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Penta-, Hexa-, and Heptanuclear Organotin–Oxygen Arsonate Clusters Constructed from an Acetate Drum Cluster Precursor and Different Arsonate Anions

Yun-Peng Xie,[a] Jian-Fang Ma,*[a] Jin Yang,*[a] Ying-Ying Liu,[a] Ji-Cheng Ma,[a] and Min-Zhong Su[a]

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Treatment of the acetate drum $[n\mathrm{BuSn(O)O_2CMe}]_6$ with different arsonic acids gave seven organotin arsonate clusters: $[(n\mathrm{BuSn})_5(\mu_3\text{-O})(\mathrm{OH})(\mathrm{R'O})_3(\mathrm{RAsO_3})_4(\mathrm{RAsO_3H})]$ [R = 2-$\mathrm{NO_2C_6H_4}$, R′ = Me (**1a** and **1b**)], $[(n\mathrm{BuSn})_3(\mathrm{RAsO_3})(\mu_3\text{-O})(\mathrm{CH_3CO_2})_3(\mathrm{R'O})_2]_2$ [R = 2,4-$(\mathrm{NO_2})_2\mathrm{C_6H_3}$, R′ = Me (**2**)], $[(n\mathrm{BuSn})_3(\mathrm{RAsO_3})_2(\mathrm{RAsO_3H})(\mu_3\text{-O})(\mathrm{R'O})_2]_2$ [R = 4-$\mathrm{NO_2C_6H_4}$, R′ = Me (**3**)], and $[(n\mathrm{BuSn})_3(\mathrm{RAsO_3})_3(\mu_3\text{-O})(\mathrm{OH})(\mathrm{R'O})_2]_2\mathrm{Sn}$ [R = $\mathrm{C_6H_5CH_2}$, R′ = Me (**4**); R = $\mathrm{C_6H_5CH_2}$, R′ = H (**5**); R = $\mathrm{C_6H_5}$, R′ = H (**6**)]. The pentanuclear motif of **1a** and **1b**, which consists of $[\mathrm{Sn_3}(\mu_3\text{-O})(\mu_2\text{-OR'})_2]$ and $[\mathrm{Sn_2(OH)}(\mu_2\text{-OR'})]$ units, was firstly found in organotin compounds. The structures of **2** and **3** possess similar organotin–oxygen clusters. However, the structure of **2** presents the first example of a hexanuclear organotin–oxygen cluster that contains both carboxylate and arsonate ligands. The heptanuclear structures of **4**–**6**, which are composed of two $[\mathrm{Sn_3}(\mu_3\text{-O})(\mu_2\text{-OR'})_2]$ units connected through hydroxy and arsonate ligands to a single tin atom, were firstly obtained by displacement reactions. The syntheses, structures, and structural interrelationship of these diverse organotin–oxygen clusters are also discussed.

Introduction

Organotin–oxygen clusters have been attracting considerable attention in recent years because of their novel structures and their efficient catalysis of various organic reactions.[1] So far, many types of organotin–oxygen clusters such as ladder,[2a,2b] drum,[2c] cube,[2d,2e] butterfly,[2e] cyclic trimer,[2f] single and double oxygen-capped,[2e,3] and doubly and triply bridged ladder[4] clusters have been reported in the literature that were synthesized by using carboxylic, phosphinic, or sulfonic acid as ligands. Until now, very few organotin–oxygen clusters based on arsonate ligands were known, owing to their relatively low solubility. In our previous work, we tried a solvothermal approach for the preparation of organotin arsonate derivatives, and a rich cluster chemistry comprising four types of structural forms of organotin/tin–oxygen arsonate clusters were discovered.[5]

In recent years, the development of alternate synthetic methods that could be used to obtain structural diversity in organotin–oxygen clusters has received particular attention. In this regard, the use of presynthesized organotin–oxygen clusters as starting materials is an important approach to construct new types of organotin–oxygen clusters. For example, when the acetate drums $[\mathrm{RSn(O)O_2CMe}]_6$ (R = *n*Bu, Me), as precursors, were treated with the di-*tert*-butylphosphinic acid, the crowns $[\{n\mathrm{BuSn(O)O_2P}(t\mathrm{Bu})_2\}\{n\mathrm{BuSn(OH)_2O_2P}(t\mathrm{Bu})_2\}][\mathrm{H}][\mathrm{O_2P}(t\mathrm{Bu})_2]$ and $[\{\mathrm{MeSn(O)O_2P}(t\mathrm{Bu})_2\}\{\mathrm{MeSn(OH)(OMe)O_2P}(t\mathrm{Bu})_2\}][\mathrm{H}][\mathrm{O_2P}(t\mathrm{Bu})_2]\cdot 4\mathrm{MeOH}\cdot 2\mathrm{H_2O}$ were obtained.[6] Treatment of the organotin carboxylate precursors $[\{\mathrm{MeSn(O)O_2CCHMe_2}\}_2\mathrm{MeSn(O_2CCHMe_2)_3}]_2$ with *tert*-butylphosphonic acid gave the organotin–oxygen cluster $[\mathrm{Me_2Sn_2O(O_2P(OH)}t\mathrm{Bu})_4]_2$.[7] In our previous work, we tried a similar approach to prepare organotin derivatives. The reactions of the precursor $[(\mathrm{Bz_2SnO})_3(\mathrm{Bz_2SnOH})_2(\mathrm{CO_3})]_2$ with different dicarboxylic acids resulted in a series of new organotin–oxygen clusters.[8] Therefore, utilizing the presynthesized clusters as starting materials proved to be a very efficient method for the syntheses of new types of organotin–oxygen clusters. In the organotin–oxygen clusters, the drum cluster is a good candidate precursor. From a structural point of view, the drum cluster can be structurally assembled in at least five ways.[1a] Thus, diverse products would be accessible by the reactions of the drum cluster with other ligands.

To produce novel organotin–oxygen clusters featuring arsonate ligands, in this work, we tried a new synthetic route in which the acetate drum cluster was used as a starting material. In our previous work, we found that the nitro substituent of the arsonate has important effects on the structures of the compounds. Therefore, arsonates with different positions and numbers of nitro substituents on the aromatic moiety were chosen in this work. The displacement reac-

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[a] Key Lab of Polyoxometalate Science, Department of Chemistry, Northeast Normal University, Changchun 130024, P. R. China
E-mail: jianfangma@yahoo.com.cn
yangjinnenu@yahoo.com.cn

