

Diorganotin dications stabilized by neutral ligands in the solid state: $[\text{R}_2\text{Sn}(\text{H}_2\text{O})_2(\text{OPPh}_3)_2](\text{O}_3\text{SCF}_3)_2$ (R = Me, Bu)

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The synthesis of $[\text{R}_2\text{Sn}(\text{H}_2\text{O})_2(\text{OPPh}_3)_2](\text{O}_3\text{SCF}_3)_2$ (R = Me (**1**), Bu (**2**)) by the consecutive reaction of R_2SnO (R = Me, Bu) with triflic acid and Ph_3PO is described. Compounds **1** and **2** feature dialkyltin(IV) dications $[\text{R}_2\text{Sn}(\text{H}_2\text{O})_2(\text{OPPh}_3)_2]^{2+}$ apparently stabilized by the neutral ligands in the solid state. Compounds **1** and **2** readily dehydrate upon heating at 105 and 86 °C, respectively. The preparative dehydration of **1** afforded $[\text{Me}_2\text{Sn}(\text{OPPh}_3)_2(\text{O}_3\text{SCF}_3)](\text{O}_3\text{SCF}_3)$ (**1a**), which features both bidentate and non-coordinating triflate anions. In compounds **1** and **2** the ligands Ph_3PO and H_2O are kinetically labile in solution and undergo reversible ligand exchange reactions. Compounds **1**, **1a** and **2** were characterized by multinuclear solution and solid-state NMR spectroscopy, IR spectroscopy, electrospray mass spectrometry, conductivity measurements, thermogravimetry and X-ray crystallography.

Introduction

The speciation of dialkyltin(IV) compounds in strongly polar solvents has been the subject of considerable research. In water, dialkyltin dichlorides R_2SnCl_2 (R = Me, Et, Bu) undergo a hydrolytic dissociation into hydrated dialkyltin dications, $[\text{R}_2\text{Sn}(\text{H}_2\text{O})_4]^{2+}$, and chloride anions.^{1,2} The same cations are also formed upon addition of strong acids, such as HNO_3 and HClO_4 , to suspensions of polymeric dialkyltin oxides, R_2SnO , in aqueous solutions.^{3,4} Extensive potentiometric studies have further demonstrated the existence of various equilibria between $[\text{R}_2\text{Sn}(\text{H}_2\text{O})_4]^{2+}$ and related deprotonated species at higher pH values.^{2,4-8} When aqueous solutions containing hydrated dialkyltin cations are slowly evaporated, the water molecules coordinated to the tin are usually substituted by the counterions and eventually non-hydrated species R_2SnX_2 (e.g. X = Cl, NO_3) are obtained.^{2,3} In many cases, however, partial hydrolysis products, such as $[\text{R}_2\text{Sn}(\text{OH})\text{X}]_2$ (e.g. X = NO_3 , ClO_4)⁹⁻¹² or $[\text{R}_2(\text{X})\text{SnOSn}(\text{Y})\text{R}_2]_2$ (e.g. X, Y = Cl, NO_3 , OH) are found.^{10,13} While simple $\text{R}_2\text{Sn}(\text{O}_3\text{SCF}_3)_2$ species have been known for a long time,^{14,15} Otera and co-workers only recently reported the rational synthesis of analogous species, $[\text{R}_2\text{Sn}(\text{OH})(\text{O}_3\text{SCF}_3)]_2$ and $[\text{R}_2(\text{X})\text{SnOSn}(\text{O}_3\text{SCF}_3)\text{R}_2]_2$ (R = alkyl; X = O_3SCF_3 , OH) by the reaction of diorganotin oxides with triflic acid in acetonitrile.¹⁶⁻¹⁸ We are aware of only two examples, namely $[\text{Me}_2\text{Sn}(\text{H}_2\text{O})_4]\text{X}_2$ (X = 1,1,3,3-tetraoxo-1,3,2-benzodithiazolidine)¹⁹ and $[\text{Bu}_2\text{Sn}(\text{H}_2\text{O})_4]\text{X}_2$ (X = 2,5-dimethylbenzene sulfonate),²⁰ in which hydrated dialkyltin dications $[\text{R}_2\text{Sn}(\text{H}_2\text{O})_4]^{2+}$ have been observed in the solid state. In these compounds, the stabilization is based on the bulkiness and weak donor strength of the organic anions and is presumably also facilitated by hydrogen bonding of the water molecules with acceptor atoms of the organic anions.

We now describe the synthesis, structure and reactivity of $[\text{R}_2\text{Sn}(\text{H}_2\text{O})_2(\text{OPPh}_3)_2](\text{O}_3\text{SCF}_3)_2$ (R = Me, Bu) which may be regarded as being derivatives of $[\text{R}_2\text{Sn}(\text{H}_2\text{O})_4]\text{X}_2$ (R = Me, Bu), in which two of the four water molecules are substituted by triphenylphosphine oxide.

Discussion

The reaction of polymeric dimethyltin oxide and dibutyltin oxide with two equivalents of triflic acid in acetonitrile afforded

a clear solution after 5 min stirring at room temperature.¹⁸ The subsequent addition of two equivalents of triphenylphosphine oxide and exposure to moist air provided $[\text{R}_2\text{Sn}(\text{H}_2\text{O})_2(\text{OPPh}_3)_2](\text{O}_3\text{SCF}_3)_2$ (R = Me (**1**), Bu (**2**)) in high yields (eqn. (1)).

