

Synthesis, structure and reactions of $[(\text{BuSn})_{12}\text{O}_{14}(\text{OH})_6]\text{Cl}_2 \cdot 2\text{H}_2\text{O}$: solution studies using ^{119}Sn NMR and electrospray mass spectrometry

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Abstract

The compound $[(\text{BuSn})_{12}\text{O}_{14}(\text{OH})_6]\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ (1) has been made on a preparative scale and its structure determined by X-ray crystallography. Tin-119 NMR spectroscopy and electrospray mass spectrometry indicate that the cationic structure $[(\text{BuSn})_{12}\text{O}_{14}(\text{OH})_6]^{2+}$ observed in the solid state is retained in solution. Two of the hydroxyl protons at six-coordinate tin centres are acidic and react with methanol to give $[(\text{BuSn})_{12}\text{O}_{14}(\text{OH})_4(\text{OMe})_2]\text{Cl}_2$. Compound 1 can be used as a precursor for the formation of other organotin oligomers such as $[(\text{BuSn}(\text{OH})\text{O}_2\text{PPh}_2)_3\text{O}][\text{Ph}_2\text{PO}_2]$. The hydroxy groups in the latter compound can be replaced in solution in a stepwise fashion to give eventually $[(\text{BuSn}(\text{OMe})\text{O}_2\text{PPh}_2)_3\text{O}][\text{Ph}_2\text{PO}_2]$.

Key words: Tin; Crystal structure; Electrospray mass spectra; Tin cluster

1. Introduction

The chemistry of organotin(IV) oligomers has become the focus of many recent studies. Some of these oligomers exhibit catalytic activity in transesterification and polymerisation processes [1]. They also have some potential as precursors of intercalates in montmorillonite clays to produce new materials with catalytic applications. A principal route to the formation of organoostannic(IV) oligomers utilises condensation reactions of organostannonic acids with carboxylic and phosphinic acids [2]. The compositions of organoostannic(IV) compounds resulting from condensation reactions between alkylstannonic acids and carboxylic acids such as $[\text{R}'\text{Sn}(\text{O})(\text{O}_2\text{CR})]_n$ and $[(\text{R}'\text{Sn}(\text{O})\text{O}_2\text{CR})_2\text{R}'\text{Sn}-$

$(\text{O}_2\text{CR})_3]_2$ have been known for some time [3] and although there were further reports on related compounds [4–6], the first definitive structural assignment did not appear until 1985, with the report of the drum-shaped molecule, $[\text{PhSn}(\text{O})\text{O}_2\text{CC}_6\text{H}_{11}]_6$ [7]. Subsequently, various structural types including oxygen-capped, cube, crown, extended ladder, butterfly, double cube and cage clusters, have been studied [8–18]. Some interconversion routes between different types of clusters have been proposed [1] on the basis of these studies. However, the structure of the most common starting material, butylstannonic acid, remains unknown.

Organostannonic acids, $\text{RSn}(\text{O})\text{OH}$, are usually prepared by hydrolysis of organotin(IV) trihalides, and are considered to be polymeric or oligomeric [18,19]. There is some evidence that organostannonic acids may exist as cyclic trimers when freshly prepared [19] but no

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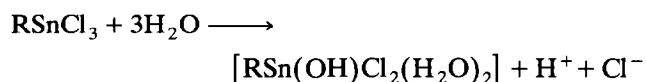
definite structural data are available nor does there appear to be a good understanding of the hydrolysis processes involved. Reported recently were the structures of (¹PrSn)₉O₈(OH)₆Cl₅ · 6(dmsO) and [(¹PrSn)₁₂O₁₄(OH)₆]Cl₂ which were serendipitous products of hydrolysis reactions of ¹PrSnCl₃ [20,21]. Study of the properties of these oligomers has been restricted by the lack of efficient synthetic procedures. Electrospray mass spectrometry (ESMS) provides a new method of investigating labile species in solution. The technique was first used to investigate the mass spectra of very large biomolecules [22–24], but we have also shown that it is applicable to a wide range of organometallic systems. In particular, it has been used to investigate alkyl derivatives of several metals [25,26] and it is also applicable to polynuclear complexes such as [Cr₃O(O₂-CR)₆L₃]⁺ [27] species and polynuclear heterometallic dithiocarbamate cationic species [28]. We now report on the synthesis, structure and reactions of the oligomer [(BuSn)₁₂O₁₄(OH)₆]Cl₂.

2. Results and discussion

2.1. ¹¹⁹Sn NMR and ESMS spectra

Organotin(IV) trichlorides, RSnCl₃ (R = Me, Bu), dissolve in water to give clear solutions with a strong acidic reaction. The pH values of these solutions varies a little depending on the organyl substituent and the concentration, but suggest formation of one molar equivalent of proton for each mole of RSnCl₃. The ¹¹⁹Sn NMR spectra of aqueous butyltin(IV) trichloride and methyltin(IV) trichloride solutions show resonances at -497 and -485 ppm, respectively. These values are about 500 ppm to lower frequency than

those in dichloromethane solution (2 and 12 ppm, respectively) and suggest the formation of six-coordinate tin(IV) species in aqueous solution [29–35].



