxyl- and/or oxo-bridged derivatives,[80,81] whereas organotin(IV) compounds with terminal Sn−OH groups are rather rare.[79] The encapsulation of the organotin(IV) fragment and the bulky crown ether seem to be the key factors that prevent the dimerisation of **4** and **5** The ring size is also of prime importance, since the replacement of [16]crown-5 by [13]crown-4 or [19]crown-8 did not give the corresponding crown ether encapsulated organotin cations.

Structures in solution: The intramolecular encapsulation of the tin atom in the diorganotin compound **3** as well as in the monoorganotin compounds **4** and **5** is retained in solution, as observed by the ^{119}Sn NMR chemical shifts and also by the ^{13}C and ^{1}H NMR spectroscopy data. Thus, the ^{119}Sn NMR spectra of **3**, **4** and **5** in CD_3CN show single resonances at δ −452 ($\nu_{1/2}$ = 27 Hz) and −550 ppm ($\nu_{1/2}$ = 27 Hz), respectively. Both values are low-frequency shifted and the first one falls in the range of the heptacoordinated diorganotin compound $[(Bu_2Sn)_3O(Hpurpurine)_2]$ (δ = −416 ppm)[82] with a SnC_2O_5 substituent pattern and of $R_2Sn(dib)$ (R = Me, δ = −437 ppm; R = *n*Bu, δ = −441 ppm; dib = dianion of diacetylpyridine bis(benzoyl)hydrazone)[83] with a $SnC_2O_2N_3$ substituent pattern. The second one is even more low-frequency shifted and close to the chemical shifts of δ = −537 and −561 ppm reported for the heptacoordinated tin atoms in trimeric $[MeSn(OC_2H_4)_3N]_3$[84–86] ($SnCO_5N$ substituent pattern) and *n*BuSn(Oxinate)$_3$[87] ($SnCO_3N_3$ substituent pattern), respectively. To the best of our knowledge, we are not aware of a heptacoordinated organotin compound with a $SnCO_6$ substituent pattern. Notably, the ^{119}Sn MAS chemical shift for compound **5** of δ = −550 ppm is identical to the ^{119}Sn NMR chemical shift in solution.

The ^{13}C NMR spectra show significant upfield shifts for the Sn*C*H$_2$ (**3**, $\Delta\delta$ = 12.2; **4**, $\Delta\delta$ = 20.4 ppm)) and C15 carbon atoms (**3**, $\Delta\delta$ = 3.8; **4**, $\Delta\delta$ = 4.8 ppm) and downfield shifts for the C14/C16 carbon atoms (**3**, $\Delta\delta$ = 2.2; **4**, $\Delta\delta$ = 2.8 ppm) with respect to the parent compounds $[PhI_2SnCH_2$([16]crown-5)] and $[I_3SnCH_2$([16]crown-5)], respectively. Moreover, the $^1J(^{13}CH_2,^{117/119}Sn)$ coupling constants of 920/964 Hz (**3**) and 1120/1174 Hz (**4**), and the $^1J(^{13}C_i,^{117/119}Sn)$ coupling of 1256/1302 Hz are typical for seven-coordinated species.[83]

The ^{1}H NMR (400.13 MHz, CD_3CN) spectra of **3**, **4** and **5** show complex patterns for the OCH_2 protons at δ = 3.81–4.55 ppm (**3**) and δ = 3.72–4.50 ppm (**4**, **5**). They are low-field shifted and show a broader distribution than the parent compound **1** (δ = 3.30–3.90 ppm). The SnC*H*$_2$ and C*H* protons appear as a doublet and unresolved multiplet resonances at δ = 1.67 (d, $^3J(^1H,^1H)$ = 3, $^2J(^1H,^{117/119}Sn)$ = 85 Hz; **3**) and 1.67 ppm (d, $^3J(^1H,^1H)$ = 4, $^2J(^1H,^{117/119}Sn)$ = 106 Hz; **4**, **5**), and δ = 2.99–3.05 (m, $^3J(^1H,\ ^{117/119}Sn)$ = 377 Hz; **3**), 2.95–3.01 ppm (m, $^3J(^1H,^{117/119}Sn)$ = 470 Hz; **4**, **5**), respectively, that are, with respect to compound **1**, shifted by 0.49 ppm to high and by 0.45 ppm to low field. A remarkable feature in the ^{1}H as well as in the ^{1}H-coupled ^{119}Sn NMR spectra of compounds **3**–**5** are the unprecedentedly large $^3J(^1H,^{117/119}Sn)$ coupling constants of 377 (**3**) and 470 Hz (**4**, **5**). So far, we have no straightforward explanation for this yet. One hypothesis is that these couplings are composed of contribu-

tions from the H-C-C-Sn and H-C-C-O-Sn pathways and that these have the same sign so that the absolute value actually observed is big.

