Polyoxocatonic antimony oxide cluster with acidic protons

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The success and continued expansion of research on metal-oxo clusters owe largely to their structural richness and wide range of functions. However, while most of them known to date are negatively charged polyoxometalates, there is only a handful of cationic ones, much less functional ones. Here, we show an all-inorganic hydroxyiodide \([\text{HSbOI}^{-}]\), such as \([\text{HSbOI}^{-}][\text{H}_2\text{O}]_n\), forming a face-centered cubic structure with cationic \([\text{HSbO}_2\text{I}_2]_{22+}\) and two types of anionic clusters in its interstitial spaces. Although it is submicrometer in size, electron diffraction tomography of \(\text{HSbOI}\) allowed the construction of the initial structural model, followed by powder Rietveld refinement to reach the final structure. The cationic cluster is characterized by the presence of acidic protons on its surface due to substantial \(\text{Sb}^{3+}\) deficiencies, which enables \(\text{HSbOI}\) to serve as an excellent solid acid catalyst. These results open up a frontier for the exploration and functionalization of cationic metal-oxo clusters containing heavy main group elements.

INTRODUCTION

Polyoxometalates (POMs) are anionic metal oxide clusters consisting of interconnected metal-oxygen polyhedral units, which are present in a solution or as a crystalline solid when combined with counter ions \((I, 2)\). Since its first discovery in the 1800s, a large variety of negatively charged POMs has been found, including Lindqvist type \([\text{M}_2\text{O}_{16}]^{18−}\) \((M = \text{Mo, W, V}, \text{etc.})\), Anderson type \([\text{H}_2(\text{MoO}_6)\text{M}_6\text{O}_{18}]^{18−}\), Keggin type \([\text{XM}_{12}\text{O}_{40}]^{n−}\) \((X = \text{S, P, Si, etc.})\), and Wells-Dawson type \([\text{XM}_{18}\text{O}_{62}]^{n−}\), to name only a few. In addition to the compositional diversity of each POM, the intrinsic isomerism and ability to form lacunary and substituted structures further increase the structural diversity and expand the reaction possibilities \((3)\). The resulting structures permit a wide range of chemical and physical properties such as homo- and heterogeneous catalysis \((4, 5)\), selective ion capturing \((6)\), and biochemical applications \((7)\) arising from the redox activity of transition metals in POMs, as well as quantum computing \((8)\).

Contrary to the negatively charged POMs, positively charged metal-oxo clusters (metal-oxo polycations) are quite rare \((8, 9)\), but in recent years, special attention has been paid to the development of the synthesis of cationic metal-oxo clusters \((11–15)\), such as \([\text{Al}_{13}\text{O}_{4}(\text{OH})_2(\text{H}_2\text{O})_{12}]^{17+}\) \((\text{Al}_{13})\) \((16)\), \([\text{Dy}_2(\text{H}_2\text{O})_8\text{V}_{12}\text{O}_{32}]^{2+}\) \((17)\), and \([\text{Zr}_{25}\text{O}_{30}(\text{OH})_2(\text{H}_2\text{O})_{8}]^{8+}\) \((18, 19)\), and isolation of these clusters. While applications ranging from water purification to catalysis have been searched for \(\text{Al}_{13}\) and its analogs \((20–22)\), the research on cationic metal-oxo clusters, in general, is in its infancy, and most studies focus on the synthetic and structural aspects, while their functions remain practically unexplored. Thus, the finding of a previously unknown cationic metal-oxo clusters not only provides a structural impact of its own but also promises unique functions in a solution or as various complexes when combined with negatively charged counter anions.

In this study, we report on \([\text{HSbO}_2\text{I}_2]_{22+}\) \([\text{HSbOI}^{-}]\), the cationic cluster in \(\text{HSbOI}\) serendipitously found during the search for an antimony oxyiodide for photocatalytic applications. This product has cationic clusters of \([\text{H}_{10.7}\text{Sb}_{32.1}\text{O}_{44}]^{19.0+}\) \([\text{HSbOI}^{-}]\) that form a face-centered cubic (fcc) packed lattice with \([\text{HSbO}_2\text{I}_2]_{22+}\) and \([\text{Sb}_{0.76}\text{I}_6]^{3.7−}\) clusters at the interstitial sites (Fig. 1A). Unlike the structurally related \(\text{Sb}_{35}\text{O}_{44}X_5\) cluster in \(\text{Cu}_{20}\text{Sb}_{35}\text{O}_{44}X_{37}\) \((X = \text{Cl, Br})\) \((11, 23)\), the cationic cluster in \(\text{HSbOI}\) carries protons, of which the surface protons are acidic, achieving excellent activity in heterogeneous acid-catalyzed reactions. Thus, this study opens a frontier in the study of metal-oxo clusters as solid catalysts, which has so far been limited to anionic transition metal oxide clusters.

