Organometallics **2007,** *26,* 2125−2128

Synthesis of an Organotin Oligomer Containing a Heptanuclear Tin Phosphonate Cluster by Debenzylation Reactions: X-ray Crystal Structure of $\{Na_6(CH_3OH)_2(H_2O)\}$-$\{[(BzSn)_3(PhPO_3)_5(\mu_3\text{-}O)(CH_3O)]_2Bz_2Sn\}\cdot CH_3OH$

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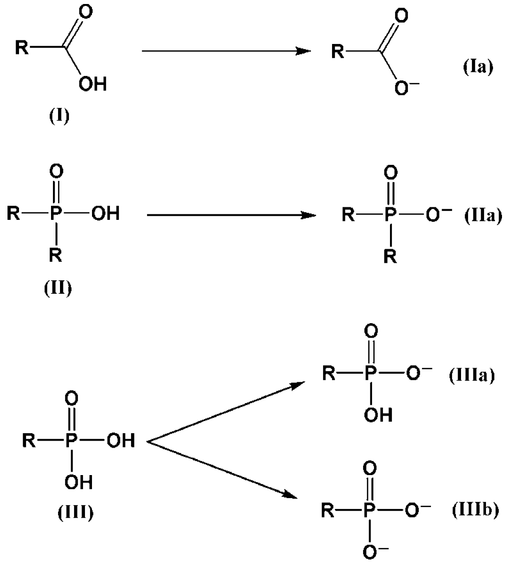
Received November 4, 2006

Summary: The first organotin phosphonate oligomer composed of alternating heptanuclear tin phenylphosphonate and hexanuclear sodium phenylphosphonate clusters was synthesized by a debenzylation process under solvothermal conditions.

Introduction

There is significant interest in the assembly and structural analysis of organotin clusters and coordination polymers.[1] Reagents such as carboxylic acids, phosphinic acids, and phosphonic acids can react with an organotin precursor to produce various organotin compounds containing carboxylate, phosphinate, and phosphonate substituents (Scheme 1). A large number of organotin carboxylates have been prepared and structurally characterized during the last few decades because of their biological properties as well as their interesting structural motifs.[2] Organotin derivatives that involve phosphinate substituents also have been reported.[3] Since both the carboxylate group and the phosphinate group have two coordinating oxygen atoms and one negative charge, in many cases organotin phosphinates show structural motifs similar to those of the carboxylates.[4] Unlike the carboxylate group, the phosphonate group contains three potentially coordinating oxygen atoms and can coordinate as a monoanionic group (IIIa in Scheme 1) and as a dianionic group (IIIb in Scheme 1). Generally, organotin phosphonate compounds, particularly those containing dianionic phosphonate ligands, show low solubility due to their oligomeric nature, and this causes difficulty in obtaining single crystals of such compounds. Therefore, a much less clear picture of the structural coordination chemistry of organotin phosphonates has developed over the years. To the best of our knowledge, only four crystal structures of organotin compounds containing monoanionic phosphonate substituents have been reported,[5a−d] and one crystal structure of an organotin compound containing both monoanionic phosphonate and dianionic phosphonate groups is known.[5e]

Scheme 1. Schematic Representation of Ligands for Organotin Synthesis



Conventionally, the syntheses of such organotin derivatives have been carried out by the reaction of an appropriate organotin precursor such as $R_3SnOSnR_3$, R_3SnOH, $(R_2SnO)_n$, or RSn(O)-

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10.1021/om061015u CCC: $37.00

(OH) with a carboxylic, phosphinic, or phosphonic acid at room or reflux temperature.[6] By means of this synthetic route a large number of structurally diverse organotin assemblies with various ligands have been realized and several types of organotin clusters such as *ladder, drum, cube, O-capped cluster, butterfly cluster, extended cage, crown cluster, and football cage* have been prepared and structurally characterized.[7−9] However, this strategy presents difficulties in obtaining crystal structures of organotin phosphonates, owing to their relatively low solubility. Therefore, other synthetic methods for the preparation of organotin phosphonates have been developed.[2a,10] In our previous work, we have tried a solvothermal approach for the preparation of organotin derivatives, and product crystallization was successful.[2a] Continuing our work on this new synthetic route and on the structural characterization of organotin clusters, we now report the first organotin phosphonate oligomer composed of alternating heptanuclear tin phenylphosphonate and hexanuclear sodium phenylphosphonate clusters formed by the reaction of tribenzyltin chloride ((Bz_3SnCl) with monosodium phenylphosphonate ($PhPO_3HNa$) under solvothermal conditions.