The first hydrolysis products of RSnCl₃ (R = Bu, ¹Pr and ¹Bu, Et) have, in fact, been isolated [36,38] and are hydroxy-bridged dimers [RSn(OH)Cl₂ · (H₂O)]₂ containing six-coordinated tin. These dimers probably dissociate to monomeric [RSn(OH)Cl₂(H₂O)₂] in solution since the ¹¹⁹Sn resonances for R = Me and Bu analogues do not show ¹¹⁷Sn satellites. Precipitation begins after addition of two molar equivalents of aqueous sodium hydroxide to solutions of BuSnCl₃ in water. The pH of the solution increases very steeply after addition of 3.1 molar equivalent of NaOH, and the degree of the precipitation reaches a maximum after addition of 3.5 molar equivalents of sodium hydroxide. This precipitate is usually regarded as butylstannonic acid, with the general formula BuSn(O)OH [20]. Freshly prepared butylstannonic acid is usually soluble in solvents such as ethanol, acetone and dichloromethane, but the solubility decreases markedly as the product is aged. The ¹¹⁹Sn NMR spectra of butylstannonic acid solutions are complex, usually containing a number of both sharp and broad resonances in the range -450 and -550 ppm. Furthermore, spectra are dependent on a number of parameters including the solvent, the rate of base addition to promote hydrolysis, and the age of the compound, all of which probably reflect the occurrence of complicated oligomerisation processes. However, we have been able consistently to prepare one pure compound by the slow base hydrolysis of

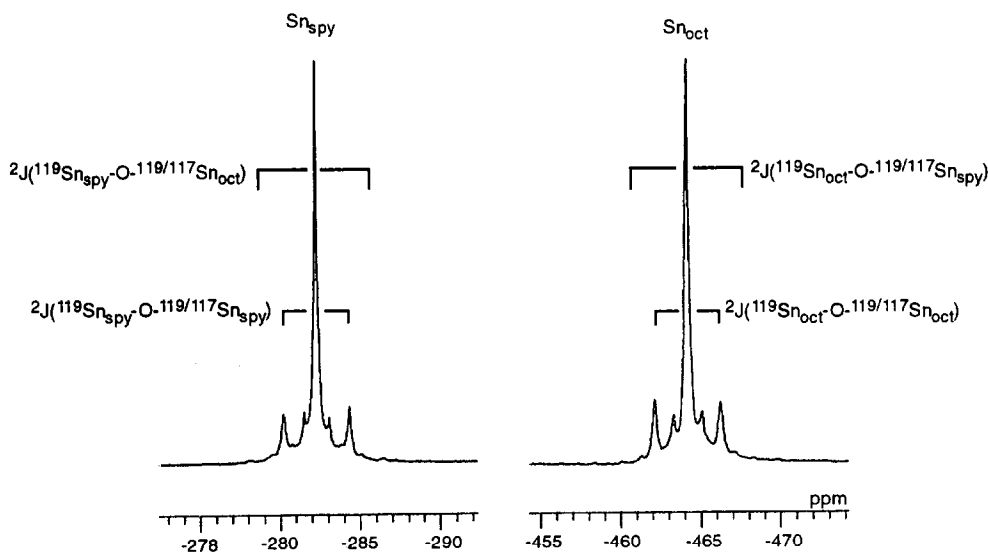


Fig. 1. ¹¹⁹Sn NMR spectrum of [(BuSn)₁₂O₁₄(OH)₆]Cl₂ · 2H₂O in dichloromethane solution at 24°C.

BuSnCl₃. The ¹¹⁹Sn NMR spectrum of this material is relatively simple and reproducible. An X-ray structural analysis (see below) has shown this compound to be [(BuSn)₁₂O₁₄(OH)₆]Cl₂ · 2H₂O.

The ¹¹⁹Sn NMR spectrum of [(BuSn)₁₂O₁₄(OH)₆]Cl₂ · 2H₂O in dichloromethane at 24°C (Fig. 1) contains two resonances, of equal intensity, at -283.1 and -468.1 ppm indicating five- and six-coordinate tin atoms, respectively [29–35]. Furthermore, each ¹¹⁹Sn resonance is accompanied by ^{117/119}Sn satellites (δ -283.1 ppm $J(^{119}\text{Sn}-\text{O}-^{119}\text{Sn}) = 425$ Hz, $J(^{119}\text{Sn}-\text{O}-^{117}\text{Sn}) = 408$ Hz, $J(^{119}\text{Sn}-\text{O}-^{117}\text{Sn}) = 156$ Hz; δ -468.1 ppm $J(^{119}\text{Sn}-\text{O}-^{119}\text{Sn}) = 425$ Hz, $J(^{119}\text{Sn}-\text{O}-^{117}\text{Sn}) = 410$ Hz, $J(^{119}\text{Sn}-\text{O}-^{117}\text{Sn}) = 188$ Hz).

The addition of 1,8-diazabicyclo[5.4.0]undec-7-ene(1,5-5) (dbu), which is a good proton acceptor but a poor Lewis base, to [(BuSn)₁₂O₁₄(OH)₆]Cl₂ in dichloromethane solution causes no change to the high frequency ¹¹⁹Sn resonance, but the ¹¹⁹Sn resonance for the six-coordinate tin broadens, such that ^{117/119}Sn satellites are no longer observed, and moves slightly to higher frequency (-466 ppm). This implies that the oligomer remains intact, and that at least some of the hydroxide groups in [(BuSn)₁₂O₁₄(OH)₆]Cl₂ are acidic

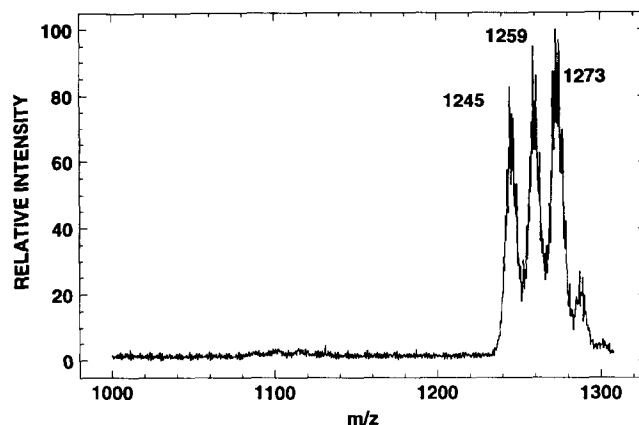


Fig. 3. ES mass spectrum of [(BuSn(OH)O₂PPh₂)₃O][Ph₂PO₂] in dichloromethane solution.

and that these acidic hydroxides are attached to six coordinate tin.

