Monoorganooxotin cage, diorganotin ladders, diorganotin double chain and triorganotin single chain formed with phosphonate and arsonate ligands[†]

Yun-Peng Xie, Jian-Fang Ma,* Jin Yang* and Min-Zhong Su

Received 27th July 2009, Accepted 29th October 2009 First published as an Advance Article on the web 11th December 2009 DOI: 10.1039/b915255e

The solvothermal reaction of *n*-BuSn(O)OH with PhPO₃H₂ afforded the hexanuclear monoorganooxotin phosphonate cage, {[(n-BuSn)₃(MeO)₃O]₂(O₃PPh)₄}·MeOH **1**. When the *n*-Bu₂Sn(PhCO₂)₂ precursor reacted with PhPO₃H₂ in a 1 : 1 stoichiometric ratio, the diorganotin phosphonate ladder [*n*-Bu₂SnO₃PPh]_{*n*} **2** was obtained. The reaction of [*n*-Bu₂(PrO)Sn]₂O with 4-OH-3-NO₂-C₆H₃AsO₃H₂ affords the diorganotin arsonate ladder [*n*-Bu₂Sn(4-OH-3-NO₂-C₆H₃AsO₃)]_{*n*} **3**, while the reaction of [*n*-Bu₂(PrO)Sn]₂O with 4-NO₂-C₆H₄AsO₃H₂ and 4-Me-C₆H₄SO₃H gives an diorganotin double chain [*n*-Bu₂Sn(4-Me-C₆H₄SO₃)(4-NO₂-C₆H₄AsO₃H)]_{*n*} **4**, which contains both sulfonate and arsonate ligands. The reaction of 4-NO₂-C₆H₄AsO₃H₂, EtONa, and Ph₃SnCl yields a new triorganotin arsonate single chain [(Ph₃Sn)₄(4-NO₂-C₆H₄AsO₃)₂·H₂O]_{*n*} **5**. The NMR (¹H, ¹³C, ¹¹⁹Sn) spectra of compounds **1** and **4** were studied.

Introduction

Organostannoxanes are a very interesting class of compounds which have been attracting interest in view of their remarkable structural diversity¹ as well as their utility as catalysts² in organic reactions. So far, organotin carboxylates, phosphinates and sulfonates have been extensively prepared and structurally characterized.³⁻⁵ But very few organotin compounds based on phosphonate and arsonate ligands are known because of the difficulty in obtaining their crystals. Particularly, crystal structures of the polymeric organotin phosphonates and arsonates, such as chain and ladder, have not been documented, and only were surmised through the IR, Mössbauer, and X-ray powder diffraction.⁶ Therefore, exploration of the crystal structures of the polymeric organotin phosphonates and arsonates attracted our intense interest.

Development of new synthetic strategies is important for the discovery of new structural types in organotin compounds. In this regard, we have been endeavouring to develop new synthetic approaches for organotin compounds. Accordingly, a series of new organotin clusters were firstly obtained through a solvothermal method.⁷ For example, the solvothermal reaction of $(n-Bu_2SnO)_x$ with 1,1'-ferrocenedicarboxylic acid gave the first tin–oxygen cluster $Sn_8O_4L_6$ ($H_2L = 1,1'$ -ferrocenedicarboxylic acid).^{7a} The solvothermal reaction of Bz_3SnCl with monosodium phenylphosphonate yielded the first organotin phosphonate oligomer, $[Na_6(CH_3OH)_2(H_2O)][{(BzSn)_3(PhPO_3)_5(\mu_3-O) (CH_3O)}_2Bz_2Sn]\cdotCH_3OH.^{7b}$ When the triphenyltin compounds were treated with arsonic acids under solvothermal conditions, four new types of organotin/tin–oxygen arsonate clusters were obtained. $^{7\mathrm{c}}$

The suitability of pre-synthesized organotin compounds to serve as precursors for new types of organotin compounds is currently being actively investigated. For instance, Shankar *et al.* have synthesized a series of novel diorganotin derivatives by utilizing di-*n*-butyltin(alkoxy)alkanesulfonates as precursors.⁸ Among the organotin precursors, distannoxane [*n*-Bu₂(PrO)Sn]₂O is an attractive candidate precursor, where the PrO groups are easily replaced by other ligands, leading to new types of organotin structures. For example, when the [*n*-Bu₂(PrO)Sn]₂O precursors were treated with methylphosphonic acid and phenylphosphonic acid, compounds [Bu₂Sn(HO₃PMe)₂]₂ and Bu₂Sn(O₃PPh) were obtained, respectively.^{9a} However, only the structure of the former was determined by single-crystal X-ray diffraction.

The above results stimulated our research interest toward further exploring the structural variations of the organotin phosphonates and arsonates. In this work, the solvothermal reaction of *n*-BuSn(O)OH with PhPO₃H₂ in methanol leads to the formation of {[(*n*-BuSn)₃(MeO)₃O]₂(O₃PPh)₄}·MeOH **1**, while the reaction of *n*-Bu₂Sn(PhCO₂)₂ with PhPO₃H₂ gives [*n*-Bu₂SnO₃PPh]_{*n*} **2**. The reaction of [*n*-Bu₂(PrO)Sn]₂O precursor with 4-OH-3-NO₂-C₆H₃AsO₃H₂ affords the diorganotin arsonate ladder [*n*-Bu₂Sn(4-OH-3-NO₂-C₆H₃AsO₃)]_{*n*} **3**, while the reaction of [*n*-Bu₂(PrO)Sn]₂O precursor with 4-Me-C₆H₄SO₃H gives an diorganotin double chain [*n*-Bu₂Sn(4-Me-C₆H₄ASO₃H₂, EtONa, and Ph₃SnCl yields a new triorganotin arsonate single chain [(Ph₃Sn)₄(4-NO₂-C₆H₄ASO₃)₂·H₂O]_{*n*} **5**.

