Communication

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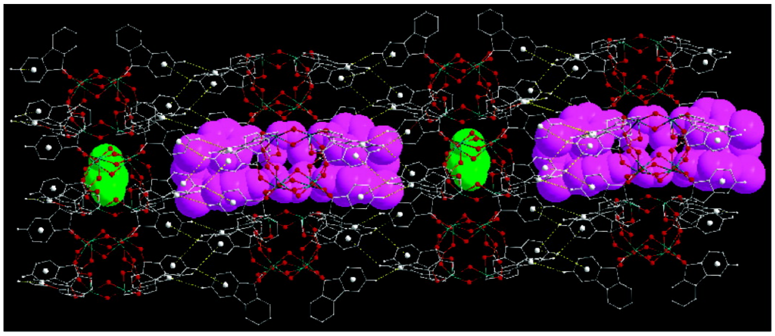

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Alternating Hydrophilic and Hydrophobic Pockets in the Channel Structures of Organostannoxane Prismanes: Preferential Confinement of Guest Molecules

Vadapalli Chandrasekhar,*,† Pakkirisamy Thilagar,† James F. Bickley,‡ and Alexander Steiner‡

Department of Chemistry, Indian Institute of Technology, Kanpur 208 016, India, and Department of Chemistry, University of Liverpool, Liverpool L69 7ZD, U.K.

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Although metal-directed self-assembly of new materials, in general, and porous materials, in particular, is of contemporary interest, the use of organometallic motifs for the preparation of such architectures is still quite rare.[1] Recently, Höpfl and co-workers have reported the formation of a 3D network containing diorganotin units formed by a combination of coordination and hydrogen bonding interactions.[2] The assembly of porous structures by utilizing organostannoxane motifs, although a nascent field, has considerable potential in view of the remarkable structural plasticity of organo-oxotin cages.[3] Herein, we report the synthesis of an unprecedented structural form of a hexanuclear organostannoxane cage whose supramolecular structure, formed by weak and strong hydrogen bonds, shows regular channels and contains alternating hydrophobic and hydrophilic pockets. These channels selectively entrap different types of guest molecules.

The reaction of *n*-BuSn(O)OH with 9-hydroxy-9-fluorenecarboxylic acid in the presence of *p*-iodophenol afforded [{*n*-BuSn(OH)L}$_6$·6H_2O·6ROH·$CHCl_3$] (**2**) in about 70% yield (Scheme). If this reaction is carried out in the absence of phenol, [{*n*-BuSn(OH)L}$_6$·3H_2O·2$CHCl_3$] (**3**) is formed. The molecular structures of **2** and **3** are very similar and contain three {$Sn_2(\mu\text{-}OH)_2$} motifs that are linked to each other by the dianionic tridentate ligand L. Previously known hexaorganostannoxane compounds are present in either a cage-like *drum* or an open *ladder* structure.[3] Compounds **2** and **3** represent the first examples where an oligomer of the basic [Sn_2OH_2] unit has been isolated and characterized.

The ^{119}Sn NMR spectra of compounds **2** and **3** reveal a singlet at −466.6 ppm, suggesting the structural similarity of these compounds as well as the equivalence of the six tin atoms present in each assembly. The ^{119}Sn chemical shifts observed for **2** and **3** are comparable with that observed for organooxotin compounds containing a 5O, 1C coordination environment.[3]