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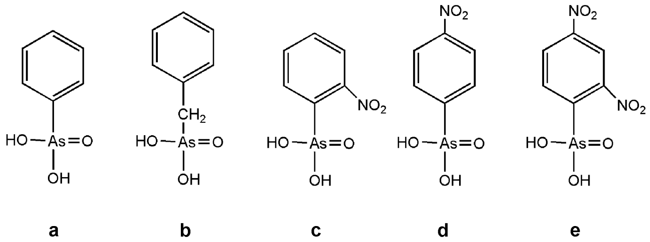
tions of the acetate drum cluster with five different arsonate ligands (Scheme 1) afford seven new organotin–oxygen clusters, namely, $[(n\text{BuSn})_5(\mu_3\text{-O})(\text{OH})(\text{R}'\text{O})_3(\text{RAsO}_3)_4(\text{RAsO}_3\text{H})]$ [R = 2-$\text{NO}_2\text{C}_6\text{H}_4$, R′ = Me (**1a** and **1b**)], $[(n\text{BuSn})_3(\text{RAsO}_3)(\mu_3\text{-O})(\text{CH}_3\text{CO}_2)_3(\text{R}'\text{O})_2]_2$ [R = 2,4-$(\text{NO}_2)_2\text{C}_6\text{H}_3$, R′ = Me (**2**)], $[(n\text{BuSn})_3(\text{RAsO}_3)_2(\text{RAsO}_3\text{H})(\mu_3\text{-O})(\text{R}'\text{O})_2]_2$ [R = 4-$\text{NO}_2\text{C}_6\text{H}_4$, R′ = Me (**3**)], and $[(n\text{BuSn})_3(\text{RAsO}_3)_3(\mu_3\text{-O})(\text{OH})(\text{R}'\text{O})_2]_2\text{Sn}$ [R = $\text{C}_6\text{H}_5\text{CH}_2$, R′ = Me (**4**); R = $\text{C}_6\text{H}_5\text{CH}_2$, R′ = H (**5**); R = C_6H_5, R′ = H (**6**)]. The pentanuclear motif of **1a** and **1b** was firstly found and structurally characterized in organotin compounds. Compound **2** is an unprecedented hexanuclear organotin–oxygen cluster that contains both carboxylate and arsonate ligands. For the first time, hexanuclear (**2** and **3**) and heptanuclear (**4**–**6**) motifs were obtained by displacement reactions of the acetate drum cluster with arsonic acids. The syntheses, structures, and structural interrelationship of these diverse organotin–oxygen clusters are also discussed.



Scheme 1. Schematic drawing of the arsonic acid ligands.

Results and Discussion

Syntheses

All the reactions are summarized in Scheme 2. In this work, we studied the displacement reactions of the acetate drum cluster $[n\text{BuSn(O)O}_2\text{CMe}]_6$ with arsonic acids. Compounds **1**–**6** were prepared by displacement reactions of $[n\text{BuSn(O)O}_2\text{CMe}]_6$ with RAsO_3H_2 in a 1:6 stoichiometry. When $[n\text{BuSn(O)O}_2\text{CMe}]_6$ was treated with 2-$\text{NO}_2\text{C}_6\text{H}_4\text{AsO}_3\text{H}_2$, block-shaped crystals of **1a** were obtained together with small needle-shaped crystals of **1b**. The latter can be manually selected from the mixture by means of their shapes. On exposure to air, the crystals of compounds **1**–**6** became opaque within minutes as a result of the loss of solvents. These compounds are insoluble in common solvents such as THF, C_6H_6, CH_3OH, DMSO, and CH_2Cl_2.