Results and discussion

Synthesis and characterization of compounds 1-5

Compound 1 was obtained through the reaction of *n*-BuSn(O)OH with $PhPO_3H_2$ in methanol at 140° C (Scheme 1). Upon exposure to air, crystals of compound 1 became opaque within minutes,

Key Lab of Polyoxometalate Science, Department of Chemistry, Northeast Normal University, Changchun, 130024, People's Republic of China. E-mail: jianfangma@yahoo.com.cn yangjinnenu@yahoo.com.cn

[†] Electronic supplementary information (ESI) available: Five X-ray crystallographic files (CIF), selected bond distances and angles. CCDC reference numbers 737801–737805. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b915255e



Scheme 1 Synthetic route of compound 1.

indicating a loss of solvent. The syntheses of compounds 2–5 are summarized in Schemes 2 and 3. The single crystals of 2–4 were directly obtained by crystallization of the respective reaction mixtures at room temperature, while the crystals of compound 5 were obtained at a refluxing temperature.



Scheme 2 Synthetic routes of compounds 2–5.



Scheme 3 Synthetic route of compound 5.

Molecular structure of ${[(n-BuSn)_3(MeO)_3O]_2(O_3PPh)_4}$ ·MeOH (1)

The crystal data of **1–5** are summarized in Table 1, whereas selected bond lengths and angles are given in Table S1 (see ESI[†]).

In view of the isolation of the organotin phosphonate $\{Na_{6}(CH_{3}OH)_{2}(H_{2}O)\} \{(BzSn)_{3}(PhPO_{3})_{5}(\mu_{3}-O)(CH_{3}O)]_{2}Bz_{2}Sn\}$ CH₃OH, we performed an analogous solvothermal reaction. The hexanuclear cage $\{[(n-BuSn)_3(MeO)_3O]_2(O_3PPh)_4\}$ ·MeOH 1 was obtained through the reaction of n-BuSn(O)OH with PhPO₃H₂ in methanol at 140° C (Scheme 1). As shown in Fig. 1, 1 contains two tritin units $[(n-BuSn)_3(O)(MeO)_3]$, where three tin atoms (Sn1, N)Sn2 and Sn3) are joined together by a μ_3 -oxygen ligand. Two adjacent tin atoms are further connected by one μ_2 -MeO⁻ group. The two $[(n-BuSn)_3(O)(MeO)_3]$ units are linked through four PhPO₃²⁻ ions, affording the first hexanuclear monoorganooxotin phosphonate cage. Each of the phenylphosphonate groups shows the μ_3 -bridging coordination mode. All of the tin atoms are hexacoordinated, bonding to one carbon atom and five oxygen atoms in octahedral coordination geometries. The average μ_3 -O-Sn bond length is 2.06 Å, while the average μ_2 -O-Sn bond length is 2.15 Å. The average Sn–O distance involving the bridging phosphonate is 2.08 Å. These values are comparable to those observed in other organotin phosphonate clusters.7b



Fig. 1 Molecular structure of **1**. All H atoms have been omitted for clarity. Symmetry code: $^{#1}$ 1–x, 1–y, z.

A hexanuclear monoorganooxotin phosphite cage {[(n- $BuSn_{3}(PhO)_{3}O_{2}(O_{3}PPh)_{4}$ and a hexanuclear inorganic tinoxygen arsonate cage { $[Sn_3Cl_3(O)(MeO)_3]_2(2-NO_2-C_6H_4AsO_3)_4$ } have been reported.7d,7e The compound 1 is clearly related to the two previously reported hexanuclear structures, however, there are a number of significant differences. In comparison with the reported {[(n-BuSn)₃(PhO)₃O]₂(O₃PPh)₄}, the μ_2 -PhO⁻ groups of the $[(n-BuSn)_3(O)(PhO)_3]$ unit are replaced by the μ_2 - MeO^{-} groups of the $[(n-BuSn)_3(O)(MeO)_3]$ for 1. The two $[(n-BuSn)_3(O)(MeO)_3]$ for 1. $BuSn_{3}(O)(PhO)_{3}$ units are further connected to each other by four HPO₃²⁻ ions, affording the hexanuclear monoorganooxotin phosphite cage. However, in contrast to {[Sn₃Cl₃(O)(MeO)₃]₂(2- $NO_2-C_6H_4AsO_3_4$, the Cl⁻ groups of the $[Sn_3Cl_3(O)(MeO)_3]$ unit are replaced by *n*-Bu groups of the $[(n-BuSn)_3(O)(MeO)_3]$ for 1. The two [Sn₃Cl₃(O)(MeO)₃] units are further linked through four $2-NO_2-C_6H_4AsO_3^{2-}$ ions, giving the hexanuclear tin-oxygen arsonate cage. Thus, compound 1 represents the hexanuclear monoorganooxotin phosphonate cage.