The structure of **3** is in accordance with the interpretation of the ^{1}H NMR and IR spectra of the complex $[Ph_2SnL]^{2+}$ $2ClO_4^-$ (L = [15]crown-5)[57] by Shuklar et al. with the difference here being that the tin atom in compound **3** is heptacoordinated and bonded to all five oxygen atoms of the crown ether.

The ESIMS spectrum (positive mode) of compound **3** shows an intense mass cluster centred at *m*/*z* 565.1 that is assigned to $[\{Ph(CH_3O)(OH)SnCH_2([16]crown-5)\}+H_2O+CH_3OH+Na^+]$. A less intense mass cluster was observed at *m*/*z* 919.3 that corresponds to the species $[(\{PhSnCH_2([16]crown-5)\}_2(OH))O]^+$. ESIMS analysis of complex **4** shows a mass cluster centred at *m*/*z* 649.2 that is tentatively assigned to $[(ClO_4)_2(CH_3CN)SnCH_2([16]crown-5)+Na]^+$.

Conclusion

Organotin(IV) cations intramolecularly encapsulated by crown ethers have been synthesised and characterised. The molecular structures of these compounds reveal that the tin atom fits perfectly in the cavity and is coordinated by all five oxygen atoms of the ring. Compounds **3**–**5** are the first examples of structurally characterised cationic organotin(IV) crown ether complexes and in addition, compounds **4** and **5** are the first compounds that contain a monomeric monoorganotin(IV) dication. They are also rare examples of a monomeric organotin(IV) hydroxide. An interesting feature in the structures of the monoorganotin hydroxides **4** and **5** are the SnOH(6)···O(51), SnOH(16)···O(44) and SnOH(6)···O(13) hydrogen bonds. They suggest that deprotonation of the terminal SnOH group by an appropriate non-nucleophilic base should be possible. On the other hand, protonation of the OH function should give the aqua complex of a, so far unknown, monoorganotin trication.

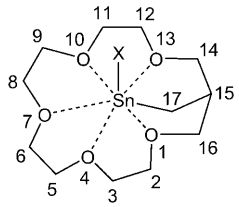
Experimental Section

General methods: Solvents were dried and distilled from the appropriate desiccants prior to use. All manipulations were performed under an inert atmosphere of argon, except the crystallisation of compounds **3**–**5**. The reactions with the silver salts were light protected. ***Caution!*** Metal perchlorates are explosives on some occasions. Only small quantities (max. 500 mg with respect of the parent organotin compound) have been used for synthesis and we have encountered no troubles during all the manipulations. The atom numbering of the crown ether fragments is shown in Scheme 2.

NMR and IR spectroscopy: NMR spectra were recorded on Bruker DRX 400 and DPX 300, spectrometers with broad-band decoupling of ^{119}Sn at 111.92 MHz and ^{13}C at 100.61 MHz. Chemical shifts (δ) are given in ppm and referenced to tetramethylstannane (^{119}Sn) and tetramethylsilane (^{1}H, ^{13}C). The ^{119}Sn MAS NMR spectra were recorded with a Bruker Avance III 400 spectrometer using cross polarisation and high-power proton decoupling (conditions: 3.7 μS (90°) pulse, 2 ms contact time, 10 s recycle delay). Spectra with five different spinning rates between 6.5 and 10 kHz were recorded to unambiguously determine the isotropic chemical shift. Tetracyclohexyltin was used as secondary reference (δ = 97.35 ppm).

IR spectra were recorded on a Bruker IFS 28 spectrometer.

Electrospray mass spectra were recorded on a Thermoquest-Finnigan instrument using CH_3CN as the mobile phase. The samples were introduced as solutions in CH_3CN by a syringe pump operating at 0.5 μL min^{-1}. The capillary voltage was 4.5 kV, while the cone skimmer voltage varied between 50 and 250 kV. Identification of the expected ions was assisted by comparison of experimental and calculated isotope distribution patterns. The *m*/*z* values reported correspond to those of the most intense peak in the corresponding isotope pattern.



3: X = Ph ; **4**, **5**: X = OH

Scheme 2. Numbering scheme for the crown ether ring in **3**–**5**.