The ES mass spectrum of a freshly prepared solution of [(BuSn)₁₂O₁₄(OH)₆]Cl₂ in dichloromethane/methanol is shown in Fig. 2a. It consists of a single peak covering a wide isotopic mass distribution (due to the multiplicity of tin isotopes) centered at m/z 1218, which is assigned to the intact ion [(BuSn)₁₂O₁₄(OH)₆]²⁺. When a sample of [(BuSn)₁₂O₁₄(OH)₆]Cl₂ is left in methanol solution for 5 days, the ES mass spectrum then obtained is shown in Fig. 2b. The main peak is now centered at m/z 1232 and it is significantly broader than the peak in Fig. 2a. Expansion of the spectrum shows a broad shoulder at m/z 1225. This spectrum shows that in methanol solution two of the hydroxy ligands are replaced by methoxy groups.

The corresponding *i*-propyl derivative, [(ⁱPrSn)₁₂O₁₄(OH)₆]Cl₂ also gives its intact ion as the only significant peak in its ES mass spectrum at m/z 1134.

The reaction of [(BuSn)₁₂O₁₄(OH)₆]Cl₂ with 16 molar equivalents of diphenylphosphinic acid, Ph₂PO₂H, in dichloromethane solution at room temperature gives rise only to a triplet resonance at -496.6 ppm with ² $J(\text{Sn}-\text{O}-\text{P})$ 132 Hz and ² $J(^{119}\text{Sn}-\text{O}-^{117}\text{Sn})$ 194 Hz. The corresponding ³¹P NMR spectrum shows a single resonance with ^{119/117}Sn satellites at 31.0 ppm (² $J(\text{P}-\text{Sn})$ 131 Hz) and a singlet at 19.4 ppm without ^{119/117}Sn satellites. The relative intensities of these two resonances are 3:1. These ¹¹⁹Sn and ³¹P NMR data are consistent with formation of [(BuSn(OH)O₂PPh₂)₃O][Ph₂PO₂], previously obtained by reaction between butylstannic acid and diphenylphosphinic acid [8].

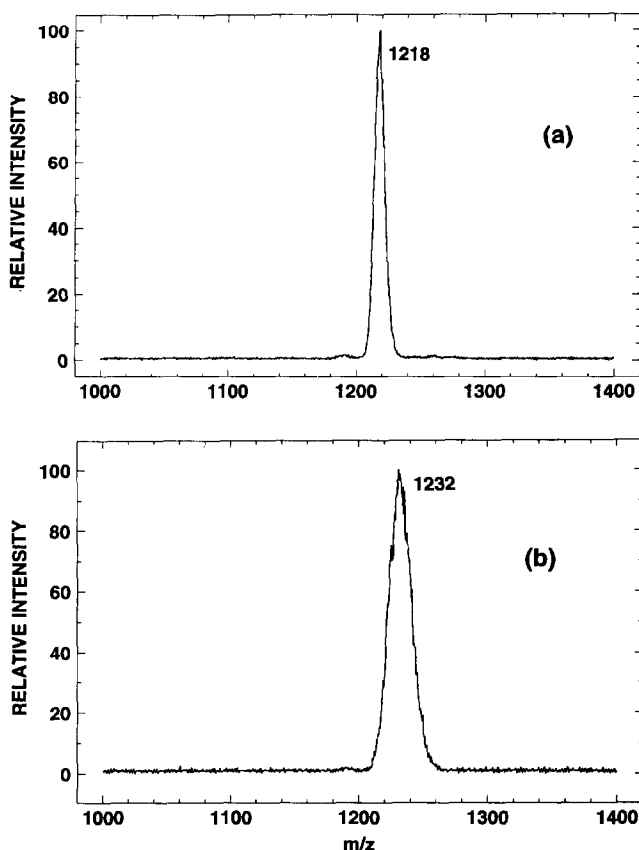
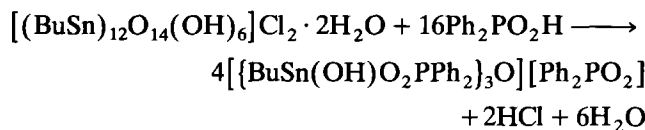


Fig. 2. ES mass spectrum (a) of a freshly prepared solution of [(BuSn)₁₂O₁₄(OH)₆]Cl₂ in dichloromethane/methanol (b) of a sample of [(BuSn)₁₂O₁₄(OH)₆]Cl₂ after 5 days in methanol.

