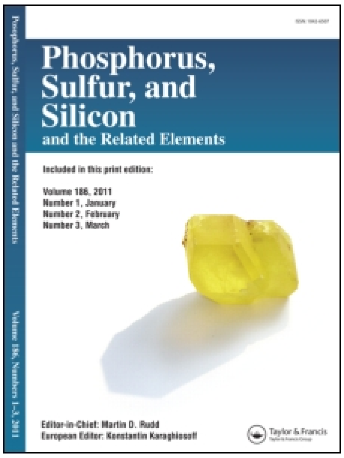

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# ORGANOSTANNOXANE MOTIFS IN CAGES AND SUPRAMOLECULAR ARCHITECTURES

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# ORGANOSTANNOXANE MOTIFS IN CAGES AND SUPRAMOLECULAR ARCHITECTURES

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*The reactions of* n-*butyl stannonic acid with* $(PhO)_2P(O)H$ *leads to the formation of a hexameric tin cage* $[\{(\text{n-}BuSn)_3(PhO)_3O\}_2\{HPO_3\}_4]$. *This reaction involves an in situ P—O bond cleavage and the generation of a* $[HPO_3]^{2-}$ *ion. A direct reaction of six equivalents of* n-$BuSnO(OH)$ *acid with six equivalents of* $C_6H_5OH$ *and four equivalents of* $H_3PO_3$ *also leads to the formation of same cage structure. A tetranuclear organooxotin cage* $[(PhCH_2)_2Sn_2O(O_2P(OH)\text{-t-}Bu)_4]_2$ *has been assembled by debenzylation involving the reaction of* $(PhCH_2)_2SnCl_2$, $(PhCH_2)_2SnO{\cdot}H_2O$ *or* $(PhCH_2)_3SnCl$ *with two equivalents of* t-$BuP(O)OH_2$. *A half-cage intermediate* $[(PhCH_2)_2Sn_2O(O_2P(OH)\text{-t-}Bu)_4]$ *has been detected. New organotin cations of the type* $[\text{n-}Bu_2Sn(H_2O)_4]^{2+}[2,5\text{-}Me_2\text{-}C_6H_3SO_3]_2^-$ *and* $\{[\text{n-}Bu_2Sn(H_2O)_3LSn(H_2O)_3(\text{n-}Bu)_2]^{2+}[1,5\text{-}(SO_3)_2\text{-}C_{10}H_6]^{2-}\}$ *have been obtained in the reactions of* n-$Bu_2SnO$ *or* $(\text{n-}Bu_3Sn)_3O$ *with 2,5-dimethyl sulfonic acid and 1,5-naphthalene disulfonic acid respectively. These organotin cations form interesting supramolecular structures in the solid state as a result of O—H$\cdots$O hydrogen bonding.*

*Keywords:* Cages; hydrogen bonding; organotin cations; stannoxanes; supramolecular structures

A variety of structural forms are known in the literature for mono organooxotin compounds.[1] These include drums, ladders, cubes, oxygen capped clusters, foot ball cages, butterfly compounds, extended cages, and so on.[2] Most of these clusters are obtained from reactions involving *n*-$BuSn(OH)_2Cl$ with carboxylic acids and phosphorus based acids such as $RP(O)(OH)_2$, $(OR)_2P(O)OH$, and $R_2P(O)OH$. Utilization

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of alternative synthetic strategies to assemble organooxotin cages are rare.[3] We have shown that a debenzylation reaction strategy is effective in generating a tetranuclear oxotin cage.[4] We also have shown that reaction of $n$-BuSnO(OH) with phenol and $H_3PO_3$ leads to the formation of a hexanuclear oxotin cage.[5] Although organotin cations have long been of interest there have not been many structural studies on these compounds.[6] We report facile synthetic methods for the assembly of organotin cations.[7] A novel feature of the solid-state structures of these cations is their organization into supramolecular assemblies. The latter are assisted by strong O—H· · ·O hydrogen bonds.

## RESULTS AND DISCUSSION

In order to explore alternative methods for the assembly of organooxotin clusters we first pursued the debenzylation reactions of benzyltin compounds. Benzyltin compounds are similar to allyltin compounds in terms of the sensitivity of the Sn—O bond cleavage reaction.[3] We used $(PhCH_2)_3SnCl$, $(PhCH_2)_2SnCl_2$, and $(PhCH_2)_2SnO{\cdot}H_2O$ as the starting materials.[8] Reaction of any of these three benzyltin substrates with *tert*-butyl phosphonic acid, first leads to the formation of a half-cage $[(PhCH_2)_2Sn_2O(O_2P(OH)\text{-}t\text{-}Bu)_4]$ (**1**) which is quickly converted to the tetranuclear cage $[(PhCH_2)_2Sn_2O(O_2P(OH)\text{-}t\text{-}Bu)_4]_2$ (**2**).

The half-cage **1** shows two sets of $^{31}P$ NMR signals at 33.7 and 31.8 ppm and a triplet of doublets centered at −657.6 ppm in its $^{119}Sn$ NMR. Conversion to the full cage **2**, is indicated by the $^{31}P$ NMR chemical shifts at 32.2 and 23.2 ppm. The $^{119}Sn$ NMR of **2** shows a triplet of triplet centered at −661.6 ppm.[9]

The reaction of $n$-BuSnO(OH) with $H_3PO_3$ and $C_6H_5OH$ affords a hexameric tin cage $[\{n\text{-}BuSn)_3(PhO)_3O\}_2\{HPO_3\}_4]$ (**3**).[5]

$$6\ n\text{-}BuSnO(OH) + 6\ PhOH + 4H_3PO_3 \xrightarrow[10\,h, 110^\circ C]{Toluene}$$

$$[\{(n\text{-}BuSn)_3(PhO)_3O\}_2\{HPO_3\}_4] + 10H_2O$$

The structure of **3** shows that it contains three $Sn_2O_2$ rings that are nearly perpendicular to each other. The role of the four $HPO_3$ ligands is to bridge the two separate trinuclear tin centers.

The weakly coordinating nature of the sulfonate ligand has been utilized to generate organotin cations. Thus, the reaction of $n$-$Bu_2SnO$ with 2,5-$Me_2$-$C_6H_3$-$SO_3H$ leads to the isolation of the organotin dication, $[n\text{-}Bu_2Sn(H_2O)_4]^{2+}[2,5\text{-}Me_2\text{-}C_6H_3\text{-}SO_3]_2^-$ (**4**).[6] The structure of the cation portion of **4** contains a central tin with a coordination number of six. The two alkyl groups are *trans* with respect to each other. In the solid-state **4** is present as a two-dimensional grid-like supramolecular structure which is formed by intermolecular O—H···O bonding. In order to explore if three-dimensional structures are possible we have carried out the reaction of $(n\text{-Bu}_3\text{Sn})_2\text{O}$ with 1,5-naphthalene disulphonic acid. This reaction leads to the formation of a Sn-butyl cleaved dication, $[n\text{-Bu}_2\text{Sn}(\text{H}_2\text{O})_3(\text{L})\text{Sn}(\text{H}_2\text{O})_3\text{-}n\text{-Bu}_2]^{2+}[\text{L}]^{2-}$(L = 1,5-naphthalene disulfonate) (**5**).[10] In **5** while one of the disulfonate units is involved in bridging the two tin centers the other disulfonate assists in forming a pillared 3-D supramolecular architecture.[11]

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