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Direct Hydrolysis of Hydrated Organotin Cations: Synthesis and Structural Characterization of $\{[n\text{-Bu}_2\text{Sn(OH}_2)(\text{Phen})(\text{O}_3\text{SC}_6\text{H}_3\text{-2,5-Me}_2)]^+[2,5\text{-Me}_2\text{C}_6\text{H}_3\text{SO}_3]^-\}$ (Phen = 1,10-phenanthroline) and $\{[n\text{-Bu}_2\text{Sn}(\mu\text{-OH})(\text{O}_3\text{SC}_6\text{H}_3\text{-2,5-Me}_2)]_2\}_n$

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The reaction of $\{[n\text{-Bu}_2\text{Sn(OH}_2)_4]^{2+}[2,5\text{-Me}_2\text{C}_6\text{H}_3\text{SO}_3^-]_2\}$ (**2**) with 1,10-phenanthroline affords $\{[n\text{-Bu}_2\text{Sn(OH}_2)(\text{Phen})(\text{O}_3\text{SC}_6\text{H}_3\text{-2,5-Me}_2)]^+[2,5\text{-Me}_2\text{C}_6\text{H}_3\text{SO}_3]^-\}$ (**3**) by the displacement of two water molecules by the chelating phenanthroline ligand and one water molecule by a sulfonate ligand. In contrast, **2** undergoes hydrolysis on treatment with pyridine, resulting in the formation of $\{[n\text{-Bu}_2\text{Sn}(\mu\text{-OH})(\text{O}_3\text{SC}_6\text{H}_3\text{-2,5-Me}_2)]_2\}_n$ (**4**). Formation of **4** also occurs in the reaction of **3** with pyridine as well as in a 1:1 reaction of $[n\text{-Bu}_2\text{SnO}]_n$ with $2,5\text{-Me}_2\text{C}_6\text{H}_3\text{SO}_3\text{H}\cdot 2\text{H}_2\text{O}$. The molecular structure of **3** contains a six-coordinate tin with a coordination environment comprising the chelating phenanthroline ligands, two butyl substituents, one water molecule, and one sulfonate ligand. Extensive hydrogen-bonding interactions (O−H- - -O, C−H- - -O, and O- - -π) in the crystal structure result in the formation of a three-dimensional supramolecular architecture for **3**. The crystal structure of **4** reveals that it is a two-dimensional coordination polymer. The basic repeat unit of the coordination polymer contains a $[\text{Sn}(\mu\text{-OH})]_2$ distannoxane ring. Anisobidentate coordination action of the sulfonate ligand results in the generation of 20-membered macrocycles, which are linked to each other to form the two-dimensional coordination polymer network.

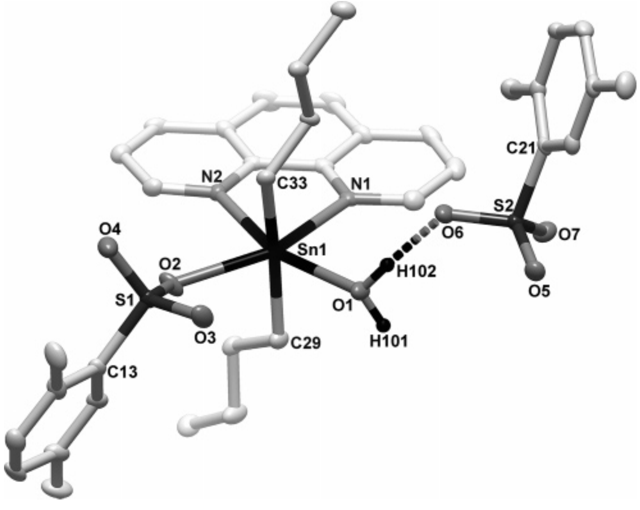

Figure 1. Molecular structure of **3** shown at the 50% ellipsoidal probability level. One of the sulfonate anions is bound to tin, while the other is involved in a O−H- - -O hydrogen bonding with the coordinated water proton. All the hydrogen atoms (except those of the coordinated water) have been removed for the sake of clarity.

Introduction

Organotin oxides, hydroxides, and oxide-hydroxides are the hydrolysis products of organotin halides and serve as important precursors for the preparation of a large variety of organostannoxane assemblies.[1] Unlike in the case of organosilicon compounds, the hydrolysis of organotin halides has been speculated to occur through the intermediacy of hydrated organotin cations such as $[\text{R}_2\text{Sn(OH}_2)_4]^{2+}$ and analogous mono- or triorgano compounds.[2] Our recent report on synthesis and structural characterization of $\{[n\text{-Bu}_2\text{Sn(OH}_2)_4]^{2+}[2,5\text{-Me}_2\text{C}_6\text{H}_3\text{-SO}_3^-]_2\}$ (**2**)[3a] and $\{[n\text{-Bu}_2\text{Sn(OH}_2)_3\text{-}[\mu\text{-L}]\text{-}n\text{-Bu}_2\text{Sn(OH}_2)_3]^{2+}\text{-}[\text{L}]^{2-}\}$ ($\text{L} = 1,5\text{-C}_6\text{H}_{10}(\text{SO}_3^-)_2$)[3b] lends credence to the existence of hydrated organotin cations. Prior to our work only one such example, viz., $\{[\text{Me}_2\text{Sn(OH}_2)_4]^{2+}[\text{X}^-]_2\}$ (X^- = 1,1,3,3-tetraoxo-1,3,2-benzodithiazide), was known that was structurally characterized.[4a] Subsequently, compounds such as $\{[\text{R}_2\text{Sn(OH}_2)_2(\text{OPPh}_3)_2]^{2+}[\text{CF}_3\text{SO}_3^-]_2\}$ (R = Me, *n*-Bu) were synthesized and characterized.[4b] The availability of hydrated organotin cations gives an opportunity to examine if indeed such compounds can serve as precursors for direct hydrolysis to afford products containing Sn−OH or Sn−O bonds. In this context it may be mentioned that the four-membered distannoxane rings $[\text{Sn}_2(\text{OH})_2]$ and $[\text{Sn}_2\text{O}_2]$ containing bridging hydroxide and oxide ligands, respectively, are ubiquitous building blocks of organostannoxanes.[1] But in all cases such building blocks are formed in situ in reactions involving organotin oxides, hydroxides, or

