A New Polyantimonate with an Sb_4O_{16} Core

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Polymerization of the antimonate ion, $Sb(OH)_6^-$, has been known to chemists for many decades.[3] However, knowledge of the chemistry of polyantimonate is still very sketchy. Structural chemistry of oligomeric antimony−oxo complexes has attracted some interest during the last quarter of the 20th century, but virtually all of these are organoantimonates that have direct Sb−C bonds,[4−18] the only exception being the polychloroantimonate, $[Sb_6O_{10}Cl_{14}]^{4-}$, whose synthetic details have not been published.[19] The study of inorganic polyantimonate has been stalled. Only recently the first inorganic polyantimonate was isolated,[20] and the $[Sb_8O_{12}(OH)_{20}]^{4-}$ anion remains the only polyantimonate that has been isolated and structurally characterized to date.

In our study of this unexplored branch of inorganic chemistry, we found that $[Sb_8O_{12}(OH)_{20}]^{4-}$ reacts with silanol to yield a new polyantimonate that has an Sb_4O_{16} core. Here we report its synthesis and structural characterization.

The $[Sb_8O_{12}(OH)_{20}]^{4-}$ anion reacts with $(CH_3)_2(t\text{-}C_4H_9)SiOH$ at 80 °C to yield a silylated polyantimonate $[Sb_4O_6(OH)_4\{OSi(CH_3)_2(t\text{-}C_4H_9)\}_6]^{2-}$.[21]

$$[Sb_8O_{12}(OH)_{20}]^{4-} + 12(CH_3)_2(t\text{-}C_4H_9)SiOH \rightarrow 2[Sb_4O_6(OH)_4\{OSi(CH_3)_2(t\text{-}C_4H_9)\}_6]^{2-} + 12H_2O$$

The compound $[(n\text{-}C_4H_9)_4N]_2[Sb_4O_6(OH)_4\{OSi(CH_3)_2(t\text{-}C_4H_9)\}_6]$ crystallizes as a CH_2Cl_2 solvate (**1**) when CH_2Cl_2/Et_2O is used as a solvent for crystallization and as an CH_3CN solvate (**2**) when crystallized from CH_3CN. X-ray diffraction studies revealed that both **1** and **2** are composed of discrete $[Sb_4O_6(OH)_4\{OSi(CH_3)_2(t\text{-}C_4H_9)\}_6]^{2-}$ anions, $[(n\text{-}C_4H_9)_4N]^+$ cations, and respective solvent molecules of crystallization.[22−24] Figure 1 shows the structure of the $[Sb_4O_6(OH)_4\{OSi(CH_3)_2(t\text{-}C_4H_9)\}_6]^{2-}$ anion. It is made up of four octahedral SbO_6 units that share edges with each other to form a planar Sb_4O_{16} core. Of the 10 terminal oxygens of this Sb_4O_{16} core, six are bound to silyl groups. The Sb−O bond lengths of the remaining four (∼1.96 Å) suggest that these oxygens are protonated,[20,25] although hydrogen atoms could not be located

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(21) A 6-mL screw-cap vial was charged with $[(n\text{-}C_4H_9)_4N]_4[Sb_8O_{12}(OH)_{20}]$ (1.0 g, 0.40 mmol), $(CH_3)_2(t{-}C_4H_9)SiOH$ (3.0 mL), and a magnetic stir bar. The vial was capped and taped, and the suspension was heated to 80 °C with stirring in an oil bath. The suspension was maintained at 80 °C and stirred for 18 h. The white precipitate that formed was collected by decantation, washed with 3 × 5 mL of diethyl ether, and dried under vacuum. This crude product (0.78 g) was dissolved in 2.3 mL of CH_3CN with heating. After centrifuging the solution at 3000 rpm for 10 min to remove a small amount of insoluble material, the clear supernatant solution was separated and allowed to stand at −15 °C. Block-shaped crystals started to appear within 1 h. The crystals were collected by decantation after 12 h and dried under vacuum for 12 h to yield 0.63 g (0.33 mmol, 41% based on Sb) of analytically pure compound. Anal. Calcd for $C_{68}H_{166}N_2S_{b4}Si_6O_{16}$: C, 42.46; H, 8.70; N, 1.46; Sb, 25.3; Si, 8.8. Found: C, 42.36; H, 8.77; N, 1.12; Sb, 25.2; Si, 8.2. IR (Nujol mull, 1250 − 400 cm^{-1}): 1245 (s), 1054 (w), 1010 (w), 948 (s), 916 (s), 834 (s), 804 (s), 680 (s), 600 (s), 529 (w), 490 (w). 1H NMR (CD_3CN): δ 3.07 (t, 16H), 2.49 (s, 4H), 1.59 (m, 16H), 1.33 (m, 16H), 0.97 (t, 24H), 0.884 (s, 24H), 0.882 (s, 18H), 0., 15 (s, 12H), 0.13 (s, 12H), 0.08 (s, 12H). The crystals of the CH_2Cl_2 solvate were obtained by dissolving 0.10 g of the crude product in 2.0 mL of CH_2Cl_2, adding 2.0 mL of diethyl ether gently to make a second layer, and allowing the mixture to stand at ambient temperature. The compound thus obtained gave spectra identical with those of the material described above.