$[\text{Me}_2\text{Sn}(\text{H}_2\text{O})_2(\text{OPPh}_3)_2](\text{O}_3\text{SCF}_3)_2$ (**1**) was obtained as large regular crystals, however, once isolated from the mother-liquor they turn opaque within a few days. This observation is attributed to a phase transition taking place and not to the beginning of water loss. The elemental analysis and the IR spectrum of an opaque sample stored at room temperature for several months were identical to those of a crystalline sample. $[\text{Bu}_2\text{Sn}(\text{H}_2\text{O})_2(\text{OPPh}_3)_2](\text{O}_3\text{SCF}_3)_2$ (**2**) shows an apparent tendency to form supersaturated solutions in hexane- CH_2Cl_2 , from which at first only needle-like crystals grew in a star-burst fashion. After approximately one third of the material was deposited, crystals with a more regular shape crystallized. The observation of different crystal shapes is attributed to the concomitant presence of two crystal forms. To prove this idea a few specimens of both polymorphs were hand-selected and investigated separately by ^1H NMR spectroscopy and elemental analysis, which indeed showed that both crystals have the same composition. Differences between the polymorphs were observed in the IR spectra (KBr). The needle shaped crystals show broad OH stretching vibrations at 3426 and 3234 cm^{-1} , whereas the regular shaped crystals reveal the same vibrations at 3305 and 3148 cm^{-1} . A representative specimen of the regular crystals was selected for X-ray crystallography.

The X-ray structure of $[\text{Me}_2\text{Sn}(\text{H}_2\text{O})_2(\text{OPPh}_3)_2](\text{O}_3\text{SCF}_3)_2$ (**1**) comprises two crystallographically independent, albeit similar $[\text{Me}_2\text{Sn}(\text{H}_2\text{O})_2(\text{OPPh}_3)_2]^{2+}$ dications featuring two Sn atoms both of which lie across crystallographic centres of inversion, as shown in Fig. 1; selected crystal data and bond parameters are collected in Tables 1 and 2, respectively. The two independent Sn sites are confirmed by an ^{119}Sn MAS NMR spectrum of **1** that shows two signals at δ -370.8 and -377.8. The X-ray structure of $[\text{Bu}_2\text{Sn}(\text{H}_2\text{O})_2(\text{OPPh}_3)_2](\text{O}_3\text{SCF}_3)_2$ (**2**) contains a centrosymmetric $[\text{Bu}_2\text{Sn}(\text{H}_2\text{O})_2(\text{OPPh}_3)_2]^{2+}$ dication, as shown in Fig. 2; selected crystal data and bond parameters are collected in Tables 1 and 3, respectively. No reasonable ^{119}Sn MAS NMR spectrum could be obtained for **2**, most likely because of the concomitant presence of the two polymorphs in the bulk material. The Sn atoms of **1** and **2** adopt slightly distorted

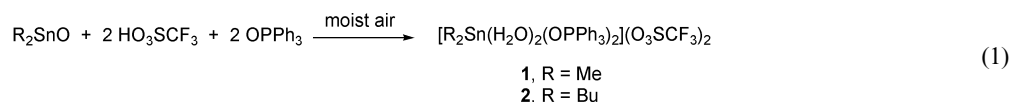
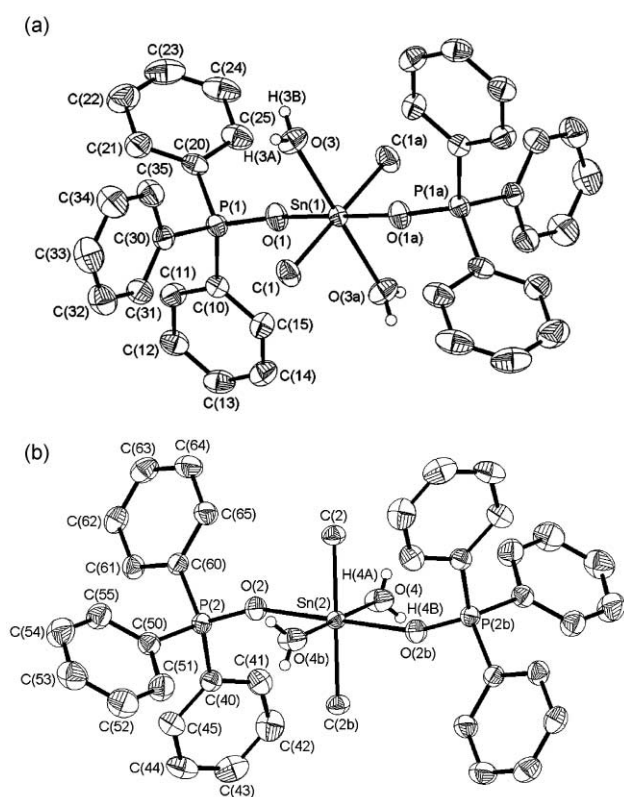


Table 1 Crystal data and structure refinement for **1** and **2**

	1	2
Formula	C ₄₀ H ₄₀ F ₆ O ₁₀ P ₂ S ₂ Sn	C ₄₆ H ₅₂ F ₆ O ₁₀ P ₂ S ₂ Sn
<i>M</i> _r /g mol ⁻¹	1039.47	1123.63
Crystal system	Triclinic	Monoclinic
Crystal size/mm	0.13 × 0.20 × 0.25	0.30 × 0.30 × 0.40
Space group	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> /Å	13.3965(7)	12.126(3)
<i>b</i> /Å	13.6189(7)	20.297(4)
<i>c</i> /Å	14.0117(7)	10.295(2)
<i>α</i> /°	64.9720(10)	90
<i>β</i> /°	89.6460(10)	93.037(4)
<i>γ</i> /°	82.3290(10)	90
<i>V</i> /Å ³	2292.0(2)	2530.4(9)
<i>Z</i>	2	2
<i>D</i> _s /Mg m ⁻³	1.506	1.475
<i>T</i> /K	293(2)	293(2)
<i>μ</i> /mm ⁻¹	0.795	0.726
No. of refls. collcd.	17842	15183
Completeness to <i>θ</i> _{max} (%)	94.4	97.5
No. of indep. refls. (<i>R</i> _{int})	9991	5690
No. of refls. obsd. (<i>I</i> > 2σ(<i>I</i>))	8232	4650
No. refined params.	629	365
GOF (<i>F</i> ²)	1.024	1.043
<i>R</i> ₁ (<i>F</i>) (<i>I</i> > 2σ(<i>I</i>))	0.0381	0.0403
<i>wR</i> ₂ (<i>F</i> ²) (all data)	0.1069	0.1063
(Δ/ <i>σ</i>) _{max}	<0.001	<0.001
Largest diff. peak, hole/e Å ⁻³	0.559, -0.343	0.664, -0.357

