## A Nonanuclear Organostiboxane Cage

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Summary: The first example of a nonanuclear organostiboxane cage,  $[(Ph_2Sb)_2(PhSb)_7(\mu-O)_{11}(\mu_3-O)_3(\mu-OH)_2(\mu-cycPO_2)_2(cyc-PO_2)_2(H_2O)_2] \cdot 2CH_3CN \cdot H_2O$ , containing Sb(V) has been assembled by a mild hydrolysis and Sb–C bond cleavage reaction of  $[(Ph_3Sb)_2(\mu-O)(\mu-cycPO_2)_2]$  (cycPO\_2 = 1,1,2,3,3-pentamethyltrimethylene phosphinate).

## Introduction

In contrast to the well-studied family of organostannoxanes,<sup>1</sup> the corresponding organostiboxanes have received much less attention, although initial efforts by the group of Sowerby were successful in the isolation of a diphenylantimony oxide whose cation consisted of a planar Sb<sub>6</sub>O<sub>6</sub> ring apart from two Sb<sub>2</sub>O<sub>2</sub> rings.<sup>2</sup> The latter motif was also found in di- and tetranuclear oxodiarylantimony phosphinates or arsinates.<sup>3</sup> Breunig and coworkers have also synthesized many Sb<sub>2</sub>O<sub>2</sub>-cored antimony complexes.<sup>4</sup> Recently in a significant breakthrough Beckmann and co-workers have isolated the first example of a well-defined stibonic acid,  $[2,6-Mes_2C_6H_3Sb(O)(OH)_2]_2$ , which also consists of a four-membered distiboxane ring.5a This group also succeeded in preparing mixed-valent antimony(III/V) oxo clusters [(2,6-Mes<sub>2</sub>C<sub>6</sub>H<sub>3</sub>Sb)<sub>4</sub>(SbCl)<sub>4</sub>(SbOH)<sub>2</sub>O<sub>14</sub>] by a controlled hydrolysis of 2,6-Mes<sub>2</sub>C<sub>6</sub>H<sub>3</sub>SbCl<sub>2</sub>.<sup>5b</sup> In a new dimension to stiboxane chemistry, Winpenny and co-workers have recently shown that  $[(ArSb)_4O_2(PhPO_3)_4(PhPO_3H)]$  and  $[(ArSb)_2(t-ArSb)_4(PhPO_3H)]$  $BuPO_{3}H_{6}O$  (Ar = *p*-chlorophenyl) function as ligands to afford a variety of polymetallic cages.<sup>6a,b</sup> Such approaches have also been extended to other systems.<sup>6c</sup> We have been involved for some time in delineating the chemistry arising out of the reactions of phosphonic and phosphinic acids with organotin oxides, hydroxides, and oxide-hydroxides.<sup>7</sup> In view of the rich structural diversity among the products obtained in such reactions we initiated a program on the study of analogous reactions involving organoantimony halides. Herein, we report the synthesis and structural characterization of  $[(Ph_3Sb)_2(\mu-O)(\mu$  $cycPO_2)_2]$  (1) and  $[(Ph_2Sb)_2(PhSb)_7(\mu-O)_{11}(\mu_3-O)_3(\mu-OH)_2(\mu$  $cycPO_2)_2(cycPO_2)_2(H_2O)_2] \cdot 2CH_3CN \cdot H_2O$  (2)  $(cycPO_2 = 1, 1, -$ 2,3,3-pentamethyltrimethylene phosphinate). The latter is an unprecedented nonanuclear organostiboxane cage containing a Sb<sub>9</sub>O<sub>16</sub> core. Unlike the mixed-valent Sb(III)/Sb(V) cages reported earlier, **2** is an all Sb(V) cage. Additionally, two putative stibinic acid motifs Ph<sub>2</sub>Sb(O)(OH) are trapped in the cage structure of **2** and serve as the two extremes of this ellipsoid molecule. Another interesting structural feature of **2** is that it possesses a partially hydrolyzed antimony center containing two molecules of water. Remarkably, **2** is formed by a concomitant Sb–C bond cleavage and hydrolysis reaction that occurs at very mild reaction conditions.

