Articles

Hydrolysis of Dinuclear Spacer-Bridged Diorganotin(IV) Triflates. A Novel Cationic Double Ladder with Supramolecular Association[†]

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A series of oligomethylene-bridged diorganotin triflates $R(OTf)_2Sn(CH_2)_nSn(OTf)_2R$ ($R = CH_2SiMe_3$; $n = 3, 4, 8, 10$) were synthesized by reaction of triflic acid with the precursor oxides $R(O)Sn(CH_2)_nSn(O)R$. On the basis of ^{119}Sn NMR (in acetonitrile) the triflates appear to be the simple six-coordinated ionic species $[(MeCN)_4(RSn(CH_2)_nSnR)(MeCN)_4]^{2+}$. These triflates readily undergo hydrolysis to give products, the identity of which depends on the length of the oligomethylene bridge. For $n = 3$ (**5**), the solid-state structure shows association of two dimeric units, which results in a tetracationic double ladder. Extensive hydrogen bonding gives rise to a supramolecular association. Solution ^{119}Sn NMR and ES MS suggest some dissociation of **5** into dimers containing four tin atoms and possibly monomers containing two tin atoms. A rudimentary solid-state structure for $n = 4$ (**6**) indicates a linear polymer based on dimeric (four tin atoms) units. The structure of **6** also features extensive hydrogen bonding, this time effectively giving rise to alternating layers of cations and anions.

Introduction

The speciation of cationic dialkyltin(IV) compounds in strongly polar solvents, such as water and acetonitrile, has attracted appreciable interest over the past 50 years.[1−9] In aqueous solution, dialkyltin dichlorides, R_2SnCl_2 (R = Me, Et, Bu), dissociate into hydrated dialkyltin dications, $[R_2Sn(H_2O)_4]^{2+}$, and chloride anions.[1] Solvated dialkyltin dications, $[R_2SnL_4]^{2+}$ ($L = H_2O$, MeCN), are also formed upon addition of strong acids HX, such as HNO_3, $HClO_4$, and HO_3SCF_3, to suspensions of dialkyltin oxides, R_2SnO, in polar solvents such as water and acetonitrile.[10−17] When solutions containing solvated dialkyl dications $[R_2SnL_4]^{2+}$ are slowly evaporated under air, the nature of the deposited diorganotin products strongly depends on the identity and concentration of the counterions. Dialkyltin dichlorides, R_2SnCl_2, are obtained at high concentrations of chloride ions,[1] whereas in the presence of weakly coordinating oxygen anions partly hydrolyzed dialkyltin−oxo species, such as $[R_2Sn(OH)X]_2$[10−14,16,18] ($X = NO_3^-$, ClO_4^-, $O_3SCF_3^-$) (**A**) and $[R_2(X)SnOSn(Y)R_2]_2$ [11,16,17] (X, Y = OH^-, NO_3^-, ClO_4^-, $O_3SCF_3^-$) (**B**), are dominant (Chart 1).

Due to the current interest in the utilization of highly charged organotin−oxo clusters as selective catalysts in organic synthesis,[15−17] we now report, as a continuation of previous work on oligomethylene-bridged tetraorganodistannoxanes with double-ladder structures, {[R(Cl)-

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[†] This paper is dedicated to Prof. J. Otera on the occasion of his 60th birthday.

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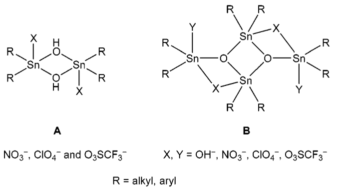
Chart 1



$Sn(CH_2)_nSn(Cl)R]O\}_4$,[19−31] a series of oligomethylene-bridged diorganotin triflates, $R(OTf)_2Sn(CH_2)_nSn(OTf)_2R$ ($R = CH_2SiMe_3$; $n = 3, 4, 8, 10$), and studies on their hydrolysis in moist air. In the case of $n = 3$, we isolated the first cationic double ladder compound, $\{[R(H_2O)Sn(CH_2)_3Sn(OH)R]O\}_4(OTf)_4$. For $n > 3$ we obtained the polymeric products $\{[R(H_2O)(HO)Sn(CH_2)_nSn(OH)(H_2O)R](OTf)_2\}_m$, featuring dimeric diorganotin hydroxide units.