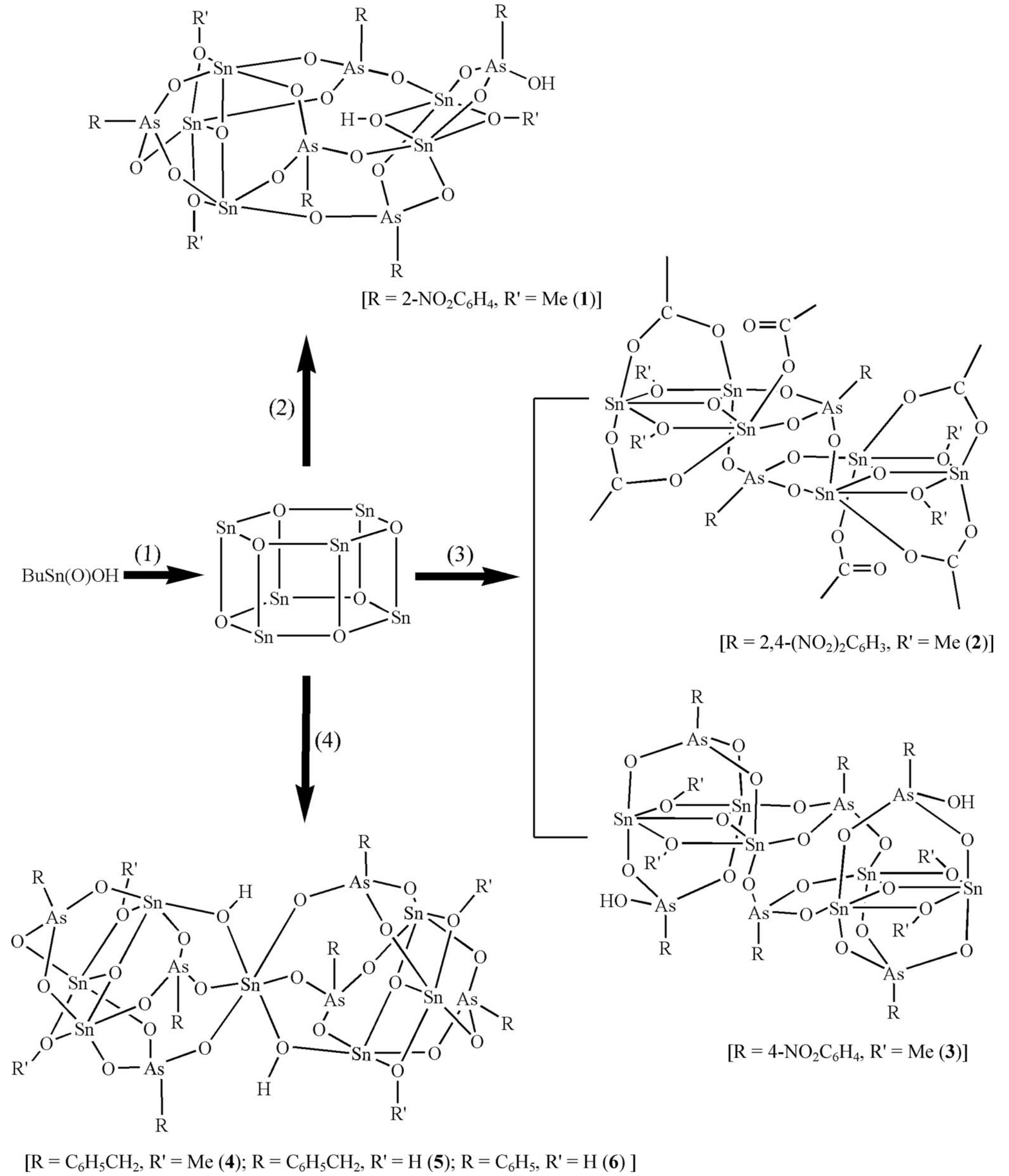
Molecular Structures of 1–6

Selected metric parameters for all the structures are listed in Table S1 (Supporting Information). When the acetate drum cluster precursor $[n\text{BuSn(O)O}_2\text{CMe}]_6$ was treated with 2-$\text{NO}_2\text{C}_6\text{H}_4\text{AsO}_3\text{H}_2$, block-shaped crystal of **1a** were obtained together with small needle-shaped crystals of **1b**. The structural motifs of **1a** and **1b** are entirely different from the reported pentameric organotin–oxygen clusters $[(\text{Bz}_2\text{SnO})_3(\text{Bz}_2\text{SnOH})_2(\text{PhCO}_2)_2]$ and $[\text{Sn}_5\text{Ph}_7(\mu_3\text{-dipp})_4(\mu\text{-dippH})(\mu_3\text{-O})(\mu\text{-OH})(i\text{PrOH})(\text{H}_2\text{O})\text{Cl}]\cdot i\text{PrOH}$ (dippH_2 = 2,6-diisopropylphenylphosphate).[8,9] To the best of our knowledge, **1a** and **1b** are the first examples of such entities in organotin chemistry. Notably, though compounds **1a** and **1b** possess similar compositions, their structures slightly differ in the details (Figures 1 and 2). The molecular structures of **1a** and **1b** contain $[\text{Sn}_3(\mu_3\text{-O})(\mu_2\text{-OR}')_2]$ and $[\text{Sn}_2(\mu_2\text{-OH})(\mu_2\text{-OR}')]$ motifs that are linked to each other by three 2-$\text{NO}_2\text{PhAsO}_3^{2-}$ units.

The Sn_2O_2 core of the four-membered $[\text{Sn}_2(\mu_2\text{-OH})(\mu_2\text{-OR}')]$ ring comprises two tin atoms held together by a μ_2-oxygen atom of the hydroxy group and a μ_2-alkoxido ligand, which bind two adjacent tin atoms. The four atoms of the Sn_2O_2 core are coplanar. To the best our knowledge, few crystal structures of monoorganotin compounds containing the $[\text{Sn}_2(\mu_2\text{-OH})(\mu_2\text{-OR}')]$ unit have been reported. For example, the butterfly compound $[n\text{BuSn(OH)}\{\text{O}_2\text{P}(\text{C}_6\text{H}_{11})_2\}_2]$ contained one $[\text{Sn}_2(\mu_2\text{-OH})(\mu_2\text{-OR}')]$ unit, which was spanned on both sides by symmetrical phosphinate bridges between the tin atoms,[2e] whereas the crown compound $[\{n\text{BuSn(O)O}_2\text{P}(t\text{Bu})_2\}\{n\text{BuSn(OH)}_2\text{O}_2\text{P}(t\text{Bu})_2\}][\text{H}][\text{O}_2\text{P}(t\text{Bu})_2]$ contains two $[\text{Sn}_2(\mu_2\text{-OH})(\mu_2\text{-OR}')]$ units, which are held together by two phosphinic acids and two hydroxy groups.[6] However, in the reported hexanuclear organotin–oxygen cluster $\{[n\text{BuSn}(\mu\text{-OH})(\text{L})]_6\cdot 3\text{H}_2\text{O}\cdot 2\text{CHCl}_3\}$, three $[\text{Sn}_2(\mu_2\text{-OH})(\mu_2\text{-OR}')]$ units are held together by six 9-hydroxy-9-fluorenecarboxylic acids (L) (Scheme 3).[10]

The Sn_3O_3 core of the $[\text{Sn}_3(\mu_3\text{-O})(\mu_2\text{-OR}')_2]$ unit comprises three tin atoms held together by a μ_3-oxygen atom; further, two alkoxides are involved as bridging ligands, and the μ_2-oxygen atom of each alkoxide is bound to two adjacent tin atoms. The unit contains two Sn_2O_2 four-membered rings. The six atoms of the Sn_3O_3 core are almost coplanar, and the largest deviation from the Sn_3O_3 plane is 0.17 Å for O26 (**1a** and **1b**). Notably, the angle between the Sn_2O_2 and Sn_3O_3 planes is 77.2° in **1a** and 77.8° in **1b**.

In **1a** and **1b**, the five 2-nitrophenylarsonate groups in the molecule form bridges between the tin atoms. The 2-nitrophenylarsonate group (As1) arranges around the outside of one of the symmetry-related $[\text{Sn}_3(\mu_3\text{-O})(\mu_2\text{-OMe})_2]$ unit, whereas the As2 and As3 groups share two of their oxygen atoms with the $[\text{Sn}_3(\mu_3\text{-O})(\mu_2\text{-OMe})_2]$ unit and their third oxygen atom with the $[\text{Sn}_2(\mu_2\text{-OH})(\mu_2\text{-OR}')]$ unit. However, for these third oxygen atoms, there are two coordination approaches: the third oxygen atom of the As3 group coordinates to Sn5, whereas that of the As2 group coordinates to Sn4 (in **1a**); the third oxygen atom of the As3 group coordinates to Sn4, whereas that of the As2 group coordinates to Sn5 (in **1b**). The 2-nitrophenylarsonate group (As4) shares two of its oxygen atoms with the $[\text{Sn}_2(\mu_2\text{-OH})(\mu_2\text{-OR}')]$ unit and its third oxygen atom with the $[\text{Sn}_3(\mu_3\text{-O})(\mu_2\text{-OMe})_2]$ unit. The 2-nitrophenylarsonate groups (As1 to As4) show the 3.111 binding mode (Harris notion).[11] The remaining 2-nitrophenylarsonate group (As5) forms symmetrical bridges between Sn4 and Sn5, whereas the third oxygen atom is not coordinated. The lat-



Scheme 2. Synthetic routes to compounds **1**–**6**.

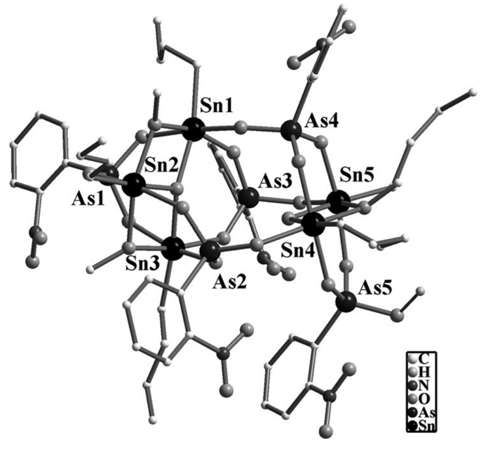


Figure 1. Molecular structure of **1a**.