X-ray crystallography: Intensity data for the colourless (**3**, **4**, **5**) crystals were collected on a Bruker SMART CCD (**3**, **4**) and an Oxford Diffraction Xcalibur S (**5**) diffractometer with graphite-monochromated $Mo_{K\alpha}$ (0.71073 Å) (**4**, **5**) and $Cu_{K\alpha}$ (1.54178 Å) (**3**) radiation at 173(1) K. The data collection covered almost the whole sphere of reciprocal space with 4 (**3**, **4**) and 9 (**5**) sets at different ϕ (**3**, **4**) and κ angles (**5**) with 1131 (**3**), 1376 (**4**) and 399 (**5**) frames through ω rotation (Δ/ω = 0.5° (**3**, **4**) and 1° (**5**)) at two times 10 (**3**, **5**) and 60 s (**4**) per frame. The crystal-to-detector distance was 4 (**3**), 4.5 (**5**) and 6 cm (**4**). Crystal decay was monitored by repeating the initial frames at the end of data collection. When analysing the duplicate reflections there was no indication for any decay. The structure was solved by direct methods SIR-97[88] (**3**, **4**) and SHELXS97[89] (**5**) and successive difference Fourier syntheses. Refinement applied full-matrix least-squares methods SHELXL97.[90]

The H atom position of the OH group (**4**, **5**) was refined (ref_{xyz}) and the other H atoms were placed in geometrically calculated positions using for all a riding model U_{iso} constrained at 1.2 for non methyl and at 1.5 for methyl groups times U_{eq} of the carrier C atom.

In **3** two O atoms are disordered over two positions with occupancies of 0.25 (O(12′), O(14′)) and 0.75 (O(12), O(14)), and in **4** one perchlorate molecule is disordered over two positions with occupancies of 0.4 (O(52A), O(53A), O(54A)) and 0.6 (O(52), O(53), O(54)) and in **5** the triflate molecules are disordered over two positions with occupancies of 0.5 (F(1), F(2) F(3), F(1′), F(2′) F(3′), F(4), F(5), F(6), F(4′), F(5′), F(6′), C(2), C(2′), O(15), O(16), O(15)′, O(16′)). Atomic scattering factors for neutral atoms and real and imaginary dispersion terms were taken from International Tables for X-ray Crystallography.[91] The figures were created by SHELXTL.[92] Crystallographic data are given in Table 3 and selected bond lengths and angles are given in Tables 1 and 2. The molecular structure of compound **5**, showing 30% probability displacement ellipsoids and the crystallographic numbering scheme, is shown in Figure S1 of the Supporting Information.

CCDC-755953 (**3**), 755952 (**4**) and 773004 (**5**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Synthesis of 3: $AgClO_4$ (0.30 g, 1.44 mmol) was added to a solution of **1**[65] (0.5 g, 0.72 mmol) in CH_3CN (30 mL) and the mixture was stirred in darkness at room temperature for five days. The insoluble AgI was filtered off and the solvent was removed in vacuo. The remaining slightly yellow solid was washed with CH_2Cl_2(20 mL) and dried in vacuo. Colourless crystals of **3** suitable for X-ray diffraction analysis were obtained by vapour diffusion of Et_2O into a solution of the compound in CH_3CN. Yield 46%; m.p. >300°C; ^{1}H NMR (400.13 MHz, CD_3CN, 20°C, TMS): δ = 1.67 (d, ^3J(H,H) = 3, ^2J(H,Sn) = 84 Hz, 2H; $SnCH_2$), 2.99–3.05 (m, ^3J(H,Sn) = 377 Hz, 1H; CH), 3.81–4.55 (m, 20H; O-CH_2), 7.42–7.69 ppm (m, 5H; Ph); ^{13}C NMR (100.63 MHz, CD_3CN, 25°C, TMS): δ = 18.9 (^1J(C,Sn) = 920.0, 964.0 Hz; C_{17}), 33.7 (^2J(C,Sn) = 70.0 Hz; C_{15}), 68.7–70.7

Table 3. Crystallographic data and structure refinements for compounds **3**-**5**.

	3	**4**	**5**
formula	$C_{18}H_{28}Cl_2O_{13}Sn$	$C_{12}H_{24}Cl_2O_{14}Sn$	$C_{14}H_{24}F_6O_{12}S_2Sn$
M_w	641.99	581.90	681.14
crystal system	monoclinic	orthorhombic	monoclinic
cryst size [mm]	$0.39\times0.22\times0.13$	0.05x 0.08×0.25	0.26x 0.20×0.18
space group	*P21/c*	*Pbca*	*P21/c*
a [Å]	15.6961(6)	10.1832(4)	9.9339(4)
b [Å]	9.4464(4)	23.6348(10)	18.8890(7)
c [Å]	15.7016(6)	33.2858(14)	12.8482(4)
α [°]	90	90	90
β [°]	91.7827(12)	90	105.905(4)
γ [°]	90	90	90
V [Å^3]	2326.97(16)	8011.2(6)	2318.6(2)
Z	4	16	4
ρ_{calcd} [mg m^3]	1.833	1.930	1.951
μ [mm^{-1}]	11.460	1.613	1.389
$F(000)$	1296	4672	1360
θ range [°]	2.82 to 89.66	1.22 to 27.54	2.16 to 25.5
index ranges	$-20\le h\le20$ $-12\le k\le12$ $-20\le l\le20$	$-13\le h\le13$ $-30\le k\le30$ $-43\le l\le43$	$-12\le h\le11$ $-22\le k\le22$ $-14\le l\le15$
no. of reflns collected	75808	78581	16695
completeness to θ_{max}	100.0	99.8	100.0
no. of indep reflns/ R_{int}	5321/0.0284	9223/0.0556	4311/0.0369
no. of reflns obsd with ($I>2\sigma(I)$)	4953	7298	16695
no. of refined params	325	556	400
GooF (F^2)	1.102	1.035	0.929
$R1$ (F) ($I>2\sigma(I)$)	0.0196	0.0438	0.0261
$wR2$ (F^2) (all data)	0.0514	0.1110	0.0571
$(\Delta/\sigma)_{max}$	0.001	0.001	0.001
largest diff. peak/ hole [e Å^{-3}]	0.567/−0.440	2.520/−1.183	1.184/−0.430