Results and Discussion

The addition of triflic acid to suspensions of polymeric α,ω-bis(trimethylsilylmethyloxostannyl)alkanes, $[R(O)Sn(CH_2)_nSn(O)R]_m$ ($R = CH_2SiMe_3$; $n = 3, 4, 8, 10$), in acetonitrile gave clear solutions after stirring for 5 min at room temperature. Removal of the solvent resulted in oligomethylene-bridged diorganotin triflates, $R(OTf)_2Sn(CH_2)_nSn(OTf)_2R$ (**1** ($n = 3$), **2** ($n = 4$), **3** ($n = 8$), **4** ($n = 10$); $R = CH_2SiMe_3$), which were obtained as colorless oils (eq 1).

$$[R(O)Sn(CH_2)_nSn(O)R]_m \xrightarrow[-2H_2O]{4TfOH} [R(OTf)_2Sn(CH_2)_nSn(OTf)_2R] \qquad (1)$$

$$n = 3\ (\mathbf{1}),\ 4\ (\mathbf{2}),\ 8\ (\mathbf{3}),\ 10\ (\mathbf{4})$$

$$R = CH_2SiMe_3$$

Compounds **1**−**4** were characterized by their ^{119}Sn NMR chemical shifts (CD_3CN) of δ −316.3, −332.7, −326.4, and −326.0, respectively, which closely resemble those of the previously reported diorganotin ditriflates, $R_2Sn(OTf)_2$ (R = Et (δ −367.0), *n*-Bu (δ −342.0), C_8H_{17} (δ −343.0)), and are indicative of hexacoordinate tin environments of the type $[R_2Sn(L)_4]^{2+}$ ($L = H_2O$, MeCN).[17]

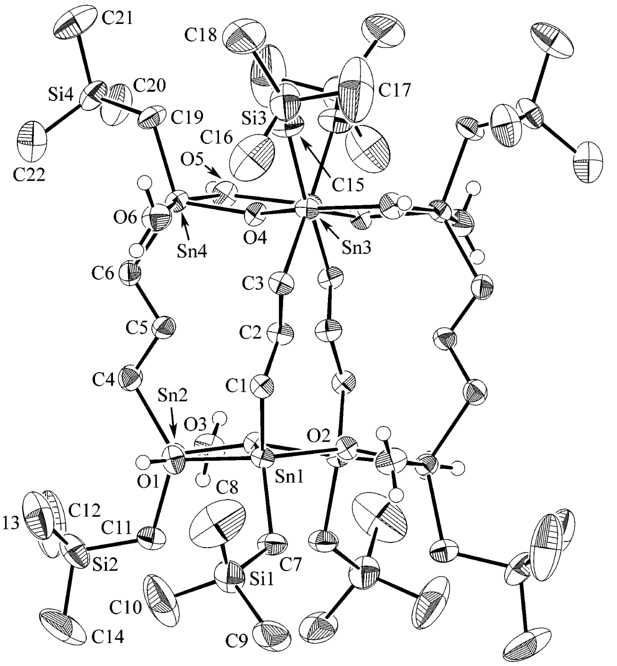


Figure 1. Molecular structure and crystallographic numbering scheme employed for the cation in **5**. For reasons of clarity, only the oxygen-bound hydrogen atoms are shown. Selected geometric parameters (bond distances in Å and angles in deg): $Sn_{endo}-O_{oxo} = 2.058(3)-2.163(3)$, $Sn_{exo}-O_{oxo} = 2.000(3)-2.005(3)$, $Sn-O_{hydroxide} = 2.118(4)-2.178(4)$, $Sn-O_{water} = 2.313(4)-2.324(4)$, $Sn-C_{CH_2} = 2.122(5)-2.128(6)$, $Sn-C_{CH_2Si} = 2.107(6)-2.120(6)$ Å; $O_{axial}-Sn-O_{axial} = 146.52(13)-159.38(15)$°.