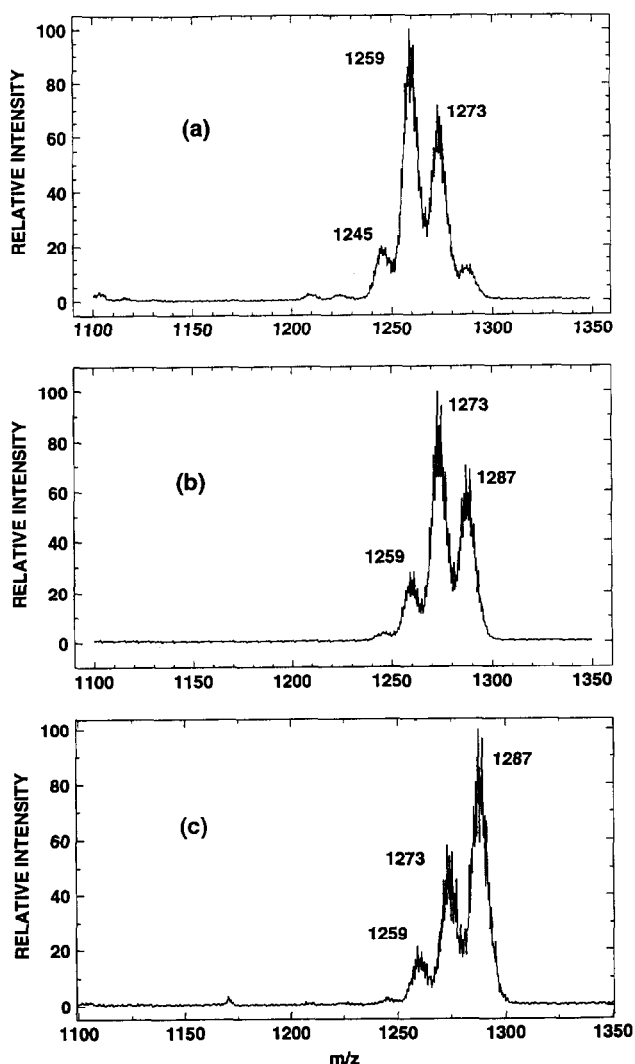


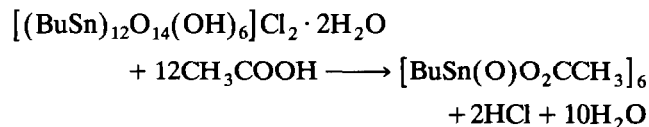
Fig. 4. ES mass spectrum of $[(\text{BuSn}(\text{OH})\text{O}_2\text{PPh}_2)_3\text{O}][\text{Ph}_2\text{PO}_2]$ (a) ca. 3 min after dissolution in methanol (b) ca. 45 min after dissolution (c) 4 days after dissolution.

ESMS confirms that $[(\text{BuSn}(\text{OH})\text{O}_2\text{PPh}_2)_3\text{O}]^+$ is the product of this reaction. Figure 3 shows the ES mass spectrum of a solution of the compound in dichloromethane. The peak at m/z 1245 is due to the intact ion $[(\text{BuSn}(\text{OH})\text{O}_2\text{PPh}_2)_3\text{O}]^+$, while the other peaks at m/z 1259, 1273 and 1287 are due to species in which the hydroxyl groups are replaced successively by methoxy groups derived from methanol in the mobile phase used in the spectrometer.

Since the substitution of the hydroxyl by methoxy groups proceeds at a reasonable rate, a solution of $[(\text{BuSn}(\text{OH})\text{O}_2\text{PPh}_2)_3\text{O}]^+$ was prepared in methanol and a sample was diluted to the appropriate concentration and immediately injected into the spectrometer. About three minutes elapses between sample injection and the appearance of the sample at the vaporisation

nozzle and the resulting ES mass spectrum is shown in Fig. 4a. Only a small proportion of the trihydroxy species remains (m/z 1245), and the most abundant species are those containing one and two methoxy groups (m/z 1259 and 1273 respectively). Figure 4b shows the ES mass spectrum of another sample of the original solution 45 min after dissolution. The substitution has clearly proceeded further, and the peak at m/z 1287, assigned to the tris(methoxy) species, is now strong. Figure 4c shows the ES mass spectrum after 4 days. Almost none of the original trihydroxy compound remains, and the major peak is now that due to the fully substituted species $[(\text{BuSn}(\text{OMe})\text{O}_2\text{PPh}_2)_3\text{O}]^+$. Unlike $[(\text{BuSn})_{12}\text{O}_{14}(\text{OH})_6]^{2+}$, in the $[(\text{BuSn}(\text{OH})\text{O}_2\text{PPh}_2)_3\text{O}]^+$ cation all of the hydroxyl groups are equivalent and are susceptible to substitution. ESMS provides a convenient way of counting active hydroxyl groups in complexes of this type.

A direct reaction of $[(\text{BuSn})_{12}\text{O}_{14}(\text{OH})_6]\text{Cl}_2$ with 12 molar equivalents of acetic acid in dichloromethane solution at room temperature produces a ^{119}Sn singlet resonance at -485 ppm with satellites ($^2J(^{119}\text{Sn}-\text{O}-^{117}\text{Sn})$ 70, 247 Hz), consistent with the presence of the drum-shaped compound $[\text{BuSn}(\text{O})\text{O}_2\text{CCH}_3]_6$ [1]. Apparently the following interconversion occurs.