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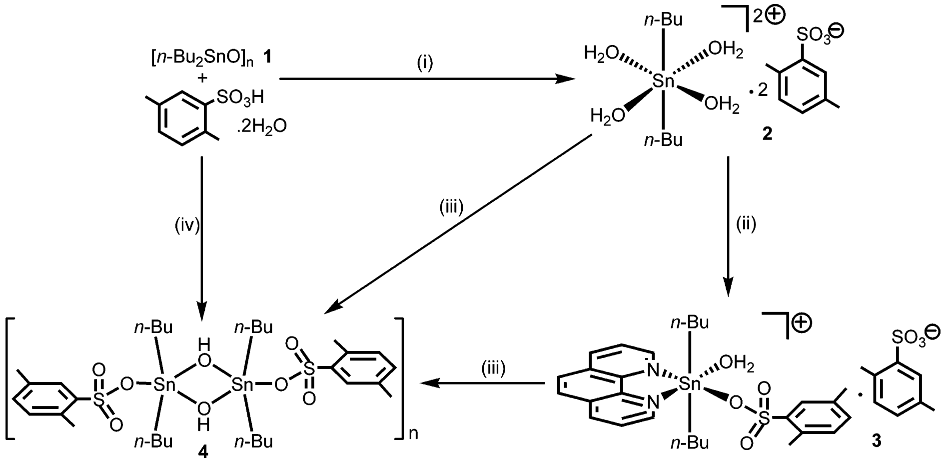
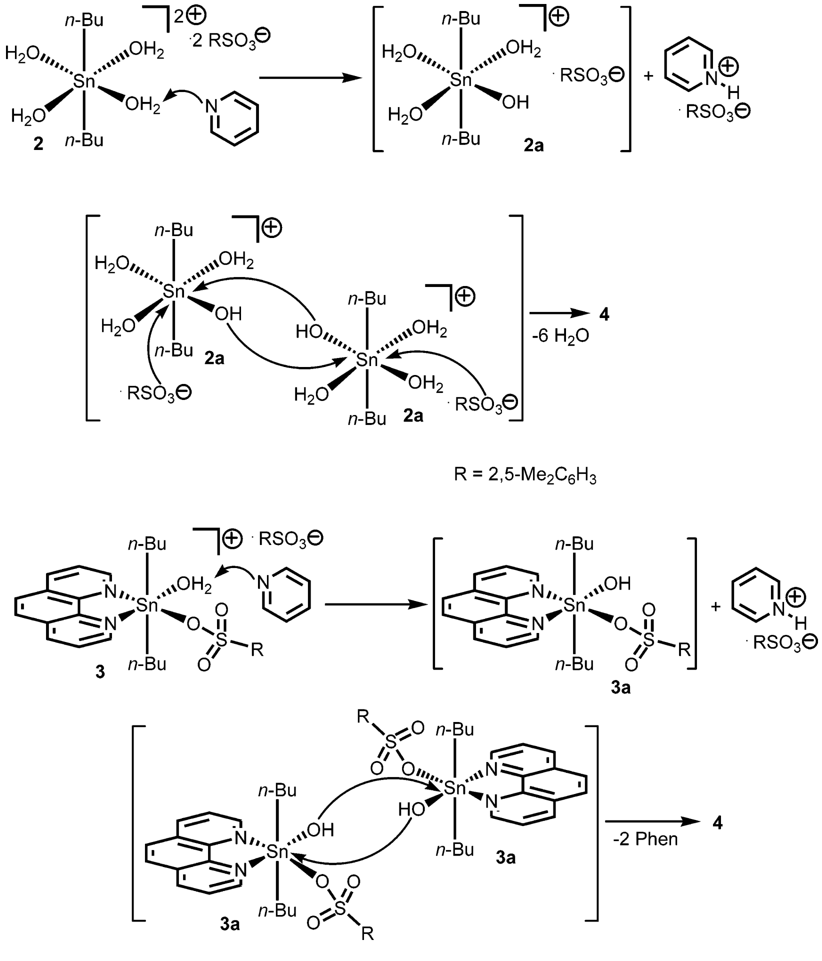
Scheme 1. Synthesis of 2−4[a]



[a] (i) 1:2, toluene, reflux, 8 h; (ii) 1,10-phenanthroline, toluene, 60 °C, 15 min; (iii) pyridine, toluene, 60 °C, overnight; (iv) 1:1, toluene, reflux, 8 h.

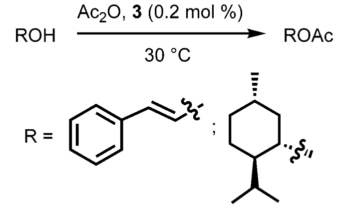
Scheme 2. Possible Formation of 4 from 2 and 3 by Reacting with Pyridine



R = 2,5-$Me_2C_6H_3$

oxide-hydroxides with protic acids.[1] Herein we provide the first example of hydrolysis of organotin cation to organotin hydroxide. Accordingly we report the synthesis and characterization of $\{[n\text{-}Bu_2Sn(OH_2)(Phen)(O_3SC_6H_3\text{-}2,5\text{-}Me_2)]^+[2,5\text{-}Me_2C_6H_3SO_3]^-\}$ (Phen = 1,10-phenanthroline) (**3**) and $\{[n\text{-}Bu_2Sn(\mu\text{-}OH)(O_3SC_6H_3\text{-}2,5\text{-}Me_2)]_2\}_n$ (**4**).