In view of the similarity of the molecular structures of the tin cages **2** and **3**, only the structure of the former is described herein. The details of the X-ray crystal structure of **3** are given in the Supporting Information. Compound **2** crystallizes in the hexagonal $P6_3/m$ (No. 176) space group.[4,5] The asymmetric unit of **2** contains 1/6 of the stannoxane cage [*n*-BuSn(OH)$_2$L] and two water molecules (both of which have 50% occupancy along with one *p*-iodophenol molecule). The molecular structure of **2** consists of two centrosymmetrically related tritin halves (Figure 1a). The three tin centers present in each half of **2** are located in the vertices of an equilateral triangle (Figure 1a). The two halves are joined together (such that the two equilateral triangles perfectly eclipse each other) by means of bridging hydroxyl groups (Figure 1b). This leads to an overall cage where the six tin atoms are present in the vertices of a trigonal prism (Figure 1b). The short edges of the prism are spanned by four-membered $Sn_2(OH)_2$ units (Figure 1b), while the long edge contains a μ-O. The short Sn−Sn edge distance (3.32 Å) is quite comparable with the Sn−Sn single bond (2.95 Å) found in tin clusters.[6] Two types of Sn−O distances are found in the prism edge; a short Sn−O distance of 2.15(3) Å and long Sn−O distance of 3.44(2) Å. In contrast to the known organooxotin cages, such as the drum,[3] the hexatin cage **2** does not have a capping μ_3-O and, also, is not built from Sn_2O_2 units.

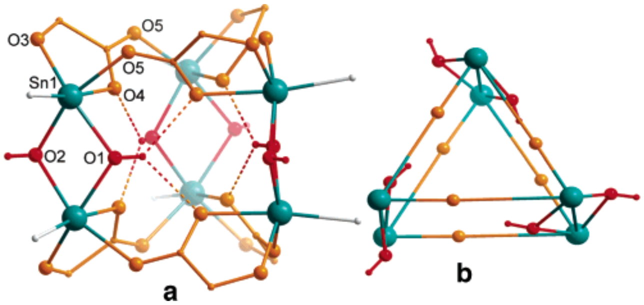
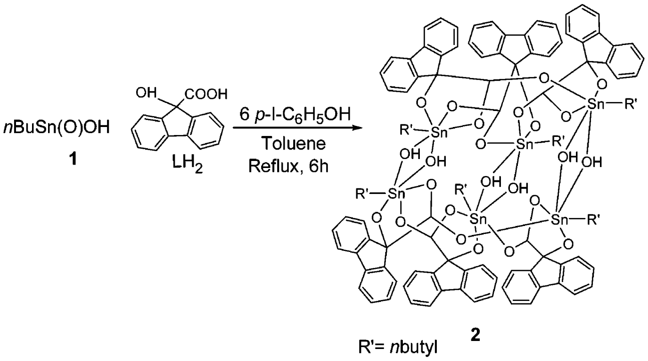


Figure 1. (a) Core structure of **2**. Only the α-carbon of the butyl groups is shown. The two six-membered rings of the fluorenyl groups are omitted for clarity. Among the six Sn−OH motifs present in **2**, three are inwardly directed and form bifurcated intramolecular hydrogen bonds with the carboxylate oxygen atoms. (b) The prismatic arrangement of tin atoms in **2**. Color scheme: hydroxyl groups are shown in red, and the carboxylate ligands are in orange. Tin atoms are shown in green.

The three discrete $Sn_2(OH)_2$ units in **2** are stitched together by six tridentate dianionic ligands. This is accomplished in the following way. The carboxylate part of the ligand bridges two adjacent tins; the hydroxylate oxygen of the ligand functions as a monodentate ligand and is attached to one tin (Figure 1a and Scheme 1). The coordination environment around each tin in **2** has five oxygen atoms and one carbon atom; the coordination geometry around tin can be described as distorted octahedral. The bond parameters found in **2** are consistent with those found in other oxotin

Scheme 1



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† Indian Institute of Technology.
‡ University of Liverpool.

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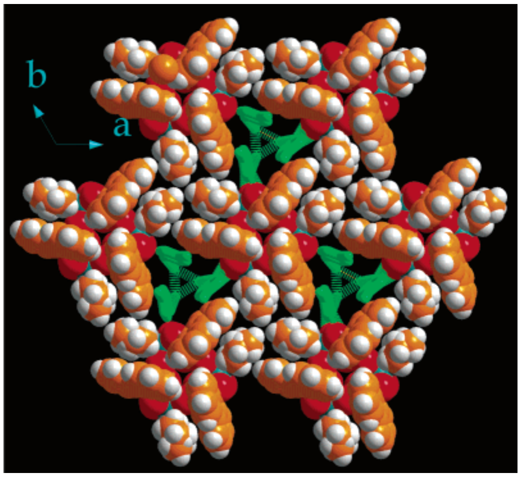