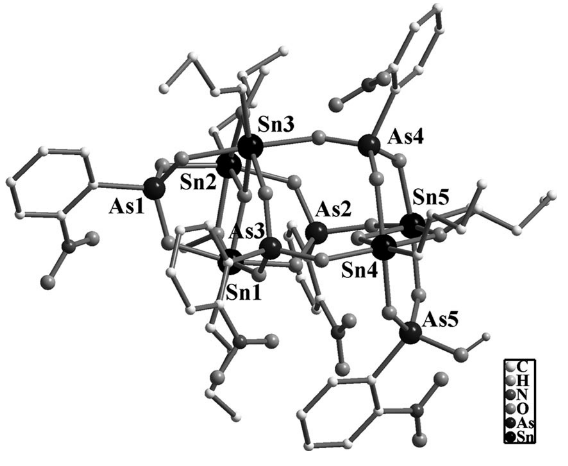
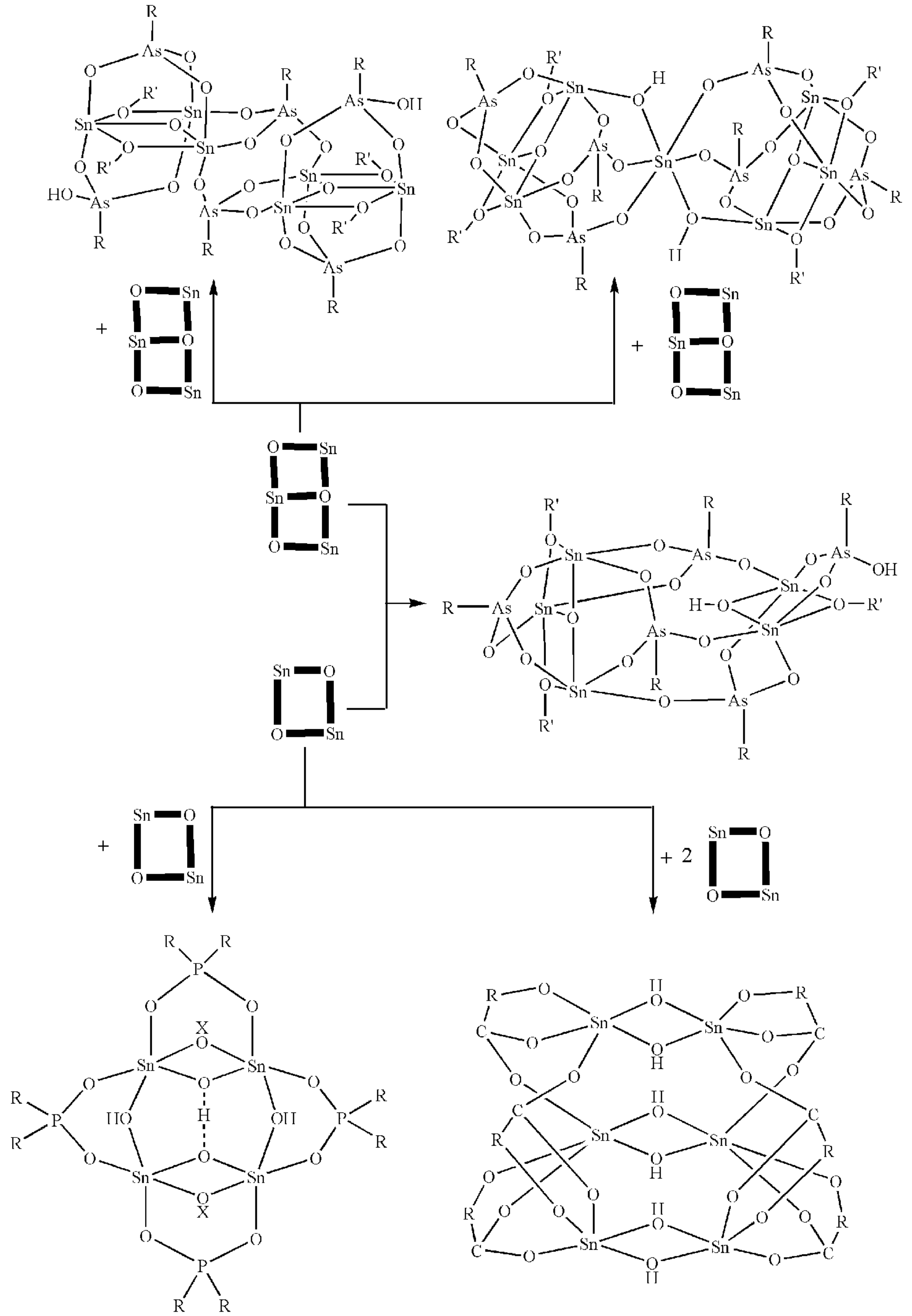


Figure 2. Molecular structure of **1b**.



Scheme 3. Structural assembly of the various stannoxane cores.

ter oxygen atom is protonated. The 2-nitrophenylarsonate group (As5) shows the 2.110 binding mode (Harris notion). All tin atoms in **1a** and **1b** are hexacoordinate, bond to one carbon atom and five oxygen atoms, and have octahedral coordination geometries. The average Sn–O distance involving the bridging arsonate is 2.090 Å. The average Sn–O(μ_3) bond length is 2.064 Å, whereas the Sn–O(μ_2) bond length is 2.131 Å.

The acetate drum cluster undergoes a displacement reaction with 2,4-$(NO_2)_2C_6H_3AsO_3H_2$ to yield the unprecedented mixed-ligand monoorganotin–oxygen cluster $[(n\text{BuSn})_3\{2,4\text{-}(NO_2)_2C_6H_3AsO_3\}(\mu_3\text{-O})(CH_3CO_2)_3(MeO)_2]_2$ (**2**), which contains two $[Sn_3(\mu_3\text{-O})(\mu_2\text{-OMe})_2]$ units (Figure 3, Scheme 3). In the tritin unit, three tin atoms (Sn1, Sn2, and Sn3) are joined together by a μ_3-oxygen ligand. The Sn1 and Sn2 atoms are further connected by one μ_2-MeO^- group and one carboxylate group. The Sn2 and Sn3 atoms are also further linked by one μ_2-MeO^- group and one carboxylate group; the Sn1 atom is further coordinated by one oxygen atom of one carboxylate group. The two $[Sn_3(\mu_3\text{-O})(\mu_2\text{-OMe})_2]$ units are linked through two arsonate ligands, affording a hexanuclear organotin oxygen cluster.

The arsonate groups show the 3.111 binding mode (Harris notion). All tin atoms are hexacoordinate, bonded to one carbon atom and five oxygen atoms, and form octahedral coordination geometries. The average Sn–O distance involving the bridging arsonate is 2.078 Å, whereas the average Sn–O distance involving the carboxylate group is 2.176 Å. The average Sn–O(μ_3) bond length is 2.035 Å, whereas the Sn–O(μ_2) bond length is 2.105 Å.