RESULTS AND DISCUSSION

Synthesis and structural characterization of \(\text{HSbOI}\)

\(\text{HSbOI}\) was obtained by accident in an attempt to prepare an unreported \(\text{Sb}_4\text{O}_5\text{Cl}_2\), which we expected to be isostructural with \(\text{Sb}_4\text{O}_5\text{Cl}_2\) and \(\text{Sb}_4\text{O}_5\text{Br}_2\) \((24)\), but has a smaller bandgap, using a solution process suitable for solar cell applications. This oxyiodide \((\text{Fig. 2C, bright orange, and fig. S1})\) was obtained by dissolving antimony oxide in an aqueous hydrogen iodide solution at room temperature \((\text{RT})\), followed by dilution with water. The powder synchrotron x-ray diffraction (SXRD) pattern (Fig. 2C) differs markedly from the expected pattern for the monoclinic \(\text{Sb}_4\text{O}_5\text{Cl}_2\) structure, with numerous peaks at low angles that prevented us from even determining the unit cell.
Because of its particle size of <200 nm (fig. S2), to resolve the crystal structure, we used three-dimensional electron diffraction (3D-ED) tomography, a powerful technique that allows to determine structures from submicrometer single crystals and has recently been applied to a variety of materials from metal oxide to proteins (25–27), but not to metal-oxo cluster compounds. The combination of selected area ED patterns (Fig. 2A, fig. S3, and table S1), high-resolution high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) images (Fig. 2B and fig. S4), and structure solution from 3D-ED data using charge flipping methods provides the initial structure model in the cubic Fm-3m space group with a large lattice parameter $a = 21.3305(1)$ Å (details in the Supplementary Materials). The 3D-ED analysis revealed large pseudo-spherical $\text{Sb}_{38-36}$ clusters with a diameter of ~13 Å (fig. S5A), assembled in an fcc packed lattice. Subsequent Rietveld refinement from the powder SXRD data (Fig. 2C) revealed additional oxygen in the large clusters and the presence of small- and medium-sized clusters. There are considerable amounts of Sb vacancies in each cluster type, with average compositions of $\text{Sb}_{38-36} \text{O}_{44}$ ($\delta = 5.95(5)$), $\text{Sb}_{6-8} \text{O}_{6}$ ($\delta = 3.89(3)$), and $\text{Sb}_{1-3} \text{O}_{6}$ ($\delta = 0.241(5)$) for the large, medium, and small clusters, respectively (table S2).

The chemical composition of $[\text{Sb}_{24} \text{O}_{36}]^{3-}[\text{Sb}_{2} \text{I}_{6}]^{3+}[\text{Sb}_{0.76} \text{I}_{6}]^{3.7-2}$ estimated above is not charge-neutral, but the presence of substantial amounts of protons is suggested by the intense background of a neutron powder diffraction profile originating from the incoherent scattering on hydrogen (fig. S11). To maintain charge neutrality, 12.8 protons should be present per formula unit. As discussed later, magic angle spinning nuclear magnetic resonance (MAS-NMR) experiments and ab initio calculations demonstrate that protons bind to the large and medium clusters, together with water of crystallization (fig. S12).

