Inorganic Chemistry

Communication

pubs.acs.org/IC

# A Cationic Antimonite Chain Templated by Sulfate: $[Sb_6O_7^{4+}][(SO_4^{2-})_2]$

Honghan Fei, Cari S. Han, and Scott R. J. Oliver*

Department of Chemistry and Biochemistry, University of California, Santa Cruz, 1156 High Street, Santa Cruz, California 95064, United States

Supporting Information

**ABSTRACT:** An extended metal oxide possessing a cationic charge on the host has been synthesized by hydrothermal methods. The structure consists of 1D antimony oxide $[Sb_6O_7]^{4+}$ chains with a new structural motif of four Sb atoms wide and unprotonated sulfate anions between the chains. The material was characterized by powder and single-crystal X-ray diffraction. Thermal behavior and chemical resistance in aqueous acidic conditions (pH ∼2) indicate a highly stable cationic material. The stability is attributed to the entirely inorganic composition of the structure, where 1D covalently extended chains are electrostatically bound to divalent anions.

Research on open-framework metal oxides has steadily increased following the discovery of zeolites, which are a family of aluminosilicates having enormous applications in catalysis, molecular separation, and water purification.[1] The overall neutral or anionic charge on the framework, however, limits their importance in anion-based applications. Two 3D cationic zeotypes were also reported based on thorium and ytterbium, with borate clusters and chloride residing in 1D channels, respectively.[2] Meanwhile, many of the metals listed as EPA-priority pollutants are in the oxohydroxo anionic form.[3] The trapping, immobilization, and recognition of both inorganic and organic anionic species (e.g., DNA polyanions, pharmaceutical pollutants, and their metabolites) are important in biological and environmental systems.[4]

Cationic inorganic materials are a family of positively charged extended architectures where charge-balancing anions reside in 0D capsules, 1D channels, or 2D interlamellar regions. Layered double hydroxides (LDHs) are the most widely studied examples, with the general formula $[M^{2+}{}_{1-x}M^{3+}{}_{x}(OH)_2][A^{n-}{}_{x/n}\cdot mH_2O]$, where $M^{2+}$ and $M^{3+}$ are a range of metals (e.g., $Mg^{2+}$ and $Al^{3+}$), $x$ is the ratio of $M^{3+}/(M^{2+} + M^{3+})$, and $A^{n-}$ is the $n$-valent counteranion (e.g., $CO_3^{2-}$, $n = 2$).[5] They demonstrate reversible anion exchange but form a paste in aqueous solution, making recovery and reusability more difficult. Indeed, the Bronsted basicity of their hydroxyl groups limits their chemical stability in acidic conditions and thus their application in corrosive wastewater.[6] Layered rare-earth hydroxides are another emerging series of cationic inorganic layered materials with halide, nitrate, sulfate, and organosulfonate as interlamellar anions, although with intrinsic basicity as for LDHs.[7]

Our group has reported a class of cationic inorganic materials based on lower p-block metals where inert electron pairs on the metal point away from the inorganic connectivity and cap the 2D layers.[8] Usually this group of materials has little or no bridging hydroxyl groups, unlike the fully hydroxylated metals of LDHs that give rise to their overall positive charge.[9] One example is lead fluoride, $[Pb_2F_2]^{2+}$, which completely anion exchanges its $\alpha,\omega$-alkanedisulfonates for $\alpha,\omega$-alkanedicarboxylates.[10] Antimony oxides are used as fire retardants and catalysts, including our previously reported 2D $[Sb_4O_4(OH)_2][O_3SC_2H_4SO_3]$.[9c] Two examples of antimony oxide chains have been previously reported: one anionic, $[Sb_2O_4]^{2-}$, and the other cationic, $[Sb(OH)]^{2+}$. The latter is one Sb atom wide, zigzags, and is covalently bridging to oxalate.[11]

Herein, we report the synthesis and characterization of an entirely new cationic 1D antimony oxide $[Sb_6O_7^{4+}][(SO_4)_2^{4-}]$ (which we denote as SLUG-34 for University of California, Santa Cruz, structure no. 34). The array of 1D $[Sb_6O_7]^{4+}$ chains interact electrostatically with sulfate groups. Although the initial anion-based host–guest experiments were not successful, this rare example of an entirely inorganic cationic material along with 1D M–O–M connectivity gives rise to high thermal stability to ∼500 °C and chemical resistance in aqueous acidic conditions.