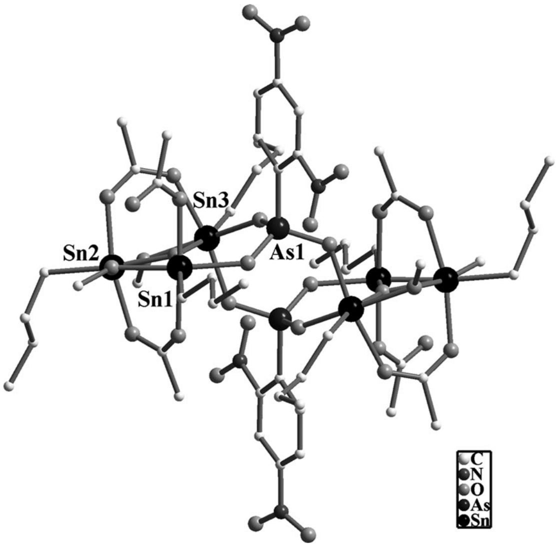


Figure 3. Molecular structure of **2**. All H atoms are omitted for clarity. The unlabeled atoms are symmetry related to the labeled atoms.

Treatment of the drum cluster [nBuSn(O)O_2CMe]$_6$ with 4-NO_2PhAsO_3H_2 gave the organotin–oxygen cluster [(nBuSn)$_3$(4-NO_2PhAsO_3)$_2$(4-NO_2PhAsO_3H)(μ_3-O)(MeO)$_2$]$_2$ (**3**). Cluster **3** again contains two [Sn_3(μ_3-O)(μ_2-OMe)$_2$] units similar to that of **2**, but from which six carboxylate groups have been displaced by four arsonate groups (Figure 4). The four arsonate ligands fall into two categories, two of those with 3.111 and the remaining two with 2.110 binding modes. The two [Sn_3(μ_3-O)(μ_2-OMe)$_2$] units are linked through two arsonate groups, affording a hexanuclear organotin–oxygen arsonate cluster. The two arsonate groups show the 3.111 binding mode. All tin atoms are six-coordinate. The average Sn–O distance involving the bridging arsonate is 2.113 Å. The average Sn–O(μ_3) bond length is 2.058 Å, whereas the Sn–O(μ_2) bond length is 2.140 Å. In comparison with **2**, the Sn–O distances are slightly longer.

The structures of **2** and **3** both contain two [Sn_3(μ_3-O)(μ_2-OR$'$)$_2$] units. Cluster **2** may be an intermediate product that is eventually converted into an architecture similar to that of **3**. Compounds **2** and **3** are clearly related to the previously reported organotin–oxygen arsonate cluster [(PhSn)$_3$(4-NO_2PhAsO_3)$_2$(4-NO_2PhAsO_3H)(μ_3-O)(MeO)$_2$]$_2$,[5] but there are some differences. compound **2** is the first hexanuclear organotin–oxygen cluster containing both carboxylate and arsonate ligands. For the first time, they are obtained by treatment of the drum cluster precursor [nBuSn(O)O_2CMe]$_6$ with the arsenic acid ligands.

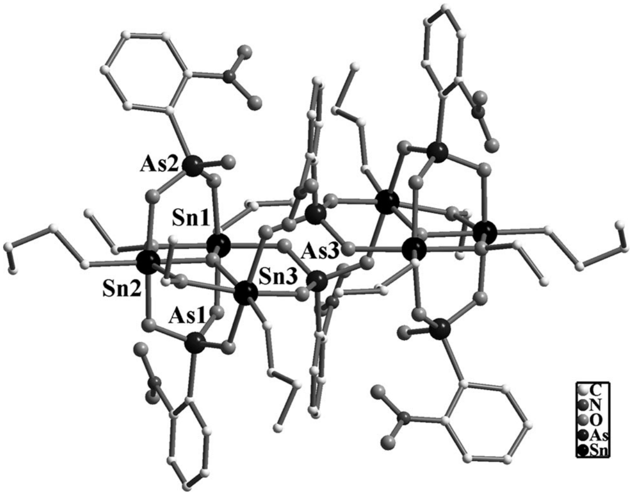


Figure 4. Molecular structure of **3**. The unlabeled atoms are symmetry related to the labeled atoms.

The reactions of the acetate drum cluster with $C_6H_5CH_2AsO_3H_2$ and $C_6H_5AsO_3H_2$ led to the formation of heptanuclear clusters [(nBuSn)$_3$(RAsO_3)$_3$(μ_3-O)(OH)-(R$'$O)$_2$]$_2$Sn [R = $C_6H_5CH_2$, R$'$ = Me (**4**); R = $C_6H_5CH_2$, R$'$ = H (**5**); R = C_6H_5, R$'$ = H (**6**)]. The structures of **4**–**6** are composed of two [Sn_3(μ_3-O)(μ_2-OR$'$)$_2$] units connected through hydroxy and arsonate ligands to a single tin atom. Because of the similarity of the three structures, only the description of **4** will be given in detail (Figure 5). The Sn_3O_3 core of the [Sn_3(μ_3-O)(μ_2-OR$'$)$_2$] unit is capped by a tridentate arsonate ligand. The four arsonate groups share two of their oxygen atoms with one [Sn_3(μ_3-O)(μ_2-OR$'$)$_2$] unit and their third oxygen atom with Sn4. The bridging action is augmented by the two hydroxide ligands, which further interconnect two pairs of tin atoms (Sn3 and Sn4; Sn3$'$ and Sn4$'$). All the arsonate groups show the 3.111 mode.

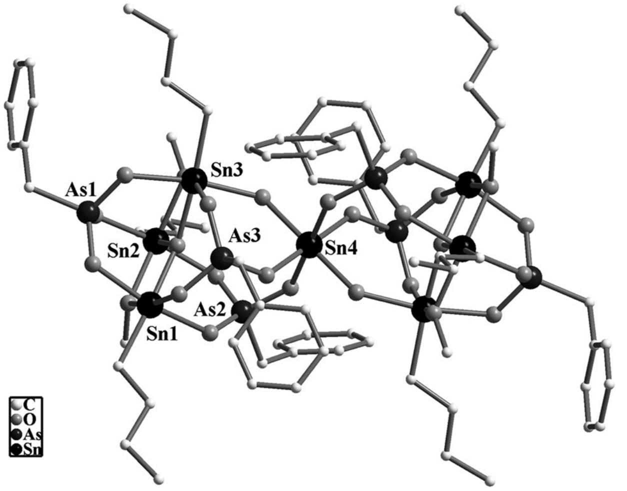
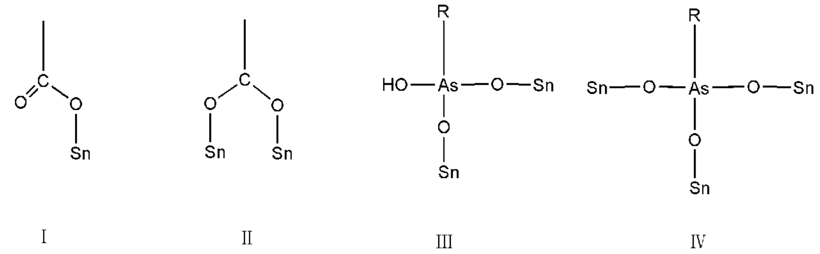


Figure 5. Molecular structure of **4**. All H atoms are omitted for clarity. The unlabeled atoms are symmetry related to the labeled atoms.