Assuming that each cluster takes on two specific compositions around the average H or Sb value, the final formula can be given by $[(\text{H}_5 \text{Sb}_1 \text{O}_8)_{0.5}(\text{H}_6 \text{Sb}_2 \text{O}_8)_{0.5}]_{0.92}[(\text{H}_2 \text{Sb}_1 \text{O}_3)_{0.5}(\text{H}_2 \text{Sb}_1 \text{O}_3)_{0.5}]_{0.90}[(\text{H}_5 \text{Sb}_3 \text{O}_3)_{0.5}(\text{H}_6 \text{Sb}_3 \text{O}_3)_{0.5}]_{0.90}[(\text{H}_2 \text{Sb}_4 \text{I}_8 \text{O}_6)_{0.8}(\text{H}_3 \text{Sb}_4 \text{I}_8 \text{O}_6)_{0.2}]_{0.9}[(\text{H}_2 \text{Sb}_4 \text{I}_8 \text{O}_6)_{0.8}(\text{H}_3 \text{Sb}_4 \text{I}_8 \text{O}_6)_{0.2}]_{0.9}[(\text{H}_2 \text{Sb}_4 \text{I}_8 \text{O}_6)_{0.8}(\text{H}_3 \text{Sb}_4 \text{I}_8 \text{O}_6)_{0.2}]_{0.9}$. Unless otherwise stated, we will hereafter use a simplified chemical formula of $[\text{H}_{10.7} \text{Sb}_{32.1} \text{O}_{44}]^{8.3+}[\text{H}_{2.1} \text{Sb}_{2.1} \text{I}_{8} \text{O}_{6}]^{11.54-}[\text{Sb}_{0.76} \text{I}_{6}]^{3.7-2}$.

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**Structural features of clusters in HSB0I**

The HSB0I cluster $[\text{Sb}_{32} \text{O}_{44}]^{8.3+}$ ($\text{Sb}_{38-36} \text{O}_{44}$, where $\delta = 6$) consists of an $\text{Sb}_{32-36} \text{O}_{36}$ ($\delta = 2$) outer shell and an $\text{Sb}_{6-8} \text{O}_{8}$ ($\delta = 4$) inner shell (Fig. 1B). The outer shell is composed of a $[\text{Sb}_{24-36} \text{O}_{36}]$ cage and eight $[\text{Sb}_{1-8} \text{O}_{8}]$ cations (Fig. 1B and C, and fig. S7c). The $[\text{Sb}_{24-36} \text{O}_{36}]$ cage contains the $\text{Sb}_{24}$ framework with truncated octahedron of $4^6 8^2$ geometry (Fig. 1D), which is also seen in other compounds (28–30), as discussed later. The outer shell $\text{Sb}^{8+}$ (Sb2 and Sb3) cations are strongly asymmetric, with a triangular oxygen environment ($\text{SbO}_3$), where Sb 5s lone electron pair (E) is pointing outward, thereby stabilizing the cluster structure, which is theoretically validated as shown in Fig. 3A. A similar $\text{Sb}_{38-36} \text{O}_{44}$ cluster is found in $\text{Cu}_{20} \text{Sb}_{35} \text{O}_{44} \text{X}_{37}$ ($\text{X} = \text{Cl}, \text{Br}$) (fig. S6), where the cluster appears to be
The medium \[\text{[Sb}_{2.1}\text{I}_{8}\text{O}_{6}]^{13.7-}\] cluster (Fig. 1E) resembles the face-capped \[\text{M}_{2}\text{Ch}_{8}\text{X}_{6}\] units of the well-known Chevrel-type compounds with transition metals (\(M = \text{Mo}, \text{Re}, \ldots; \text{Ch} = \text{S}, \text{Se}, \ldots; \text{X} = \text{Cl}, \text{PET}_{3}, \ldots\)) (31). The formation of Chevrel-type clusters can be interpreted in terms of electronic stabilization, where the highest occupied molecular orbitals are mainly of metal-metal bonding nature. In contrast, the \(d\) orbitals of \(\text{Sb}^{3+}\) ion in \(\text{Sb}_{6-3\text{I}_{6}\text{O}_{6}}\) are fully occupied (4d$^{10}$), indicating that this medium cluster is not stable by itself but is somehow stabilized by the “nanospace” formed by the fcc network of \(\text{HSbO}\) clusters through covalent interactions. The \(O^{2-}\) ions in \(\text{Sb}_{6-3\text{I}_{6}\text{O}_{6}}\) bind not only to \(\text{Sb}4\) within this cluster but also to \(\text{Sb}3\) in the \(\text{HSbO}\) cluster, indicating a substantial interaction between the two clusters, which is supported by bond valence sum (BVS) calculations (see Supplementary Text). Thus, the six \(\text{Sb}4\) ions appear to be assembled merely to orient the \(\text{Sb}5s\) orbitals toward the octahedral center. Such “clustering” of cations with lone-pair electrons has been observed in solids with \(\text{Sb}, \text{Bi}, \text{Pb}, \text{and Te}\) (32).

