J. Am. Chem. Soc. **1995,** *117,* 12007−12008

Synthesis and Characterization of the First Polyantimonate, $[Sb_8O_{12}(OH)_{20}]^{4-}$

H. Nakano,[1a] Y. Ozawa,*[1b] and A. Yagasaki*[1a]

School of Science, Kwansei Gakuin University
Uegahara, Nishinomiya 662, Japan
Department of Material Science
Himeji Institute of Technology
Harima Science Park City, Kamigori 678-12, Japan

Received August 11, 1995

Antimonate is known to polymerize in aqueous acidic solution.[2] The polymerization of antimonate was studied by several different physical techniques during the 1960s,[2a−e] and Lefebvre and Maria proposed that a dodecamer was formed in aqueous solution on the basis of their potentiometric study.[2a] Attempts to isolate the polyantimonate from aqueous solution, however, have always been frustrated by the formation of sparingly soluble, often amorphous precipitates.[2d,f,g] Hence the chemistry of polyantimonate has been left virtually uninvestigated and scarcely documented.

After encountering trouble working with the aqueous antimonate system ourselves, we initiated a study of antimonate in nonaqueous media and succeeded in isolating octaantimonate as a tetra-*n*-butylammonium salt, which is the first example of a discrete polyantimonate.

To an antimonic acid solution prepared by passing a $KSb(OH)_6$ solution (20.0 g, 76.1 mmol, in 2000 mL of deionized water) through a cation exchange column was added a 10% aqueous solution of $[(n\text{-}C_4H_9)_4N]OH$ (98.0 g, 37.8 mmol). The mixed solution was evaporated to dryness, and the resulting sticky solid was washed with diethyl ether and dried under vacuum to yield 21.1 g of a crude product. Single crystals of $[(n\text{-}C_4H_9)_4N]_4[Sb_8O_{12}(OH)_{20}]$ were obtained as a chloroform solvate by dissolving 10.0 g of the crude product in 20 mL of chloroform, adding 10 mL of diethyl ether gently to make a second layer, and allowing the mixture to stand for 10 days at ambient temperature (0.60 g, 0.24 mmol, after drying in vacuo).[3]

X-ray structural analysis[4] of crystalline $[(n\text{-}C_4H_9)_4N]_4[Sb_8O_{12}(OH)_{20}]\cdot 5CHCl_3$ revealed the presence of $[(n\text{-}C_4H_9)_4N]^+$ cations, disordered $CHCl_3$ molecules of crystallization, and discrete $[Sb_8O_{12}(OH)_{20}]^{4-}$ anions having the structure shown in Figure 1. The structure is built up from four Sb_2O_{10} subunits. Each subunit consists of two SbO_6 octahedra connected by sharing a common edge. This type of building block is commonly found in the structures of complex antimony oxides.[6] The Sb_2O_{10} subunits connect to each other in a centrosymmetric manner by sharing the corners of the octahedra to form the Sb_8O_{32} framework. The connection pattern of octahedra in the $[Sb_8O_{12}(OH)_{20}]^{4-}$ anion is the same as that observed in rutile, one of the polymorphs of TiO_2.[7] Thus the current compound can be viewed as a molecular oxide that has a cut-out rutile structure.