Scheme 4. Coordination modes of the carboxylate and arsonate ligands.

The tin atoms of the two $[Sn_3(\mu_3\text{-}O)(\mu_2\text{-}OR')_2]$ units are hexacoordinate, bonding to one carbon atom and five oxygen atoms in octahedral coordination geometries, whereas the central tin site is bound to four O donors from four distinct arsonate groups and two other O donors from two bridging oxido groups. The average Sn–O(μ_3) bond length is 2.070 Å, whereas the average Sn–O(μ_2) bond length is 2.125 Å. The average Sn–O distance involving the bridging arsonate ligand is 2.084 Å. These values are comparable to those observed in other organotin arylarsonate clusters.

Although **4**–**6** are related to the previously reported organotin arsonates $[(PhSn)_3(RAsO_3)_3(\mu_3\text{-}O)(OH)(R'O)_2]_2Sn$ (R = C_6H_5, 2-$NH_2C_6H_4$, 4-$NH_2C_6H_4$, 2-$NO_2C_6H_4$, 3-$NO_2C_6H_4$, 2-ClC_6H_4, 2,4-$Cl_2C_6H_3$, and 3-NO_2-4-OHC_6H_3; R′ = Me or Et),[5] there are a number of differences. The previously reported structures were obtained by solvothermal reactions, whereas **4**–**6** were obtained by treatment of the drum cluster $[n\text{BuSn(O)}O_2CMe]_6$ with $C_6H_5CH_2AsO_3H_2$ and $C_6H_5AsO_3H_2$. In comparison with the previously reported structures, the $MeO^–$ groups at the corner positions of the $[Sn_3(\mu_3\text{-}O)(\mu_2\text{-}OMe)_2]$ units have been replaced by $HO^–$ groups (**5** and **6**) through changing the reaction conditions.

Compounds **1**–**6** were obtained from the acetate drum $[n\text{BuSn(O)}O_2CMe]_6$ in displacement reactions with the arsonic acids. It is noteworthy that the basic $[Sn_3(\mu_3\text{-}O)(\mu_2\text{-}OR')_2]$ unit is observed in the molecular structures of compounds **1**–**6**. It is immediately evident that organotin–oxygen clusters **1**–**6** are structurally related to the drum. The drum compound (Sn_6O_6 core) could be thought of as forming from a condensation of the two $[Sn_3(\mu_3\text{-}O)(\mu_2\text{-}OR')_2]$ units. However, if the two $[Sn_3(\mu_3\text{-}O)(\mu_2\text{-}OR')_2]$ units are joined to each other with the help of arsonic acid ligands, clusters **2**–**6** are obtained. The formation of **1a** and **1b** resulted from displacement reactions of the drum with 2-$NO_2C_6H_4AsO_3H_2$. The molecular structures of **1a** and **1b** contain $[Sn_3(\mu_3\text{-}O)(\mu_2\text{-}OR')_2]$ and $[Sn_2(\mu_2\text{-}OH)(\mu_2\text{-}OR')]$ units that are linked to each other by three 2-$NO_2PhAsO_3^{2–}$ units. They are structurally different from the crown $[\{n\text{BuSn(O)}O_2P(t\text{Bu})_2\}\{n\text{BuSn(OH)}_2O_2P(t\text{Bu})_2\}][H][O_2P(t\text{Bu})_2]$.[6] The crown contains two $[Sn_2(\mu_2\text{-}OH)(\mu_2\text{-}OR')]$ units, which are held together by two phosphinic acids and two hydroxy groups.

In **2**, carboxylic acids have two types of coordination modes (Scheme 4): (I) One oxygen atom coordinates to one tin ion, whereas the remaining oxido group is not coordinated. (II) Two oxygen atoms coordinate to two different tin ions. In **1**–**6**, arsonic acids also display two kinds of coordination modes (Scheme 4). (III) Two oxygen atoms coordinate to two different tin ions, whereas the remaining –OH group is not coordinated. (IV) Three oxygen atoms coordinate to three different tin ions.

From the structures of these compounds, it can be seen that the arsonic acids play important roles in the formation of clusters **1**–**6**. Generally, the role of arsonic acid ligands can be explained in terms of their differences in organic substituent groups. In this work, arsonic acids such as $PhAsO_3H_2$ (**a**), $BzAsO_3H_2$ (**b**), 2-$NO_2C_6H_4AsO_3H_2$ (**c**), 4-$NO_2PhAsO_3H_2$ (**d**), and 2,4-$(NO_2)_2C_6H_3AsO_3H_2$ (**e**) (Scheme 1) were used under similar synthesis conditions. In contrast to **a** and **b**, **c**–**e** contain nitro substituent groups. Treatment of arsonic acids **a** and **b** with the acetate drum cluster gave the heptanuclear organotin–oxygen clusters **4**–**6**, whereas the reactions of arsonic acids **c**–**e** with the acetate drum cluster resulted in the penta- and hexanuclear organotin–oxygen clusters **1**–**3**. Further, the positions and numbers of the nitro substituents on the aromatic moiety are also critical factors in determining the formation of organotin–oxygen arsonate clusters. For example, through varying the position and number of nitro substituents on the aromatic moiety of the arsonic acid ligands **c**–**e**, pentanuclear organotin–oxygen cluster **1** and hexanuclear organotin–oxygen arsonate clusters **2** and **3** were obtained, respectively.

It should be pointed out that compounds **4**–**6** can be obtained by using both the drum as the starting material and the previously reported methods. However, compounds **1** and **2** cannot be obtained by using other precursors and methods. The syntheses of compounds **4**–**6** with the use of the drum as the starting material indicate that the drum precursors can provide a variety of different units in the products.

Conclusions

The acetate drum cluster $[n\text{BuSn(O)}O_2CMe]_6$ undergoes displacement reactions with different arsonic acid ligands to yield three types of organotin–oxygen arsonate clusters. The pentanuclear motif of **1a** and **1b** was firstly found and structurally characterized in organotin compounds. Compound **2** is an unprecedented hexanuclear organotin–oxygen cluster that contains both carboxylate and arsonate ligands. For the first time, hexanuclear (**2** and **3**) and heptanuclear (**4**–**6**) motifs were obtained by displacement reactions. The results reveal that the employment of the acetate drum cluster as a reagent in the syntheses of organotin–oxygen arsonate clusters is very effective. Also, the organic substituent groups of the arsonate ligands in the reaction played key roles in determining the final cluster types.

Experimental Section

Materials: $2\text{-NO}_2C_6H_4AsO_3H_2$, $2,4\text{-(NO}_2)_2C_6H_3AsO_3H_2$, and $BzAsO_3H_2$ were prepared by literature methods.[12] $C_6H_5AsO_3H_2$, $4\text{-NO}_2C_6H_4AsO_3H_2$, and reagents were purchased from commercial sources.