The small \(\text{[Sb}_{0.76}\text{I}_{6}\text{O}_{6}]^{3.7-}\) cluster (Fig. 1F) is also unusual because the \(\text{Sb}\) deficiency (24\%) implies a cation-vacant \((\text{I}_{6})^{6-}\) octahedron. For inorganic molecules and metal complexes, \(\text{MX}_{6}\) octahedra (e.g., \([\text{Fe(CN)}_{6}]^{3-}\) and \([\text{SiF}_{6}]^{2-}\) do not permit a metal deficiency without being accompanied by a ligand defect (33). The situation differs markedly from extended oxides such as perovskite oxides where octahedral metal defects are often seen (34). The strong interaction with the \(\text{HSbO}\) cluster is once again expected to stabilize this cluster; when only the octahedral center (\(\text{Sb}5\)) is considered, the BVS value of \(\text{I}2\) is as small as −0.44, but it rises to −0.86 when \(\text{Sb}2\) and \(\text{Sb}3\) sites of the large cluster are included.

Acidic protons and catalysis

$^1\text{H}$ MAS-NMR profile of the dehydrated \(\text{HSbO}\) was collected to obtain information about the states of protons. As shown in Fig. 4A, the spectrum mainly consists of three peaks centered at 10, 6, and 4.5 parts per million (ppm) with a peak area ratio of about 25:10:26 (see fig. S13 for the spectrum of the as-prepared sample). We computationally determined the stable proton positions for an extended cluster of \([\text{Sb}_{34}\text{O}_{44}]^{14+}\) that has a large cluster (consisting of outer \([\text{Sb}_{45}\text{Sb}_{2}\text{O}_{50}]\)) and inner \([\text{Sb}_{3}\text{O}_{8}]\) taking into account \(\text{Sb}\) vacancies, plus two capping \((\text{O}−\text{Sb}4)\) and four \([\text{O}−\text{V}_{\text{Sb}}]\) units of the middle cluster \([\text{Sb}_{46-\text{I}_{6}\text{O}_{6}}]\) (where \(V_{\text{Sb}}\) represents an antimony vacancy).
The density functional theory (DFT) and the gauge-independent atomic orbital (GIAO) method were used to compute chemical shifts (see the “Computational methods” section). The extended $[\text{Sb}_{36}\text{O}_{50}]^{8+}$ structure was fixed as the experimentally determined one, while the position of an added proton was fully optimized. As shown in Fig. 4B, there are roughly three stable $\text{H}^+$ positions at 9.5 to 10.5 ppm for $\text{H}^+$ bound to $\text{O}_2$ and $\text{O}_3$ in the outer shell, 4.7 ppm for $\text{H}^+$ bound to $\text{O}_4$ in the inner shell, and 6.0 ppm for $\text{H}^+$ bound to the capped $\text{O}_1$. These calculated chemical shifts reproduced the experimental data extremely well. The 1H MAS-NMR spectrum after soaking in heavy water (Fig. 4C) supports the 10-ppm signal being assigned to protons on the surface of large clusters. Moreover, a 2D 1H radio frequency–driven recoupling (RFDR) NMR spectrum (Fig. 4D), which recouples the homonuclear dipolar couplings depending on the nuclear distance, further validates the aforementioned computational assignment because the observed cross peak between 6 and 10 ppm means that protons corresponding to each chemical shift are close in distance.

The relationship between 1H MAS-NMR chemical shift and acidity has been well known both experimentally (35) and theoretically (36); the larger the chemical shift in solid-state NMR, the higher the acidity. For instance, the silanol groups of zeolites (H-mordenite) exhibit 1H MAS-NMR chemical shifts of ca. 2 ppm (37), while those of the Bronsted acid sites of zeolites (H-mordenite) (37) and acidic Nafion (38) are observed at ca. 4 and 9.7 ppm, respectively. The chemical shift of the protons in the outer shell (10 ppm) of the HSbO cluster is as large as those of the typical acidic salts of Keggin-type POM (39) and the acidic polymer of Nafions (38), suggesting that the surface of the HSbO cluster in HSboI must be acidic.