Colorless needlelike crystals of SLUG-34 were synthesized under acidic hydrothermal conditions with high yield and phase purity at 150 °C, as supported by the match of the experimental powder X-ray diffraction (PXRD) pattern to the theoretical pattern simulated from single-crystal data (see the Supporting Information). Hydrothermal conditions higher than 150 °C produced a mixed phase of SLUG-34 and $SbO_2$ (ICDD PDF no. 01-074-0127). Lower temperature (125 °C) resulted in lower crystallinity, as evidenced by lower intensity and broadening of the X-ray diffraction peaks. A more concentrated hydrothermal aqueous solution and/or a higher molar ratio of the metal source to sulfuric acid gave rise to $Sb_2O_3$ (ICDD PDF no. 99-000-3357).

SLUG-34 crystallizes in a high-symmetry *Ccc*2 space group of the orthorhombic crystal system. Single-crystal X-ray crystallography reveals that the structure contains isolated 1D cationic antimony oxide chains with charge-balancing sulfate anions between adjacent chains (Figure 1).[12] Each $[Sb_6O_7]^{4+}$ chain propagates along the $c$ axis and is surrounded by sulfate anions in the $ab$ plane. The $[Sb_6O_7]^{4+}$ chains consist of three

**Received:** June 23, 2012
**Published:** July 30, 2012

dx.doi.org/10.1021/ic3013409 | *Inorg. Chem.* 2012, 51, 8655−8657

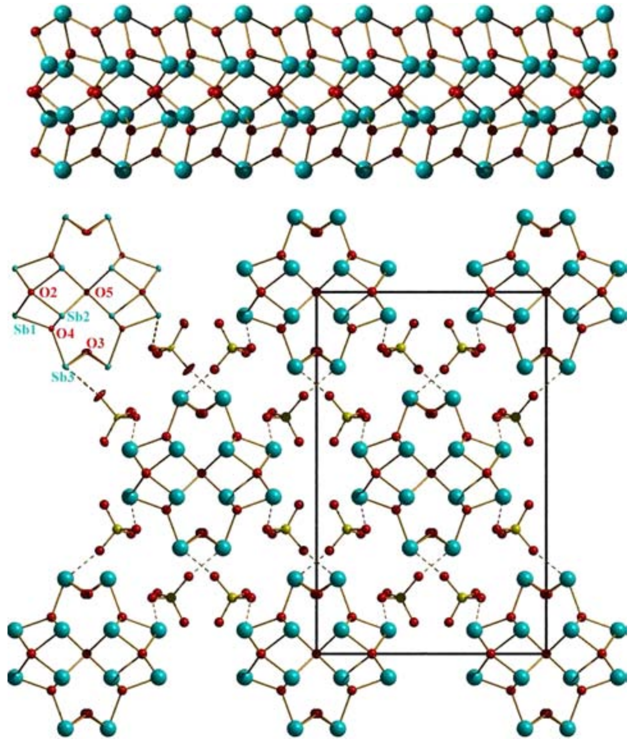

**Figure 1.** Top: *b* projection of one cationic $[Sb_6O_7]^{4+}$ chain of SLUG-34. Bottom: *c* projection of SLUG-34 showing the chains end-on and interchain sulfates. The top left chain and two neighboring weakly bound sulfates are shown as thermal ellipsoids with 50% probability (Sb, turquoise; S, yellow; O, red).

crystallographically independent Sb centers, all with a similar trigonal-pyramidal coordination environment. The inert pair effect of the lower p-block metals allows umbrella-like coordination, with the inert pair of the outer Sb centers (Sb1 and Sb3; Figures 1 and S4 in the Supporting Information, SI) pointing outward and capping the chains. All of the O atoms in the antimonite chains are unprotonated, supported by both charge balance and X-ray crystallography ($R_1$ = 0.0115 and $wR_2$ = 0.0278) and attributable to the semimetal nature of Sb. Two of four crystallographically independent intrachain O atoms (O2 and O4) triply bridge to metal centers as for LDHs, while two other O atoms (O3 and O5) doubly bridge to Sb. The positive charge feature of this 1D extended structure is due to the trivalent, tricoordinate Sb centers and $\mu_3$-O atoms.