Hydrolysis of $R(OTf)_2Sn(CH_2)_3Sn(OTf)_2R$. $R(OTf)_2Sn(CH_2)_3Sn(OTf)_2R$ (**1**; $R = CH_2SiMe_3$) was diluted in a mixture of acetonitrile and chloroform (80:20) and was exposed to moist air for 14 days, upon which colorless crystals of $\{[R(H_2O)Sn(CH_2)_3Sn(OH)R]O\}_4(OTf)_4$ (**5**; $R = CH_2SiMe_3$) were obtained in good yield (eq 2).

$$\underset{\mathbf{1}}{R(OTf)_2Sn(CH_2)_3Sn(OTf)_2R} \xrightarrow[-3TfOH\ (hydrated)]{moist\ air} \qquad (2)$$

$$\underset{\mathbf{5}}{{}^1/_4\{[R(HO)Sn(CH_2)_3Sn(H_2O)R]O\}_4(OTf)_4}$$

$$R = CH_2SiMe_3$$

The molecular structure of the tetravalent cation in **5** is shown in Figure 1, and selected geometric parameters are included in the figure caption. The cation comprises an octanuclear diorganotin cluster consisting of two dimeric tetraorganodistannoxane layers linked by four trimethylene spacers. There is molecular symmetry in the cation such that a crystallographic 2-fold axis runs through both Sn_4O_6 faces of the approximately rectangular box. Each tetraorganodistannoxane layer features a central Sn_2O_2 core with links to exocyclic tin atoms afforded by the two oxo groups of the central Sn_2O_2 core, giving μ_3-oxygen, and two hydroxides. The water molecules occupy terminal positions, and the remaining bonds to the tin atoms are to carbon atoms, so that the coordination geometries are distorted trigonal bipyramidal with oxygen atoms in the axial positions in each case. As can be seen from Figure 1, the tin and

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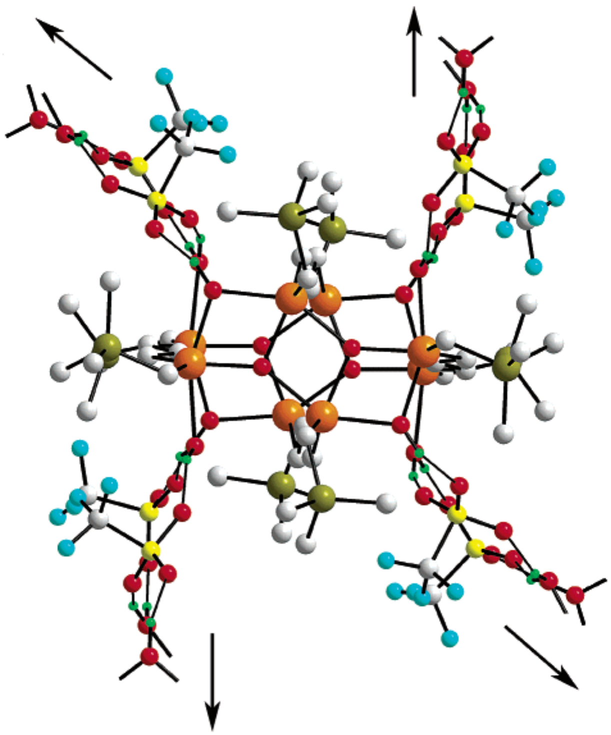
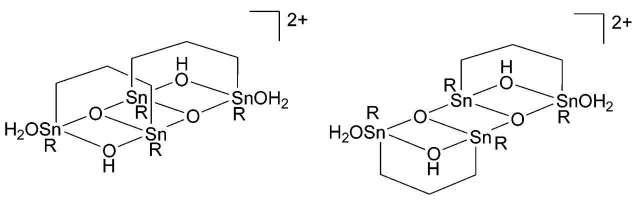


Figure 2. Supramolecular association between cationic clusters in **5** mediated by hydrogen-bonding interactions viewed normal to (001).

oxygen atoms of each of the tetraorganodistannoxane layers are effectively in a plane, and the approximate separation between the two planes is 5.9 Å. The two Sn_4O_6 faces are not superimposable, as there is a twist angle of approximately 16° between them; this can be seen from Figure 2. In the lattice there are substantial interactions (see the Supporting Information) between the cations and the triflate counterions that are facilitated by hydrogen-bonding interactions. Each of the hydroxide- and water-bound hydrogen atoms is involved in a hydrogen bond interaction. In the same way, each triflate oxygen participates in hydrogen bonding. Pairs of triflate anions straddle each of the $Sn(CH_2)_3Sn$ edges, forming three interactions. Thus, along each edge, the water molecule bridges two triflates and one of the triflates also forms a hydrogen bond to the hydroxide. In this way there are a total of eight triflate molecules associated with each Sn_8 cluster, implying that the triflates bridge neighboring clusters. Indeed, this is the case, and because the tops of the boxes are occupied by hydrophobic groups, the ions are associated into layers that are separated by hydrophobic interactions. In other words, the crystal structure can be thought of as being comprised of columns of Sn_8 clusters, with each cluster separated by hydrophobic interactions. In turn, the adjacent columns are connected via the triflate anions, as represented in Figure 2. The key links between adjacent clusters are afforded by two coordinated water molecules that are linked via two triflate anions, resulting in the formation of a 12-membered [$\cdots$H−O−H$\cdots$O−S−O$\cdots$]$_2$ ring. Each of the two remaining oxygen atoms of the triflates hydrogen bonds to the hydroxide.