The reaction of Ph<sub>3</sub>SbCl<sub>2</sub>·H<sub>2</sub>O with *cyc*P(O)(OH) in the presence of 2 equiv of triethylamine afforded **1** (Chart 1, Figure 1), whose molecular structure was determined by single-crystal X-ray analysis<sup>8</sup> (*vide infra*). The <sup>31</sup>P NMR spectrum of **1** in C<sub>6</sub>D<sub>6</sub> revealed the presence of two closely spaced resonances at 48.02 and 48.56 ppm, respectively, which may be due to the slight nonequivalence of the phosphorus centers in **1**, which may be a result of variation of coordination modes (monodentate and bidentate).<sup>3a</sup> The <sup>1</sup>H NMR spectrum of **1** also is consistent with the presence of two nonequivalent phosphinate ligands. The <sup>31</sup>P chemical shifts of **1** are slightly upfield shifted in comparison to *cyc*P(O)(OH) (59.83 ppm, CDCl<sub>3</sub>). Such an upfield shift of <sup>31</sup>P resonance was noted before in [(*n*Bu<sub>2</sub>Sn)<sub>2</sub>( $\mu$ -OH)( $\mu$ -*cyc*PO<sub>2</sub>)<sub>3</sub>]<sub>n</sub> and [(*n*Bu<sub>3</sub>Sn)( $\mu$ -*cyc*PO<sub>2</sub>)]<sub>4</sub>.<sup>7c</sup>

The crystal structure of **1** reveals that its asymmetric unit contains one full molecule. The molecular structure of **1** (Figure 1) shows that it is made up of two triphenylantimony units that are bridged to each other by a  $\mu$ -O and two  $(cycPO_2)^-$  ligands. The latter bind the two antimony centers in a 2.11 mode,<sup>9</sup> affording two six-membered Sb<sub>2</sub>O<sub>3</sub>P rings, which are nearly perpendicular to each other (dihedral angle 86.7°) (Supporting Information). The six-membered rings themselves are nearly planar, although one oxygen atom (O2) deviates from the mean plane by 0.4 Å. The Sb–O–Sb angle found in **1** is quite wide (146.40(16)°) in comparison with (Ph<sub>3</sub>SbO)<sub>2</sub> (av 102.5(2)°).<sup>3d</sup> Two types of Sb–O distances are found in **1**. The bond distance involving the  $\mu$ -O is shorter (av 1.9537(25) Å) in comparison with that involving the phosphinate ligand (av 2.1926(31) Å). Only three other organoantimony compounds are known in the

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literature possessing similar structural features to those shown by 1.<sup>3a,10</sup> Interestingly the reaction of *cyc*PO<sub>2</sub>H with organotin substrates results in the formation of polymeric or macrocyclic compounds.<sup>7c</sup>



Figure 1. ORTEP diagram of 1. Thermal ellipsoids are set at 30%, and hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and bond angles (deg): Sb(1)-O(5) 1.959(3), Sb(2)-O(5) 1.949(3), Sb(1)-O(1) 2.160(3), Sb(1)-O(4) 2.204(3), Sb(2)-O(2) 2.214(3), Sb(2)-O(3) 2.194(3), Sb(2)-O(5)-Sb(1) 146.40(16).