In expectation of the high catalytic activity of the HSbO surface as a Bronsted acid, we carried out pinacol rearrangement reaction, which is a typical acid-catalyzed reaction (40). In the pinacol rearrangement reaction, elimination of water from pinacol (a diol) gives pinacolone (a ketone) via 1,2-methyl shift as a major product and 2,3-dimethyl-1,3-butadiene (an olefin) via simple dehydration as a minor product (40). As shown in Fig. 5A, HSboI exhibits high catalytic activity as a solid catalyst (entry 1, 100% conversion and >99% selectivity to pinacolone) at 373 K and 1 hour in toluene [see figs. S14 and S15 for the 1H NMR and gas chromatography (GC) chart, respectively]. The catalytic performance of HSboI is comparable to...
Z = 4). Note that the amounts of metal-oxo clusters (unit cell) Asterisk indicates that 300 mg of 1-phenyl-3-butene-1-ol was identified. Figure 5B lists the results of the Barbier-Grignard reaction in water and an environmentally friendly C─C bond formation in organic media. TON and TOF were calculated from the equation TON = [yield (%)\/amount of catalyst (mol)/amount of substrate (mol)] and TOF (hour⁻¹) = TON\/reaction time (hours). Astarisk indicates that 300 mg of HSBOI corresponds to 0.01 mmol based on its unit cell (Z = 4). Note that the amounts of metal-oxo clusters (HSBO or [PW₁₂O₃₇⁻]) are the same in entries 1 and 2. Dagger indicates that no other products were detected in entry 2 (2,3-dimethyl-1,3-butadiene was not detected). Unidentified peaks at long retention times were observed in the GC chart of the reaction solution of entry 2.

those of Keggin-type heteropolyacids (100% conversion and 43 to 78% selectivity to pinacolone at 423 K and 1 hour), which are well-known superacids (41). The reaction under the same conditions using the well-known POM-based solid acid catalyst Cs₂.₅H₀.₅PW₁₂O₄₀ (42) showed 100% conversion of pinacol and 93% selectivity to pinacolone, demonstrating that the performance of HSBOI is comparable. The powder XRD pattern of HSBOI after the reaction is analogous to that before the reaction (fig. S16), showing that the crystal structure of the catalyst is maintained during the reaction. As shown in Fig. 5A, HSBOI can be easily recovered from the reaction mixture by simple filtration and washing with toluene and can be reused at least once (entry 2, 100% conversion and >92% selectivity to pinacolone).

In addition, we carried out allylation of aldehydes using the Barbier-Grignard reaction, which is a typical acid-catalyzed reaction in water and an environmentally friendly C―C bond formation method (43). Figure 5B lists the results of the Barbier-Grignard reaction catalyzed by HSBOI; 1-phenyl-3-buten-1-ol was identified as the sole reaction product of this reaction by GC and ¹H NMR. Removing the catalyst stopped the reaction, indicating that the observed catalysis is truly heterogeneous (fig. S17). Elemental analysis of the reaction solution by inductively coupled plasma mass spectrometry (ICP-MS) showed that the amount of Sb that leached from HSBOI after 24 hours was ca. 0.4% and negligible. The yield and turnover number (TON) with 0.2 mole percent (mol %) of HSBOI (based on benzaldehyde) in H₂O at 353 K and 24 hours were 63% and 315, respectively. Notably, the turnover frequency (TOF) reached a high value of 50 per hour with 0.1 mol % of HSBOI at 1 hour, which is higher than that of a typical solid acid catalyst, a scandium triflate–grated mesoporous silica (TON ~ 200 and TOF < 1 at 353 K) (44). It is known that the activity in the Barbier-Grignard reaction increases by increasing the acid strength of POM-based solids as catalysts [i.e., pKₘ (where Kₘ is the acid dissociation constant) of the metal aqua ions as counter cations] (45), so these results confirm the highly acidic property of HSBOI. Because HSBOI is not porous (fig. S18), the activity per proton is high, given that the reaction with benzaldehyde in this case occurred only on the small surface of HSBOI particles. We note that no by-products due to the redox property of iodine were observed in both reactions.

