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First Example of a Hydrogen-Bonded Three-Dimensional *Pillared* Structure Involving an Organotin Motif: Synthesis and X-ray Crystal Structures of $\{[^n\mathrm{Bu_2Sn(H_2O)_3(L)Sn(H_2O)_3}{}^n\mathrm{Bu_2}]^{2+}[\mathrm{L}]^{2-}\}\cdot 2\mathrm{MeOH}\cdot 2\mathrm{H_2O}$ and $\{[\mathrm{Ph_3Sn(L)Sn(H_2O)Ph_3}]_n\}\cdot\mathrm{THF}$ (L = 1,5-Naphthalenedisulfonate)

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*Summary: The reaction of a disulfonic acid with $^n\mathrm{Bu_3SnOSn}{}^n\mathrm{Bu_3}$ generates the Sn−alkyl-cleaved dicationic species $\{[^n\mathrm{Bu_2Sn(H_2O)_3(L)Sn(H_2O)_3}{}^n\mathrm{Bu_2}]^{2+}[\mathrm{L}]^{2-}\}\cdot 2\mathrm{MeOH}\cdot 2\mathrm{H_2O}$ (**4**; L = 1,5-naphthalenedisulfonate, 1,5-$\mathrm{C_{10}H_6\text{-}(SO_3)_2}$). The corresponding reaction with $\mathrm{Ph_3SnOSnPh_3}$ leads to the unusual zigzag polymer $\{[\mathrm{Ph_3Sn(L)Sn(H_2O)Ph_3}]_n\}\cdot\mathrm{THF}$ (**5**), which contains an Sn−O motif in the backbone as well as a pendant group.*

There is considerable interest in the use of intermolecular hydrogen-bonding interactions to drive the formation of supramolecular structures.[1] Initial efforts in this regard have been to prove the robustness of synthons and reproducibility of interactions between them. Using such synthons, many two-and three-dimensional structures have been realized in the solid state for organic compounds.[2] Conventionally, in inorganic systems the generation of supramolecular organizations has been through covalent interactions, including ligand−metal coordinate bonds.[3] In recent years the applicability of sulfonate ligands in engaging metal complexes with second-sphere coordination involving hydrogen bonding, leading to the formation of novel supramolecular architectures, has been shown.[4] In view of our interest in organometallic assemblies involving the Sn−O motifs,[5] we have been trying to design molecules that can form extended structures assisted by weak and strong intermolecular hydrogen bonds. Thus, we have recently shown a lamellar layered structure[6a] in $[^n\mathrm{Bu_2Sn(H_2O)_4}]^{2+}[\mathrm{2,5\text{-}Me_2\text{-}C_6H_3SO_3}]^-{}_2$ and supramolecular grids[6b] in $[^n\mathrm{BuSnOCOR}]_6$ (R = ferrocenyl methyl or mesityl groups). No example of a hydrogen-bond-assisted three-dimensional *pillared network*, however, is known to this date for Sn−O assemblies, although there have been a few reports on two- and three-dimensional hydrogen-bonded assemblies.[7] We now report a pillared three-dimensional lamellar structure involving the ditin complex $\{[^n\mathrm{Bu_2Sn(H_2O)_3(L)Sn(H_2O)_3}{}^n\mathrm{Bu_2}]^{2+}[\mathrm{L}]^{2-}\}\cdot 2\mathrm{MeOH}\cdot 2\mathrm{H_2O}$ (**4**; L = 1,5-naphthalenedisulfonate ligand, 1,5-$\mathrm{C_{10}H_6\text{-}(SO_3)_2}$). The formation of this compound involves a Sn−alkyl cleavage reaction. We also report a two-dimensional polymeric network in the crystal structure of $\{[\mathrm{Ph_3Sn(L)Sn(H_2O)Ph_3}]_n\}\cdot\mathrm{THF}$ (**5**). This structure includes both coordinate and hydrogen-bonding interactions.