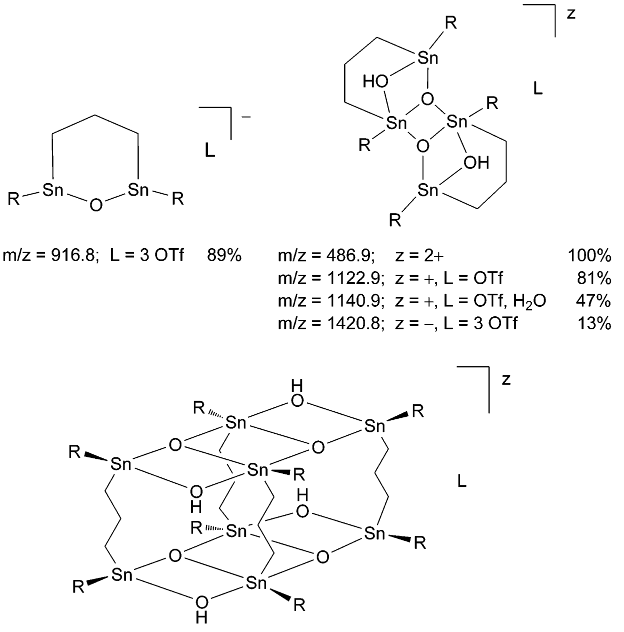
The IR spectrum (KBr) of **5** shows two absorptions at 3250 and 3365 cm^{-1}, which were assigned to the hydroxide group and the coordinated water molecules, respectively. Compound **5** is readily soluble in polar solvents. The ^{119}Sn NMR spectrum (CD_3CN) of an analytically pure sample of **5** shows two signals of equal intensity at δ −119.0 and −128.5 (total integral 64%) that were assigned to the exo- and endocyclic tin sites present in the double-ladder structure. In addition, two pairs of signals, each of equal intensity, are observed at δ −110.0 and −152.0 (total integral 9%) and at δ −115.8 and −126.5 (total 23%) and are tentatively assigned to two dimeric tetraorganodistannoxane isomers,[25,29−30] *cis*-{[R(H_2O)Sn(CH_2)$_3$Sn(OH)R]O}$_2$(OTf)$_2$ (**5a**; R = CH_2SiMe_3) and *trans*-{[R(H_2O)Sn(CH_2)$_3$Sn(OH)R]O}$_2$(OTf)$_2$ (**5b**; R = CH_2SiMe_3) (Chart 2). The driving force is not only the entropy gain in going from one particle to two particles but also the decrease in energy associated with charge separation in going from a tetracation to two dicationic species.

Chart 2



5a **5b**

Chart 3



m/z = 916.8; L = 3 OTf 89%

m/z = 486.9; z = 2+ 100%
m/z = 1122.9; z = +, L = OTf 81%
m/z = 1140.9; z = +, L = OTf, H_2O 47%
m/z = 1420.8; z = −, L = 3 OTf 13%

m/z = 2394.8; z = +, L = 3 OTf 15%
m/z = 2691.9; z = −, L = 5 OTf 16%

This assignment is in agreement with electrospray mass spectrometry. In the positive mode, the ES MS spectrum of **5** is comparatively simple. The most intense peak at *m/z* 486.9 (100%) is assigned to the doubly charged species [$^1/_2$**5** − $2H_2O$ − 2OTf]$^{2+}$. The peaks at *m/z* 1122.9 (81%), 1140.9 (47%), and 2394.8 (15%) are assigned to the cations [$^1/_2$**5** − $2H_2O$ − OTf]$^+$, [$^1/_2$**5** − H_2O − OTf]$^+$, and [**5** − $4H_2O$ − OTf]$^+$, respectively (Chart 3). In the negative mode, the ES MS spectrum of **5** exhibits an intense peak at *m/z* 916.8 (89%) and two peaks of low intensity at *m/z* 1420.8 (13%) and *m/z* 2691.9 (16%), which are assigned to the anions [$^1/_4$**5** − H_2O − OH + 2OTf]$^-$, [$^1/_2$**5** − $2H_2O$ + OTf]$^-$ and [**5** − $4H_2O$ + OTf]$^-$, respectively (Chart 3).