$Table \ 1 \quad Crystal \ data \ and \ structure \ refinements \ for \ compounds \ 1-5$

	1	2	
Formula	$C_{55}H_{96}O_{21}P_4Sn_6$	$C_{42}H_{69}O_9P_3Sn_3$	
FW	1929.34	1166.95	
Cryst. syst.	Triclinic	Monoclinic	
Space group	$P\overline{1}$	$P2_{1}/c$	
a/Å	12.437(7)	14.794(3)	
b/Å	12.829(6)	21.870(5)	
c/Å	14.246(6)	17.051(4)	
α (°)	63.359(14)	90	
β (°)	82.908(19)	109.379(8)	
γ (°)	70.228(19)	90	
$V/Å^3$	1910.8(16)	5204.4(19)	
Ζ	1	4	
$D_{\rm c}/{\rm g}~{\rm cm}^{-3}$	1.677	1.489	
F(000)	954	2352	
Reflns collected/unique	18475/8514	47860/11628	
GOF on F^2	1.093	1.050	
$R_{\rm int}$	0.0253	0.0646	
$R_1[I > 2\sigma(I)]$	0.0362	0.0525	
R_1 [all data]	0.0438	0.0857	
$WR_2[I > 2\sigma(I)]$	0.1152	0.1374	
wR_2 [all data]	0.1211	0.1605	
	3	4	5
Formula	$C_{14}H_{22}AsNO_6Sn$	$C_{21}H_{30}AsNO_8SSn$	$C_{84}H_{70}As_2N_2O_{11}Sn_4$
FW	493.94	649.92	1908.02
Cryst. syst.	Monoclinic	Triclinic	Triclinic
Space group	C2/c	<i>P</i> 1	<i>P</i> 1
a/Å	21.3171(10)	9.393(6)	12.806(3)
b/Å	16.9883(11)	10.437(5)	14.635(4)
c/Å	12.3270(15)	14.206(6)	23.623(7)
α (°)	90	91.074(14)	80.774(11)
β (°)	122.929(2)	92.744(19)	88.419(10)
γ (°)	90	107.485(18)	65.454(10)
$V/Å^3$	3746.9(5)	1326.0(1)	3971.4(19)
Ζ	8	2	2
$D_{\rm c}/{\rm g~cm^{-3}}$	1.751	1.628	1.588
F(000)	1952	650	1874
Reflns collected/unique 9411/3329	13180/6007	38320/17825	
GOF on F^2	1.054	1.036	1.038
$R_{\rm int} 0.0340 0.0553 0.0483$			
$R_1[I > 2\sigma(I)]$	0.0514	0.0507	0.0613
R_1 [all data]	0.0707	0.0839 0.1083	
$wR_2[I > 2\sigma(I)]$	0.1396	0.0992	0.1414
wR_2 [all data]	0.1535	0.1036 0.1667	

Molecular structure of $[n-Bu_2SnO_3PPh]_n$ (2)

To the best of our knowledge, the only studies on dibutyltinphosphonates with a basic structural unit of the type Bu₂SnO₃PR were made at the end of the 1960s by Ridenour *et al.* ($\mathbf{R} = C_6 H_{13}$, $CH_2 C_6 H_5$, $C_8 H_{17}$),^{9b} Freireich *et al.* ($\mathbf{R} = C_6 H_5$)^{9c} and Ribot et al. ($R = C_6H_5$, CH_3).^{9a} However, crystals have not been obtained for these compounds. Here, the n-Bu₂Sn(PhCO₂)₂ precursor reacted with PhPO₃H₂ in a 1:1 stoichiometric ratio, the ladder-like dibutyltinphosphonate chain $[n-Bu_2SnO_3PPh]_n$ 2 was obtained (Scheme 2). As shown in Fig. 2a, the asymmetric unit of 2 is composed of three crystallographically unique tin atoms (Sn1 to Sn3) and three phenylphosphonate ligands which are bound to the three tin atoms in two different coordination modes. The phenylphosphonate group (P2) is bound to three tin atoms (Sn1 to Sn3). On the other hand, the phenylphosphonate group (P1or P3) is bound to two tin atoms (Sn1, Sn3 for P1 and Sn2, Sn3 for P3) through its two O atoms contributing to the formation of the eightmembered ring $(Sn_2P_2O_4)$, and it employs the third oxygen atom



Fig. 2 (a) Structure of the asymmetric unit of **2**. (b) Molecular structure of $[n-Bu_2SnPhPO3]_n$, **2**. (c) Sn–O–P core of **2** showing a ladder-like structure along the *b*-axis. Symmetry codes: ^{#1} 2–x, 2–y, –z+1; ^{#2} 1–x, 2–y, –z.

to coordinate to the adjacent asymmetric unit. The cumulative effect of the coordination of the phenylphosphonates leads to the formation of the ladder-like diorganotin phosphonate chain (Fig. 2b). The chain is built from edge-sharing eight-membered rings ($Sn_2P_2O_4$), with strictly alternating Sn and P nodes. However, the chain is non-planar, when looking along the *a*-axis (Fig. 2c). Each tin is five-coordinate with a C_2O_3 coordination environment. The geometry around each tin is distorted trigonal bipyramid (oxygen atoms in the apical position, angle O–Sn–O = $170.6(2)-175.8(2)^{\circ}$). The average Sn–O bond length is 2.16 Å.