Scheme 3. Acetylation Reactions of 3



Results and Discussion

Synthesis. The hydrated organotin cation $\{[n\text{-}Bu_2Sn(OH_2)_4]^{2+}\text{-}[2,5\text{-}Me_2C_6H_3SO_3^-]_2\}$ (**2**) can be conveniently synthesized in reasonable yields in a reaction involving $[n\text{-}BuSnO]_n$ (**1**) and $2,5\text{-}Me_2C_6H_3SO_3H{\cdot}2H_2O$ in a 1:2 stoichiometry.[3a] We have

Table 1. Selected Bond Parameters for the Molecular Structure of 3 and 4

compound **3**		compound **4**	
bond distance (Å)	bond angle (deg)	bond distance (Å)	bond angle (deg)
Sn1−O1 2.273(3)	C29−Sn1−C33 165.96(16)	Sn1−O4 2.058(2)	O4−Sn1−O1* 76.41(78)
Sn1−O2 2.283(3)	O1−Sn1−O2 119.11(12)	Sn1−O2 2.341(2)	O4−Sn1−O2 74.80(8)
Sn1−N1 2.332(3)	O1−Sn1−N2 159.21(12)	Sn1−O1* 2.624(2)	O4−Sn1−O4* 69.82(11)
Sn1−N2 2.310(3)	O1−Sn1−N1 87.30(12)	Sn1−O4* 2.112(2)	O1*−Sn1−O2 139.01(68)
Sn1−C29 2.115(4)	O2−Sn1−N2 81.67(11)	Sn1−C9 2.109(3)	O1*−Sn1−O4* 146.19(82)
Sn1−C33 2.118(4)	O2−Sn1−N1 153.21(12)	Sn1−C13 2.121(3)	O2−Sn1−O4* 144.56(8)
S1−O2 1.491(3)	N2−Sn1−N1 71.93(12)	O4−H101 0.740(4)	C9−Sn1−C13 143.04(11)
S1−O3 1.439(3)	Sn1−O2−S1 124.98(17)	S1−O1 1.455(2)	Sn1−O2−S1 124.85(11)
S1−O4 1.439(3)	H101−O1−H102 104.25(54)	S1−O2 1.474(2)	Sn1−O4−Sn1* 110.18(11)
S1−C13 1.778(4)		S1−O3 1.450(2)	
S2−O5 1.449(3)		S1−C1 1.778(3)	
S2−O6 1.465(3)			
S2−O7 1.464(3)			
S2−C21 1.776(4)			
O1−H101 0.877(5)			
O1−H102 0.846(6)			

Table 2. Hydrogen-Bonding Parameters for Compounds 3 and 4

D−H---A	D−H (Å)	H---A (Å)	D---A (Å)	D−H---A (deg)	symmetry
		Compound **3**			
O1−H101- - -O7	0.877(5)	1.784(5)	2.658(5)	174.24(47)	1+*x*, *y*, 1+*z*
O1−H102- - -O6	0.846(6)	1.811(6)	2.655(5)	174.97(61)	1+*x*, *y*, 1+*z*
C6−H6- - -O3	0.931(6)	2.471(4)	3.242(7)	140.24(37)	1+*x*, *y*, *z*
C4−H4- - -O6	0.930(4)	2.697(3)	3.550(6)	152.96(34)	2−*x*, 1−*y*, 2−*z*
C4−H4- - -O5	0.930(4)	2.538(3)	3.384(5)	151.45(29)	2−*x*, 1−*y*, 2−*z*
C3−H3- - -O5	0.929(4)	2.663(3)	3.471(6)	145.75(34)	2−*x*, 1−*y*, 2−*z*
C19−H19C- - -O3	0.960(6)	2.419(4)	3.372(8)	171.73(36)	−1−*x*, −*y*, 1−*z*
		Compound **4**			
O4−H101- - -O3	0.740(4)	2.047(4)	2.731(7)	153.96(39)	0.5+*x*, 0.5−*y*, *z*

shown that **2** and related hydrated organotin cations are effective catalysts for acetylation and transacetylation reactions.[5] The lability of the water molecules of the in situ-generated dication $[R_2Sn(OH_2)_4]^{2+}$ was examined by Beckmann and co-workers, and the compounds $\{[R_2Sn(OH_2)_2(OPPh_3)_2]^{2+}[CF_3SO_3^{-}]_2\}$ (R = Me, *n*-Bu) were isolated by displacement of two coordinated water molecules by two phosphine oxide ligands.[4b] In order to understand the reactivity of **2**, we examined its reaction with the chelating ligand Phen. We were able to isolate the monohydrate derivative $\{[n\text{-}Bu_2Sn(OH_2)(Phen)(O_3SC_6H_3\text{-}2,5\text{-}Me_2)]^{+}\text{-}[2,5\text{-}Me_2C_6H_3SO_3]^{-}\}$ (**3**) in appreciable yields (Scheme 1). It is of interest to note that the formation of **3** is accomplished by replacement of three water molecules: two by the Phen ligand and one by a sulfonate ligand. It may be mentioned that in **2** the four water molecules that are coordinated to tin are involved in an extensive hydrogen-bonding network with the uncoordinated sulfonate ligands to generate a lamellar two-dimensional sheet.[3a] Disruption of this network by removal of two water molecules presumably causes one of the noncoordinating sulfonate ligands of **2** to enter into the coordination sphere of **3**. Because of this, the organotin cation in **3** bears a unit positive charge. The ^{119}Sn NMR of **3** in $CDCl_3$ solution shows a single resonance at −413.5 ppm, confirming the six-coordinate nature of tin. Also, the chemical shift of **3** is consistent with the observation of Otera and co-workers, who have noticed that ^{119}Sn chemical shifts move upfield in the presence of chelating ligands.[6]