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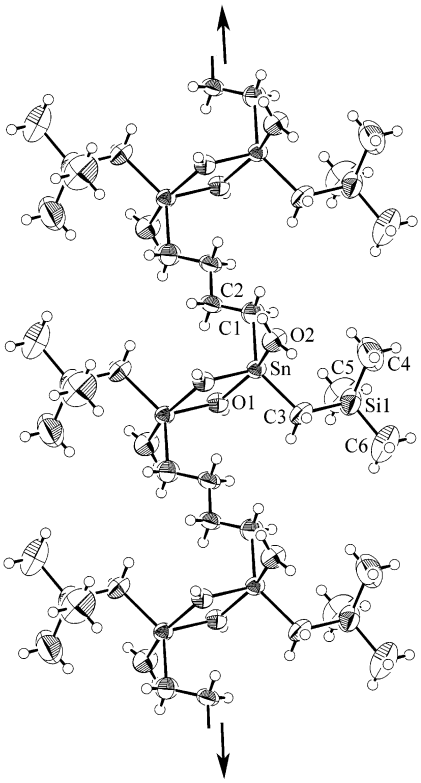

Figure 3. Polymeric structure and crystallographic numbering scheme employed for the cation in **6**·$2H_2O$.

Hydrolysis of $R(OTf)_2Sn(CH_2)_nSn(OTf)_2R$ (n = 4, 8, 10). $R(OTf)_2Sn(CH_2)_nSn(OTf)_2R$ species (n = 4 (**2**), 8 (**3**), 10 (**4**)) were exposed to air moisture in a mixture of acetonitrile and chloroform (80:20) to provide colorless precipitates of $\{R(H_2O)(HO)Sn(CH_2)_nSn(OH)(H_2O)R](OTf)_2\}_m$ (n = 4 (**6**), 8 (**7**), 10 (**8**)) (eq 3).

$$\underset{n = 4\ (\mathbf{2}),\ 8\ (\mathbf{3}),\ 10\ (\mathbf{4})}{R(OTf)_2Sn(CH_2)_nSn(OTf)_2R} \xrightarrow[-3\text{TfOH (hydrated)}]{\text{moist air}} \qquad (3)$$

$$\underset{n = 4\ (\mathbf{6}),\ 8\ (\mathbf{7}),\ 10\ (\mathbf{8})}{(1/m)\{[R(H_2O)(HO)Sn(CH_2)_nSn(OH)(H_2O)R](OTf)_2\}_m}$$

$$R = CH_2SiMe_3$$

All attempts to obtain good-quality crystals of **6**−**8** failed. However, a preliminary analysis was conducted on a crystal of **6**·$2H_2O$. This analysis is far from ideal but establishes the molecular connectivity unambiguously and provides vital information about the composition of **6**−**8**. The crystallographic asymmetric unit of **6**·$2H_2O$ comprises half the dication $[R(H_2O)(HO)Sn(CH_2)_4Sn(OH)(H_2O)R]^{2+}$, one triflate, and a water molecule of crystallization. The structure is constructed about a centrosymmetric Sn_2O_2 core (Sn−O1 = 2.179(8) and 2.024(9) Å). These are linked to translationally related Sn_2O_2 cores via the tetramethylene links (Sn−C1 = 2.115(14) Å), which are also disposed about a center of inversion. In this way a linear polymer is established as illustrated in Figure 3. The coordination geometry is completed by a CH_2SiMe_3 group (Sn−C3 2.098(12) Å) and a water molecule (Sn−O2 = 2.250(9) Å) so that the tin atom shows a trigonal-bipyramidal configuration with the O1 and O2 atoms occupying the axial positions (O−Sn−O is 156.3(4)°). As for the structure of **5**, there are extensive hydrogen-bonding interactions operating in the crystal lattice of **6**·$2H_2O$.