The reactions of $^n\mathrm{Bu_3SnOSn}{}^n\mathrm{Bu_3}$ and $\mathrm{Ph_3SnOSnPh_3}$ with 1,5-naphthalenedisulfonic acid tetrahydrate lead to two different kinds of products.[8] Thus, the first reaction generates the Sn−butyl-cleaved dication $[^n\mathrm{Bu_2Sn(H_2O)_3(L)Sn(H_2O)_3}{}^n\mathrm{Bu_2}]^{2+}[\mathrm{L}]^{2-}$ (**4**). This product is formed in nearly quantitative yields and contains a ditin unit bridged by naphthalenedisulfonate. The cleavage of the Sn−butyl group to afford **4** in very high yields, as observed in the present instance, is quite unusual. There are only a few scattered reports on Sn−alkyl cleavage reactions, leading to products in poor yields.[9] It must be mentioned that the most common Sn−R cleavage reactions occur with benzyl- and allyltin

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(8) Synthetic details of **4** and **5** are given in Supporting Information.

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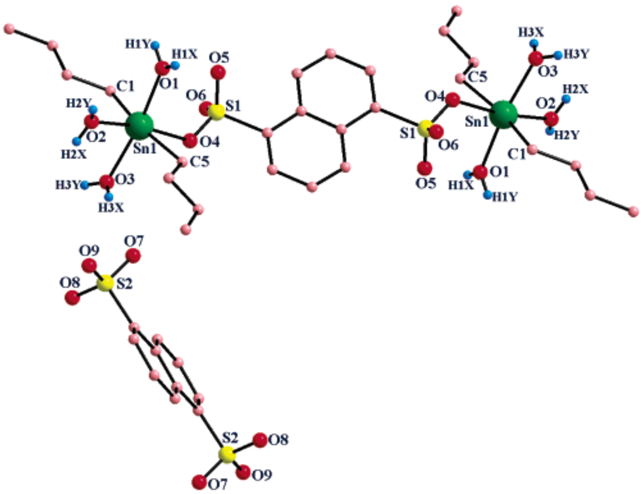

Figure 1. X-ray crystal structure of **4** showing the naphthalenedisulfonate-bridged ditin dication along with the naphthalenedisulfonate dianion. The metric parameters of **4** are given in Table S1 in the Supporting Information.

compounds.[10] The Sn−butyl cleavage reaction occurs in the present instance, presumably because of the stability associated with the formation of the dication.[11] The remaining two *n*-butyl groups on each tin are required to stabilize the positive charge. In the case of $Ph_3SnOSnPh_3$ the phenyl groups remain intact in the product $[Ph_3Sn(L)Sn(H_2O)Ph_3]_n$ (**5**). This may be due to the higher electronegativity of the phenyl moiety, which cannot assist in alleviating the positive charge of the cation. Consequently, the formation of a neutral product is preferred in this reaction.

Compound **4** crystallizes with two molecules of water and methanol. The X-ray crystal structure of **4** shows that the two tin centers have similar coordination geometries (Figure 1).[12] Thus, both have an approximate octahedral environment containing two alkyl groups, three molecules of water, and a sulfonate oxygen. The disposition of the alkyl groups is trans with respect to each other. The metric parameters found in **4** are quite normal, except for the Sn−O bond distances involving the sulfonate oxygens. Thus, the Sn−O4 distance is 2.515(57) Å. This is longer than the normal Sn−O distance of 2.15 Å.[13] The coordinated water molecules and the sulfonates (coordinated and uncoordinated) in **4** provide an ideal platform for a rich inter- and intramolecular O−H···O hydrogen bonding. The overall effect of all the hydrogen-bonding interactions is to generate a three-dimensional structure containing a pillared pattern analogous to those found in the guanidinium−sulfonate (GS) complexes of Ward and coworkers.[14] Other types of pillared structures in organic solids as well as transition-metal phosphonates are known, although in these examples the pillared structures possess various functionalities such as diamines, dicarboxylates, diphosphonates, etc.[15] The extended structure in **4** may be understood by analyzing it in a stepwise manner. Thus, a layered structure may be first visualized. This is formed by the hydrogen bonding of coordinated water molecules (O1, O2, O3) with coordinated (O4, O5, O6) and free (O7, O8, O9) sulfonates. Within the layers the different sheet segments (for example I and II) are glued to each other by the sheet III, which arises as a result of the interactions emanating from free sulfonate with a water (O10) and a molecule of methanol (O11). This leads to a nearly planar sheet (Figure 2a).