(C_2–C_{12}), 75.3 (^3J(C,Sn) = 37.0 Hz; C_{14}, C_{16}), 130.35 (^3J(C,Sn) = 119.0 Hz, Ph; C_m), 131.8 (^4J(C,Sn) = 22.0 Hz, Ph; C_p), 133.8 (^2J(C,Sn) = 71.0 Hz; Ph, C_o), 138.0 ppm (Ph; C_i); ^{119}Sn{^{1}H NMR (300 MHz, CD_3CN, 20 °C): δ = −452 ($\nu_{1/2}$ = 27 Hz); ^{119}Sn NMR (^{1}H coupled, 300 MHz, CD_3CN, 20 °C) δ = −452 (br d, ^3J(Sn,H) = 385.0 Hz); elemental analysis calcd (%) for $C_{18}H_{28}Cl_2O_{13}Sn$ (641.99): C 33.6, H 4.7; found C 33.6, H 4.5.

Synthesis of 4: $AgClO_4$ (0.38 g, 1.83 mmol) was added to a solution of **2**[72] (0.46 g, 0.61 mmol) in CH_3CN (30 mL) and the mixture was stirred in darkness at room temperature for ten days. The insoluble AgI was filtered off and the solvent was removed in vacuo. The remaining slightly grey solid was washed with CH_2Cl_2(20 mL) and dried in vacuo. Single crystals of **4** suitable for X-ray diffraction analysis were obtained by vapour diffusion of Et_2O into a solution of the compound in CH_3CN. Yield 59 %; m.p. > 300 °C; ^{1}H NMR (400.13 MHz, CD_3CN, 25 °C, TMS): δ = 1.67 (d, ^3J(H,H) = 3.0, ^2J(H,Sn) = 106.0 Hz, 2H; $SnCH_2$), 2.95–3.01 (m, 1H; CH), 3.72–4.48 ppm (m, 20H; O-CH_2); ^{13}C NMR (100.63 MHz, CD_3CN, 25 °C, TMS): δ = 17.6 (C_{17}), 32.1 (^2J(C,Sn) = 78.0 Hz; C_{15}), 68.4–70.1 (C_2-C_{12}), 74.7 ppm (^3J(C,Sn) = 62.0 Hz; C_{14}/C_{16}); ^{119}Sn{^{1}H NMR (300 MHz, CD_3CN, 20 °C,): δ = −550 ppm ($\nu_{1/2}$ = 27 Hz); ^{119}Sn NMR (^{1}H coupled, 300 MHz, CD_3CN, 20 °C): δ = −550 ppm (dt, ^2J(Sn,H) = 110.0, ^3J(Sn,H) = 474.0 Hz); IR(KBr): $\tilde{\nu}$ = 3449 cm^{-1} (Sn-OH); elemental analysis calcd (%) for $C_{12}H_{23}Cl_2O_{14}Sn$(580.91): C 24.8, H 4.0; found C 24.4, H 4.3.

Synthesis of 5: $AgOSO_2CF_3$ (2.140 g, 8.324 mmol) was added to a solution of **2**[72] (2.073 g, 2.776 mmol) in CH_3CN (40 mL) and the mixture was stirred in darkness at room temperature for ten days. The insoluble AgI was filtered off, water (0.1 mL) was added to the filtrate and the resulting mixture was magnetically stirred for 30 min. After the solvent had been removed in vacuo the remaining solid was washed with CH_2Cl_2(20 mL) and dried in vacuo. Single crystals of **5** suitable for X-ray diffraction analysis were obtained by vapour diffusion of Et_2O into a solution of the compound in CH_3CN. Yield 50 %; m.p. 108 °C. The ^{1}H and ^{119}Sn NMR data are virtually identical with those of compound **4**. No ^{13}C NMR spectrum was recorded. Elemental analysis calcd (%) for $C_{14}H_{24}F_6O_{12}S_2Sn$-(580.91): C 24.7, H 3.5; found C 24.6, H 3.6.

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