In contrast to the above, reaction of **2** with nonchelating pyridine does not proceed by ligand replacement but involves hydrolysis to afford $\{[n\text{-}Bu_2Sn(\mu\text{-}OH)(O_3SC_6H_3\text{-}2,5\text{-}Me_2)]_2\}_n$ (**4**) (Scheme 1). The possible mechanism for the hydrolysis of **2** is shown in Scheme 2. The Lewis acidity of the tin atom renders the coordinated water molecules readily susceptible to proton abstraction. It is reasonable to postulate that pyridine abstracts a proton to afford a tin monohydroxide (**2a**) with the removal of pyridinium sulfonate.[7] The intermediate **2a**, containing the highly nucleophilic −OH group, dimerizes readily to afford **4**, which contains the hydroxide-bridged distannoxane core $[Sn_2(\mu\text{-}OH)_2]$. Dimerization is accompanied by the simultaneous displacement of the remaining six water ligands at the tin centers with a concomitant coordination action of the sulfonate ligand (Scheme 2).

Interestingly, **4** is also generated in two other reactions. First, the direct reaction of **1** with $2,5\text{-}Me_2C_6H_3SO_3H\cdot 2H_2O$ in a 1:1 stoichiometry affords **4** (Scheme 1). This observation is similar to that of Otera and co-workers, who have reported the formation of the dimeric organotin compound $[n\text{-}Bu_2Sn(\mu\text{-}OH)(OH_2)(O_3SCF_3)]_2$ in a 1:1 reaction involving **1** and CF_3SO_3H.[8a] On the other hand, the reaction between **3** and pyridine also yielded **4**, testifying to the stability of the distannoxane, $[Sn_2(\mu\text{-}OH)_2]$, core. The ^{119}Sn NMR of **4** shows two resonances at −167.6 and −258.8 ppm. The upfield signal observed for **4** is similar to that observed for $[n\text{-}Bu_2Sn(\mu\text{-}OH)(OH_2)(O_3SCF_3)]_2$ (−249.7 ppm).[8a] We were unable to isolate any independent chemical species that could be assigned the downfield signal at −167.6 ppm. However, it must noted that solution behavior of organotin hydroxides is complex. Thus, the closely related compound $\{[n\text{-}Bu_2Sn(\mu\text{-}OH)OSO_2Me]_2\}_n$ showed six resonances in its solution ^{119}Sn NMR with chemical shifts ranging from −189.3 to −162.7 ppm.[8c] Further, it has been observed that $[R_2Sn(\mu\text{-}OH)(OSO_2CF_3)(H_2O)]_2$ (R = Et, *n*-Bu, *n*-octyl) showed chemical shifts in the range −205 to −214 ppm in solution. In

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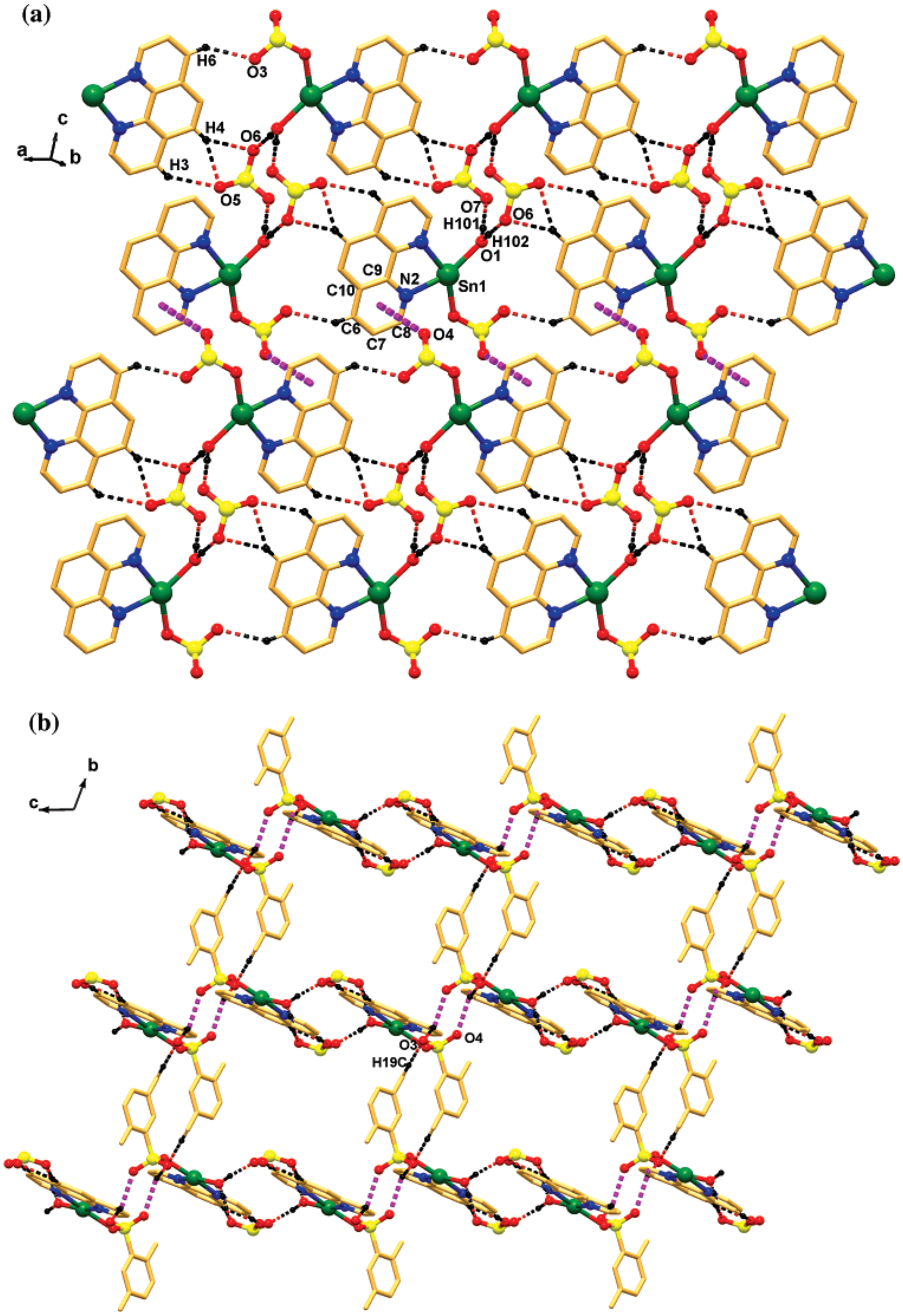