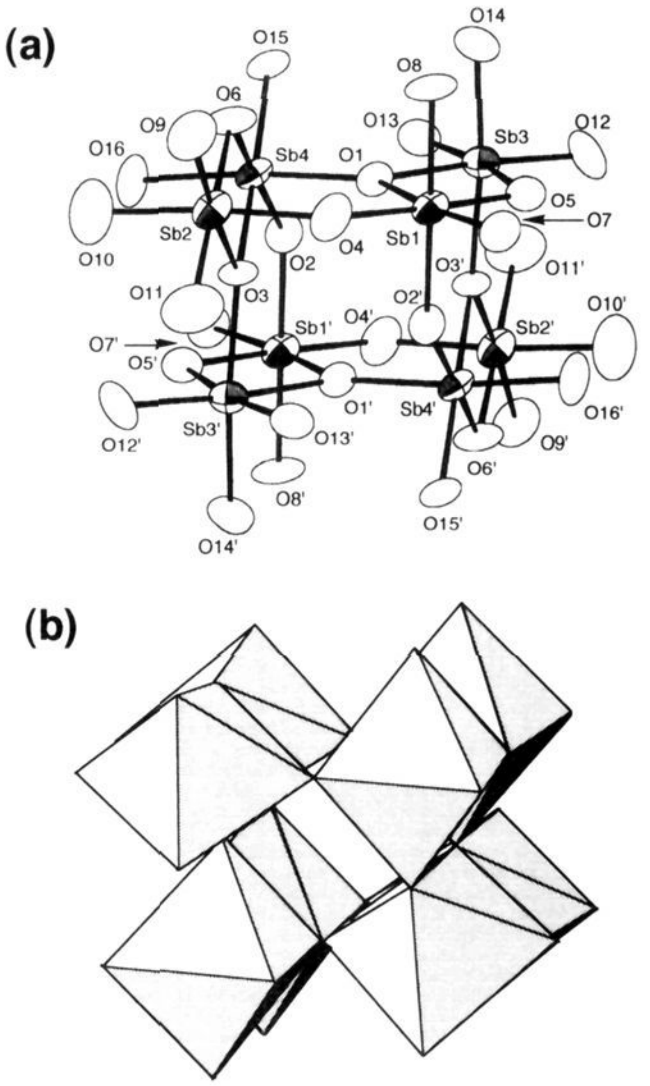

Figure 1. (a) The structure of $[Sb_8O_{12}(OH)_{20}]^{4-}$. Ellipsoids are drawn to encompass 50% of the electron density. The anion possesses rigorous crystallographic $\bar{1}$ symmetry in the solid state. Selected distances (Å): Sb1−O1 2.11(1), Sb1−O2′ 1.96(1), Sb1−O4 1.93(2), Sb1−O5 1.97(2), Sb1−O7 1.95(1), Sb1−O8 1.96(2), Sb2−O3 2.09(1), Sb2−O4 1.94(2), Sb2−O6 1.93(1), Sb2−O9 1.96(1), Sb2−O10 2.01(2), Sb2−O11 1.94(2), Sb3−O1 2.07(2), Sb3−O3′ 2.03(1), Sb3−O5 1.97(1), Sb3−O12 1.95(2), Sb3−O13 1.92(2), Sb3−O14 1.95(2), Sb4−O1 2.01(2), Sb4−O2 1.95(1), Sb4−O3 2.04(1), Sb4−O6 1.95(1), Sb4−O15 1.98(1), Sb4−O16 1.99(2). (b) Polyhedral representation of $[Sb_8O_{12}(OH)_{20}]^{4-}$.

The MO_6 octahedra in $[Sb_8O_{12}(OH)_{20}]^{4-}$ are much less distorted than those of transition metal polyoxometalates.[8] The difference between the shortest and the longest Sb−O bonds in

---

(1) (a) Kwansei Gakuin University. (b) Himeji Institute of Technology.

(2) (a) Lefebvre, J.; Maria, H. *C. R. Hebd. Seances Acad. Sci.* **1963**, *256*, 3121−3124. (b) Gate, S. H.; Richardson, E. *J. Inorg. Nucl. Chem.* **1961**, *23*, 257−263. (c) Baetsle, L. H.; Hyus, D. *J. Inorg. Nucl. Chem.* **1968**, *30*, 639−649. (d) Jander, G.; Ostmann, H.-J. *Z. Anorg. Allg. Chem.* **1962**, *315*, 241−249. (e) Jander, G.; Ostmann, H.-J. *Z. Anorg. Allg. Chem.* **1962**, *315*, 250−258. (f) Bailor, J. C., Emeléus, H. J., Nyholm, R., Trotman-Dickenson, A. F., Eds. *Comprehensive Inorganic Chemistry*; Pergamon Press: New York, 1973; Vol. 2, p 656. (g) Baes, C. F.; Mesmer, R. E. *The Hydrolysis of Cations*; John Wiley & Sons: New York, 1976; pp 370−375.

(3) The crystals lost the solvate molecules easily, and no $CHCl_3$ peak was observed in the ^1H NMR spectrum of the dried sample. Anal. Calcd for $C_{64}H_{164}N_4Sb_8O_{32}$: C, 31.05; H, 6.68; N, 2.26; Sb, 39.3. Found: C, 30.79; H, 6.77; N, 2.22; Sb, 38.7. ^1H NMR (CD_3SOCD_3, TMS): δ 7.24 (s, 2H), 4.82 (s, 2H), 3.79 (s, 2H), 3.70 (s, 2H), 3.41 (s, 2H), 3.19 (s, 2H), 3.18 (m, 32H), 3.11 (s, 2H), 3.06 (s, 2H), 2.84 (s, 2H), 2.82 (s, 2H), 1.57 (m, 32H), 1.32 (m, 32H), 0.94 (t, 48H). IR (Nujol mull, 1000−350 cm^{-1}): 968 (w), 942 (w), 882 (w), 784 (m), 708 (s), 594 (s), 540 (m), 456 (m), 366 (s).