**Fig. 1** General view of the two crystallographically independent [Me₂Sn(H₂O)₂(OPPh₃)₂]²⁺ dications of **1** showing 30% probability displacement ellipsoids and the crystallographic numbering scheme (symmetry operation used to generate equivalent atoms: *a* = -*x*, -*y*, -*z*).

octahedral geometries defined by C₂O₄ donor sets with chemically and crystallographically identical ligands being situated in the *trans* positions to one another. The largest distortion is found for **1** in the O(1a)–Sn(1)–C(1) and O(2)–Sn(2)–C(2) angles being 86.63(12) and 87.85(9)°, and for **2** in the O(3a)–Sn(1)–C(1) angle being 86.19(12), respectively. This presumably results from steric crowding between the alkyl group and the Ph₃PO molecule. The coordination of the water molecules to

Table 2 Selected bond lengths (Å) and angles (°) for the two independent molecules of **1**^a

Molecule 1		Molecule 2	
Sn(1)–O(1)	2.197(3)	Sn(2)–O(2)	2.192(2)
Sn(1)–O(3)	2.237(3)	Sn(2)–O(4)	2.238(3)
Sn(1)–C(1)	2.099(4)	Sn(2)–C(2)	2.086(3)
P(1)–O(1)	1.501(2)	P(2)–O(2)	1.500(2)
O(1)–Sn(1)–O(1a)	180	O(2)–Sn(2)–O(2a)	180
O(1)–Sn(1)–O(3)	88.76(9)	O(2)–Sn(2)–O(4)	88.65(12)
O(1)–Sn(1)–O(3a)	91.24(9)	O(2)–Sn(2)–O(4a)	91.35(12)
O(3)–Sn(1)–O(3a)	180	O(4)–Sn(2)–O(4a)	180
O(1)–Sn(1)–C(1)	93.37(12)	O(2)–Sn(2)–C(2)	87.85(9)
O(1a)–Sn(1)–C(1)	86.63(12)	O(2b)–Sn(2)–C(2)	92.15(9)
O(3)–Sn(1)–C(1)	88.98(14)	O(4)–Sn(2)–C(2)	90.17(13)
O(3a)–Sn(1)–C(1)	91.02(14)	O(4b)–Sn(2)–C(2)	89.83(13)
C(1)–Sn(1)–C(1a)	180	C(2)–Sn(2)–C(2a)	180
Sn(1)–O(1)–P(1)	151.84(13)	Sn(2)–O(2)–P(2)	158.67(14)

^a Symmetry operations to generate equivalent atoms: *a* = -*x*, -*y*, -*z*.**Table 3** Selected bond lengths (Å) and angles (°) for **2**^a

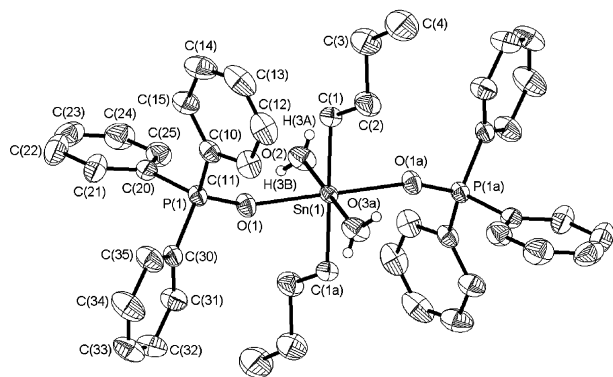
Sn(1)–O(1)	2.205(2)	Sn(1)–O(3)	2.254(2)
Sn(1)–C(1)	2.109(3)	P(1)–O(1)	1.505(2)
O(1)–Sn(1)–O(1a)	180	O(1)–Sn(1)–O(3)	91.39(10)
O(1)–Sn(1)–O(3a)	88.61(10)	O(3)–Sn(1)–O(3a)	180
O(1)–Sn(1)–C(1)	93.28(9)	O(1a)–Sn(1)–C(1)	86.72(9)
O(3)–Sn(1)–C(1)	93.81(12)	O(3a)–Sn(1)–C(1)	86.19(12)
C(1)–Sn(1)–C(1a)	180	Sn(1)–O(1)–P(1)	154.26(13)

^a Symmetry operations to generate equivalent atoms: *a* = -*x*, -*y*, -*z*.

the Sn atoms, defined for **1** by the Sn(1)–O(3) and Sn(2)–O(4) distances of 2.237(3) and 2.238(3) Å, and for **2** by the Sn(1)–O(3) distance of 2.254(2) Å, is comparable with those found in [Me₂Sn(H₂O)₄]²⁺ (average Sn–O 2.230(3) Å, CN 6)¹⁹ and [Bu₂Sn(H₂O)₄]²⁺ (average Sn–O 2.271(2) Å, CN 6).²⁰ However, it appears to be stronger than that of the dimer [Bu₂Sn(OH)(H₂O)(O₃SCF₃)₂]₂ (average Sn–O: 2.409(3) Å, CN 6),¹⁷ and the crown-ether stabilized Me₂SnCl₂ water adducts: [Me₂SnCl₂·H₂O]₂·18-crown-6 (average Sn–O 2.336(3) Å, CN 5 + 1)²¹ and [Me₂SnCl₂·H₂O]·1,3-xylyl-18-crown-5 (Sn–O 2.407(9) Å, CN