Results and Discussion

In view of the isolation of the inorganic tin cluster $Sn_8O_4L_6$ (H_2L = 1,1′-ferrocenedicarboxylic acid) by the reaction of (n-$Bu_2SnO)_x$ with 1,1′-ferrocenedicarboxylic acid under solvothermal conditions, where the reaction proceeded with complete dealkylation of (n-$Bu_2SnO)_x$, we probed an analogous reaction involving Bz_3SnCl and monosodium phenylphosphonate.[2a] The solvothermal reaction of Bz_3SnCl with monosodium phenylphosphonate in methanol was performed at 160 °C for 5 days to give colorless crystals of the oligomer $\{Na_6(CH_3OH)_2(H_2O)\}$-$\{[(BzSn)_3(PhPO_3)_5(\mu_3\text{-}O)(CH_3O)]_2Bz_2Sn\}\cdot CH_3OH$ (**1**) (eq 1).

$$Bz_3SnCl + PhPO_3HNa \xrightarrow[160°C,\ 5\ days]{MeOH} \{Na_6(CH_3OH)_2(H_2O)\} - \{[(BzSn)_3(PhPO_3)_5(\mu_3\text{-}O)(CH_3O)]_2Bz_2Sn\}\cdot CH_3OH \quad (1)$$

In addition to the colorless crystals of **1**, the reaction also gave some white amorphous powders. The XRD pattern of this powder is shown in Figure S1 (in the Supporting Information). Since both the compound **1** and the white powder are insoluble in common organic solvents, no solution NMR spectra could be recorded. In the IR spectrum of **1**, the bands of −OH groups of water and methanol appear at 3736 and 3621 cm^{-1}, and the band at 2962 cm^{-1} can be attributed to the methyl group. TGA shows that compound **1** gradually decomposes when it is heated from room temperature to 600 °C. Also, there is no melting point for compound **1**.

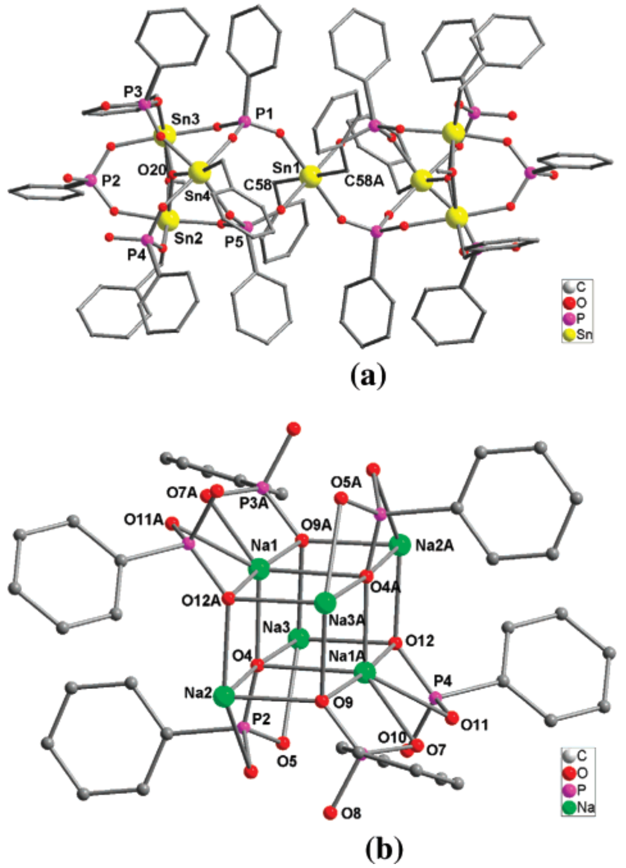

Figure 1. Views of the heptanuclear tin phenylphosphonate cluster (a) and the hexanuclear sodium phenylphosphonate cluster (b).