(4) Single crystals of $[(n\text{-}C_4H_9)_4N]_4[Sb_8O_{12}(OH)_{20}]\cdot 5CHCl_3$ are, at 166 K, orthorhombic, space group *Pcab*, with $a = 23.211(3)$ Å, $b = 31.292(6)$ Å, $c = 17.477(2)$ Å, and $Z = 4$ [$d_{calcd} = 1.608$ g cm^{-3}; $\mu(\text{Mo K}\alpha) = 2.066$ mm^{-1}]. X-ray diffraction measurements were performed on an Enraf-Nonius CAD-4 diffractometer with graphite-monochromated Mo Kα ($\lambda = 0.710\,73$ Å) radiation. A colorless prismatic crystal with 0.45 × 0.45 × 0.33 mm dimensions was sealed in a glass capillary and kept at 166 K by using an Enraf-Nonius FR558NH liquid nitrogen cryostat. Unit cell parameters were determined by least-squares using 25 well-centered reflections ($12.5° < \theta < 15.0°$). Intensity data were collected with the ω-scan technique up to $\theta = 25°$. Three standard reflections monitored every 2 h showed no intensity decreases. Of the total of 11 167 reflections measured, 4749 independent data having $F > 3\sigma(F)$ were used for structure determination and refinement. Lorentz, polarization, and numerical absorption corrections were applied. The positions of Sb atoms were determined from the Patterson maps. All of the other atoms were found from successive Fourier syntheses. No hydrogen atoms were located. Anisotropic thermal parameters were applied for the Sb and O atoms. All atomic parameters were refined by full-matrix least-squares techniques based on F, and the calculation converged to $R = 0.064$. All calculations were carried out using the Xtal3.2 program.[5]

(5) Hall, S. R.; Flack, H. D.; Stewart, J. M. *Xtal 3.2*; University of Western Australia: Nedlands, Australia, 1992.

(6) (a) DeBoer, B. G.; Young, R. A.; Sakthivel, A. *Acta Crystallogr., Sect. C* **1994**, *C50*, 476−482. (b) Hong, H. Y.-P. *Acta Crystallogr., Sect. B* **1974**, *B30*, 945−952 and references cited therein.

(7) Wells, A. F. *Structural Inorganic Chemistry*, 5th ed.; Clarendon Press: Oxford, 1984; pp 247−250.

0002-7863/95/1517-12007$09.00/0 © 1995 American Chemical Society

the current complex is only 0.19 Å. The Sb−O bond lengths to the terminal oxygen atoms lie in the range 1.92−2.01 Å, while those to the doubly and triply bridged oxygen atoms are in the ranges 1.93−1.96 Å and 2.01−2.11 Å, respectively. On the other hand, the bond length differences between different types of M−O bonds in transition metal polyoxometalates are much more distinct and the longest and shortest M−O bond lengths often differ by more than 0.5 Å.

As indicated in the formula, $[Sb_8O_{12}(OH)_{20}]^{4-}$, all 20 terminal oxygen atoms are protonated.[9−12] The exchange of those protons seems to be slow on the NMR time scale in polar aprotic solvents. In dimethyl sulfoxide, $[Sb_8O_{12}(OH)_{20}]^{4-}$ showed 10 peaks of equal intensity besides the peaks of the cation in its ^{1}H NMR spectrum. This is consistent with the $\bar{1}$ symmetry observed in the solid state.

The $[Sb_8O_{12}(OH)_{20}]^{4-}$ salt reported here has good solubility in polar organic solvents such as acetonitrile, 1,2-dichloroethane, dimethyl sulfoxide, dimethylformamide, and nitromethane. It also dissolves readily in water, methanol, and ethanol. Preliminary experiments indicate that $[Sb_8O_{12}(OH)_{20}]^{4-}$ undergoes further condensation on heating or on acidification. We believe that the current compound will serve as an entrance to polyantimonate chemistry.

Acknowledgment. This work was supported in part by a Grant-in-Aid for Scientific Research on Priority Areas No. 07242269 from the Ministry of Education, Science and Culture of Japan (Monbusho). We thank Prof. K. Toriumi of Himeji Institute of Technology for the use of the X-ray diffractometer.

Supporting Information Available: Full X-ray data for $[(n\text{-}C_4H_9)_4N]_4[Sb_8O_{12}(OH)_{20}]\cdot 5CHCl_3$ (6 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

JA952754X

---

(8) Pope, M. T. *Heteropoly and Isopoly Oxometalates*; Springer-Verlag: Berlin, 1983; pp 20−30.

(9) Hydrogen atoms could not be located directly from the X-ray data. Their existence, however, was inferred from the terminal Sb−O bond lengths, which were reasonable for Sb−OH bonds.[10] Terminal Sb=O bonds have never been structurally characterized to our knowledge, and its existence has been questioned by Doak and his co-workers recently.[11] According to Brown et al.,[12] the bond length of a Sb=O double bond should be about 1.69 Å. The terminal Sb−O bonds in the current compound are much longer than this, and their bond orders fall in the range 0.83−1.01. The result of the elemental analysis is also consistent with the existence of 20 OH groups.[3] The possibility of $Sb-OH_2$ groups disordered with Sb=O groups was also excluded because the temperature factors of the terminal oxygen atoms showed no sign of anomaly expected to manifest if such disorder existed.

(10) (a) Asai, T. *Bull. Chem. Soc. Jpn.* **1975**, *48*, 2677−2679. (b) Wieber, M.; Simonis, U.; Kraft, D. *Z. Naturforsch.* **1991**, *48b*, 139−142.

(11) Bordner, J.; Doak, G. O.; Everett, T. S. *J. Am. Chem. Soc.* **1986**, *108*, 4206−4213.

(12) Brown, I. D.; Altermatt, D. *Acta Crystallogr., Sect. B* **1985**, *B41*, 244−247.