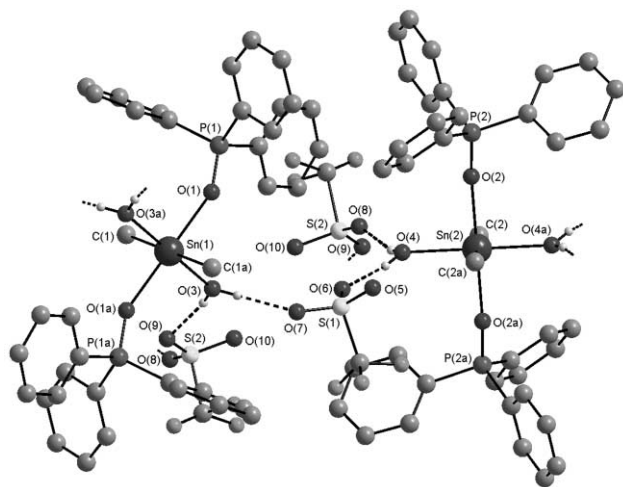
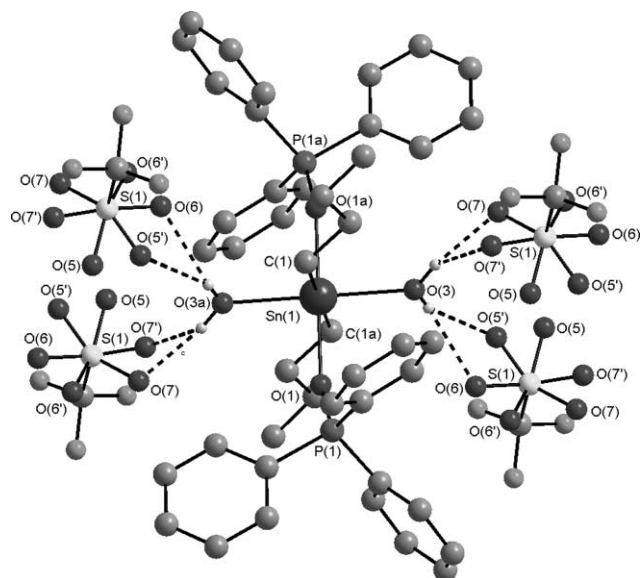
Table 4 Hydrogen bond lengths (Å) and angles (°) for **1**

D–H ⋯ A	D–H	H ⋯ A	D ⋯ A	D–H ⋯ A	Symmetry operation used to generate A
O(3)–H(3A) ⋯ O(7)	0.78(4)	1.91(4)	2.674(4)	172(4)	$x, y + 1, z - 1$
O(3)–H(3B) ⋯ O(9)	0.80(5)	1.93(5)	2.705(5)	164(6)	$x, y + 1, z$
O(4)–H(4A) ⋯ O(8)	0.67(4)	1.99(5)	2.634(8)	164(5)	$x, y + 1, z$
O(4)–H(4B) ⋯ O(6)	0.78(6)	1.93(7)	2.699(7)	169(6)	$x, y + 1, z - 1$

**Fig. 2** General view of the $[\text{Bu}_2\text{Sn}(\text{H}_2\text{O})_2(\text{OPPh}_3)_2]^{2+}$ dication of **2** showing 30% probability displacement ellipsoids and the crystallographic numbering scheme (symmetry operation used to generate equivalent atoms: $a = -x, -y, -z$).

5).²² This observation might be attributed to the higher charge situated at the Sn atoms of $[\text{R}_2\text{Sn}(\text{H}_2\text{O})_2(\text{OPPh}_3)_2]^{2+}$ and $[\text{R}_2\text{Sn}(\text{H}_2\text{O})_4]^{2+}$ ($\text{R} = \text{Me}, \text{Bu}$), respectively. The coordination of the Ph_3PO molecules is characterized for **1** by the $\text{Sn}(1)\text{--O}(1)$ and $\text{Sn}(2)\text{--O}(2)$ distance being 2.197(3) and 2.192(2) Å, and for **2** by the $\text{Sn}(1)\text{--O}(1)$ distance being 2.205(2) Å, respectively, and seems to be generally stronger than that of the water molecules, possibly due to the greater dipole moment. The coordination of the Ph_3PO molecules in **1** and **2** appears to be comparable with that in $\text{Ph}_2\text{Sn}(\text{OPPh}_3)(\text{NO}_3)_2$ ($\text{Sn}\text{--O}$ 2.148(6) Å, CN 7),²³ but somewhat stronger than in $\text{Ph}_2\text{Sn}(\text{OPPh}_3)_2\text{Cl}_2$ ($\text{Sn}\text{--O}$ 2.214(4) Å, CN = 6), $\text{Ph}_2\text{Sn}(\text{OPPh}_3)\text{Cl}_2$ ($\text{Sn}\text{--O}$ 2.278(2) Å, CN = 5)²⁴ and $[\text{Me}_2\text{Sn}(\text{OH})(\text{NMs}_2)(\text{OPPh}_3)]_2 \cdot 2\text{MeCN}$ ($\text{Sn}\text{--O}$ 2.326(1) Å, CN = 7).²⁵ The ^{31}P MAS NMR spectrum of **1** shows two signals at δ 36.6 and 35.7. The IR spectrum (KBr) of **1** and **2** reveals a strong absorption at 1144 and 1161 cm^{-1} (shoulder at 1142 cm^{-1}), respectively, that were assigned to the PO stretching vibration. The position of this absorption resembles that found in $\text{Me}_2\text{Sn}(\text{OPPh}_3)_2\text{Cl}_2$ (1159 cm^{-1}),²⁴ $\text{Me}_2\text{Sn}(\text{OPPh}_3)_2\text{Cl}_2$ (1139 cm^{-1}),²⁴ $[\text{Me}_2\text{Sn}(\text{OPPh}_3)_4](\text{PF}_6)_2$ (1147 cm^{-1})²⁶ and $[\text{Me}_2\text{Sn}(\text{OPPh}_3)_4](\text{ClO}_4)_2$ (1144 cm^{-1}).²⁶ The corresponding absorption of the free ligand was reported to be at 1192 cm^{-1} .²⁷ The $\text{Sn}\text{--O}\text{--P}$ angles of **1** and **2** lie in the range from 151.84(13) to 158.67(14)° and fall between the related angles in $\text{Ph}_2\text{Sn}(\text{OPPh}_3)_2\text{Cl}_2$ (145.66(18)),²⁴ $\text{Ph}_2\text{Sn}(\text{OPPh}_3)\text{Cl}_2$ (148.04(13)°)²⁴ and $\text{Ph}_2\text{Sn}(\text{OPPh}_3)(\text{NO}_3)_2$ (162.5(4)°).²³