2.2. Molecular structure of $[(\text{BuSn})_{12}\text{O}_{14}(\text{OH})_6]\text{Cl}_2 \cdot 2\text{H}_2\text{O}$

The molecular structure of $[(\text{BuSn})_{12}\text{O}_{14}(\text{OH})_6]^{2+}$ is shown in Fig. 5, and selected bond distances and bond

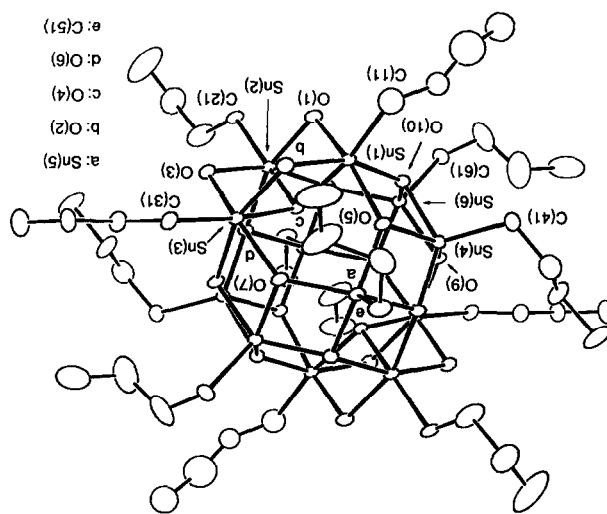


Fig. 5. ORTEP diagram of $[(\text{BuSn})_{12}\text{O}_{14}(\text{OH})_6]\text{Cl}_2 \cdot 2\text{H}_2\text{O}$.

TABLE 1. Selected bond distances (Å) and bond angles (deg) for [(BuSn)₁₂O₁₄(OH)₆]Cl₂ · 2H₂O