In view of the recent interest in the hydrolytic chemistry of organoantimony and organotin compounds and recognizing that compounds such as **1** are hydrolytically sensitive, <sup>3a</sup> we effected a mild hydrolysis of **1** in a mixture of CH<sub>3</sub>CN and water (99:1, v/v) at 45 °C. In contrast to previous literature observations, where Sb(V)–C bonds were found to be stable, <sup>5b</sup> we find a facile Sb–C cleavage reaction accompanied by hydrolysis to afford [(Ph<sub>2</sub>Sb)<sub>2</sub>(PhSb)<sub>7</sub>( $\mu$ -O)<sub>11</sub>( $\mu$ <sub>3</sub>-O)<sub>3</sub>( $\mu$ -OH)<sub>2</sub>( $\mu$ -cycPO<sub>2</sub>)<sub>2</sub>-(cycPO<sub>2</sub>)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>] • 2CH<sub>3</sub>CN • H<sub>2</sub>O (**2**) (Chart 1), which could be characterized in the solid state by single-crystal X-ray analysis.<sup>8</sup> Its poor solubility, however, precluded its characterization in solution.

2 is an unprecedented nonanuclear organostiboxane cage containing a Sb<sub>9</sub>O<sub>16</sub> core (Figure 2). Seven of the nine antimony atoms have only one phenyl substituent, while two others possess two phenyl groups each. Although four phosphinate ligands are involved in binding to six of the antimony atoms, the bulk of the core structure is entirely built from bridging oxide ( $\mu_3$  and  $\mu_2$ ) and hydroxide ligands. Interestingly, **2** also

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<sup>(8)</sup> Crystal data for 1: triclinic;  $P\overline{1}$ ; a = 10.8548(17) Å, b = 12.1442(19)Å, c = 19.956(3) Å;  $\alpha = 95.080(3)^\circ$ ,  $\beta = 99.305(3)^\circ$ ,  $\gamma = 103.353(2)^\circ$ ; V = 2504.1(7) Å<sup>3</sup>, T = 273(2) K, Z = 2;  $\rho_{calcd} = 1.422$  g cm<sup>-3</sup>; crystal dimensions 0.2 × 0.2 × 0.1 mm;  $2\theta_{max} = 25.00$ ; 13 051 reflections measured; 8680 unique reflections; 564 parameters; R1 = 0.0428; wR2 = 0.1071. Crystal data for **2**: monoclinic; P2/n; a = 15.420(3) Å, b = 15.122(3) Å, c = 25.599(5) Å;  $\beta = 92.52(3)^\circ$ ; V = 5963(2) Å<sup>3</sup>, T = 100(2) K, Z = 2;  $\rho_{calcd} = 1.692$  g cm<sup>-3</sup>; crystal dimensions 0.3 × 0.2 × 0.2 mm;  $2\theta_{max} = 25.00$ ; 30 217 reflections measured; 10 482 unique reflections; 630 parameters; R1 = 0.0395; wR2 = 0.0981. CCDC 716145 and 716146 contain the crystallographic data for this publication.



Figure 2. ORTEP diagram of the  $Sb_9O_{16}$  core of 2. Thermal ellipsoids are set at 30%; phenyl groups, phosphinate ligands, and water molecules are omitted for clarity. Selected bond distances (Å) and bond angles (deg): Sb(1)-O(7) 1.925(3), Sb(1)-O(4) 1.985(3), Sb(1)-O(3) 2.058(3), Sb(2)-O(9) 1.962(3). Sb(2)-O(4) 2.051 (3), Sb(2)-O(3) 2.092(3), Sb(3)-O(6) 1.953(3), Sb(3)-O(8) 1.955(3), Sb(3)-O(7) 1.955(3), Sb(3)-O(12) 2.107(3), Sb(3)-O(5) 2.116(3), Sb(4)-O(9) 1.940(3), Sb(4)-O(13) 1.959(3), Sb(4)-O(8) 1.998(3), Sb(4)-O(5) 2.157(3), Sb(5)-O(13) 1.917(3), Sb(5)-O(12) 2.016(4), Sb(1)-O(4)-Sb(2) 105.97(14), Sb(1)-O(3)-Sb(2) 101.87(14).

contains an antimony atom (Sb5) that is partially hydrolyzed and contains two water molecules of coordination. It is of interest to note that recently we have shown that hydrated organotin cations are the precursors to further hydrolyzed products.<sup>11</sup> In light of this, it is clear that the coordination environment around Sb5 represents a snapshot of an intermediate before its final hydrolysis to form hydroxides or their condensed products.