In the crystal lattice, the $[\text{R}_2\text{Sn}(\text{H}_2\text{O})_2(\text{OPPh}_3)_2]^{2+}$ dications ($\text{R} = \text{Me}, \text{Bu}$) of **1** and **2** are associated with triflate anions *via* hydrogen bonding with H atoms of water molecules, as shown in Figs. 3 and 4; relevant bond parameters are collected in Tables 4 and 5, respectively. For **1** the distance between the donor and acceptor O atoms varies from 2.634(8) to 2.705(5) Å, which is consistent with medium strength hydrogen bonding. Consistently, the IR spectrum (KBr) of **1** showed a broad absorption at 3175 cm^{-1} that is assigned to an OH stretching vibration.^{28,29} The O sites of the triflate anions of **2** are disordered with occupancies of 70% (O(5), O(6) and O(7)) and 30% (O(5'), O(6') and O(7')) (Fig. 4). Consequently, two different sets of distances between the donor and acceptor O atoms are observed, namely at 2.618(20) and 2.608(20) Å (30% occupancy) and at 2.730(7) and 2.796(8) Å (70% occupancy). The IR spectrum

**Fig. 3** Perspective view of **1** showing the hydrogen-bonding between $[\text{Me}_2\text{Sn}(\text{H}_2\text{O})_2(\text{OPPh}_3)_2]^{2+}$ dications and triflate anions.**Fig. 4** Perspective view of **2** showing the hydrogen-bonding between $[\text{Bu}_2\text{Sn}(\text{H}_2\text{O})_2(\text{OPPh}_3)_2]^{2+}$ dications and triflate anions.

shows two broad OH stretching vibrations at 3305 and 3148 cm^{-1} . The question whether the triflate anions are coordinated to the Sn atoms or not, may also be answered solely on the basis of IR spectroscopy.³⁰ Thus, for (nearly) free triflate anions (C_{3v}) the asymmetric SO_3 stretching vibration $\nu_{\text{as}}(\text{SO}_3)$ is doubly degenerate. However, in the presence of sufficiently large cation–anion interactions the axial symmetry is diminished (C_s) and the asymmetric SO_3 stretching vibration $\nu_{\text{as}}(\text{SO}_3)$ splits into two components. Accordingly, for $[\text{R}_2\text{Sn}(\text{H}_2\text{O})_2(\text{OPPh}_3)_2](\text{O}_3\text{SCF}_3)_2$ ($\text{R} = \text{Me}$ (**1**), Bu (**2**)) the two non-coordinating triflate anions give rise to two IR absorptions (KBr) at 1285 and 1031 cm^{-1} and at 1283 and 1028 cm^{-1} , respectively, which were assigned to the asymmetric and symmetric stretching SO_3 vibrations, respectively, by comparison with appropriate IR vibrations in $\text{Bu}_4\text{N}(\text{O}_3\text{SCF}_3)$ ($\nu_{\text{as}}(\text{SO}_3)$ 1273, $\nu_{\text{s}}(\text{SO}_3)$ 1032 (KBr)).³¹

Table 5 Hydrogen bond lengths (Å) and angles (°) for **2**

D–H···A	D–H	H···A	D···A	D–H···A	Symmetry operation used to generate A
O(3)–H(3A)···O(5') ^a	0.64(5)	2.01(5)	2.608(20)	155(6)	$x - 1, y, z$
O(3)–H(3A)···O(6) ^b	0.64(5)	2.16(5)	2.730(7)	150(6)	$x - 1, y, z$
O(3)–H(3B)···O(7) ^b	0.86(5)	1.97(5)	2.796(8)	161(5)	$-x, -y, 1 - z$
O(3)–H(3B)···O(7') ^a	0.86(5)	1.83(5)	2.618(20)	151(5)	$-x, -y, 1 - z$

^a Occupancy 30%. ^b Occupancy 70%.

Dehydration

Thermogravimetry (heat rate 20 °C min⁻¹) of [R₂Sn(H₂O)₂(OPPh₃)₂](O₃SCF₃)₂ (R = Me (**1**), Bu (**2**)) reveals that both water molecules are lost between 55 and 105 °C (mass loss 3.4%; theoretical 3.5%) and 30 and 86 °C (mass loss 3.7%; theoretical 3.2%), respectively, in a single mass loss incident. Taking into account the result of thermogravimetry, a bulk sample of **1** was heated for 5 h at 110 °C in vacuum to give the dehydrated material, confirmed by a satisfying elemental analysis and the absence of H₂O in the IR spectrum. Based on the following discussion the constitution of this material is best described as [Me₂Sn(OPPh₃)₂(O₃SCF₃)₂](O₃SCF₃) (**1a**), in which one of the triflate group is coordinated in a bidentate fashion between two adjacent tin atoms, while the other triflate group is not involved in coordination to Sn atoms; a proposed structure is given in Chart 1.