The water molecules and O^{2-} anions in **1** should come from the wet methanol. It is attractive to probe the product when the reaction was carried out in absolutely anhydrous methanol, and so we have carried out the synthesis using anhydrous methanol. Unfortunately, no crystals suitable for X-ray diffraction analysis were obtained, and the reaction only gave some amorphous powders. The X-ray powder diffraction pattern is provided as Figure S2 (in the Supporting Information). Since the powder is insoluble in common organic solvents, its NMR spectra cannot be recorded. The low solubility implies that the powder has a polymeric structure. Since the XRD pattern, IR data, and the results of elemental analysis of this white powder are almost the same as those of the powder formed in the reaction which gave compound **1**, these two powders may be the same compound.

The structure of compound **1** is shown in Figures 1 and 2. Compound **1** can be described as a one-dimensional chain structure formed by alternating heptanuclear tin phenylphosphonate and hexanuclear sodium phenylphosphonate clusters. We believe that compound **1** is the first such structural entity found for organotin compounds. As shown in Figure 1a, the heptanuclear tin cluster is composed of two centrosymmetrically related tritin subunits and one Bz_2Sn^{2+} group. In the tritin subunit, three tin atoms (Sn2, Sn3, and Sn4) are joined together by a μ_3-O^{2-} ion (O20). Sn2 and Sn4 are further connected by

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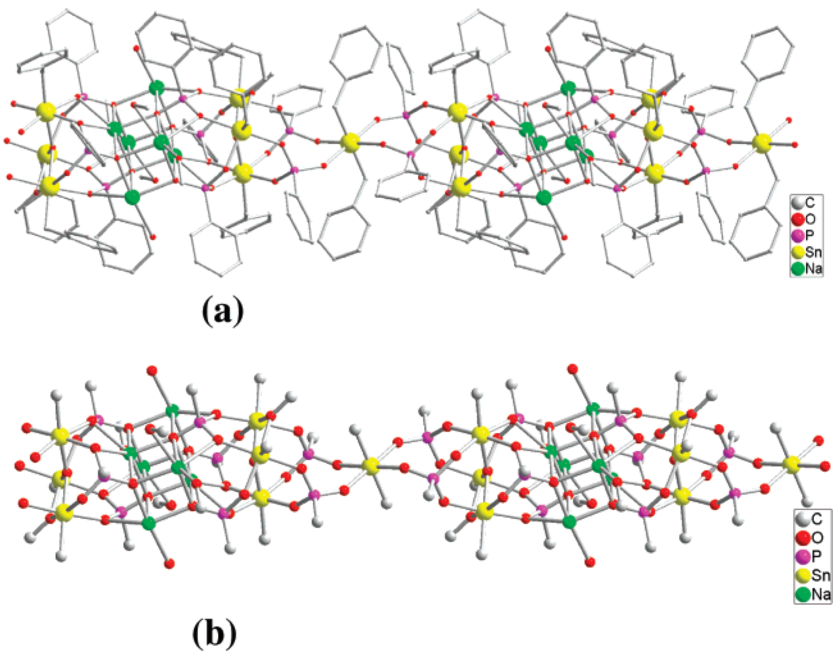
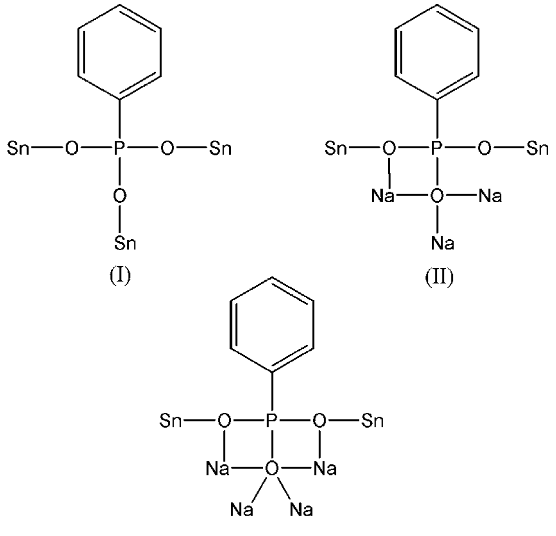