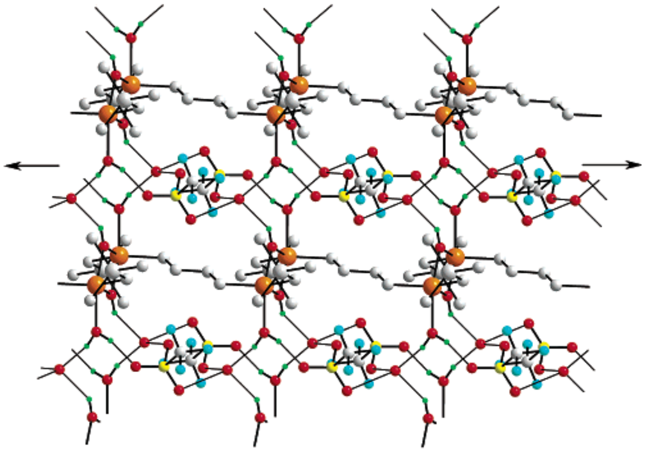

Figure 4. Supramolecular association between the cationic polymeric chains in **6**·$2H_2O$ mediated by hydrogen-bonding interactions viewed down the *z* axis.

Each coordinated water molecule forms two interactions, one to the lattice water and the other to one of the triflate oxygen atoms. The hydroxide also forms a hydrogen bond with a lattice water molecule. Finally, the lattice water forms two donor interactions, one with each of the remaining triflate oxygen atoms, derived from two different triflates, so that all potential donor and acceptor sites are utilized in the hydrogen-bond network in the lattice of **6**·$2H_2O$. The hydrogen bonds serve to connect adjacent cationic rows, as can be seen from the view shown in Figure 4. The links between the polymeric chains are provided by the association between facing pairs of coordinated water molecules and hydroxides that are linked via two lattice water molecules, resulting in the formation of 12-membered $[H_{hydroxide}\cdots O_{water}\cdots H-O-Sn-O_{hydroxide}-]_2$ rings. The second hydrogen of the coordinated water molecule links a triflate. The remaining hydrogen bonds described above serve to stabilize the anionic layer. Thus, the structure may be described as comprising alternating layers of cations and anions.

The IR spectrum (KBr) of **6** reveals two absorptions at 3233 and 3334 cm^{-1}, which were assigned to the hydroxy group and the coordinating water molecules, respectively. The ^{119}Sn NMR spectrum (CD_3CN) of an analytically pure sample of **6** shows two signals at δ −165.5 ppm (broad, integral 26%) and −185.7 ppm (sharp, integral 74%), consistent with tetracoordinated tin centers. The ^{119}Sn NMR spectrum of a hydrated sample (**6**·$2H_2O$) reveals the same signals, indicating that the complex dissociates to give **6** and two water molecules in solution. The electrospray mass spectrum (MeCN) of **6** in the positive mode is comparatively simple. The predominant peaks at *m*/*z* 632.9 (100%) and *m*/*z* 1432.9 (56%) are assigned to species with two and four tin atoms, respectively, and are related to **6** by dehydration; proposed structures of these species are shown in Chart 4.

Attempts to obtain single crystals of **7** and **8** failed. The IR spectra of **7** and **8** (KBr) reveal two absorptions

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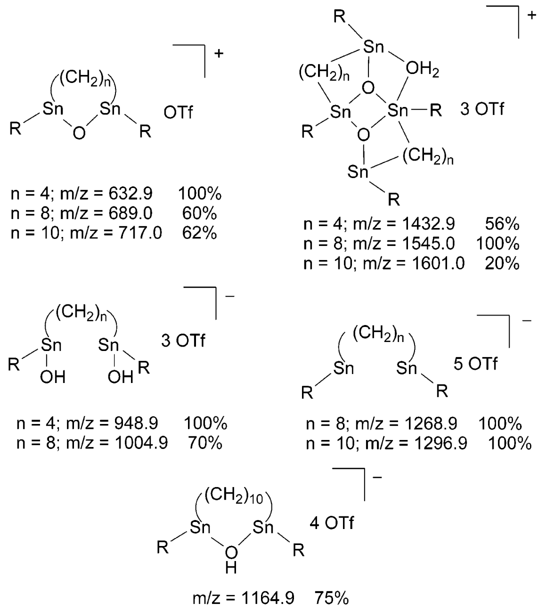
Chart 4



at 3215/3364 and 3225/3354 cm^{-1}, respectively, which are assigned to hydroxy groups and coordinating water molecules.