Bond distances (Å)					
Sn _{oct} -O(H)	2.114	Sn _{oct} -O _{tpl}	2.116	Sn _{spy} -O (m-6)	2.031
Sn(1)-O(1)	2.115(4)	Sn(1)-O(5)	2.118(4)	Sn(4)-O(6) ^Y	2.033(4)
Sn(1)-O(2)	2.112(4)	Sn(1)-O(10)	2.098(4)	Sn(4)-O(9) ^Y	2.026(4)
Sn(2)-O(1)	2.103(4)	Sn(2)-O(6)	2.115(4)	Sn(5)-O(5)	2.023(4)
Sn(2)-O(3)	2.124(4)	Sn(2)-O(8)	2.109(4)	Sn(5)-O(7)	2.028(4)
Sn(3)-O(2)	2.111(4)	Sn(3)-O(7)	2.119(4)	Sn(6)-O(8) ^Y	2.032(4)
Sn(3)-O(3)	2.121(4)	Sn(3)-O(9)	2.134(4)	Sn(6)-O(10) ^Y	2.043(4)
Sn _{oct} -O _{tpy}	2.085	Sn _{oct} -C	2.141	Sn _{spy} -C	2.137
Sn(1)-O(4)	2.095(4)	Sn(1)-C11	2.150(6)	Sn(4)-C41	2.137(7)
Sn(2)-O(4)	2.087(4)	Sn(2)-C21	2.144(7)	Sn(5)-C51	2.130(7)
Sn(3)-O(4)	2.073(4)	Sn(3)-C31	2.128(6)	Sn(6)-C61	2.145(7)
Sn _{spy} -O (m-4)	2.088				
Sn(4)-O(5)	2.086(4)	Sn(5)-O(6) ^Y	2.090(4)	Sn(6)-O(7)	2.093(4)
Sn(4)-O(10) ^Y	2.093(4)	Sn(5)-O(8) ^Y	2.086(4)	Sn(6)-O(9) ^Y	2.082(4)
Bond angles (deg)					
O(H)-Sn _{oct} -C (<i>cis</i>)	98.4	O _{tpl} -Sn _{oct} -C (<i>cis</i>)	99.1	O(H)-Sn _{oct} -O _{tpl} (m-6, sleeping-chair)	90.0
O(1)-Sn(1)-C11	99.1(2)	O(5)-Sn(1)-C11	99.1(3)	O(1)-Sn(1)-O(10)	89.7(2)
O(2)-Sn(1)-C11	97.0(2)	O(10)-Sn(1)-C11	100.4(3)	O(2)-Sn(1)-O(5)	89.9(2)
O(1)-Sn(2)-C21	97.3(3)	O(6)-Sn(2)-C21	99.5(3)	O(1)-Sn(2)-O(8)	89.9(2)
O(3)-Sn(2)-C21	96.7(3)	O(8)-Sn(2)-C21	100.2(3)	O(3)-Sn(2)-O(6)	90.1(2)
O(2)-Sn(3)-C31	100.5(3)	O(7)-Sn(3)-C31	98.0(3)	O(2)-Sn(3)-O(7)	90.0(2)
O(3)-Sn(3)-C31	99.2(3)	O(9)-Sn(3)-C31	97.1(3)	O(3)-Sn(3)-O(9)	90.3(2)
O(H)-Sn _{oct} -O _{tpy} (m-4)	76.2	O _{tpy} -Sn _{oct} -O _{tpl} (m-6)	87.7	O(H)-Sn _{oct} -O _{tpl} (<i>trans</i>)	159.1
O(1)-Sn(1)-O(4)	76.7(2)	O(4)-Sn(1)-O(5)	86.9(2)	O(1)-Sn(1)-O(5)	158.5(2)
O(2)-Sn(1)-O(4)	75.4(2)	O(4)-Sn(1)-O(10)	88.3(2)	O(2)-Sn(1)-O(10)	159.0(2)
O(1)-Sn(2)-O(4)	77.2(2)	O(4)-Sn(2)-O(6)	87.8(2)	O(1)-Sn(2)-O(6)	159.7(2)
O(3)-Sn(2)-O(4)	76.0(2)	O(4)-Sn(2)-O(8)	88.4(2)	O(3)-Sn(2)-O(8)	159.6(2)
O(2)-Sn(3)-O(4)	75.9(2)	O(4)-Sn(3)-O(7)	87.4(2)	O(2)-Sn(3)-O(9)	158.8(2)
O(3)-Sn(3)-O(4)	76.3(2)	O(4)-Sn(3)-O(9)	87.5(2)	O(3)-Sn(3)-O(7)	159.1(2)
O _{tpy} -Sn _{oct} -C (<i>trans</i>)	171.3	O _{tpl} -Sn _{oct} -O _{tpl} (m-4)	75.9	O(H)-Sn _{oct} -O(H) (m-6, chair)	98.9
O(4)-Sn(1)-C11	170.5(3)	O(5)-Sn(1)-O(10)	75.9(2)	O(1)-Sn(1)-O(2)	99.2(2)
O(4)-Sn(2)-C21	169.8(3)	O(6)-Sn(2)-O(8)	76.0(2)	O(1)-Sn(2)-O(3)	99.2(2)
O(4)-Sn(3)-C31	173.6(3)	O(7)-Sn(3)-O(9)	75.8(2)	O(2)-Sn(3)-O(3)	98.4(2)
O-Sn _{spy} -C (long Sn-O)	110.7	O-Sn _{spy} -C (short Sn-O)	112.1	O-Sn _{spy} -O (<i>trans</i>)	135.9
O(6) ^Y -Sn(4)-C41	109.8(3)	O(5)-Sn(4)-C41	108.4(3)	O(5)-Sn(4)-O(9) ^Y	136.1(2)
O(9) ^Y -Sn(4)-C41	114.1(3)	O(10)-Sn(4)-C41	111.9(3)	O(6) ^Y -Sn(4)-O(10)	136.0(2)
O(5)-Sn(5)-C51	108.6(3)	O(6) ^Y -Sn(5)-C51	110.7(3)	O(5)-Sn(5)-O(8) ^Y	135.5(2)
O(7)-Sn(5)-C51	112.0(3)	O(8) ^Y -Sn(5)-C51	114.3(3)	O(6) ^Y -Sn(5)-O(7)	136.4(2)
O(8) ^Y -Sn(6)-C61	108.6(3)	O(7)-Sn(6)-C61	112.7(3)	O(7)-Sn(6)-O(10) ^Y	135.7(2)
O(10) ^Y -Sn(6)-C61	110.0(3)	O(9)-Sn(6)-C61	114.6(3)	O(8) ^Y -Sn(6)-O(9)	135.8(2)
O _{tpl} -Sn _{spy} -O _{tpl} (m-4)	77.7	O _{tpl} -Sn _{oct} -O _{tpl} (m-4)	76.9	O _{tpl} -Sn _{spy} -O _{tpl} (m-6)	96.8
O(5)-Sn(4)-O(6) ^Y	77.6(2)	O(5)-Sn(4)-O(10)	76.7(2)	O(6) ^Y -Sn(4)-O(9) ^Y	97.5(2)
O(9) ^Y -Sn(4)-O(10)	77.8(2)	O(6) ^Y -Sn(5)-O(8) ^Y	77.0(2)	O(5)-Sn(5)-O(7)	96.8(2)
O(5)-Sn(5)-O(6) ^Y	77.7(2)	O(7)-Sn(6)-O(9)	77.5(2)	O(8) ^Y -Sn(6)-O(10) ^Y	96.0(2)
O(7)-Sn(5)-O(8) ^Y	77.8(2)				
O(7)-Sn(6)-O(8) ^Y	77.6(2)				
O(9)-Sn(6)-O(10) ^Y	77.7(2)				
Sn _{oct} -O _{tpl} -Sn _{spy} (m-6)	134.9	Sn _{oct} -O _{tpl} -Sn _{spy} (m-4)	103.6	Sn _{spy} -O _{tpl} -Sn _{spy} (m-4)	102.1
Sn(1)-O(5)-Sn(5)	135.4(1)	Sn(1)-O(5)-Sn(4)	103.4(1)	Sn(4)-O(5)-Sn(5)	102.5(1)
Sn(2)-O(6)-Sn(4) ^Y	134.6(1)	Sn(2)-O(6)-Sn(5) ^Y	103.3(1)	Sn(4) ^Y -O(6)-Sn(5) ^Y	102.0(1)
Sn(3)-O(7)-Sn(5)	135.2(1)	Sn(3)-O(7)-Sn(6)	103.7(1)	Sn(5)-O(7)-Sn(6)	102.0(1)
Sn(2)-O(8)-Sn(6) ^Y	135.2(1)	Sn(2)-O(8)-Sn(5) ^Y	103.8(1)	Sn(5) ^Y -O(8)-Sn(6) ^Y	102.2(1)
Sn(3)-O(9)-Sn(4) ^Y	133.8(1)	Sn(3)-O(9)-Sn(6)	103.4(1)	Sn(4) ^Y -O(9)-Sn(6)	102.4(1)

TABLE 1 (continued)