The molecular structure of 2 contains two symmetrically related trimer units that are present an either end of the structure. Thus, Sb1, Sb2, and Sb4 are part of a six-membered Sb<sub>3</sub>O<sub>3</sub> ring, where Sb2 and Sb1 are further bridged by a  $\mu$ -OH (O3) ligand to generate a bicyclic ring system. The central portion of the cage contains two symmetrically related antimony atoms (Sb3 and Sb3\*), which are connected to each other by two  $\mu$ -O ligands (O12 and O6). The partially hydrolyzed antimony (Sb5) containing two water molecules is associated in bridging the two trimeric (through O13 and O13\*) as well as the central dimeric unit (through O12). The latter is connected to the trimeric poles through the bridging action of two  $\mu$ -O (O7 and O8) and one  $\mu_3$ -O (O5) ligand. The formation of this Sb<sub>9</sub>O<sub>16</sub> core leads to the presence of many Sb-O ring systems including Sb<sub>2</sub>O<sub>2</sub>, Sb<sub>3</sub>O<sub>3</sub>, and Sb<sub>4</sub>O<sub>4</sub> rings (Supporting Information). Two of the four phosphinate ligands act as a 2.11 coordination mode<sup>9</sup> and bridge the Sb<sub>2</sub>O(OH) motifs present on either end of the cage. The other two phosphinate ligands are monodentate and bind to the third antimony of the trimeric units. The three antimony atoms present in the center of the cage do not have phosphinate ligands.

Some of the bond parameters of **2** are summarized in the caption for Figure 2. The others are given in the Supporting Information. The cage structure of **2** represents the largest structure containing Sb(V) centers. Another novel feature of the structure of **2** is that the two extremes of the cage are in fact capped by two putative stibinic acid [Ph<sub>2</sub>Sb(O)(OH)] units. Thus, **2** is a unique cage containing motifs related to stibonic and stibinic acids as well as a partially hydrolyzed organoantimony center.

## **Experimental Section**

**Reagents and General Procedures.** Solvents and other general reagents used in this work were purified according to standard

procedures. 2,4,4-Trimethyl-2-pentene and triphenylantimony were purchased from Sigma Aldrich Ltd. Aluminum chloride was purchased from s. d. Fine Chemicals, Mumbai. Triphenylantimony dichloride and 1,1,2,3,3-pentamethyltrimethylenephosphinic acid were synthesized according to well-known literature procedures.<sup>12</sup>

Instrumentation. Melting points were measured using a JSGW melting point apparatus in glass capillaries and are uncorrected. Elemental analyses were carried out using a Thermoquest CE Instruments model EA/110 CHNS-O elemental analyzer. IR spectra were recorded from 4000 to 400 cm<sup>-1</sup> on a Bruker FT-IR Vector 22 model in the solid state using KBr pellets and in the solution state using dichloromethane. <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR were recorded on a JEOL-JNM LAMBDA model 400 spectrometer using C<sub>6</sub>D<sub>6</sub> and  $C_7D_8$  operating at 400 and 100 MHz, respectively. <sup>31</sup>P{<sup>1</sup>H} NMR spectra were recorded on a JEOL-JNM DELTA model 500 spectrometer using C<sub>6</sub>D<sub>6</sub> operating at 162 MHz. ESI-MS analyses were performed on a Waters Micromass Quattro Micro triple quadrupole mass spectrometer. Electrospray ionization (positive ion, full scan mode) was used keeping acetonitrile as solvent and nitrogen gas for desolvation. Capillary voltage was maintained at 2 kV, and cone voltage was kept at 31 kV. The temperature maintained for the ion source was 100 °C and for desolvation 350 °C.