The ^{119}Sn NMR spectra (CD_3CN) of analytically pure samples of **7** and **8** each show two signals at δ −166.6 ppm (broad, integral 39%)/−170.5 ppm (broad, integral 61%) and at δ −132.0 ppm (broad, integral 5%)/−178.2 ppm (broad, integral 95%), respectively. The electrospray mass spectra of **7** and **8** show peaks analogous to those of **6** (Chart 4).

We anticipate that these new three-dimensional organotin−oxo clusters will open new opportunities in selective Lewis acid catalysis.

Experimental Section

All solvents were dried and purified by standard procedures. The polymeric α,ω-bis(trimethylsilylmethyloxostannyl)alkanes $[R(O)Sn(CH_2)_nSn(O)R]_m$ ($R = CH_2SiMe_3$; $n = 3, 4, 8, 10$) were prepared according to a previously disclosed procedure.[19,21,28] The NMR spectra were recorded using a Varian 300 Unity Plus (^1H, ^{13}C) and a JEOL-GX 270 spectrometer (^{119}Sn) and were referenced to $SiMe_4$ (^1H, ^{13}C) and $SnMe_4$ (^{119}Sn). Uncorrected melting points were determined on a Reichert hot stage. The IR spectra were recorded using a BioRad FTIR spectrophotometer. Microanalysis was performed by CMAS, Belmont, Australia. The ESMS spectrum was obtained with a Platform II single-quadrupole mass spectrometer (Micromass, Altrincham, U.K.) 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 vaporization nozzle of the electrospray ion source at a flow rate of 10 μL min^{-1}. Nitrogen was used as both a drying gas and for nebulization with flow rates of approximately 200 and 20 mL min^{-1}, respectively. Pressure in the mass analyzer region was usually about 4×10^{-5} mbar. Typically 10 signal averaged spectra were collected.

Synthesis of $Me_3SiCH_2(OTf)_2Sn(CH_2)_nSn(OTf)_2CH_2SiMe_3$ (n = 3, 4, 8, 10). A suspension of $[(Me_3SiCH_2)(O)Sn(CH_2)_nSn(O)(CH_2SiMe_3)]_m$ (1.03 mmol, 0.50 g for $n = 3$, 0.51 g for $n = 4$, 0.57 g for $n = 8$, 0.60 g for $n = 10$) and TfOH (0.62 g, 4.16 mmol) in acetonitrile (80 mL) was stirred at room temperature for 12 h. Removal of solvent in vacuo yielded $Me_3SiCH_2(TfO)_2Sn(CH_2)_nSn(TfO)_2CH_2SiMe_3$ (n = 3 (**1**), 4 (**2**), 8 (**3**), 10 (**4**)) as pale yellow oils.

^{119}Sn NMR: δ −316.3 (**1**), −332.7 (**2**), −326.4 (**3**), −326.0 (**4**).

Hydrolysis of $Me_3SiCH_2(OTf)_2Sn(CH_2)_nSn(OTf)_2CH_2SiMe_3$ (n = 3, 4, 8, 10). A sample of **1**−**4** in acetonitrile/chloroform (80:20) was exposed to air moisture to give $\{[(Me_3SiCH_2)(H_2O)Sn(CH_2)_3Sn(OH)(CH_2SiMe_3)]O\}_4(OTf)_4$ (**5**) and $\{[(Me_3SiCH_2)(HO)(H_2O)Sn(CH_2)_nSn(OH)(H_2O)(CH_2SiMe_3)](OTf)_2\}_m$ ($n = 4$ (**6**), $n = 8$ (**7**), $n = 10$ (**8**)) as colorless solids.

5: mp 193−195 °C; ^{119}Sn NMR δ −110.0 (integral 5%), −115.8 (integral 13%), −119.0 (integral 30%), −126.5 (integral 10%), −128.5 (integral 34%), −152.0 (integral 4%); IR (KBr) ν(OH) 3250.0, 3365.3 cm^{-1}. Anal. Calcd for $C_{48}H_{124}F_{12}S_4O_{24}Si_8Sn_8$ (2616.30): C, 22.0; H, 4.8. Found: C, 22.3; H, 4.8.