It is noteworthy that the architecture of the present diorganotin phosphonate chain is entirely different from that of the reported diorganotin phosphinate chain $\{[(n-Bu_2Sn)_2(OH)][cycPO_2]_3\}_n$ $(cvcPO_2H = 1, 1, 2, 3, 3$ -pentamethyltrimethylene phosphinic acid), consisting of alternate planar six- (Sn₂PO₃), and eight-membered rings (Sn₂P₂O₄).⁹ The adjacent six- and eight-membered rings are nearly coplanar. The bridging bidentate mode of phosphinate ligands leads to the formation of the chain. However, in 2 the phenylphosphonate groups, in unusual dianionic tridentate modes, linked the n-Bu₂Sn groups into a non-planar ladderlike chain structure, which is only built from eight-membered rings $(Sn_2P_2O_4)$. Also, the eight-membered ring $(Sn_2P_2O_4)$ is non-planar. Obviously, the third coordinating oxygen atom of the phenylphosphonate unit plays a significant role in the formation of the diorganotin phosphonate chain of 2. On the other hand, compound $[Me_2Sn(\mu_3-dipp)]_n$ (dipp-H₂ = 2,6diisopropylphenylphosphate) has been reported.9a In [Me₂Sn(µ₃ $dipp)]_{n}$, each dipp ligand bridges three different tin atoms to form an infinite ladder-chain structure. In comparison with $Me_2Sn(\mu_3$ dipp)], the dipp groups are replaced by phenylphosphonates for 2. Consequently, the P–O bonds [1.50 (5)–1.55(5) Å] in 2 are longer than the ones [1.49 (7)-1.51(6) Å] in $[\text{Me}_2\text{Sn}(\mu_3\text{-dipp})]_n$.

Molecular structure of $[n-Bu_2Sn(4-OH-3-NO_2-C_6H_3AsO_3)]_n$ (3)

The reaction of [n-Bu₂(PrO)Sn]₂O with 4-OH-3-NO₂- $C_6H_3AsO_3H_2$ in a 1:2 molar ratio affords a diorganotin arsonate ladder $[n-Bu_2Sn(4-OH-3-NO_2-C_6H_3AsO_3)]_n$ 3. X-ray crystallographic study reveals that the structure of ${\bf 3}$ shows an infinite ladder. To the best of our knowledge, there have been no reports on the crystal structures of diorganotin arsonates, and therefore the diorganotin arsonate ladder of 3 was firstly found in organotin arsonate compounds. As shown in Fig. 3a, the asymmetric unit of 3 is composed of one crystallographically unique tin atom (Sn1) and one arsonate ligand. The arsonate group is bound to the tin atom (Sn1) through its one O atom, and it employs the remaining two oxygen atoms to coordinate to the two adjacent asymmetric units. The μ_3 -O₃As bonding mode of arsonates leads to the formation of the distorted diorganotin arsonate ladder running along the b-axis (Fig. 3b). The ladder is built from edge-sharing eight-membered rings $(Sn_2As_2O_4)$, with strictly alternating Sn and As nodes. However, the ladder is non-planar, when looking along the a-axis (Fig. 3c). Each tin atom is in a distorted trigonal bipyramid coordination environment surrounded by three arsonate-oxygen atoms and two carbon atoms of two of the *n*-butyl groups. The average Sn-O bond length is 2.11 Å.

In addition, there are intramolecular hydrogen bonding (O4–H4 \cdots O5) and intermolecular interactions (O4–H4 \cdots O5^{#1})



Fig. 3 (a) Structure of the asymmetric unit of **3**. (b) Molecular structure of **3** along the *b*-axis. (c) Molecular structure of **3** along the *a*-axis. The α -carbon of phenyl ring (As–Ph) is reserved, and the other atoms, which are omitted for clarity. Symmetry codes: ^{#1} 1–x, y, –z+3/2; ^{#2} x, –y, z+1/2; ^{#3} x, –y+1, z–1/2.

between chains, forming a two-dimensional supramolecular structure (Fig. 4). The oxygen atoms (O5) and the hydrogen atoms (H4) are involved in these hydrogen-bonding interactions to form a 4-membered hydrogen-bonding ring. The distances of $O \cdots O$ interactions for O4–H4 \cdots O5 and O4–H4 \cdots O5^{#1} are 2.60(1) and 3.01(2) Å, respectively (Table 2).



Fig. 4 The two-dimensional supramolecular network structure of **3**. The hydrogen atoms which are not involved in hydrogen-bonding interactions are omitted for clarity. The butyl groups on tin are omitted except for the carbon atoms bonded to tin atoms.

Compounds 2 and 3 are 1D polymers with similar architectures. Two polymeric chains are built from edge-sharing eight-membered rings $Sn_2E_2O_4$ (E = P or As), with strictly alternating Sn and E nodes. It is noteworthy that polymeric chains of compounds 2 and 3 display beautiful sinusoidal ruffles (Fig. 2c and Fig. 3c), and the period of compound 3 is shorter than that of compound 2.