Sn(1)–O(10)–Sn(6)′	135.4(1)	Sn(1)–O(10)–Sn(4)	103.6(1)	Sn(4)–O(10)–Sn(6)′	101.7(1)
Sn–O _{ipy} –Sn	104.7	Sn–O(H)–Sn	103.0		
Sn(1)–O(4)–Sn(2)	103.6(1)	Sn(1)–O(1)–Sn(2)	102.9(1)		
Sn(1)–O(4)–Sn(3)	105.2(1)	Sn(1)–O(2)–Sn(3)	103.6(1)		
Sn(2)–O(4)–Sn(3)	105.2(1)	Sn(2)–O(3)–Sn(3)	102.5(1)		

angles are listed in Table 1. The structure determination confirms the stoichiometry of the compound, and is very similar to that reported for [(¹PrSn)₁₂O₁₄(OH)₆]Cl₂ [21]. The molecule is situated about a crystallographic centre of inversion. As expected there are weak associations in the lattice between the cationic cluster core and the water molecules of crystallization and the chloride anions. The oxygen atom of the water molecule, *i.e.* O(w), is situated near to the three hydroxyl O atoms, and the most significant interaction occurs between the O(w) and O(1) atoms, such that the O(1) ··· O(w) separation is 2.683(8) Å; there are weaker interactions of 3.709(9) and 3.73(1) Å between O(2) ··· O(w) and O(3) ··· O(w), respectively. The O(w) atom also forms weak interactions with the chloride anions such that O(w) ··· Cl is 3.202(6) and O(w) ··· Cl′ is 3.157(8) Å (symmetry operation: 1 – x, 1 – y, 1 – z). The closest contact between the chloride anion and the cluster cation is between O(3) and Cl′ of 3.111(5) Å (symmetry operation: 1 – x, 1 – y, – z). Apparently the core of the structure is a soccerball-like Sn–O framework, to which the butyl groups are attached. Inspection of the framework of [(BuSn)₁₂O₁₄(OH)₆]²⁺ shows three sub-frameworks. Two of them are three-Sn-atom units (Sn₃), which contain all six-coordinate Sn atoms. The other one is a macro-ring containing six five-coordinate Sn atoms (Sn₆), bonding through all the basal O atoms. The geometry of the Sn₃ units is very similar to that in the phosphinic acid based cluster [(BuSn(OH)O₂PPh₂)₃O][Ph₂PO₂] [8]; the structural features, such as bond angles and bond distances, are very similar. Further, these structural units, such as four- and six-membered rings and five- and six-coordinate geometries about tin atoms, are also found in [(¹PrSn)₉O₈(OH)₆Cl₅] · 6dmsO [39] and [(¹PrSn)₁₂O₄(OH)₂₄Na]⁴⁺ [40] clusters.

3. Conclusion

It was generally believed that the dehydration of monoorganotin(IV) hydroxide occurs in the last step in the base hydrolysis of RSnCl₃, *i.e.* from RSn(OH)₃ [19,20,37]. However, it appears that the dehydration may occur at earlier stages of hydrolysis, such as at RSn(OH)₂Cl, and between RSn(OH)₂Cl and RSn(OH)₃. The final dehydration product may depend on

the hydrolysis speed, the temperature, and perhaps the solvent. Nevertheless, the [(RSn)₁₂O₁₄(OH)₆]²⁺ cluster may be regarded as a stable product, which may be brought into reaction with other ligands. Changing the hydrolysis conditions may result in other types of clusters.

This work also confirms that the combination of NMR and ESMS methods is very powerful for solution studies. One limitation of ESMS is that it only detects charged species, so any neutral species in solution may be unobserved. However, in this work, tin-119 NMR spectroscopy has shown that in each system there is only one species present in solution, and ESMS gives an unequivocal identification.

4. Experimental section

¹¹⁹Sn NMR spectra were recorded at 100.75 Hz with broad band proton decoupling using a JEOL GX270 MHz spectrometer and referenced against external Me₄Sn. ³¹P NMR spectra were recorded at 109.38 MHz and referenced against external 85% H₃PO₄.

TABLE 2. Crystal and data collection summary for [(BuSn)₁₂O₁₄(OH)₆]Cl₂ · 2H₂O

formula	C ₄₈ H ₁₁₈ O ₂₂ Cl ₂ Sn ₁₂
f _w	2542.6
crys. sys.	triclinic
space group	P $\bar{1}$
a, Å	13.071(1)
b, Å	13.811(2)
c, Å	12.825(2)
α, deg.	111.73(1)
β, deg.	106.54(1)
γ, deg.	81.51(1)
V, Å ³	2059.4
Z	1
D _{calc} , gcm ⁻³	2.050
F(000)	1216
μ, cm ⁻¹	34.20
T, K	293
No. of data collected	5425
No. of unique data	5382
No. of data with I ≥ 2.5σ(I)	4776
R	0.031
g	0.0014
R _w	0.039

TABLE 3. Atomic coordinates ($\times 10^5$ for Sn and $\times 10^4$ for remaining atoms) for [(BuSn)₁₂O₁₄(OH)₆]Cl₂ · 2H₂O