While metal-oxo cluster materials have been extensively studied as catalysts for a variety of acid-base and redox reactions (4, 5, 46), most of the clusters are composed of transition metals and/or light main group metals. In this regard, HSBOI composed of late main group elements (Sb) is unprecedented in demonstrating excellent properties as a solid acid. In addition to the large chemical shift, the unusually weak binding of the protons in the large cluster’s surface (attached to O₂ or O₃) can be presumed from the computed O–H bond length of 1.013 to 1.045 Å, which is longer than 1.010 Å for O₁–H and 0.979 Å for O₄–H (fig. S19). To obtain further insights into the bonding nature of H⁺, we calculated electrostatic potentials (ESPs) (47). Figure 3B shows that the DFT-optimized ESPs of the extended [Sb₅O₅Sb]⁺⁺ cluster increase in the order of outer shell oxygen, inner shell oxygen, and capped oxygen. The reason for the presence of acidic protons attached to the outer shell is not immediately available but is speculated to be as follows. A large number of vacancies are created in the inner shell to relieve the overbonding of antimony sites (Sb1), which, in turn, generate a large number of charge balancing protons (three H⁺ for each Sb³⁺ defect). However, because there are only a limited number of oxygen sites (O1) in the inner shell that can bond more strongly with hydrogen than oxygen sites of the outer shell, the extra protons should bond to oxygen of the outer shell, resulting in high Bronsted acidity. In addition, the stereochemically active lone-pair electrons of the HSBOI surface (Fig. 3A) may somehow contribute to the reaction process.

**Outlook**

We have successfully synthesized an all-inorganic hydroxyiodide containing a large cationic antimony-based cluster, featuring acidic protons. Considering that acid reactions have mainly been catalyzed by anionic POM clusters containing early transition metals (W, Mo, V, etc.) (4, 5, 46), using positively charged clusters with heavy main group elements and controlling the metal ion defects as in this study may open up possibilities in the design of solid-state catalysts. As there are many metal-oxo clusters containing B and Sb (48, 49), they should also exhibit acidity by protonation via introducing defects.

It is noted that sodalites [Al₆Si₆O₂₄] framework (28), uranium clusters [(UO₂)₂O₃(OH)]₃⁻ (29), and M₃P₁₆ (M = Cu, Ni) in clathrate compounds AM₃P₄ (A = Sr, Ba) (30) have a structure with similar topology (truncated octahedron, 4₆⁶⁻) as the [Sb₄₈₋₄O₃₆] cage in the outer shell of the HSBOI clusters (fig. S6). In these compounds, this framework can be modified to yield, e.g., the inner space to be used as a reaction field (50). Likewise, our HSBOI clusters could be structurally modified, for example, we may be able to synthesize antimony oxido cage structures with different topologies (51, 52) and higher-order structures (53). In addition, dissolving and isolating HSBOI clusters would permit the use of single clusters for homogeneous catalysis and a broader deployment as building blocks for various organic-inorganic composites. For example, if we
can introduce permanent porosity into HSbO-based polycation composites, then the catalytic activity would be greatly enhanced because the reactant molecules can access not only the HSbO clusters on the crystal surface but also all the HSbO clusters inside.

Recall that various functions have been explored in anionic POM clusters such as the Keggin and Wells-Dawson types by modifying the clusters themselves, e.g., through elemental substitution (3) and addition of organic functional groups (54), and by forming organic-inorganic complexes in combination with various cations (1). Such synthetic approaches should be possible in our Sb-based cluster system, which can adjust the acidity and introduce porosity to improve the acid catalytic properties or to add other functions such as proton conductivity. It would also be interesting to examine how the catalysis of HSbOI is altered by elemental substitution, e.g., halide substitution at the iodine sites. To this end, it is important to understand the reaction mechanism, including the condensation process during the cluster formation.

MATERIALS AND METHODS

Synthesis

The powder sample of HSbOI was prepared as follows: Sb$_2$O$_3$ (99.9%, Wako; 2.0 g; 6.86 mmol) was dissolved in a mixture of HI (Wako; 6.8 M, 15.6 ml) and water (10 ml) and was stirred for 1 hour at 75°C. Adding water (500 ml) to this solution resulted in the precipitation of an orange powder. The suspension was stirred at 75°C for 1 hour and then at 0°C for 1 hour. The resulting product was recovered by filtration, washed with filtrate, and dehydrated through drying at 100°C under vacuum.