Molecular structure of $[n-Bu_2Sn(4-Me-C_6H_4SO_3)(4-NO_2-C_6H_4AsO_3H)]_n$ (4)

The reaction of $[n-Bu_2(PrO)Sn]_2O$ with $4-NO_2-C_6H_4AsO_3H_2$ and $4-Me-C_6H_4SO_3H$ gives an unusual diorganotin double chain

D-H····A	D…A/Å	H · · · A/Å	$D\text{-}H\cdots A(deg)$	Symmetry
Compound 3				
O4-H4O5 O4-H4O5 ^{#1}	2.60(1) 3.01(2)	1.90 2.33	141.4 140.4	1-x, -y, 2-z
Compound 4				
$\begin{matrix} 06\text{-}H6\cdots O3^{\#1} \\ C11\text{-}H11\cdots O3^{\#1} \\ C21\text{-}H21\cdots O6^{\#2} \\ C13\text{-}H13\cdots O8^{\#3} \end{matrix}$	2.64(5) 3.39(8) 3.29(8) 3.47(1)	2.05 2.48 2.54 2.56	128.8 166.7 137.8 167.0	2-x, 1-y, 2-z 2-x, 1-y, 2-z 2-x, -y, 2-z 2-x, 1-y, 3-z

[*n*-Bu₂Sn(4-Me-C₆H₄SO₃)(4-NO₂-C₆H₄AsO₃H)]_{*n*} **4**. A part of the molecular structure of **4** corresponds to a dimer based on an eight-membered ring formed by the μ_2 -O₂As bonding mode of the hydrogenarsonate group. Further, the sulfonate groups act in a μ_2 -O₂S bonding mode to form a weak bond with a tin atom of the neighboring dimer, resulting in the formation of a double chain comprising alternate eight-membered rings being formed by the hydrogenarsonate and sulfonate ligands, respectively (Fig. 5). Each tin atom adopts a distorted octahedral geometry with the SnO₄ core occupying the basal plane and *trans* disposition of n-butyl groups. The mean Sn–O₅ bond lengths [2.45(1)–2.53(2) Å] across the two sulfonate groups are found to be much longer than those observed for Sn–O_{As} bonds [2.05(1)–2.12(2) Å].



Fig. 5 The structure of complex **4**. All H atoms have been omitted for clarity. Symmetry codes: $^{#1}$ x, y–1, z; $^{#2}$ x, y+1, z.

It is noteworthy that the architecture of **4** is entirely different from that of **3**. In **4**, the hydrogenarsonate and sulfonate ligands show the μ_2 -bridging coordination modes. Each tin atom is sixcoordinate with a C₂O₄ coordination environment. However, in **3**, all the arsonate ligands show the μ_3 -bridging coordination modes. Each tin is five-coordinate with a C₂O₃ coordination environment. Obviously, the third coordinating oxygen atom of the arsonate unit plays a significant role in the formation of **3**. However, in **4**, the introduction of sulfonate ligands is a critical factor in the formation of the double chain.

Compound **4**, which contains a 4-nitro substituent on the aromatic moiety, shows a three-dimensional supramolecular assembly formed by O–H···O and C–H···O interactions (Fig. 6). This can be understood in the following way. These one-dimensional chains are interconnected through three intermolecular interactions (O6-H6···O3^{#1}, C11-H11···O3^{#1} and C21-H21···O6^{#2}) affording a two-dimensional supramolecular structure (Fig. 6a). The distances of the O6···O3^{#1}, C11···O3^{#1} and C21···O6^{#2} interactions are 2.64(5), 3.39(8) and 3.29(8) Å, respectively. Fur-



Fig. 6 Three-dimensional supramolecular assembly of 4 formed from $O-H\cdots O$ and $C-H\cdots O$ interactions. (a) View showing part of the supramolecular assembly of 4. (b) View showing the three-dimensional supramolecular architecture.

ther, the two-dimensional supramolecular networks are further interconnected by intermolecular interactions (C13–H13 \cdots O8^{#3}) to give a three-dimensional supramolecular architecture (Fig. 6b). The distance of the C13 \cdots O8^{#3} interaction is 3.47(1) Å.

Molecular structure of $[(Ph_3Sn)_4(4-NO_2-C_6H_4AsO_3)_2 \cdot H_2O]_n$ (5)

Through the reaction of 4-NO₂-C₆H₄AsO₃H₂, EtONa and Ph₃SnCl, a new triorganotin arsonate single chain [(Ph₃Sn)₄(4- $NO_2-C_6H_4AsO_3)_2 H_2O_{1n}$ 5 was obtained. As shown in Fig. 7, the adjacent triorganotin motifs (Sn1 and Sn2) are bridged by the μ_2 -O₂As bonding mode of arsonate groups to form a single chain. The remaining oxygen atoms are bound to the other triorganotin motifs (Sn3 and Sn4). Thus, the geometries of all the tin atoms involved can be classified into two types: the five-coordinate tin (Sn1 and Sn2) and the four-coordinate tin (Sn3 and Sn4). The tin atom (Sn1 or Sn2) is trigonal bipyramidal (C₃O₂ coordination environment), with the apical positions being taken up by the oxygen atoms of two different arsonate ligands. The apical O-Sn-O angle is almost linear. The tetrahedral coordination geometry of Sn3 is defined by three C atoms of the phenyl groups and one O atom of the arsonate ligand. However, Sn4 is weakly coordinated by one water molecule [Sn–O = 2.77(2) Å]. Although the long Sn–O distances are well inside the sum of the van der Waals radii of the



Fig. 7 The structure of complex 5. [The α -carbon of phenyl ring (Sn–Ph) is reserved, and the other carbons, which are omitted for clarity.] Symmetry codes: ^{#1} 1+x, y, z; ^{#2} x–1, y, z.