Atom	x	y	z
Sn(1)	62901(3)	15397(3)	-7367(3)
Sn(2)	36656(3)	15989(3)	-14875(3)
Sn(3)	46361(3)	26699(3)	12655(3)
Sn(4)	72204(3)	-7942(3)	-6618(3)
Sn(5)	71705(3)	6918(3)	19256(3)
Sn(6)	49580(3)	10796(3)	26655(3)
O(1)	4969(3)	1875(3)	-1978(4)
O(2)	6213(4)	2912(3)	710(4)
O(3)	3654(4)	2985(3)	-32(4)
O(4)	4974(3)	1370(3)	-204(3)
O(5)	7224(3)	772(3)	399(4)
O(6)	7268(3)	-882(3)	899(3)
O(7)	5990(3)	1810(3)	2235(3)
O(8)	6192(3)	2(3)	2459(3)
O(9)	3903(3)	1855(3)	1645(4)
O(10)	3774(3)	48(3)	1763(3)
C(11)	7552(7)	1983(7)	-1214(8)
C(12) ^a	8001(19)	1375(17)	-2036(21)
C(12') ^a	7347(22)	1224(20)	-2905(23)
C(13)	8325(27)	1206(25)	-2926(33)
C(14)	8176(16)	490(16)	-4254(19)
C(21)	2425(6)	2106(6)	-2707(7)
C(22)	1369(10)	2104(14)	-2673(16)
C(23)	469(12)	2616(14)	-3434(16)
C(24)	598(17)	3725(14)	-3171(18)
C(31)	4878(6)	4106(5)	2655(6)
C(32)	3734(7)	4542(5)	2673(7)
C(33)	3709(9)	5604(7)	3656(9)
C(34)	2583(10)	5977(10)	3662(13)
C(41)	8753(6)	-1239(6)	-1025(7)
C(42)	9403(9)	-2050(11)	-530(10)
C(43)	8926(9)	-2978(7)	-897(13)
C(44)	9594(14)	-3864(11)	-460(16)
C(51)	8658(7)	1154(6)	3146(7)
C(52)	9185(8)	1957(9)	3035(10)
C(53)	8516(12)	2974(11)	3229(18)
C(54)	9054(21)	3850(11)	3300(18)
C(61)	4978(7)	1725(6)	4471(6)
C(62)	3995(14)	1936(16)	4771(12)
C(63)	3250(20)	2631(21)	4357(14)
C(64)	2686(29)	3308(15)	4877(21)
C1	6868(2)	4917(2)	494(2)
O(w)	4967(6)	3895(4)	8286(6)

^a Atom has 50% site occupancy.

Temperatures were maintained using a JEOL GTV3 control system.

Solutions of the compounds (2.0 mM) in dichloromethane or methanol were diluted 1:10 with methanol. Electrospray mass spectra were obtained with a VG Bio-Q triple quadrupole mass spectrometer (VG BioTech, Altrincham, Cheshire, UK) using a water/methanol/acetic acid (50:50:1%) mobile phase. The diluted solutions of the compounds were injected directly into the spectrometer via a Rheodyne injector equipped with a 10 μ l loop. A Phoenix 20 micro LC syringe pump delivered the solutions to the vaporisa-

tion nozzle of the electrospray ion source at a flow rate of 3 μ l min⁻¹. Nitrogen was used as both a drying gas and for nebulisation with flow rates of approximately 3 l min⁻¹ and 100 ml min⁻¹ respectively. Pressure in the mass analyser region was usually about 3×10^{-5} torr. The compounds in this study give strong signals in their ES mass spectra and typically 8–10 signal averaged spectra were required to give good signal to noise ratio. Measurements were made at a first skimmer (B1) voltage of 40 V unless stated otherwise.

4.1. [(BuSn)₁₂O₁₄(OH)₆]Cl₂ · 2H₂O

To a stirred solution of BuSnCl₃ (14.1 g in 200 ml H₂O) was slowly added (about 40 ml over 2 h) aqueous 1 M KOH solution until the pH of the solution reached 4.0. The resulting solution containing a white precipitate was stirred for another 1 h. The white precipitate was filtered off and washed with 500 ml of distilled water. The air-dried material was dissolved in 10 ml of acetone and of 15 ml of acetonitrile were then added. This solution was left at 0°C to crystallise. After slow evaporation of solvent, a total of 8.9 g white crystals was obtained. Single crystals suitable for X-ray structure determination were obtained by recrystallisation from acetone. [(BuSn)₁₂O₁₄(OH)₆]Cl₂ · 2H₂O Found C 22.70, H 4.68; C₄₈H₁₁₈Sn₁₂O₂₂Cl₂ requires C 22.66, H 4.67%.

4.2. Crystal structure determination

Intensity data for a colourless crystal of **1** (0.10 \times 0.28 \times 0.50 mm) were collected at room temperature on an Enraf-Nonius CAD4F diffractometer fitted with Mo K α radiation; $\lambda = 0.71073$ Å. The $\omega:2\theta$ scan technique was employed to measure 5425 data ($2\theta_{\max}$ 50.0°) which were corrected for Lorentz and polarisation effects and for absorption employing an analytical procedure (maximum and minimum transmission factors: 0.531 and 0.405) [41]. Of the 5382 unique data, 4776 satisfied the $I \geq 2.5\sigma(I)$ criterion of observability and were used in the subsequent analysis; crystal data are summarised in Table 2.

The structure was solved by direct-methods [42] and refined by a full-matrix least-squares procedure based on F [41]. All non-hydrogen atom were refined anisotropically except for those constituting the C(11)–C(14) butyl group which was found to be disordered such that the C(12) atom had two sites, each modelled with 50% site occupancy. Hydrogen atoms were included in the model at their calculated positions except for the disordered butyl group. The refinement was continued after the inclusion of a weighting scheme of the form $w = [\sigma^2(F) + g|F|^2]$ when at convergence $R = 0.031$, $g = 0.0014$ and $R_w = 0.039$; other details are summarised in Table 2. The analysis of variance showed

no special features and the maximum and minimum peaks in the final difference map were 1.10 and $-0.91 \text{ e}\text{\AA}^3$, respectively. Fractional atomic coordinates are listed in Table 3 and the crystallographic numbering scheme is shown in Fig. 5 which was drawn with the ORTEP [43] program at 25% probability ellipsoids. Lists of thermal parameters, hydrogen-atom parameters, all bond distances and angles, and observed and calculated structure factors are available from E.R.T.T.

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