The cationic topology is further defined by electrostatic interaction between sulfates and positively charged chains. The sulfate O atoms interact with Sb by a weak contact [~2.290(3)−2.376(3) Å]. These contact distances not only are significantly longer than the intrachain Sb−O bonds [~1.982(2)−2.149(2) Å] but also are well outside the accepted distance for a covalent Sb−O bond (2.061 ± 0.116 Å, from the Cambridge Structural Database).[13] These bond distances indicate that the sulfates are not covalently bonded to the antimony oxide chains, supporting the theory that the material is indeed a cationic 1D extended inorganic structure. Initial attempts to exchange sulfate with other anions [e.g., chromate ($CrO_4^{2-}$), permanganate ($MnO_4^-$), perchlorate ($ClO_4^-$), and selenite ($SeO_3^{2-}$)] were unsuccessful. Likely, the divalent nature of the sulfates gives rise to strong electrostatic bonding with the cationic chains compared to weakly coordinating anions such as $BF_4^-$ and $ClO_4^-$.

The thermal behavior of this rare cationic 1D antimonite topology was probed by in situ powder X-ray thermodiffraction in air and by thermogravimetric analysis (TGA) under both $N_2$ and air purge. The TGA traces indicate that SLUG-34 is thermally stable to ca. 500 °C, which was also observed by in situ thermodiffraction, with no structural rearrangement after annealing of the crystals to 400 °C (Figures 2 and S2 in the SI).

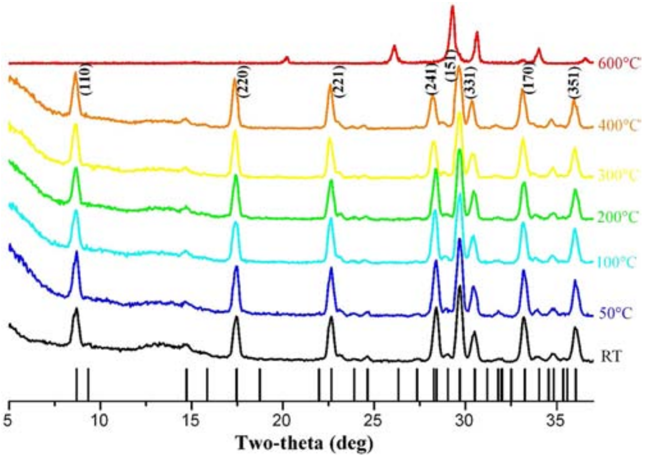

**Figure 2.** In situ variable-temperature PXRD of SLUG-34 from room temperature to 400 °C and ex situ thermodiffraction after heating to 600 °C. The theoretical pattern is shown at the bottom as bars.

This thermal stability is significantly higher than those of layered rare-earth hydroxides and almost all metal−organic frameworks.[7b,g,14] No apparent peak broadening in the in situ thermodiffraction confirms negligible loss of crystallanity upon heating. The major decomposition step occurred in the temperature range 450−600 °C, with ex situ annealing of SLUG-34 at 600 °C producing $SbO_2$ (ICDD PDF no. 01-074-0127). In agreement, TGA shows 9.90 wt % loss over this region (theoretical 10.83 wt % based on the formation of $SbO_2$). Calcination of SLUG-34 under $N_2(g)$ purge presumably condenses the structure to Sb metal with ~40 wt % loss (theoretical 30.1 wt %).