Sn and O atoms (*ca.* 3.6 Å), there does not appear to be any major distortion of the tetrahedral Sn-coordination geometry as a result of this contact. The average Sn–O_{As} bond length is 2.13 Å. All the arsonate groups show the μ_3 -bridging coordination modes.

In our previous work, the solvothermal reaction of Ph₃SnCl with 4-NO₂-C₆H₄AsO₃H₂ yielded an inorganic tin-oxygen cluster $[Sn_3Cl_3(\mu_3-O)(EtO)_3]_2(4-NO_2-PhAsO_3)_4$.^{7e} The reaction proceeded with complete dearylation of triphenyltin compound. However, the reaction of 4-NO₂-C₆H₄AsO₃H₂, EtONa, and Ph₃SnCl at a refluxing temperature gave the new triorganotin arsonate single chain, $[(Ph_3Sn)_4(4-NO_2-C_6H_4AsO_3)_2\cdot H_2O]_n$ **5**. In contrast to the solvothermal reaction, reaction conditions used for obtaining **5** are relatively mild, and the cleavage of Sn–Ph bonds does not occur. The result reveals that the reaction conditions played an important role in the formation of organotin arsonates.

Notably, the possible structures of the diorganotin arsonates and phosphonates have been surmised by Cunningham et al. through IR, Mössbauer, and X-ray powder diffraction.^{6h} As shown in Scheme 4, the possible structures include a discrete dimer [Scheme 4(a)], two singe chains [Schemes 4(b) and 4(c)], a ladder [Scheme 4(d)] and a polymer [Scheme 4(e)]. In Scheme 4(a), the dimer is composed of two tin atoms and two arsonate (or phosphonate) ligands which are bound to the two tin atoms in the μ_3 -O₃As (or μ_3 -O₃P) binding mode. In the single chain of Scheme 4(b), the four-coordinate tin atoms are bridged by the arsonates in the μ_2 -O₂As bonding mode (or phosphonates in μ_2 -O₂P bonding mode). In Scheme 4(c), the single chain is similar to that of Scheme 4(b), whereas the free oxygen atoms of arsonate (or phosphonate) groups in Scheme 4(b) coordinate to neighbouring tin atoms. All tin atoms are five-coordinated. When each arsonate (or phosphonate) ligand is bound to the three tin atoms in μ_3 -O₃As (or μ_3 -O₃P) binding mode, the ladder [Scheme 4(d)] and sheet polymer [Scheme 4(e)] could be obtained.



 $\label{eq:scheme 4} \mbox{Possible structures for complexes $R_2Sn[R'EO_3]$ (E = P \mbox{ or } As)$.}$

Apparently, the ladder structure of 2 and 3 are consistent with that of Scheme 4(d). It should be pointed out that the diorganotin phosphonate and arsonate ladders were firstly confirmed through the single-crystal X-ray diffraction method. Therefore, compounds 2 and 3 are the first examples of the diorganotin ladder surmised by Cunningham *et al.* The diorganotin arsonate double chain of 4 comprises alternate eight-membered rings being formed by the hydrogenarsonate and sulfonate ligands. However, the structure type of **4** was not found in Scheme 4. By carefully observing the structure, we found that the double chain contains the diorganotin arsonate dimer which is entirely different from that of Scheme 4(a). In **4**, two arsonates, in μ_2 -O₂As bonding mode, bridge two tin atoms to yield a dimer, while the dimer depicted in Scheme 4(a) was formed by the μ_3 -O₃As bonding mode of arsonate group. The structure of **5** shows a triorganotin arsonate single chain structure. The whole structure of **5** was similar to diorganotin arsonate single chains surmised in Schemes 4(b) and 4(c). However, the coordination modes of arsonates in **5** differ from those of Schemes 4(b) and 4(c). The structure of **5** indicates that the reaction of triorganotin with arsonate also results in a single chain.

¹H, ¹³C and ¹¹⁹Sn NMR spectra

The compounds 1 and 4 can dissolve in CHCl₃ and DMSO, respectively. However, the compounds 2, 3 and 5 could hardly dissolve in any organic solvent. Therefore, ¹H, ¹³C and ¹¹⁹Sn NMR data of the compounds 1 and 4 were measured and discussed. The ¹H NMR spectrum of 1 displays signals at 0.59-0.71 ppm for the methyl groups (CH₃ of *n*-Bu), 0.87–1.40 ppm for the methylene groups (-CH₂ of *n*-Bu), 1.53–1.73 ppm for the methyl groups (-OCH₃), and 3.48 ppm for the methyl groups (CH₃OH). Other signals at 7.06-7.90 ppm can be attributed to the phenyl groups. The ¹³C NMR spectrum of **1** shows a signal at 13.57 ppm for the methyl groups (CH₃ of *n*-Bu), and 25.92-27.04 ppm for the methylene groups (-CH₂ of n-Bu). Other signals at 126.97–131.22 ppm may result from the phenyl groups. The ¹¹⁹Sn NMR signals of 1 occurred at -507.9, -515.2 and -545.0 ppm, respectively. The high negative chemical shifts observed in the ¹¹⁹Sn NMR indicate the presence of the CO₅ coordination environment around tin.^{7d} The ¹H NMR spectrum of **4** displays signals at 0.82 and 2.31 ppm for the methyl groups (CH₃ of *n*-Bu and CH₃ of *p*-Me-Ar), 1.26 and 1.56 ppm for the methylene groups (-CH₂ of n-Bu). The signals of the phenyl groups were observed at 7.14, 7.52, 8.09 and 8.46 ppm. The ¹³C NMR spectrum of 4 shows two signals at 14.16 and 21.46 ppm for the methyl groups (CH₃ of *n*-Bu and CH₃ of *p*-Me-Ar), two signals (26.80 and 27.67 ppm) for the methylene groups (-CH₂ of *n*-Bu), and other signals (124.86, 126.15, 128.81, 132.34, 138.81, 141.01, 145.43 and 150.79 ppm) for the phenyl groups. The ¹¹⁹Sn NMR signal of 4 appeared at -294.44 ppm, which is similar to that of reported diorganotin phosphonates.9a