Figure 2. Views of the one-dimensional structure of **1**. In (b), all phenyl groups are omitted except for the carbon atoms bonded to phosphorus atoms.

two phenylphosphonate groups, and Sn3 and Sn4 are also further linked by two phenylphosphonate groups; Sn2 and Sn3 are further connected by one μ_2-MeO$^-$ ion and one phenylphosphonate group. Sn3 and Sn4 of one subunit are connected to the Bz_2Sn^{2+} ion through one phenylphosphonate group each. The two adjacent tritin motifs are bound to the same Bz_2Sn^{2+} ion, affording a heptanuclear tin phenylphosphonate cluster. It is noteworthy that the architecture of the present heptanuclear tin phenylphosphonate cluster is entirely different from that of the reported organotin phosphinates. Obviously, the third coordinating oxygen atom of the phenylphosphonate unit has a significant effect on the formation of the cluster. All tin atoms in **1** have a coordination number of 6; for Sn2, Sn3, and Sn4 atoms, this coordination is completed by one benzyl group and five oxygen atoms, while the Sn1 atom is six-coordinated by two benzyl groups and four oxygen atoms. Interestingly, partial debenzylation of Bz_3SnCl occurs in the formation of compound **1**, which plays a crucial role in the formation of the heptanuclear tin phenylphosphonate cluster. For the synthesis of the inorganic tin cluster $Sn_8O_4L_6$, complete dealkylation of n-Bu_2SnO was observed.[2a] The Sn−O distances involving the μ_3-O^{2-} ion are nearly similar, although not equal: Sn2−O20 = 2.098(7) Å, Sn3−O20 = 2.090(7) Å, and Sn4−O20 = 2.089(5) Å (Table S1 in the Supporting Information). In comparison, Sn−O distances involving the phosphonate oxygen atoms are slightly longer.

On the other hand, as shown in Figure 1b, six sodium ions are bridged by six phenylphosphonate ions to form a boxlike hexanuclear sodium phenylphosphonate cluster. The Na1 atom is bonded to six oxygen atoms from four different phenylphosphonate ions in a distorted-octahedral coordination sphere. Each of the Na2 and Na3 atoms is bonded to four oxygen atoms from three different phenylphosphonate ions. The Na−O(phosphonate) distances range from 2.205(7) to 2.757(10) Å, comparable to those observed in the related sodium compounds.[11] In addition, the Na2 atom is further bonded to two methanol molecules, and the Na3 atom is further coordinated by one water molecule. Five independent phenylphosphonate anions show three different kinds of coordination modes (Chart 1). For mode I, each O atom coordinates to one tin atom. For mode II, the anion acts as a hexadentate ligand, coordinating to two tin atoms and three Na atoms in all. For mode III, the anion acts as an octadenate ligand, coordinating to two tin atoms and four Na atoms in all. These phenylphosphonate anions with various coordination modes play an important role in the formation of the 1D oligomeric structure of **1**. Further studies on solvothermal syntheses and structural characterization of organotin clusters are under way in our laboratory.

Chart 1. Coordination Modes of the Phenylphosphonate Anion in Compound 1



Experimental Section

General Procedures. Bz_3SnCl[12] was prepared by literature methods. Other reagents were purchased from commercial sources.

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Anhydrous methanol was prepared by distilling the commercial methanol from magnesium methoxide under nitrogen.