Figure 2. Three-dimensional supramolecular assembly of **3** formed from O−H- - -O, C−H- - -O, and O- - -π interactions. (a) View showing part of the supramolecular assembly of **3**. Bonding parameters for O- - -π interaction: O4- - -π_{cent} 3.293(5) Å [O4- - -C6 3.948(8), O4- - -C7 3.393(7), O4- - -C8 2.973(7), O4- - -C9 3.699(7), O4- - -C10 4.089(8), O4- - -N2 3.172(6) Å]; O4- - -π_{plane} 3.072(6) Å with a tilt angle of ∼24°. (b) View showing the three-dimensional supramolecular architecture along the *a*-axis.

addition, resonances at −140 and −170 ppm were observed.[8b] The latter were assigned to a trinuclear compound that is present in equilibrium with the main product.

In view of the interest in the catalytic activity of organotin cations vis-à-vis acetylation reactions,[3,5,8a,b] we evaluated the role of **3** in the acetylation of cinnamyl alcohol and L-menthol (Scheme 3). We observed that by using only 0.2 mol % of **3** acetylation went to completion (100%) in 75 min (cinnamyl alcohol) and 50 min (L-menthol). On this basis it is possible to conclude that **3** is as effective as other hydrated tin cations for acetylation reactions.[3a,5,8a,b]

Molecular and Crystal Structure of 3. The molecular structure of **3** shows a central tin atom (Sn1) with an octahedral coordination environment (2N, 2C, 2O) comprising two nitrogen atoms (N1 and N2) of the Phen ligand, two oxygen atoms from water (O1) and sulfonate (O2) ligands, and two carbon atoms (C29 and C33) of the two *n*-butyl groups arranged in a trans geometry with respect to each other (Figure 1). The bond angles O1−Sn1−N2, O2−Sn1−N1, and C29−Sn1−C33 are 159.21(12)°, 153.21(12)°, and 165.96(16)°, respectively, indicating the distortion from an ideal octahedral geometry (Table 1). This may be contrasted to the situation found in **2**, where analogous bond angles involving the antipodal ligands and the central tin average to a perfect 180°.[3a] The Sn1−O1 distance (involving the coordinated water) is 2.273(3) Å and is similar to that found in **2** (average Sn−Ow 2.271(3) Å) (Table 1). Analogous distances found in $\{[R_2Sn(OH_2)_2(OPPh_3)_2]^{2+}[CF_3SO_3^-]_2\}$ are not too different (R = *n*-Bu, 2.254(2) Å and R = Me, 2.237(3) Å).[4b] The Sn1−O2 distance (involving the sulfonate ligand) is 2.283(3) Å, which is similar to the Sn1−O1 distance (Table 1). Interestingly the Sn−O distance found in $[n\text{-}Bu_2Sn(\mu\text{-}OH)(OH_2)(O_3SCF_3)]_2$ is 2.622(4) Å.[8a] Similarly in $\{[n\text{-}Bu_2Sn(OH_2)_3\text{-}[\mu\text{-}L]\text{-}n\text{-}Bu_2Sn(OH_2)_3]^{2+}[L]^{2-}\}$ (L = 1,5-$C_6H_{10}(SO_3^-)_2$) the Sn−O distance involving the sulfonate ligand is 2.515(57) Å.[3b] This indicates that in the current instance tin is bound tightly to the sulfonate ligand. The *free* sulfonate counteranion of **3** is involved in an O−H- - -O hydrogen bonding with one of the coordinated water molecules (H102- - -O6) (Figure 1). The hydrogen-bonding parameters are given in Table 2.

The supramolecular architecture of **3** is quite interesting. In **2**, the four water molecules bound to tin are involved in extensive hydrogen bonding with the two sulfonate counteranions to afford a two-dimensional lamellar network.[3a] On the other hand, in **3**, only one water molecule is attached to the tin atom and only one sulfonate is present as a counteranion. This impacts the hydrogen bonding of **3** in the following way. First two molecules of **3** are brought together to form a centrosymmetric dimer as a result of hydrogen bonding (O−H- - -O) between the coordinated water and the sulfonate counteranions. Two of the oxygen atoms (O6 and O7) of each sulfonate anion and both the hydrogen atoms (H101 and H102) of the water (O1) molecule are involved in this hydrogen-bonding interaction to form a 12-membered hydrogen-bonded ring (Figure 2a). The bond parameters involved in this interaction [O1- - -O7 2.658(53) Å, O1−H101- - -O7 174.24(47)°, O1- - -O6 2.655(5) Å, and O1−H102- - -O6 174.96(61)°] indicate that the hydrogen bonds formed are quite strong (Table 2). These parameters are comparable to those found in **2**[3a] and in $\{[n\text{-}Bu_2Sn(OH_2)_3\text{-}[\mu\text{-}L]\text{-}n\text{-}Bu_2Sn(OH_2)_3]^{2+}[L]^{2-}\}$ (L = 1,5-$C_6H_{10}(SO_3^-)_2$).[3b] The hierarchical progression of the supramolecular architecture in **3** occurs first by intermolecular C−H- - -O hydrogen bonding between the dimers to afford a polymeric tape (Figure 2a). The hydrogen atoms involved in this interaction (H3 and H4) belong to the phenanthroline moiety, while the oxygen atoms are derived from the sulfonate anions (O5 and O6) (Figure 2a; Table 2). Interestingly H4 is involved in a bifurcated hydrogen bond (with O5 and O6), while O5 is also involved in a similar interaction (with H3 and H4). The one-dimensional tape is further glued by an additional intermolecular C−H- - -O bond between the oxygen atom of the bound sulfonate ligand (O3) and a hydrogen (H6) of the phenanthroline ligand (Figure 2a; Table 2). Interestingly, these one-dimensional tapes are interconnected through O- - -π interactions involving the Phen ligand (C6−C10, N2) and the sulfonate oxygen (O4) to afford a two-dimensional network (Figure 2a). The distance between the oxygen atom (O4) and the centroid of the Phen ligand is 3.293(5) Å with a tilt angle of ∼24°. The O- - -C distances that are involved in this interaction vary from 2.973(7) Å (O4- - -C8) to 4.089(8) Å (O4- - -C10). These O- - -π interactions are highly directional and belong to the class of *orthogonal multipolar interactions*. The contributions of such orthogonal electrostatic interactions between dipoles in structural chemistry and biology have been reviewed recently.[9a] Very recently we have shown that the crystal structure of Ph_3SnO_2CFc (Fc = ferrocenyl) consists of an interesting supramolecular architecture mediated by multipolar CO_2- - -π interactions.[9b] Finally, the two-dimensional networks described above are further connected through C−H- - -O interactions involving the methyl substituent (H19C of the bound xylyl sulfonate group) and the sulfonate oxygen (O3) to afford a three-dimensional network (Figure 2b; Table 2).