Conclusion

In conclusion, five organotin phosphonates and arsonates {[$(n-BuSn)_3(MeO)_3O]_2(O_3PPh)_4$ }·MeOH 1, [$n-Bu_2SnO_3PPh]_n$ 2, [$n-Bu_2Sn(4-OH-3-NO_2-C_6H_3AsO_3)$]_n 3, [$n-Bu_2Sn(4-Me-C_6H_4SO_3)(4-NO_2-C_6H_4AsO_3H)$]_n 4 and [(Ph_3Sn)₄(4-NO_2-C_6H_4AsO_3)_2·H_2O]_n 5 have been successfully isolated. Compound 1 represents the hexanuclear monoorganooxotin phosphonate cage. The crystal structures of 2 and 3 feature diorganotin ladders. Compound 4 represents the diorganotin arsonate double chain which contains both sulfonate and arsonate ligands. Compound 5 shows the triorganotin arsonate single chain structure. From the results, we can conclude that utilizing the $n-Bu_2Sn(PhCO_2)_2$ and [$n-Bu_2(PrO)Sn$]₂O as starting precursors are a very efficient

method for the syntheses of novel diorganotin compounds. Further study of access to new organotin phosphonate and arsonate through the reactions of the organotin precursors is underway in our laboratory.

Experimental

General procedures

 $[n-Bu_2(PrO)Sn]_2O$ and $n-Bu_2Sn(PhCO_2)_2$ were prepared by literature methods.^{9a,10} C₆H₃PO₃H₂, 4-OH-3-NO₂-C₆H₃AsO₃H₂, 4-NO₂-C₆H₄AsO₃H₂, 4-Me-C₆H₄SO₃H and reagents were purchased from commercial sources. The C, H, and N elemental analysis was conducted on a Perkin-Elmer 240C elemental analyzer. The FT-IR spectra were recorded from KBr pellets in the range 4000–400 cm⁻¹ on a Mattson Alpha-Centauri spectrometer. ¹H, ¹³C and ¹¹⁹Sn NMR spectra of compounds **1** and **4** were recorded on a Mercury Plus-400 NMR spectrometer, and chemical shifts were given relative to Me₄Si and Me₄Sn.

Synthesis of compound 1

A mixture of *n*-BuSn(O)OH (0.104 g, 0.5 mmol) and PhPO₃H₂ (0.08 g, 0.5 mmol) in methanol (10 ml) was heated in a 15 ml Teflonlined autoclave at 140 °C for 3 days. When the mixture was cooled to room temperature, the resulting colorless crystals of compound **1** were collected and washed with methanol. Yield 0.347 g [36% based on *n*-BuSn(O)OH). Anal. Calcd for $C_{55}H_{96}O_{21}P_4Sn_6$ (*M*r = 1929.34): C, 34.24; H, 5.02. Found: C, 34.41; H, 5.34.¹H NMR (ppm): 0.59–0.71 (m, 18H, CH₃ of *n*-Bu), 0.87–1.73 (m, 36H, CH₂ of *n*-Bu), 1.53–1.73 (m, 18H, OCH₃), 3.48 (m, 3H, CH₃O), 7.06–7.90 (m, 20H, Ph); ¹³C NMR (ppm): 13.57 (CH₃ of *n*-Bu), 25.92–27.04 (CH₂ of *n*-Bu), 126.97–131.22 (Ph); ¹¹⁹Sn NMR (ppm): -507.9, -515.2 and -545.0. IR (cm⁻¹): 3737 (w), 3617 (w), 3588 (w), 3046 (w), 2921 (w), 2829 (w), 1519 (w), 1426 (m), 1382 (w), 1096 (m), 1026 (m), 862 (s), 814 (m), 723 (m), 690 (m), 509 (m), 437 (m).

Synthesis of compound 2

A mixture of *n*-Bu₂Sn(PhCO₂)₂ (0.210 g, 0.05 mmol) and PhPO₃H₂ (0.08 g, 0.5 mmol) was stirred in a chloroform (5 ml)/methanol (15 ml) for 6 h and filtered. The filtrated was left undisturbed to concentrate slowly by evaporation. After 1 week, colorless crystals of compound **2** were collected. Yield 0.135 g [23% based on *n*-Bu₂Sn(PhCO₂)₂. Anal. Calcd for C₄₂H₆₀O₉P₃Sn₃ (*M*r = 1166.95): C, 43.23; H, 5.96. Found: C, 43.41; H, 5.74. IR (cm⁻¹): 3748 (w), 3633 (w), 3047 (m), 2958 (w), 2932 (w), 1687 (w), 1586 (w), 1547 (m), 1494 (m), 1451 (w), 1121 (s), 1042 (s), 810 (m), 748 (m), 696 (m), 544 (m), 450 (m), 423 (m).