The lamellar structure thus formed is taken into the third dimension by the naphthalenedisulfonate units, which act as pillars. Both the coordinated and free sulfonate moieties are involved in the pillaring, as shown in parts b and c of Figure 2. The details of the entire inter- and intramolecular hydrogen bonding observed in **4** are given in the Supporting Information (Table S2). The interlayer separation (distance between two tins in adjacent layers) in **4** is 11.5 Å. The width between the pillars in a given row is 7.1 Å. It is interesting that the interlayer distance obtained in GS structures using 1,5-naphthalenedisulfonate is 6.9 Å.[16] Thus, the use of tin with a definite three-dimensional coordination sphere makes a substantial difference in increasing the interlayer distance.

The crystal structure of **5** is shown in Figure 3.[12] The structure is polymeric, and the repeating unit of the polymer has two five-coordinate tin centers (Figure 3a). One of the sulfonate groups of L acts as a bridge to connect two tins. Thus, O2 is bound to Sn2 while O1 is bound to Sn1. The coordination environment around Sn2 is trigonal bipyramidal. The equatorial positions are taken up by the phenyl groups. The apical positions are occupied by a water molecule (O7) and the sulfonate oxygen (O2). The coordination environment around Sn1 is also similar, except that the fifth coordination is provided by O5 of the disulfonate. This linkage is the crucial one and takes the ditin motif into a zigzag polymeric chain (Figure 3b) which contains a tin backbone along with pendant tin groups.[17] Individual polymeric chains are hydrogen-bonded to each other through the coordinated water (O7) and sulfonate oxygen (O4). This leads to the formation of a two-dimensional network with discrete voids (Figure 3c). In **5** these voids

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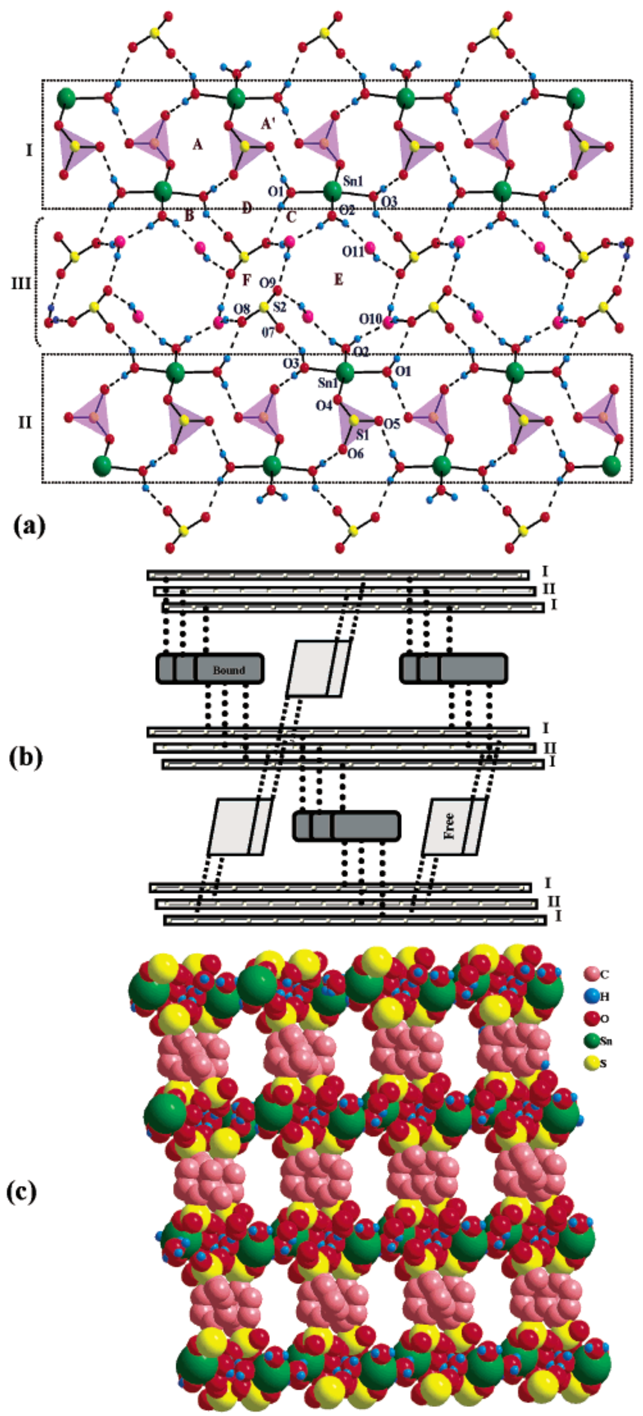