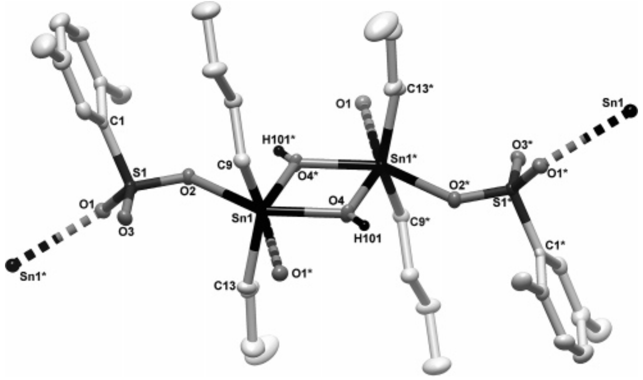

Figure 3. Repeating unit of the coordination polymer **4** shown at the 50% ellipsoidal probability level. All the hydrogen atoms (except that of the bridging hydroxyl group) have been removed.

Crystal Structure of 4. The crystal structure of **4** shows that it is a two-dimensional coordination polymer. The repeat unit of the polymeric network is shown in Figure 3 and consists of a four-membered distannoxane $[Sn_2(\mu\text{-}OH)_2]$ unit where the tin centers are bridged by two hydroxide ligands. Each tin atom is six-coordinate (4O, 2C) in a distorted octahedral geometry. Apart from the two bridging hydroxide ligands (O4 and O4*) each tin (Sn1) also contains one sulfonate ligand (O2) and two *n*-butyl substituents (C9 and C13). Another oxygen of the sulfonate ligand (O1*) belonging to an adjacent repeat unit completes the coordination environment. The Sn−O distances found in the four-membered ring are nearly equal [Sn1−O4 2.112(2) Å and Sn−O4* 2.058(2) Å] (Table 1). These distances are shorter than the Sn−O distance involving the sulfonate ligand (short distance: Sn1−O2 2.341(2) Å; long distance: Sn1−O1* 2.624(2) Å). The Sn−O−Sn bond angle of the four-membered ring is much wider (Sn1−O4-Sn1* 110.18(11)°) than the O−Sn−O (O4−Sn1−O4* 69.82(11)°) angle (Table 1). A comparison of the bond parameters of **4** with those observed in distannoxanes containing sulfonate ligands is as follows. In $[n\text{-}Bu_2Sn(\mu\text{-}OH)(OH_2)(O_3SCF_3)]_2$ the two Sn−O distances of the distannoxane ring are 2.085(3) and 2.147(3) Å, respectively,[8a] while the Sn−O distance involving the sulfonate ligand in **4** is much longer (2.622(4) Å) than found in the present instance. In $[\{n\text{-}Bu_2Sn(\mu\text{-}OH)(O_3SMe)\}_2]_n$, which also forms a two-dimensional coordination polymer, two types of Sn−O distances are found: 2.117(4) (average Sn−(μ-OH) distance) Å; 2.429(4) and 2.492(4) Å (distances involving sulfonate ligand).[8c] In another related example, $\{[n\text{-}Bu_2Sn(\mu\text{-}OH)(O_3SC_6H_2\text{-}2,4,6\text{-}Me_3)]_2\}_n$,[10] the Sn−O distances within the distannoxane ring are equal at 2.199(3) Å, while the Sn−O distance involving the sulfonate ligand is 2.313(3) Å.

The four-membered distannoxane units in **4** are linked to each other by an anisobidentate coordination mode of a sulfonate ligand to afford a two-dimensional grid-like coordination polymer network containing 20-membered $Sn_6S_4O_{10}$ macrocycle repeat units (Figure 4).[8c] Within each macrocycle the hydroxide