Synthesis of compound 3

A mixture of [n-Bu₂(PrO)Sn]₂O (0.150 g, 0.25 mmol) and 4-OH-3-NO₂-C₆H₃AsO₃H₂ (0.132 g, 0.5 mmol) was stirred in a chloroform (5 ml)/methanol (15 ml) for 6 h and filtered. The filtrated was left undisturbed to concentrate slowly by evaporation. After 1 week, colorless crystals of compound **3** were collected. Yield 0.027 g [11% based on [n-Bu₂(PrO)Sn]₂O. Anal. Calcd for C₁₄H₂₂AsNO₆Sn (Mr = 493.94): C, 34.04; H, 4.49. Found: C, 34.21; H, 4.34. IR (cm⁻¹): 3240 (w), 1612 (s), 1575 (w), 1530 (m), 1489 (m), 1432 (w),

1312 (w), 1252 (m), 1140 (w), 1102 (m), 1066 (w), 1044 (w), 897 (m), 874 (s), 828 (s), 545 (m), 507 (m), 450 (m), 423 (m).

Synthesis of compound 4

A mixture of [n-Bu₂(PrO)Sn]₂O (0.300 g, 0.5 mmol), 4-NO₂-C₆H₄AsO₃H₂ (0.124 g, 0.5 mmol) and 4-Me-C₆H₄SO₃H (0.088 g, 0.5 mmol) was stirred in a chloroform (5 ml)/methanol (15 ml) for 6 h and filtered. The filtrate was left undisturbed to concentrate slowly by evaporation. After 1 week, colorless crystals of compound 4 were collected. Yield 0.052 g [16% based on [n- $Bu_2(PrO)Sn_2O$. Anal. Calcd for $C_{21}H_{30}AsNO_8SSn$ (Mr = 649.92): C, 38.86; H, 5.96; N, 4.50. Found: C, 38.62; H, 4.74; N, 4.64.¹H NMR (ppm): 0.82 (m, 12H, CH₃ of *n*-Bu), 1.26 and 1.56 (m, 24H, CH₂ of n-Bu), 2.31 (s, 6H, CH₃ of p-Me-Ar), 7.14, 7.52, 8.09 and 8.46 (s, 16H, Ph); ¹³C NMR (ppm): 14.16 and 21.46 (CH₃ of *n*-Bu and CH₃ of *p*-Me-Ar), 26.80, and 27.67 (CH₂ of *n*-Bu), 124.86, 126.15, 128.81, 132.34, 138.81, 141.01, 145.43 and 150.79 (Ph);¹¹⁹Sn NMR (ppm): -294.4. IR (cm⁻¹): 3830 (w), 3725 (m), 3410 (m), 3100 (m), 2964 (m), 1652 (w), 1608 (w), 1533 (s), 1347 (m), 1208 (m), 1150 (m), 1095 (w), 1028 (m), 940 (m), 843 (s), 740 (w), 568 (w), 506 (w), 447 (m), 420 (m).

Synthesis of compound 5

The 4-NO₂-C₆H₄AsO₃H₂ (0.124 g, 0.5 mmol) and EtONa (0.068 g, 1 mmol) were added to the solution of dry ethanol (30 ml) in a standard Schlenk technique, and the mixture was stirred for 10 min. Triphenyltin(IV) chloride (0.386 g, 1 mmol) was then added to the mixture, and the reaction was refluxed for 6 h. The solution was filtered and the solvent of the filtrate was left undisturbed to concentrate slowly by evaporation. After 1 week, colorless crystals of compounds **5** were collected. Yield 0.109 g [23% based on Ph₃SnCI]. Anal. Calcd for C₈₄H₇₀As₂N₂O₁₁Sn₄ (*M*r = 1908.02): C, 52.87; H, 3.70; N, 1.47. Found: C, 53.32; H, 3.73; N, 1.64. IR (cm⁻¹): 3740 (w), 3649 (w), 3622 (w), 3414 (m), 3101 (w), 2927 (w), 1644 (w), 1612 (w), 1520 (s), 1482 (w), 1428 (w), 1351 (m), 1088 (m), 1037 (m), 883 (s), 848 (s), 722 (m), 678 (m), 568 (m), 445 (s), 418 (s).

X-ray crystallography

Single-crystal X-ray diffraction data for compound **3** was recorded on a Bruker Apex CCD diffractometer with graphitemonochromated Mo-K α radiation ($\lambda = 0.71073$ Å) at 293 K. Diffraction data for other compounds were collected on a Rigaku RAXIS-RAPID single-crystal diffractometer with Mo-K α radiation ($\lambda = 0.71073$ Å) at 293 K. Absorption corrections were applied using the multi-scan technique.¹¹ All the structures were solved by the Direct Method of SHELXS-97¹² and refined by full-matrix least-squares techniques using the SHELXL-97 program¹³ within WINGX.¹⁴ The detailed crystallographic data and structure refinement parameters for the compounds are summarized in Table 1.

Acknowledgements

We thank the Program for Changjiang Scholars and Innovative Research Teams in Chinese University, China Postdoctoral Science Foundation, the Postdoctoral Foundation of Northeast Normal University (NENU), the Training Fund of NENU's Scientific Innovation Project and the Analysis and Testing Foundation of NENU for support.

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