The basic nature of LDHs and layered rare-earth hydroxides does not allow for chemical stability in acidic conditions, which is often the operation parameter in environmental hazardous waste. The chemical resistance of SLUG-34 to an acidic aqueous solution was examined by suspending samples of crystals (ca. 100 mg) in Milli-Q water, a buffered solution at pH 4, and an aqueous HCl, $HNO_3$, or $H_2SO_4$ solution at pH 2. PXRD before and after acidic solution treatment for 12 h confirms the integrity of the extended 1D structure (Figure 3). The crystallanity decreased after acid treatment, as judged by the lower diffraction peak intensity (cf. Figure S1 in the SI). Nevertheless, the survival of the diffraction peaks, including the three low-angle $2\theta$ diffraction peaks with Miller indices (110), (220), and (221), indicates chemical stability in acidic conditions. Indeed, there is no phase transition, and no diffraction peaks for $SbO_2$, $Sb_2O_3$, or other antimony oxides are observed.

In conclusion, SLUG-34 is a new cationic antimony oxide with 1D Sb−O−Sb inorganic connectivity and entirely inorganic nature. The strongly bound sulfate divalent anions give rise to stability to ~500 °C and chemical resistance to acidic conditions. Although initial attempts for host−guest applications were unsuccessful, this breakthrough in both new

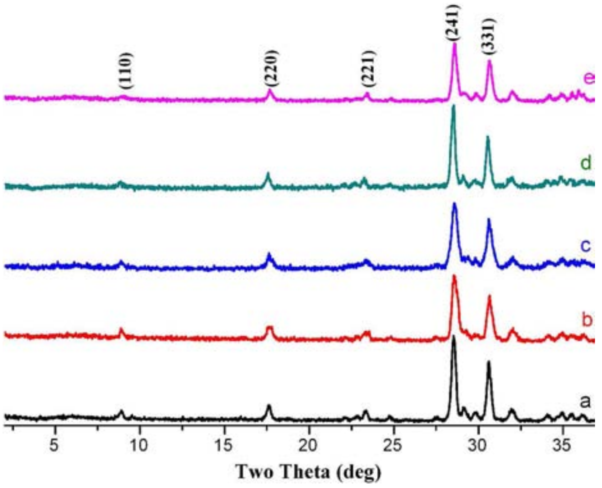

**Figure 3.** PXRD of SLUG-34 after treatment for 12 h in Milli-Q water (a), buffer at pH 4 (b), a HCl aqueous solution at pH 2 (c), a $HNO_3$ aqueous solution at pH 2 (d), and a $H_2SO_4$ aqueous solution at pH 2 (e).

cationic inorganic topology and sulfate templating opens up the possibility of cationic extended metalates with stability superior to that of LDHs for anion-based applications.

## ■ ASSOCIATED CONTENT

### Ⓢ Supporting Information

Experimental details, additional figures and tables, CIF file including refinement parameters and full bond distances. This material is available free of charge via the Internet at http://pubs.acs.org.

## ■ AUTHOR INFORMATION

### Corresponding Author

*E-mail: soliver@ucsc.edu.

### Notes

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

The single-crystal X-ray diffraction and in situ thermodiffraction data in this work were recorded on instruments supported by the NSF Major Research Instrumentation (MRI) Program under Grants CHE-0521569 and DMR-1126845. H.F thanks the University of California, Santa Cruz, Graduate Division, for a Chancellor's Dissertation Year Fellowship.

## ■ REFERENCES

(1) (a) Thomas, J. M. *Sci. Am.* **1992**, *1992*, 112–115. (b) Wight, A. P.; Davis, M. E. *Chem. Rev.* **2002**, *102*, 3589–3614. (c) Davis, M. E. *Nature* **2002**, *417*, 813–821. (d) Corma, A. *J. Catal.* **2003**, *216*, 298–312.

(2) (a) Wang, S.; Alekseev, E. V.; Diwu, J.; Casey, W. H.; Phillips, B. L.; Depmeier, W.; Albrecht-Schmitt, T. E. *Angew. Chem., Int. Ed.* **2010**, *49* (6), 1057–1060. (b) Goulding, H. V.; Hulse, S. E.; Clegg, W.; Harrington, R. W.; Playford, H. Y.; Walton, R. I.; Fogg, A. M. *J. Am. Chem. Soc.* **2010**, *132*, 13618–13620.