Figure 2. O-H⋯O bond assisted supramolecular assembly of **4.** (a) View of a single layer (along the *b* axis). This layer contains individual sheets (viz. I and II) of tin sulfonates which are connected by free sulfonates and solvents (H_2O and CH_3OH) of crystallization (III). Note the formation of rings A−F as a result of intra- and intermolecular hydrogen bonding in the sheets I−III. The hydrogen-bonding metric parameters are given in Table S2 of the Supporting Information. (b) Schematic representation showing the pillaring of two different layers by free and coordinated sulfonates. Viewing down the pillared structure, the bound and free sulfonates criss-cross each other. (c) Space-filling model of the pillared structure.

are taken up by guest molecules in the form of tetrahydrofuran. The latter are held in the voids because of hydrogen bonding to the coordinated water. It is of

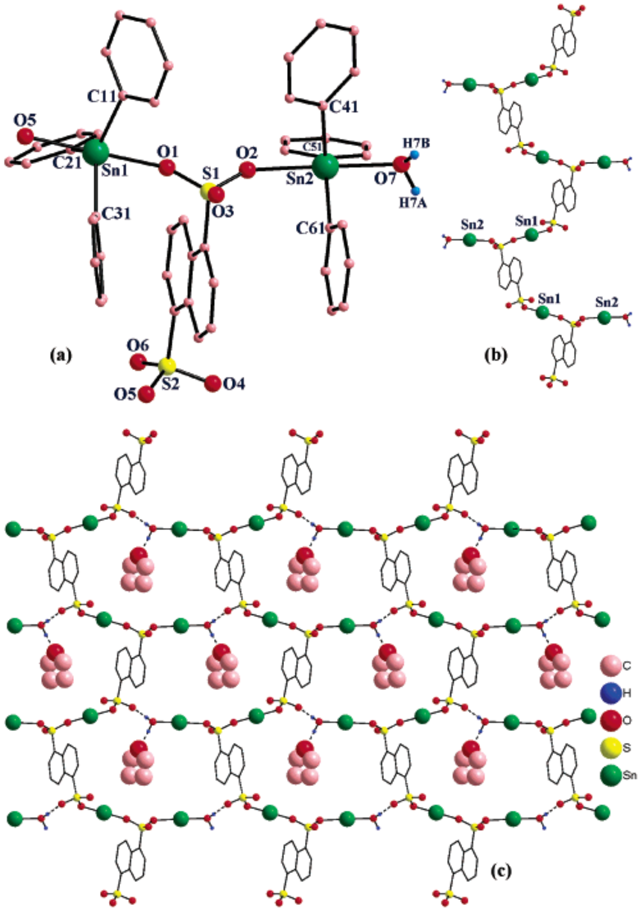

Figure 3. (a) Asymmetric unit of the zigzag polymeric compound **5**. The metric parameters for this compound are given in Table S3 of the Supporting Information. (b) Polymeric chain of **5** showing the pendant Sn−H_2O groups. (c) View of the 2D sheet of **5** along the *c* axis formed by the intermolecular hydrogen bonding. THF molecules are shown in the space-filling model.

interest to note that the O7- - -O4 distance involved in the hydrogen bonding is 2.613(2) Å, which indicates a strong interaction between the two units.

In summary, the interaction between disulfonate ligand and triorganotin precursors has led to the discovery of two unusual structural forms in organotin assemblies. While the reaction with ^{n}Bu$_3$SnOSn^{n}Bu$_3$ generates the Sn−butyl-cleaved ditin dication **4**, the corresponding reaction with $Ph_3SnOSnPh_3$ leads to the unusual zigzag polymer **5**, which contains an Sn−O motif in the backbone as well as a pendant group. Inter- and intramolecular O−H⋯O hydrogen-bonding interactions are present in both **4** and **5** and lead to the formation of three- and two-dimensional structures. Currently we are pursuing these studies further with other examples of di- and trisulfonate ligands.

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Supporting Information Available: Additional figures, scheme, synthetic procedures, and tables containing X-ray data are given in the Suppporting Information. This material is available free of charge via the Internet at http://pubs.acs.org.

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