(22) Single crystals of **1** are, at 170 K, monoclinic, space group $P2_1/c$, with $a = 20.962(2)$ Å, $b = 21.070(2)$ Å, $c = 23.672(2)$ Å, $\beta = 93.670(9)$, and $Z = 4$. A colorless crystal of dimensions 0.2 × 0.2 × 0.1 mm^3 was used for data collection. Diffraction data were collected on a MAC Science DIP-LABO imaging plate diffractometer installed on the BL04B2 beam line of the SPring−8 synchrotron radiation facility, using 38 keV ($\lambda = 0.331$ Å) monochromatized X−ray beam. The final agreement factors were $R = 0.095$ and $wR2 = 0.242$ for 6272 unique reflections. Single crystals of **2** are, at 120 K, monoclinic, space group $P2_1/n$, with $a = 14.3290(7)$ Å, $b = 16.3670(9)$ Å, $c = 22.3070(13)$ Å, $\beta = 95.985(3)$, and $Z = 2$. A colorless crystal of dimensions 0.3 × 0.3 × 0.2 mm^3 was used for data collection. Diffraction data were collected on an Enraf−Nonius diffractometer using Mo Kα radiation by a φ-axis oscillation method. Imaging plates were used as detectors. The imaging plates were read on a MAC Science DIP-420 off−line IP reader. The final agreement factors were $R = 0.063$ and $wR2 = 0.182$ for 7615 unique reflections. For both structural analyses, DENZO and the SCALEPACK programs were used for indexing, integration, scaling, and merging of the reflections.[23] Both structures were solved and refined using the Xtal 3.6 program.[24] No absorption corrections or extinction corrections were made. Atomic scattering factors and anomalous scattering factors were taken from International Tables for Crystallography, Vol. IV, Table 2.2B and 2.3.1.

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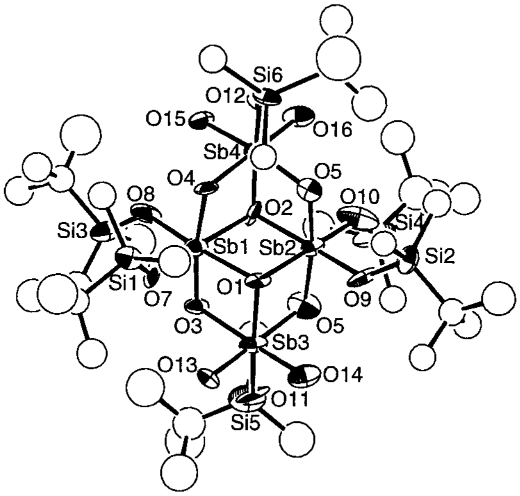

Figure 1. Perspective drawing of the $[Sb_4O_6(OH)_4\{OSi(CH_3)_2(t\text{-}C_4H_9)\}_6]^{2-}$ anion in **1**. Displacement ellipsoids are scaled to enclose 50% probability levels. Selected distances (Å): Sb1−O1 2.117(15), Sb2−O5 1.968(15), Sb3−O13 1.977(17), Sb1−O2 2.146(16), Sb2−O6 1.924(13), Sb3−O14 1.967(18), Sb1−O3 1.984(12), Sb2−O9 1.978(15), Sb4−O2 2.113(14), Sb1−O4 1.936(12), Sb2−O10 1.99(2), Sb4−O4 1.961(16), Sb1−O7 1.935(16), Sb3−O1 2.126(11), Sb4−O6 1.995(15), Sb1−O8 1.976(16), Sb3−O3 2.029(15), Sb4−O12 1.910(13), Sb2−O1 2.076(16), Sb3−O5 2.03(2), Sb4−O15 1.983(15), Sb2−O2 2.056(15), Sb3−O11 1.980(13), Sb4−O16 1.960(19), C69···O13 3.20(3), C69···O14 3.25(4), C70···O15 2.97(6), C70···O16 3.01(5)

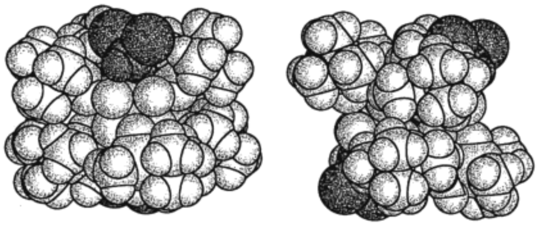

Figure 2. Front (left) and side (right) views of the $[Sb_4O_6(OH)_4\{OSi(CH_3)_2(t\text{-}C_4H_9)\}_6]^{2-}$ anion holding CH_2Cl_2 molecules in its pockets. The CH_2Cl_2 molecules are shaded darker. Atoms are represented by spheres having van der Waals radii (C, 1.65 Å; H, 1.20 Å; O, 1.40 Å; Cl, 1.78 Å; Si, 2.10 Å).

directly from the X-ray data. The result of elemental analysis was also consistent with four OH groups.