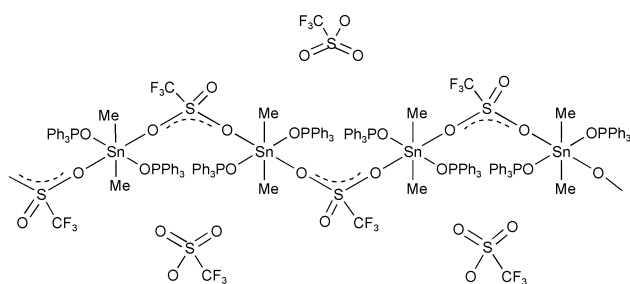


Chart 1

Thus, the ¹¹⁹Sn MAS NMR spectrum of **1a** displays a main signal at –320.0 (integral approx. 95%), which accounts for hexacoordinate Sn atoms. Also present is a low intensity signal at –237.0 (integral approx. 5%) that is assigned to a minor species with pentacoordinated Sn atoms. Consistently, the ³¹P MAS NMR shows signals at 38.5 (integral approx. 95%) and 41.1 (integral approx. 5%). The IR spectrum (KBr) of **1a** reveals the asymmetric PO vibration at 1145 cm⁻¹ almost unchanged by the dehydration. Evidence for the different coordination modes of the triflate anions stems from IR spectroscopy. [Me₂Sn(OPPh₃)₂(O₃SCF₃)₂](O₃SCF₃) (**1a**) shows three absorptions in the range of asymmetric stretching vibrations ν_{as}(SO₃); two absorptions at 1326 and 1206 cm⁻¹, which were assigned to a bidentate triflate anion (C_s symmetry) and one absorption at 1288 cm⁻¹ that was attributed to the concomitant presence of a non-coordinating triflate anion (C_{3v} symmetry).³⁰ The symmetric SO₃ stretching vibration gives rise to an absorption at 1032 cm⁻¹.

Solution studies

[R₂Sn(H₂O)₂(OPPh₃)₂](O₃SCF₃)₂ (R = Me (**1**), Bu (**2**)) are soluble in common organic solvents such as CHCl₃, THF and MeCN. At room temperature, ¹¹⁹Sn NMR spectra show very broad signals in CDCl₃ and d₃-MeCN at δ –296.4 and –343.9 for **1** and at δ –302.1 and –362.5 for **2**, respectively, which are in each case indicative for hexacoordinate tin atoms. At –40 °C, the ¹¹⁹Sn NMR spectra of **1** and **2** in d₃-MeCN are still very broad, but have shifted slightly to δ –364.3 and –387.5, respectively. The broadness of the signals suggests reversible ligand exchange processes that are fast on the NMR time scale.

This hypothesis is supported by electrospray mass spectra (positive mode, cone voltage 20 V) of **1** and **2** in MeCN that reveals doubly and singly charged mass clusters that were unambiguously assigned to the following organotin cations; the spectra are depicted in Fig. 5: [Me₂Sn(OPPh₃)_n]²⁺ (**1A_n**; n = 2 (353.1 Da), 3 (492.1), 4 (631.1 Da)), [Me₂Sn(OPPh₃)_nCl]⁺ (**1B_n**; n = 1 (463.0 Da), 2 (741.1 Da)) and [Me₂Sn(OPPh₃)_n(O₃SCF₃)]⁺ (**1C_n**; n = 1 (577.0 Da), 2 (855.1 Da), 3 (1133.2 Da)); [Bu₂Sn(OPPh₃)_nCl]⁺ (**2B_n**; n = 1 (547.1 Da), 2 (825.1 Da)), [Bu₂Sn(OPPh₃)_n(O₃SCF₃)]⁺ (**2C_n**; n = 1 (661.1 Da), 2 (939.2 Da)). The spectrum of **2** also shows heavier mass clusters that were assigned to dinuclear organotin cations, [{Bu₂Sn(OPPh₃)(O₃SCF₃)₂Cl]⁺ (**2E₂**; (1355.1 Da)) and [{Bu₂Sn(OPPh₃)(O₃SCF₃)₂Cl]₂⁺ (**2F₂**; (1469.1 Da)). The spectrum of **1** also reveals a mass cluster that was assigned to [Me₃Sn(OPPh₃)₂]⁺ (**1D₂**; (721.1 Da)). Although the origin of this triorganotin complex is not yet known it might be speculated that the starting material Me₂SnO was contaminated by a trace of a trimethyltin compound. Conductivity measurements (c = 3.3 mmol L⁻¹) of **1** (714 μS cm⁻¹) and **2** (705 μS cm⁻¹) confirm the electrolytic dissociation of **1** and **2** into charged species in MeCN. The ³¹P NMR spectrum of **1** and **2** in MeCN displays a signals at δ 43.0 and 43.7, respectively, which