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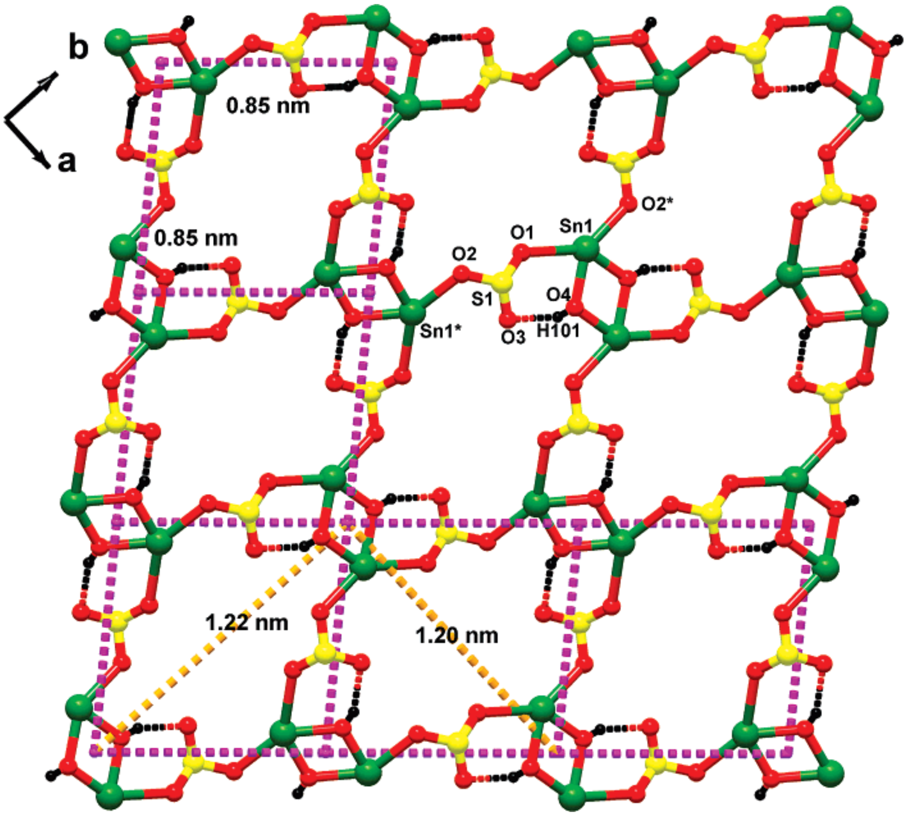

Figure 4. Two-dimensional coordination polymer of **4**. Representation of the two-dimensional polymer is shown in the background in the form of dotted lines.

ligands of the $[Sn(\mu\text{-}OH)]_2$ group are involved in hydrogen bonding (O4−H101- - -O3) with the adjacent sulfonate groups (Figure 4; Table 2). Polymeric networks containing macrocycle repeat units are quite scarce in organotin chemistry, although a few examples have been structurally elucidated in recent years.[8b,c,11] In the current system each macrocycle repeat unit of the two-dimensional coordination polymer is nearly a perfect square, with the dimensions of each side being 8.5 Å (Figure 4). The topological arrangement of the two-dimensional polymeric grids is not flat, however. A side view of the polymer reveals their wavy zigzag corrugated architecture, this being the result of the bridging sulfonate ligands undulating alternately above and below the interconnected macrocycle mean planes.[7] The interlayer distance between two adjacent zigzag layers is 14.5 Å.[7]

Conclusions

Main-group organometallic compounds containing E−OH bonds are of interest in view of their potential as synthons for building heterometallic architectures. Organotin hydroxides are generally obtained by hydrolysis of organotin halides. The availability of discrete hydrated organotin cations opens up the possibility of investigating whether such species can be hydrolyzed deliberately to generate organotin hydroxides. Accordingly we have shown that $\{[n\text{-}Bu_2Sn(OH_2)_4]^{2+}[2,5\text{-}Me_2C_6H_3SO_3^-]_2\}$ (**2**) can be deliberately hydrolyzed by a mild base such as pyridine to afford $\{[n\text{-}Bu_2Sn(\mu\text{-}OH)(O_3SC_6H_3\text{-}2,5\text{-}Me_2)]_2\}_n$ (**4**), which is a two-dimensional coordination polymer containing the four-membered distannoxane ring $[Sn_2(OH)_2]$ as its building unit. Formation of **4** can also be accomplished by a hydrolysis involving the monohydrated compound $\{[n\text{-}Bu_2Sn(OH_2)(Phen)(O_3SC_6H_3\text{-}2,5\text{-}Me_2)]^+[2,5\text{-}Me_2C_6H_3SO_3]^-\}$ (Phen = 1,10-phenanthroline) (**3**). These studies point out the utility of hydrated organotin cations as precursors for organotin hydroxides. We are currently exploring pathways that will allow the isolation of organotin hydroxides where the hydroxide groups are not involved in bridging coordination.

Experimental Section

General Remarks. Solvents were distilled and dried prior to use according to standard procedures. $[n\text{-}Bu_2SnO]_n$, 1,10-phenanthroline (Phen) (Aldrich), L-menthol (Lancaster), cinnamyl alcohol (Fluka), pyridine, and acetic anhydride (sd-fine, India) were purchased and used as such without any further purification. 2,5-$Me_2C_6H_3SO_3H{\cdot}2H_2O$[12] and **2**[3a] were prepared by literature methods. Melting points were measured using a JSGW melting point apparatus and are uncorrected. Elemental analyses were carried out using a Thermoquest CE Instruments model EA/110 CHNS-O elemental analyzer. Infrared spectra were recorded as KBr pellets on a FT-IR Bruker-Vector model. ^1H and ^{119}Sn NMR spectra were obtained on a JEOL-JNM Lambda 400 model spectrometer using $CDCl_3$, CD_3OD, and $(CD_3)_2SO$ solutions with shifts referenced to tetramethylsilane (for ^1H NMR) and tetramethyltin (for ^{119}Sn NMR). ^{119}Sn NMR spectra were recorded under broad-band decoupled conditions.