6: mp 188−190 °C; ^{119}Sn NMR δ −166.5 (integral 26%), −185.7 (integral 74%); IR (KBr) ν(OH) 3233.3, 3334.1 cm^{-1}. Anal. Calcd for $C_{14}H_{40}F_6S_2O_{12}Si_2Sn_2$ (872.22): C, 19.3; H, 4.6. Found: C, 18.9; H, 4.8.

7: mp 150−152 °C; ^{119}Sn NMR δ −166.6 (integral 39%), −170.5 (integral 61%); IR (KBr) ν(OH) 3245.6, 3363.8 cm^{-1}. Anal. Calcd for $C_{18}H_{48}F_6S_2O_{12}Si_2Sn_2$ (928.33): C, 23.3; H, 5.2. Found: C, 23.8; H, 5.6.

8: mp 145−148 °C; ^{119}Sn NMR δ −132.0 (integral 5%), −178.2 (integral 95%); IR (KBr) ν(OH) 3225.0, 3353.8 cm^{-1}. Anal. Calcd for $C_{20}H_{52}F_6S_2O_{12}Si_2Sn_2$ (956.39): C, 25.1; H, 5.5. Found: C, 25.6; H, 6.0.

Crystallography. Single crystals of **5** suitable for X-ray analysis were obtained by the slow evaporation of an acetonitrile/chloroform (80:20) solution containing compound **1**. Intensity data for a colorless crystal were measured at 218 K on a Bruker AXS SMART CCD using Mo Kα radiation so that $\theta_{max} = 30.0°$. The structure was solved by heavy-atom methods[32] and refined (anisotropic displacement parameters, H atoms in their calculated positions, and the weighting scheme $w = 1/[\sigma^2(F_o^2) + 0.055P^2 + 24.6368P]$, where $P = (F_o^2 + 2F_c^2)/3$) on F^2 with SHELXL-97.[33] The absolute structure was determined on the basis of differences in Friedel pairs included in the data set.[34] The molecular structure (ORTEP,[35] 50% displacement parameters) is shown in Figure 1 and unit cell contents, with arbitrary spheres, in Figure 2.[36] Data manipulation was performed using teXsan.[37]

Crystal data: $C_{48}H_{124}F_{12}O_{24}S_4Si_8Sn_8$, $M_r = 2615.95$, orthorhombic, $Fdd2$, $a = 33.4940(13)$ Å, $b = 37.0059(15)$ Å, $c = 18.4293(7)$ Å, $V = 22842.7(15)$ Å^3, $Z = 8$, $D_x = 1.521$, $F(000) = 10\,304$, $\mu = 1.944$ mm^{-1}, 14 257 unique data , 12 600 data with $I \geq 2\sigma(I)$, 481 parameters, R(obsd data) = 0.043, R_w(all data) = 0.101, $\rho = 1.53$ e Å^{-3} near Sn4.

Crystals of $\mathbf{6}\cdot 2H_2O$ were grown as above, using compound **2** as the starting material, and subjected to crystallographic analysis. Data were collected at 293 K on a Nonius Kappa CCD for a colorless crystal using Mo Kα radiation so that $\theta_{max} = 27.6°$. The structure was solved and refined as above, using the weighting scheme $w = 1/[\sigma^2(F_o^2) + 0.0645P^2 + 12.3954P]$, where $P = (F_o^2 + 2F_c^2)/3$. The lattice water bound hydrogen atoms were not included. The analysis is not optimal, owing to the poor quality of the crystal and the nonavailability of a low-temperature apparatus.

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Crystal data: $C_7H_{20}F_3O_6SSiSn$, $M_r = 436.07$, triclinic, $P\bar{1}$, $a = 7.9964(16)$ Å, $b = 8.1518(17)$ Å, $c = 14.356(3)$ Å, $\alpha = 73.568(4)°$, $\beta = 81.976(5)°$, $\gamma = 86.270(4)°$, $V = 888.5(3)$ Å^3, $Z = 2$, $D_x = 1.630$, $F(000) = 434$, $\mu = 1.665$ mm^{-1}, 3922 unique data, 3248 data with $I \geq 2\sigma(I)$, 178 parameters, R(obsd data) = 0.098, R_w(all data) = 0.252, $\rho = 1.76$ e Å^{-3} near Sn.

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Supporting Information Available: Further details of the structure determination, including listings of atomic coordinates, bond distances and angles, and thermal parameters. This material is available free of charge via the Internet at http://pubs.acs.org.

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