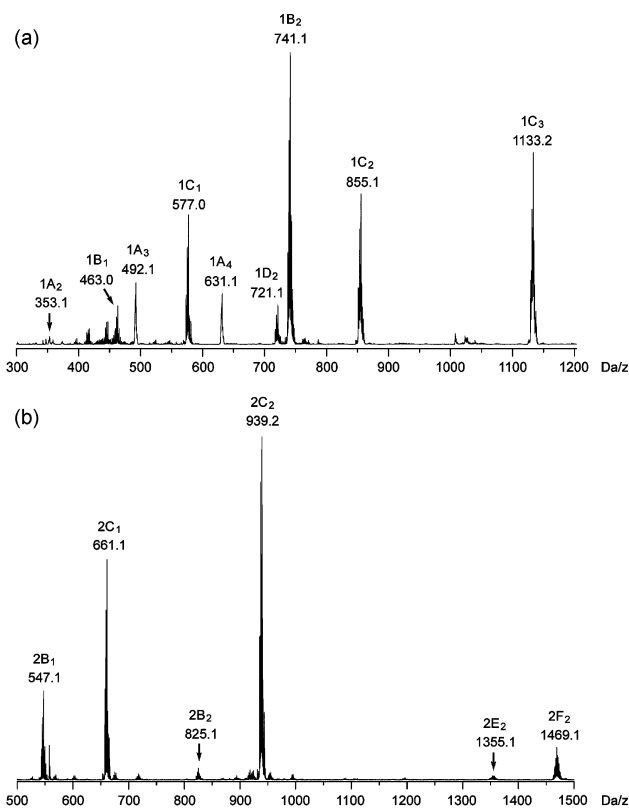


Fig. 5 ESMS spectrum (positive mode, cone voltage 20 V) of **1** and **2** showing related doubly and singly charged diorganotin cations in MeCN: (a) [Me₂Sn(OPPh₃)_n]²⁺ (**1A_n**; n = 2–4), [Me₂Sn(OPPh₃)_nCl]⁺ (**1B_n**; n = 1–2), [Me₂Sn(OPPh₃)_n(O₃SCF₃)]⁺ (**1C_n**; n = 1–3) (also present is the trimethyltin cation [Me₃Sn(OPPh₃)₂]⁺ (**1D₂**)). (b) [Bu₂Sn(OPPh₃)_nCl]⁺ (**2B_n**; n = 1–2), [Bu₂Sn(OPPh₃)_n(O₃SCF₃)]⁺ (**2C_n**; n = 1–2), [{Bu₂Sn(OPPh₃)(O₃SCF₃)₂Cl]⁺ (**2E₂**), [{Bu₂Sn(OPPh₃)(O₃SCF₃)₂Cl]₂⁺ (**2F₂**).

differs from the ^{31}P NMR chemical shift of the free ligand (δ 28.5) in the same solvent by 14.5 ppm.

It has been recently demonstrated that diorganotin(IV) compounds, which easily undergo electrolytic dissociations in polar solvents, such as $\text{Bu}_2\text{Sn}(\text{O}_3\text{SCF}_3)_2$,³² $[\text{Bu}_2\text{Sn}(\text{H}_2\text{O})_4](2,5\text{-Me}_2\text{C}_6\text{-H}_3\text{SO}_3)_2$ ²⁰ and $[\text{Bu}_2\text{Sn}(\text{OH})(\text{H}_2\text{O})_2](\text{O}_3\text{SCF}_3)_2$,¹⁶ show high catalytic activities in a number of organic reactions, such as transesterifications. It might be worthwhile for a future investigation to study whether $[\text{R}_2\text{Sn}(\text{H}_2\text{O})_2(\text{OPPh}_3)_2](\text{O}_3\text{SCF}_3)_2$ ($\text{R} = \text{Me}$ (**1**), Bu (**2**)) show similar catalytic activities or to what extent it is diminished by the Ph_3PO groups. Furthermore, the interaction of aqueous diorganotin(IV) cations with biologically active ligands, such as adenosine-5'-monophosphate, was extensively studied recently. However, little structural information has yet become available for these systems.^{33,34} It appears that $[\text{R}_2\text{Sn}(\text{H}_2\text{O})_2(\text{OPPh}_3)_2](\text{O}_3\text{SCF}_3)_2$ ($\text{R} = \text{Me}$ (**1**), Bu (**2**)) may hold some potential as model compounds to estimate the coordination environment of the Sn atoms in these complexes.

Experimental

All solvents were distilled prior to use. Me_2SnO , Bu_2SnO , triflic acid and OPPh_3 were obtained from Aldrich. The solution NMR spectra were measured using a JEOL Eclipse Plus 400 spectrometer (at 399.78 Mz (^1H), 100.54 (^{13}C), 161.84 (^{31}P) and 149.05 (^{119}Sn)) and were referenced against SiMe_4 , aqueous H_3PO_4 (90%) and SnMe_4 . The solid-state NMR spectra were measured using the same instrument equipped with a 4 mm MAS probe. Crystalline $\text{NH}_4\text{H}_2\text{PO}_4$ (δ 0.95) and $c\text{-Hex}_4\text{Sn}$ (δ -97.35) were used as secondary references. The ^{119}Sn MAS NMR spectra were obtained using cross polarization (contact time 5 ms, recycle delay 10 s). The ESMS spectra were obtained with a Platform II single quadrupole mass spectrometer (Micromass, Altrincham, UK) using an acetonitrile mobile phase. Acetonitrile solutions (0.1 mM) were injected directly into the spectrometer *via* a Rheodyne injector equipped with a 50 μL loop. A Harvard 22 syringe pump delivered the solutions to the vaporisation nozzle of the electrospray ion source at a flow rate of 10 $\mu\text{L min}^{-1}$. Nitrogen was used as both a drying gas and for nebulisation with flow rates of approx. 200 mL min^{-1} and 20 mL min^{-1} , respectively. Pressure in the mass analyser region was usually about 4×10^{-5} mbar. Typically ten signal averaged spectra were collected. The IR spectra were recorded using a BioRad FTIR spectrometer. Microanalyses were carried out by CMAS, Belmont, Australia. The thermogravimetric analysis was carried out under air using a Perkin-Elmer TGA 7 thermogravimetric analyser with TAC 7/DX controller and gas selector. The conductivity measurements were performed using a CDM80 Conductivity Meter equipped with a CDC104 Conductivity Cell (Radiometer Copenhagen, DK) at 25 °C.

Synthesis of $[\text{R}_2\text{Sn}(\text{H}_2\text{O})_2(\text{OPPh}_3)_2](\text{O}_3\text{SCF}_3)_2$ ($\text{R} = \text{Me}$ (**1**), Bu (**2**))

To a suspension of R_2SnO (1.65 g for **1** ($\text{R} = \text{Me}$), 2.49 g for **2** ($\text{R} = \text{Bu}$); 10.0 mmol) in MeCN (10 mL) two equivalents of triflic acid (1.77 mL, 20.0 mmol) were added *via* syringe to give a clear solution after 5 min stirring at room temperature. Then, two equivalents of solid Ph_3PO (5.56 g, 20.0 mmol) were added and the mixture was heated for 30 min at 40 °C before the solvent was removed in vacuum. The residue was recrystallized from hexane- CH_2Cl_2 .