Figure 2. Packing diagram of **2** showing the C_3 symmetric voids occupied by guest phenol and water molecules. The guest molecules are shown in green.

cages.[7] The molecular structure of **2** has a C_{3h} symmetry, and interestingly, the crystal structure reveals C_3 symmetric voids that are formed as a result of the packing of three molecules of **2** (Figure 2). Each of these voids contains six molecules of *p*-iodophenol and six water molecules. Each stannoxane cage is surrounded by three such voids. Thus, every molecule of **2** is associated with six phenol and six water molecules. The supramolecular formation in **2** is quite intricate and is a result of several cumulative hydrogen bonding interactions that occur between the hosts and the hosts and guests. First, three molecules of **2** are held together in a trigonal symmetric fashion by O−H···O interactions that occur between phenol hydroxyl groups and the carboxylate oxygens, as well as the oxygen atoms of the water molecules and the Sn−OH units of the stannoxane core. In addition, C−H···π hydrogen bonding interactions between the C−H of the phenol and the fluorenyl moieties of the cage strengthen these intermolecular contacts. This results in tubular layers. Further C−H···π interactions between such tubular layers leads to columnar structures in the crystallographic *c* axis (Figure 3).

The diameter of the column, thus formed, is 10 Å, and its lining contains the Sn−OH and the carboxylate oxygens, making the column hydrophilic in this segment. However, at regular intervals, the butyl groups on tin protrude into the column and reduce the column diameter to 2.5 Å. This also results in the column becoming hydrophobic. Interestingly, while the hydrophilic pocket is occupied by phenol and water molecules, the hydrophobic pocket contains chloroform molecules (Figure 3). The six water molecules present in the hydrophilic pocket interact strongly among themselves to afford a nonplanar cage (see Supporting Information). TGA studies on **2** reveal the complete loss of the guest molecules at about 250 °C. This is accompanied by an irreversible decomposition of the stannoxane cage. This suggests that the channel formation in **2** is assisted by the guest clusters. Accordingly, the absence of phenol in **3** leads to one-dimensional tape-like supramolecular structure (see Supporting Information).

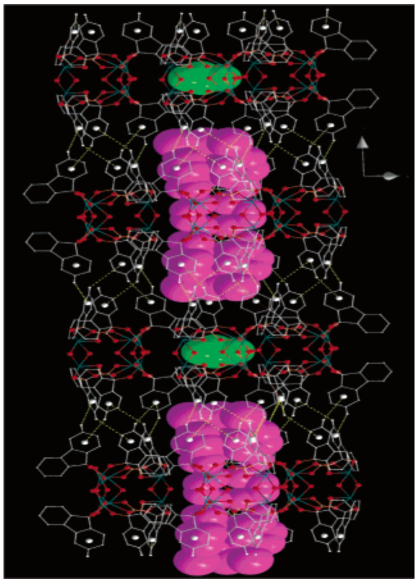

Figure 3. Formation of channel structures via intermolecular C−H···π interactions between fluorenyl groups of stannoxane cages along the crystallographic *c* axis. The selective entrapment of guest molecules inside the channels may be noted. The butyl groups attached to tin are omitted for clarity. Color scheme: oxygen atoms (carboxylate and Sn−OH) are in red; guest molecules (phenol and water) are in pink, while chloroform molecules are in green.

In conclusion, we describe the synthesis and structural characterization of a novel hexatin cage [{*n*-BuSn(OH)L}$_6$·6H_2O·6ROH·$CHCl_3$]. The hexatin cage contains three interlinked $Sn_2(OH)_2$ units, thus generating a hydroxyl-rich compound. The solid-state packing of the oxotin cage **2**, mediated by O−H···O and C−H···O interactions, leads to the generation of C_3 symmetric channels. Preferential guest entrapment in the hydrophobic and hydrophilic pockets of these channels is observed.

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Supporting Information Available: Synthetic procedure for **2** and **3**, and their crystallographic data and cif files; Figures S1−S8 showing the structural details and the thermogravimetric traces for **2** and **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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