Synthesis. Synthesis of  $[(Ph_3Sb)_2(\mu-O)(\mu-cycPO_2)_2]$  (1): Hydrated triphenylantimony dichloride (0.19 g, 0.45 mmol) was added to a clear solution of 1,1,2,3,3-pentamethyltrimethylenephosphinic acid (0.08 g, 0.45 mmol) and triethylamine (0.2 mL) in 20 mL of benzene. The solution was stirred for 24 h. Filtration followed by evaporation produced a white solid. Block-shaped crystals of 1 were formed, which were recrystallized from *n*-hexane. Yield: 0.2 g, 83%. Mp: 192-193 °C. Anal. Calcd for C<sub>52</sub>H<sub>62</sub>P<sub>2</sub>O<sub>5</sub>Sb<sub>2</sub> (1): C, 58.31; H, 5.84. Found: C, 58.12; H, 5.76. IR (KBr, cm<sup>-1</sup>): 1110 ( $\nu_{asym}PO_2$ ) and 1031, 1008 ( $\nu_{sym}$  PO<sub>2</sub>). <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>, ppm):  $\delta$ 8.27 (Ar, m), 8.09 (Ar, m), 7.96 (Ar, m), 7.84 (Ar, d, J = 6.83Hz), 7.30-7.00 (Ar, m), 1.41-1.34 (-CH<sub>3</sub>, dd, J = 8.79 and 9.51 Hz), 1.30–1.22 (–CH, m), 1.18 (–CH<sub>3</sub>, d, *J* = 4.8757 Hz), 1.13  $(-CH_3, d, J = 5.16 Hz), 0.80 (-CH_3, d, J = 18.78 Hz), 0.61$  $(-CH_3, d, J = 19.02)$ . <sup>31</sup>P NMR (202.5 MHz, C<sub>6</sub>D<sub>6</sub>, ppm):  $\delta$  48.02 (s), 48.56 (s). ESI-MS: *m*/*z* (%) 177.1065 [*cyc*-PO<sub>2</sub>H+H]<sup>+</sup> (18), 369.0209 [(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>SbOH]<sup>+</sup> (100), 411.0345 [(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>Sb(OH<sub>2</sub>)(CH<sub>3</sub>-CN)] (47), 429.0620 [(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>Sb(OH<sub>2</sub>)<sub>2</sub>(CH<sub>3</sub>CN)] (16), 527.1167  $[(C_6H_5)_3Sb(cyc-PO_2)]$  (8), 739.0409  $[\{(C_6H_5)_3Sb\}_2(O)(OH)]^+$  (8).

Synthesis of  $[(Ph_2Sb)_2(PhSb)_7(\mu-O)_{11}(\mu_3-O)_3(\mu-OH)_2(\mu-cycPO_2)_2(cycPO_2)_2(H_2O)_2] \cdot 2CH_3CN \cdot H_2O$  (2): Compound 1 (0.1 g, 0.09 mmol) was dissolved at 50 °C in 50 mL of a solution consisting of acetonitrile and water (99:1). After filtration, the filtrate was kept for slow evaporation at 45 °C. After a few weeks, parallelopiped-shaped crystals of **2** were isolated. Yield: 0.02 g, 32%. Mp > 300 °C dec. Anal. Calcd for  $C_{102}H_{133}N_2O_{27}P_4Sb_9$  (2): C, 40.31; H, 4.41; N, 0.92. Found: C, 40.20; H, 4.32; N, 0.74. IR (KBr, cm<sup>-1</sup>): 3431 ( $\nu$  O–H), 1073, 1061 ( $\nu_{asym}$  PO<sub>2</sub>), and 1023, 993 ( $\nu_{sym}$  PO<sub>2</sub>).

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**Supporting Information Available:** CIF files for **1** and **2** and Figures S1–S14. This material is available free of charge via the Internet at http://pubs.acs.org.

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