1 (8.11 g, 78%, mp 224–226 °C with loss of water between 55 and 105 °C). IR (KBr) ν : 3175vbr, 3045sh, 3020sh, 2950sh, 1640br, 1590w, 1485s, 1439s, 1281vs, 1242vs, 1144s, 1121s, 1084m, 1031vs, 998w, 803w, 750w, 726s, 691m, 639m cm^{-1} . Anal. Calc. for $\text{C}_{40}\text{H}_{40}\text{F}_6\text{O}_{10}\text{P}_2\text{S}_2\text{Sn}$ (1039.56): C, 46.22; H, 3.88. Found: C, 46.15; H, 3.69%. ^1H NMR ($d_3\text{-MeCN}$) δ : 8.4–7.8 (30H), 2.57 (6H). ^{13}C NMR ($d_3\text{-MeCN}$) δ : 134.7, 132.5, 131.0,

127.8, 119.2, 16.8. ^{31}P NMR ($d_3\text{-MeCN}$) δ : 43.0. ^{119}Sn NMR ($d_3\text{-MeCN}$) δ : -343.9. ^{31}P MAS NMR δ : 36.6, 35.7. ^{119}Sn MAS NMR δ : -370.8, -377.8.

2 (8.02 g, 72%, mixture of two polymorphs: needle crystals mp 210–216 °C, regular crystals mp 222–225 °C with loss of water between 30 and 86 °C). Needle like crystals IR (KBr) ν : 3426vbr, 3234vbr, 3078m, 3059m, 2958s, 2928s, 2866m, 1651br, 1591w, 1485w, 1439s, 1281vs, 1272sh, 1253vs, 1227sh, 1163vs, 1139sh, 1120s, 1081m, 1032vs, 997w, 883w, 854w, 751w, 725s, 693m, 638m cm^{-1} . Anal. Calc. for $\text{C}_{46}\text{H}_{52}\text{F}_6\text{O}_{10}\text{P}_2\text{S}_2\text{Sn}$ (1123.72): C, 49.17; H, 4.66. Found: C, 49.66; H, 4.70%. Regular crystals IR (KBr) ν : 3304vbr, 3148vbr, 3078m, 3060m, 2959s, 2928s, 2866m, 1656br, 1590w, 1485w, 1439s, 1288vs, 1275sh, 1248vs, 1161vs, 1142sh, 1120s, 108m, 1028s, 998w, 883w, 861w, 752w, 725s, 690m, 656w, 639m cm^{-1} . Anal. Calc. for $\text{C}_{46}\text{H}_{52}\text{F}_6\text{O}_{10}\text{P}_2\text{S}_2\text{Sn}$ (1123.72): C, 49.17; H, 4.66. Found: C, 49.76; H, 4.76%. ^1H NMR ($d_3\text{-MeCN}$) δ : 7.8–7.4 (30H), 1.61 (4H), 1.44 (4H), 0.97 (4H), 0.62 (6H). ^{13}C NMR ($d_3\text{-MeCN}$) δ : 132.7, 131.1, 128.0, 125.8, 119.2, 33.5, 25.6, 24.3, 11.5. ^{31}P NMR ($d_3\text{-MeCN}$) δ : 43.7. ^{119}Sn NMR ($d_3\text{-MeCN}$) δ : -363.5.

Dehydration of $[\text{Me}_2\text{Sn}(\text{H}_2\text{O})_2(\text{OPPh}_3)_2](\text{O}_3\text{SCF}_3)_2$ (**1**)

Heating of **1** at 110 °C under dynamic oil pump vacuum for 5 h afforded **1a**.

1a: ^{31}P MAS NMR δ : 38.5 (integral approx. 95%), 41.1 (integral approx. 5%). ^{119}Sn MAS NMR δ : -237.0 (integral approx. 5%), -320.0 (integral approx. 95%). IR (KBr) ν : 3059m, 3027m, 2925w, 1626br, 1590w, 1485w, 1438s, 1325sh, 1288s, 1249vs, 1206s, 1160s, 1145vs, 1121s, 1083m, 1032vs, 991sh, 806w, 750w, 725s, 693m, 637m, 578w, 532s, 517sh, 463w, 419w cm^{-1} . Anal. Calc. for $\text{C}_{40}\text{H}_{36}\text{F}_6\text{O}_8\text{P}_2\text{S}_2\text{Sn}$ (1003.53): C, 47.88; H, 3.62. Found: C, 47.76; H, 3.66%.

Crystallography

Single crystals of **1** and **2** suitable for X-ray crystallography were obtained from hexane- CH_2Cl_2 . Intensity data were collected on Bruker SMART Apex CCD diffractometer fitted with Mo- $\text{K}\alpha$ radiation (graphite crystal monochromator, $\lambda = 0.71073$ Å) to θ_{max} *via* ω scans. Data were reduced and corrected for absorption using the programs SAINT and SADABS.³⁵ The structure was solved by direct methods and difference Fourier synthesis using SHELX-97 implemented in the program WinGX 2002.³⁶ Full-matrix least-squares refinement on F^2 , using all data, was carried out with anisotropic displacement parameters applied to all non-hydrogen atoms. Hydrogen atoms were included in geometrically calculated positions using a riding model and were refined isotropically. Disorder was resolved for one triflate group of **1** so that the atoms S(2), C(4), F(6), O(10) were refined over two sites with occupancy ratios of 50 : 50. Disorder was resolved for the triflate group of **2** so that the atoms O(5), O(6) and O(7) were refined over two sites with occupancy ratios of 70 : 30. The Figures were created using DIAMOND.³⁷

CCDC reference numbers 207870 for **1** and 207871 for **2**.

See <http://www.rsc.org/suppdata/dt/b3/b303878e/> for crystallographic data in CIF or other electronic format.

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