General Characterization and Physical Measurements: C, H, and N elemental analyses were conducted with a Perkin–Elmer 240C elemental analyzer. FTIR spectra were recorded from KBr pellets in the range 4000–400 cm^{-1} with a Mattson Alpha-Centauri spectrometer. For free arylarsonic acids, ν(As=O) is observed in the rang 915–865 cm^{-1}. In compounds **1**–**6**, ν(As=O) is lower than those in the free acids, which can be attributed to coordination of the As=O to tin. The bands in the rang 1120–1050 cm^{-1} are assigned to ν(As–C). Bands of medium intensity, observed around 400 and 500 cm^{-1}, are assigned to ν(Sn–O) and ν(Sn–O), respectively.

$[(n\text{BuSn})_5(\mu_3\text{-O})(\text{OH})(\text{MeO})_3(2\text{-NO}_2\text{PhAsO}_3)_4(2\text{-NO}_2\text{PhAsO}_3\text{H})]\cdot\text{MeOH}$ (1a) and $[(n\text{BuSn})_5(\mu_3\text{-O})(\text{OH})(\text{MeO})_3(2\text{-NO}_2\text{PhAsO}_3)_4(2\text{-NO}_2\text{PhAsO}_3\text{H})]$ (1b): A mixture of the acetate drum $[n\text{BuSn(O)O}_2\text{CMe}]_6$ (0.151 g, 0.1 mmol) and $2\text{-NO}_2C_6H_4AsO_3H_2$ (0.148 g, 0.6 mmol) was heated in chloroform (5 mL)/methanol (15 mL) for 8 h and then filtered. The filtrate was left undisturbed to concentrate slowly by evaporation. After 1 week, colorless crystals of compounds **1a** and **1b** were collected. Data for **1a**: Yield: 0.141 g {62% based on $[n\text{BuSn(O)O}_2\text{CMe}]_6$}, block-shaped crystals. M.p. 230–232 °C. $C_{54}H_{80}As_5N_5O_{31}Sn_5$ (2263.28): calcd. C 28.66, H 3.56, N 3.09; found C 28.41, H 3.34, N 3.27. IR: ṽ = 3295 (w), 3099 (w), 2955 (m), 2927 (m), 2869 (w), 2830 (w), 1600 (w), 1540 (s), 1464 (w), 1437 (w), 1349 (s), 1309 (w), 1148 (w), 1117 (m), 1036 (m), 891 (s), 831 (s), 734 (m), 710 (m), 676 (m), 606 (w), 571 (w), 499 (m), 460 (m), 420 (m), 402 (m) cm^{-1}. Data for **1b**: Yield: 0.029 g {13% based on $[n\text{BuSn(O)O}_2\text{CMe}]_6$}, needle-shaped crystals. M.p. 231–232 °C. $C_{53}H_{76}As_5N_5O_{30}Sn_5$ (2231.24): calcd. C 28.53, H 3.43, N 3.14; found C 28.37, H 3.19, N 3.41. IR: ṽ = 3311 (w), 3099 (w), 2955 (m), 2927 (m), 2869 (w), 2830 (w), 1601 (w), 1537 (s), 1464 (m), 1437 (w), 1350 (s), 1310 (m), 1149 (w), 1117 (m), 1053 (m), 891 (s), 828 (s), 734 (m), 710 (m), 676 (m), 607 (w), 573 (w), 498 (m), 460 (m), 420 (m), 402 (m) cm^{-1}.

$\{(n\text{BuSn})_3[2,4\text{-(NO}_2)_2\text{C}_6\text{H}_3\text{AsO}_3](\mu_3\text{-O})(\text{CH}_3\text{CO}_2)_3(\text{MeO})_2\}_2$ (2): Synthesized by a procedure similar to that used for **1** except that $2,4\text{-(NO}_2)_2C_6H_3AsO_3H_2$ (0.175 g, 0.6 mmol) was used in place of $2\text{-NO}_2PhAsO_3H_2$. Yield: 0.056 g {26% based on $[n\text{BuSn(O)O}_2\text{CMe}]_6$}. M.p. 226–228 °C. $C_{52}H_{90}As_2N_4O_{32}Sn_6$ (2145.26): calcd. C 29.11, H 4.23, N 2.61; found C 28.82, H 4.52, N 2.35. IR: ṽ = 3110 (w), 2957 (m), 2928 (m), 2871 (w), 1707 (m), 1600 (m), 1541 (s), 1448 (m), 1348 (m), 1310 (m), 1158 (w), 1117 (m), 1047 (w), 850 (s), 814 (s), 736 (m), 711 (m), 677 (m), 611 (m), 533 (m), 490 (m), 449 (m), 423 (m), 404 (m) cm^{-1}.

$[(n\text{BuSn})_3(4\text{-NO}_2\text{PhAsO}_3)_2(4\text{-NO}_2\text{PhAsO}_3\text{H})(\mu_3\text{-O})(\text{MeO})_2]_2$ (3): Synthesized by a procedure similar to that used for **1** except that $4\text{-NO}_2PhAsO_3H_2$ (0.148 g, 0.06 mmol) was used in place of $2\text{-NO}_2PhAsO_3H_2$. Yield: 0.198 g {74% based on $[n\text{BuSn(O)O}_2\text{CMe}]_6$}. M.p. 242–243 °C. $C_{64}H_{92}As_6N_6O_{36}Sn_6$ (2683.10): calcd. C 28.65, H 3.46, N 3.13; found C 28.82, H 3.17, N 3.35. IR: ṽ = 3101 (w), 2955 (m), 2927 (m), 2867 (m), 1602 (m), 1528 (s), 1462 (w), 1395 (w), 1351 (s), 1287 (w), 1091 (m), 1017 (w), 847 (s), 739 (m), 717 (m), 680 (m), 610 (w), 437 (m), 420 (m), 404 (m) cm^{-1}.

$\{[(n\text{BuSn})_3(\text{BzAsO}_3)_3(\mu_3\text{-O})(\text{OH})(\text{MeO})_2]_2\text{Sn}\}\cdot\text{MeOH}$ (4): Synthesized by a procedure similar to that used for **1** except that $BzAsO_3H_2$ (0.129 g, 0.6 mmol) was used in place of $2\text{-NO}_2PhAsO_3H_2$. Yield: 0.132 g {75% based on $[n\text{BuSn(O)O}_2\text{CMe}]_6$}. M.p. 217–218 °C. $C_{71}H_{114}As_6O_{27}Sn_7$ (2679.97): calcd. C 31.82, H 4.29; found C 31.53, H 4.01. IR: ṽ = 3612 (w), 3300 (w), 3086 (w), 3062 (w), 3031 (w), 2954 (m), 2925 (m), 2868 (m), 2824 (w), 1602 (w), 1496 (m), 1455 (m), 1408 (w), 1375 (w), 1041 (m), 843 (s), 808 (s), 760 (m), 695 (m), 674 (m), 610 (w), 565 (w), 504 (m), 464 (m), 421 (m), 403 (m) cm^{-1}.