Characterization

The specimen for TEM study was prepared by grinding the powder in anhydrous hexane and putting a few drops of the resulting suspension onto Cu grids covered with a holey carbon layer. The ED experiment was performed using a FEI Tecnai G2 microscope operated at 200 kV. Energy-dispersive x-ray spectroscopy was performed using a FEI Tecnai Osiris microscope (200 kV), equipped with a Super-X detector. High-resolution STEM images were acquired using a FEI Titan 80-300 “cubed” microscope (300 kV). A Gatan double-tilt vacuum transfer holder was used to prevent the oxidation of the sample. 3D-ED tomography was used for the structure solution. Reciprocal space was scanned over an angular range of 85°, resulting in 696 reflections that were used for refinement with 590 reflections being independent. The PET software (55) was used for the 3D reconstruction of reciprocal space.

Powder XRD data were collected using a D8 ADVANCE diffractometer (Bruker AXS) with Cu-K$_a$ radiation. High-resolution powder SXRD experiments were performed at RT using a Debye-Scherrer camera, installed at SPring-8 BL02B2 of the Japan Synchrotron Radiation Research Institute. The incident beams from the bending magnet were monochromatized to $\lambda = 0.42096(1)$ Å. Sieved powder samples ($<32$ μm) were loaded into a Pyrex capillary with an inner diameter of 0.2 mm. The sealed capillary was rotated during the measurement to reduce the effect of preferred orientation of the crystallites. Powder neutron diffraction (ND) data were collected at RT using the high-resolution powder diffractometer BT-1 ($\lambda = 1.54060$ Å) at the National Institute of Standards and Technology (NIST) Center for Neutron Research. The collected SXRD patterns were analyzed by the Rietveld method using RIETAN-FP program (56).

DFT computations for the large HSbO cluster were performed with the Gaussian 09 package. Calculations were carried out using the extended cluster of [Sb$_{36}$O$_{50}$]$^{8+}$ (and protonated [HSb$_{36}$O$_{50}$]$^{9+}$), which is composed of [Sb$_{18}$O$_{44}$] from the HSbO cluster plus O─Sb ($\times 2$) and O─V$_{Sb}$ ($\times 4$) from the Sb$_{6}$─8I$_4$O$_6$ cluster (where V$_{Sb}$ represents an antimony vacancy).
For the outer shell of the HSbO cluster, a small deficiency (occupancy, \( g \approx 0.95 \)) in Sb3 (Wyckoff site 96j) was ignored, while the three-split Sb2 sites (96k, \( g \approx 0.31 \)) were placed at the ideal site (32j, \( g = 1 \)), yielding [Sb3O4]. For the inner shell, reflecting the experimental defect (\( g \approx 0.319 \)), we removed four of the six antisymmetries for Sb1 in [Sb3O4], resulting in [Sb2O4]. Thus, outer [Sb3O4] and inner [Sb2O4] are combined to give a [Sb4O6] structure, while keeping the XYZ coordinates of the framework Sb3O5. The two Sb1 atoms are arranged vertically in Fig. 4B.

As shown in Fig. 4B, O atoms of the Sb3O5 cluster can be divided into three layers according to their distance from the center of the cluster. The O atoms of HSbO cluster can be classified into five groups and the capping O atoms into two groups (Fig. S19). One proton is placed near any of the seven O atoms to form a [HSb3O5]9+ cluster. The most stable orientation of the protons bound to each O atom was determined. 3D XYZ coordinates of each proton in the [HSb3O5]9+ cluster were fully optimized using the B3LYP functional, while keeping the XYZ coordinates of the framework Sb3O5 fixed. The basis sets are LanL2DZ for Sb atoms and cc-pVDZ for O atoms. The bonding energy of the [HSb3O5]9+ cluster was calculated by setting the average of the computed NMR chemical shifts of proton in the [HSb3O5]9+ and 20. T. A. Stewart, D. E. Trudell, T. M. Alam, C. A. Ohlin, C. Lawler, W. H. Casey, S. Jett, M. Nyman, Crystallographic refinement of metal-ion battery structure refinement. J. Am. Chem. Soc. 122, 7432–7433 (2000).

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