The Sn and Na elemental analysis was obtained by inductively coupled plasma-atomic emission spectrometry (ICP-AES), with a Labtest Equipment Co. Model 710 Plasmas instrument. The C and H 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. TGA was performed on a Perkin-Elmer TG-7 analyzer heated from 35 to 600 °C under nitrogen. X-ray powder diffraction patterns were collected on a Rigaku D_{max} 2000 X-ray diffractometer with graphite-monochromated Cu Kα radiation ($\lambda = 0.154$ nm).

Synthesis of $PhPO_3HNa$. $PhPO_3HNa$ was obtained by evaporating a solution of phenylphosphonic acid (0.01 mol) and NaOH (0.01 mol) in water (10 mL) and drying at 80 °C under vacuum.

Synthesis of Compound 1. A mixture of Bz_3SnCl (0.107 g, 0.25 mmol) and $PhPO_3HNa$ (0.045 g, 0.25 mmol) in wet methanol (10 mL) was heated in a Teflon-lined autoclave at 160 °C for 5 days. When the mixture was cooled to room temperature, the resulting colorless crystals of compound **1** and some loose amorphous powders were separated, and each were washed with methanol.

Data for compound **1**: yield 30% (based on Bz_3SnCl); IR (cm^{-1}) 3736 (w), 3621 (w), 3054 (m), 2962 (w), 2924 (w), 1692 (w), 1646 (w), 1599 (m), 1547 (m), 1494 (m), 1443 (w), 1113 (vs), 1042 (vs), 807 (ms), 753 (ms), 692 (ms), 547 (ms), 457 (m). Anal. Calcd for $C_{121}H_{126}Na_6O_{38}P_{10}Sn_7$: C, 41.92; H, 3.66; Na, 3.98; Sn 23.97. Found: C, 41.86; H, 3.60; Na, 4.00; Sn, 24.04.

Data for the amorphous powder (0.060 g): IR (cm^{-1}) 3059 (w), 3024 (w), 2927 (w), 1964 (w), 1897 (w), 1598 (m), 1492 (m), 1438 (ms), 1146 (vs), 1069 (vs), 1024 (s), 999 (ms), 750 (m), 723 (m), 693 (ms), 553 (ms). Anal. Found: C, 53.46; H, 4.40; Na, 3.73; Sn, 19.44.

Reaction in Anhydrous Methanol. A mixture of Bz_3SnCl (0.107 g, 0.25 mmol) and $PhPO_3HNa$ (0.045 g, 0.25 mmol) in anhydrous methanol (10 mL) was heated in a Teflon-lined autoclave at 160 °C for 5 days. When the mixture was cooled to room temperature, some white amorphous powders were collected and washed with anhydrous methanol (0.112 g). IR (cm^{-1}): 3058 (w), 3026 (w), 2926 (w), 1964 (w), 1898 (w), 1598 (m), 1493 (m), 1439 (ms), 1146 (vs), 1069 (vs), 1024 (s), 998 (ms), 750 (m), 723 (m), 694 (ms), 553 (ms). Anal. Found: C, 53.39; H, 4.45; Na, 3.68; Sn, 19.52.

X-ray Crystallography. Single-crystal X-ray diffraction data were recorded on a Bruker Apex CCD diffractometer with graphite-monochromated Mo Kα radiation ($\lambda = 0.710\,73$ Å). Absorption corrections were applied by using multiscan techniques.[13] The structure was solved by direct methods with SHELXS-97[14] and refined by full-matrix least squares with SHELXL-97[15] within WINGX.[16] Selected crystal data are given in Table S2 of the Supporting Information.

Acknowledgment. We thank the National Natural Science Foundation of China (No. 20471014), Program for New Century Excellent Talents in Chinese University (NCET-05-0320), the Fok Ying Tung Education Foundation, and the Analysis and Testing Foundation of Northeast Normal University for support.

Supporting Information Available: A CIF file giving X-ray crystallographic data for **1**, tables giving selected bond lengths and angles for **1**, and figures giving XRD patterns for the amorphous powders and ORTEP plots of the heptanuclear tin phenylphosphonate cluster and the hexanuclear sodium phenylphosphonate cluster. This material is available free of charge via the Internet at http://pubs.acs.org.

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