$\{[(n\text{BuSn})_3(\text{BzAsO}_3)_3(\mu_3\text{-O})(\text{OH})_3]_2\text{Sn}\}\cdot 2\text{DMF}$ (5): A mixture of the acetate drum $[n\text{BuSn(O)O}_2\text{CMe}]_6$ (0.151 g, 0.1 mmol) and $BzAsO_3H_2$ (0.129 g, 0.6 mmol) was stirred in chloroform (10 mL)/DMF (5 mL) for 8 h and then filtered. The filtrate was left undisturbed to concentrate slowly by evaporation. After 6 weeks, colorless crystals of compound **5** were collected. Yield: 0.044 g {16% based on $[n\text{BuSn(O)O}_2\text{CMe}]_6$}. M.p. 210–212 °C. $C_{72}H_{112}As_6N_2O_{28}Sn_7$ (2733.99): calcd. C 31.65, H 4.06, N 1.03; found C 31.27, H 4.17, N 1.35. IR: ṽ = 3572 (w), 3306 (w), 3085 (w), 3061 (w), 3037 (w), 2955 (m), 2924 (m), 2865 (m), 2829 (w), 1760 (m), 1602 (w), 1493 (m), 1452 (m), 1408 (w), 1375 (w), 1043 (m), 846 (s), 810 (s), 764 (m), 695 (m), 674 (m), 617 (w), 566 (w), 507 (m), 468 (m), 424 (m), 405 (m) cm^{-1}.

$\{[(n\text{BuSn})_3(\text{PhAsO}_3)_3(\mu_3\text{-O})(\text{OH})_3]_2\text{Sn}\}\cdot 2\text{DMF}$ (6): Synthesized by a procedure similar to that used for **5** except that $PhAsO_3H_2$ (0.121 g, 0.6 mmol) was used in place of $PhAsO_3H_2$. Yield: 0.051 g {19% based on $[n\text{BuSn(O)O}_2\text{CMe}]_6$}. M.p. 237–238 °C. $C_{66}H_{100}As_6N_2O_{28}Sn_7$ (2649.83): calcd. C 29.94, H 3.73, N 1.06; found C 29.62, H 3.98, N 1.27. IR: ṽ = 3735 (w), 3672 (w), 3624 (w), 3590 (w), 3566 (w), 3058 (w), 2939 (w), 2821 (w), 1762 (m), 1512 (w), 1437 (m), 1379 (w), 1095 (m), 1024 (m), 861 (s), 814 (s), 730 (m), 686 (m), 506 (m), 437 (s), 405 (s) cm^{-1}.

X-ray Crystallography: Single-crystal X-ray diffraction data for compounds **1a**, **3**, and **4** were recorded with a Bruker Apex CCD diffractometer with graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å) at 293 K. Diffraction data for other compounds were collected with a Rigaku RAXIS-RAPID single-crystal diffractometer with Mo-K_α radiation (λ = 0.71073 Å) at 293 K. Absorption corrections were applied using multiscan techniques.[13] All the structures were solved by the direct methods of SHELXS-97[14] and refined by full-matrix least-squares techniques by using the SHELXL-97 program[15] within WINGX.[16] Detailed crystallographic data and structure refinement parameters for the compounds are summarized in Tables 1 and 2. CCDC-697684 (for **1a**), -697685 (for **1b**), -697686 (for **2**), -697687 (for **3**), -697688 (for **4**), -697689 (for **5**), and -697690 (for **6**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (see footnote on the first page of this article): Selected bond lengths and angles for compounds **1**–**6**.

Table 1. Crystal data and structure refinements for compounds **1**–**3**.

	1a	**1b**	**2**	**3**
Formula	$C_{54}H_{80}As_5N_5O_{31}Sn_5$	$C_{53}H_{76}As_5N_5O_{30}Sn_5$	$C_{52}H_{90}As_2N_4O_{32}Sn_6$	$C_{64}H_{92}As_6N_6O_{36}Sn_6$
Fw	2263.28	2231.24	2145.26	2683.10
Crystal system	triclinic	triclinic	monoclinic	monoclinic
Space group	$P\bar{1}$	$P\bar{1}$	$p2_1/n$	$p2_1/c$
a [Å]	13.1779(11)	13.244(6)	13.345(8)	14.9000(14)
b [Å]	15.9398(13)	15.899(6)	19.814(8)	22.642(2)
c [Å]	20.3286(17)	20.114(7)	15.666(8)	14.5363(14)
α [°]	93.109(1)	91.804(12)	90	90
β [°]	91.964(1)	90.658(14)	114.222(18)	106.214(1)
γ [°]	108.220(1)	110.232(16)	90	90
V [Å^3]	4044.1(6)	3971(3)	3778(3)	4709.0(8)
Z	2	2	2	2
$D_{calcd.}$ [g cm^{-3}]	1.859	1.866	1.886	1.892
F(000)	2204.0	2168.0	2104	2608.0
Reflections collected/unique	17729/9887	16720/7497	8344/4135	8374/4329
GOF on F^2	0.998	0.967	1.014	0.980
R_1[a] [$I>2\sigma(I)$]	0.0509	0.0893	0.0730	0.0552
wR_2[b] [$I>2\sigma(I)$]	0.1343	0.2153	0.1706	0.1435

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR_2 = |\Sigma w(|F_o|^2 - |F_c|^2)|/\Sigma|w(F_o^2)^2|^{1/2}$.

Table 2. Crystal data and structure refinements for compounds **4**–**6**.

	4	**5**	**6**
Formula	$C_{71}H_{114}As_6O_{27}Sn_7$	$C_{72}H_{112}As_6N_2O_{28}Sn_7$	$C_{66}H_{100}As_6N_2O_{28}Sn_7$
Fw	2407.5(3)	2733.99	2649.83
Crystal system	triclinic	triclinic	monoclinic
Space group	$P\bar{1}$	$P\bar{1}$	$p2_1/n$
a [Å]	12.8200(9)	13.667(8)	12.496(2)
b [Å]	13.8336(10)	15.021(6)	29.564(6)
c [Å]	15.2162(11)	15.262(7)	13.634(3)
α [°]	77.630(1)	111.181(15)	90
β [°]	68.573(0)	112.660(18)	100.86(9)
γ [°]	75.296(1)	97.244(18)	90
V [Å^3]	2407.5(3)	2565(2)	4946.6(18)
Z	1	1	2
$D_{calcd.}$ [g cm^{-3}]	1.848	1.770	1.779
F(000)	1304.0	1330.0	2564.0
Reflections collected/unique	10754/7493	11220/5537	11034/8713
GOF on F^2	1.017	0.949	1.053
R_1[a] [$I>2\sigma(I)$]	0.0416	0.0712	0.0510
wR_2[b] [$I>2\sigma(I)$]	0.0945	0.1606	0.1519

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR_2 = |\Sigma w(|F_o|^2 - |F_c|^2)|/\Sigma|w(F_o^2)^2|^{1/2}$.

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