Synthesis of 3. A suspension of **2** (0.33 g, 5.00 mmol) and Phen (0.09 g, 5.00 mmol) in 10 mL of toluene was stirred gently for 15 min at 60 °C. The solution was filtered and kept for slow

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evaporation. Thick plate-like, colorless crystals appeared after 5 days. Yield: 0.31 g (80%, for isolated crystals). Mp: 136 °C. Anal. Calcd for $C_{36}H_{49}O_7N_2S_2Sn$ (801.6 g) (%): C, 53.94, H, 5.78, N 3.49. Found: C, 53.8, H, 5.65, N, 3.26. IR (KBr, cm^{-1}): 3428 [br, $\nu(H_2O)$], 1254 [s, $\nu(SO_3)$ asym. str.], 1145 [s, $\nu(SO_3)$ assym. str.], 1083 [s, $\nu(SO_3)$ sym. str.], 995 [s, $\nu(SO_3)$ ionic]. ^1H NMR (400 MHz, $CDCl_3$): δ 0.79−0.82 (m, 6H, CH_3), 1.23−1.24 (m, 4H, $SnCH_2$), 1.45−1.54 (m, 8H, CH_2CH_2), 2.20 (s, 3H, Ar−CH_3), 2.51 (s, 3H, Ar−CH_3), 7.05 (m, 2H, Phen C*H*), 8.06 (m, 2H, Phen C*H*), 8.68 (d, 2H, Phen C*H*), 10.0 (d, 2H, Phen C*H*). ^{119}Sn NMR (150 MHz, $CDCl_3$): δ −413.5 (s).

Synthesis of 4. Method A: Pyridine (0.04 mL, 0.51 mmol) was added dropwise to a suspension of **2** under stirring (0.23 g, 0.34 mmol) in 10 mL of toluene, and the contents were stirred overnight at 60 °C. The solution turned turbid. Removal of solvent afforded a solid residue. This was dissolved in methanol, slow evaporation of which afforded colorless block-like crystals. Yield: 0.11 g (71%, isolated crystals).

Method B: A mixture of **1** (0.40 g, 1.6 mmol) and 2,5-$Me_2C_6H_3$-$SO_3H\cdot xH_2O$ (0.30 g, 1.6 mmol) in toluene (60 mL) was heated under reflux for 7 h using Dean−Stark apparatus to remove the water formed in the reaction by azeotropic distillation. A white solid that formed was filtered and dried. Yield: 0.51 g (72%, isolated solid). Crystals of **4** were grown by slow evaporation of its methanolic solution. Mp: 156 °C. Anal. Calcd for $C_{32}H_{56}O_8S_2Sn_2$ (870.3 g) (%): C 44.16, H 6.49. Found: C 43.91, H 6.25. IR (KBr, cm^{-1}): 3392 [br, $\nu(\mu\text{-OH})$], 1259 [s, $\nu(SO_3)$ assym. str.], 1183 [s, $\nu(SO_3)$ assym. str.], 1087 [s, $\nu(SO_3)$ sym. str.], 626 [m, ν(C−S) str.]. ^1H NMR (400 MHz, CD_3OD): δ 0.76−0.92 (m, 6H, CH_3), 1.21−1.28 (m, 4H, $SnCH_2$), 1.31−1.57 (m, 8H, CH_2CH_2), 2.23 (s, 3H, Ar−CH_3), 2.59 (s, Ar−CH_3), 7.08−7.18 (m, 2H, aromatic C*H*), 7.61 (s, 1H, aromatic C*H*). ^{119}Sn NMR (150 MHz, CD_3OD): δ −167.6 (s), −258.8 (s).

Acetylation. Acetylation reactions were carried out according to the procedure reported by us recently.[3a,5]

X-ray Crystallographic Study. The crystal data for compounds **3** and **4** were collected on a Bruker SMART APEX CCD diffractrometer. The SMART software package (version 5.628) was used for collecting data frames, the SAINT software package (version 6.45) for integration of the intensity and scaling, and SADABS for absorption correction. The details pertaining to the data collection and refinement for crystals are as follows. For **3**: size = 0.3 × 0.3 × 0.2 mm^3; triclinic; $P\bar{1}$; a = 10.6541(1) Å, b = 13.1098(2) Å, c = 15.8103(2) Å; α = 102.973(2)°, β = 103.614(2)°, γ = 113.463(2)°; V = 1839.1(4) Å^3; T = 100(2) K; Z = 2; D_{calcd} = 1.447 Mg m^{-3}; θ range 2.10 to 28.32°; 12 330 reflections collected; 8220 independent reflections (R_{int} = 0.0333); R1 = 0.0568, wR2 = 0.1186 [for $I > 2\sigma(I)$]; R1 = 0.0711, wR2 = 0.1263 (for all data); GOF = 1.025. For **4**: size = 0.3 × 0.2 × 0.2 mm^3; monoclinic; $P2(1)/c$; a = 11.938(5) Å, b = 12.140(5) Å, c = 14.522(5) Å; β = 112.103(5)°; V = 1950.0(13) Å^3; T = 153(2) K; Z = 4; D_{calcd} = 1.482 Mg m^{-3}; θ range 4.14 to 25.02°; 9995 reflections collected; 3432 independent reflections (R_{int} = 0.0311); R1 = 0.0285, wR2 = 0.0690 [for $I > 2\sigma(I)$]; R1 = 0.0321, wR2 = 0.0708 (for all data); GOF = 1.047. The structures were solved and refined by full-matrix least-squares on F^2 using the SHELXTL software package.[13] Non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms attached to oxygen atoms of water and hydroxyl groups were located from the difference map, and their positions were refined. All other hydrogen atoms were included in idealized positions, and a riding model was used. CCDC 630934 and 630935 contain the supplementary crystallographic data for this paper.[7] These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (int.) +44-1223/336-033; e-mail: deposit@ccdc.cam.ac.uk]. Figures 1−4 and bonding parameters were obtained from the DIAMOND 3.0 software package.[14]

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Supporting Information Available: IR spectroscopic data for the reaction mixture of **4**, ORTEP plots for compounds **3** and **4**, additional figure for compound **4**, and crystallographic information files (CIF) for compounds **3** and **4**. These materials are available free of charge via the Internet at http://pubs.acs.org.

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