The silyl groups of the $[Sb_4O_6(OH)_4\{OSi(CH_3)_2(t\text{-}C_4H_9)\}_6]^{2-}$ anion make a shallow pocket on each side of the molecular oxide anion. The mouth of these pockets is ~7 Å wide, and they appear to be capable of holding small molecules. In fact, each of the pockets contains a CH_2Cl_2 molecule in **1** (see Figure 2). There exist some short contacts between the CH_2Cl_2 molecules and the oxygen atoms of the terminal OH groups (see the caption of Figure 1). In **2**, on the other hand, the CH_3CN molecules locate themselves relatively far from the anion, and the pockets are left vacant. The confinement of the CH_2Cl_2 molecules in the pockets seems to have some influence on the size of the molecular oxide anion. The Sb···Sb distances in **1** are slightly yet significantly longer than those in **2**.[26] The position and orientation of the CH_2Cl_2 molecule in the pocket suggest that it is acting as a hydrogen-bond donor.

So far there is no direct evidence that the $[Sb_4O_6(OH)_4\{OSi(CH_3)_2(t\text{-}C_4H_9)\}_6]^{2-}$ anion keeps CH_2Cl_2 molecules in its pocket in solution. However, ^1H NMR data indicate significant interaction between this molecular antimonate anion and the solvent molecules. Chemical shifts of the OH groups vary very much in different solvents and they correlate well with Gutmann's donor numbers[27] and Dimroth and Reichardt's E_T[28,29] of the solvents (Figure S1). The order observed here is the same as that observed for the chemical shifts of ^{23}Na in different solvents.[30]

The $[Sb_4O_6(OH)_4\{OSi(CH_3)_2(t\text{-}C_4H_9)\}_6]^{2-}$ anion hydrolyzes spontaneously in $CDCl_3$. The peaks for the silyl groups of the anion completely disappear in 15 h, and free silanol peaks appear instead in the ^1H NMR spectra. Such hydrolysis does not occur in dry CD_3CN, for which the ^1H NMR spectra do not change even after 60 h. However, the hydrolysis reaction completes within 1 h, even in CD_3CN, if 100 equiv of H_2O is added to the solution. In both solvents the reaction appears to proceed cleanly. Only peaks for the free silanol and the $[(n\text{-}C_4H_9)_4N]^+$ cation are observed in the ^1H NMR spectra when the hydrolysis is complete. This implies the formation of a new polyantimonate, such as $[Sb_4O_6(OH)_{10}]^{2-}$.

$$[Sb_4O_6(OH)_4\{OSi(CH_3)_2(t\text{-}C_4H_9)\}_6]^{2-} + 6H_2O \rightarrow [Sb_4O_6(OH)_{10}]^{2-} + 6(CH_3)_2(t\text{-}C_4H_9)SiOH$$

Effort is underway to isolate this species.

One more thing that deserves notice is the apparent nonlability of the OH protons of the title anions. The OH groups of the $[Sb_4O_6(OH)_4\{OSi(CH_3)_2(t\text{-}C_4H_9)\}_6]^{2-}$ anion give a single relatively sharp ^1H NMR peak in $CDCl_3$, CD_3CN, CD_2Cl_2, acetone-d_6, and DMSO-d_6. Furthermore, the OH peak persists in the ^1H NMR spectra even after 100 equiv of H_2O is added to the solution. This implies that the terminal Sb−O oxygen atoms are quite basic.

Supporting Information Available: X-ray crystallographic files in CIF format for the structures of **1** and **2**, plots showing the correlation between the chemical shifts of the OH peak and DN's and E_T's of the solvents (Figure S1), and packing diagrams for **1** and **2** (Figures S2 and S3). This material is available free of charge via the Internet at http://pubs.acs.org.

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(26) Distances between Sb atoms in **1** (Å): Sb1···Sb2 3.254(3), Sb1···Sb3 3.158(2), Sb1···Sb4 3.149(2), Sb2···Sb3 3.153(2), Sb2···Sb4 3.140(2). Distances between Sb atoms in **2** (Å): Sb1···Sb1* 3.1884(7), Sb1···Sb2 3.1157(7), Sb1···Sb2* 3.1290(7). Atoms with and without * are related by a center of inversion.

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