(3) (a) Keith, L. H.; Teillard, W. A. *Environ. Sci. Technol.* **1979**, *13*, 416. (b) Hogue, C. *Chem. Eng. News* **2011**, *89*, 6.

(4) (a) Weitkamp, J. *Solid State Ionics* **2000**, *131*, 175–188. (b) Wu, M.; Janssen, S. *Environ. Sci. Technol.* **2011**, *45*, 366–367.

(5) (a) Rives, V. *LDHs: Layered Double Hydroxides: Present and Future*; Nova Science Publishers Inc.: Hauppauge, NY, 2001. (b) Slade, D. G. E. a. R. C. T. *Layered Double Hydroxides*; Duan, X., Evans, D. G., Eds.; Springer-Verlag: New York, 2006; pp 1–87.

(6) Rao, K. K.; Gravelle, M.; Valente, J. S.; Figueras, F. *J. Catal.* **1997**, *173*, 115–121.

(7) (a) Geng, F.; Ma, R.; Sasaki, T. *Acc. Chem. Res.* **2010**, *43*, 1177–1185. (b) Geng, F.; Matsushida, Y.; Ma, R.; Xin, H.; Tanaka, M.; Izumi, F.; Lyi, N.; Sasaki, T. *J. Am. Chem. Soc.* **2008**, *130*, 16344–16350. (c) Liu, Z.; Ma, R.; Osada, M.; Iyi, N.; Ebina, Y.; Takada, K.; Sasaki, T. *J. Am. Chem. Soc.* **2006**, *128*, 4872–4880. (d) Poudret, L.; Prior, T. J.; McIntyre, L. J.; Fogg, A. M. *Chem. Mater.* **2008**, *20*, 7447–7453. (e) McIntyre, L. J.; Jackson, L. K.; Fogg, A. M. *Chem. Mater.* **2008**, *20*, 335–340. (f) Gandara, F.; Perles, J.; Snejko, N.; Iglesia, M.; Gomez-Lor, B.; Gutierrez-Puebla, R.; Monge, M. A. *Angew. Chem., Int. Ed.* **2006**, *45*, 7998–8001. (g) Liang, J.; Ma, R.; Geng, F.; Ebina, Y.; Sasaki, T. *Chem. Mater.* **2010**, *22*, 6001–6007.

(8) (a) Oliver, S. R. J. *Chem. Soc. Rev.* **2009**, *38*, 1868–1881. (b) Orgel, L. E. *J. Chem. Soc.* **1959**, 3815–3819. (c) Stoltzfus, M. W.; Woodward, P. M.; Seshadri, R.; Klepeis, J. H.; Bursten, B. *Inorg. Chem.* **2007**, *46*, 3839–3850.

(9) (a) Tran, D. T.; Zavalij, P. Y.; Oliver, S. R. J. *J. Am. Chem. Soc.* **2002**, *124*, 3966–3969. (b) Rogow, D. L.; Russell, M. P.; Wayman, L. M.; Swanson, C. H.; Oliver, A. G.; Oliver, S. R. J. *Cryst. Growth Des.* **2010**, *10*, 823–829. (c) Swanson, C. H.; Shaikh, H. A.; Rogow, D. L.; Oliver, A. G.; Campana, C. F.; Oliver, S. R. J. *J. Am. Chem. Soc.* **2008**, *130*, 11737–11741. (d) Fei, H.; Oliver, S. R. J. *Angew. Chem., Int. Ed.* **2011**, *50*, 9066–9070. (e) Rogow, D. L.; Fei, H.; Brennan, D. P.; Ikehata, M.; Zavalij, P. Y.; Oliver, A. G.; Oliver, S. R. J. *Inorg. Chem.* **2010**, *49*, 5619–5624.

(10) Fei, H.; Pham, C. H.; Oliver, S. R. J. *J. Am. Chem. Soc.* **2012**, *134*, 10729–10732.

(11) (a) Kaduk, J. A.; Toft, M. A.; Golab, J. T. *Powder Diffr.* **2009**, *25*, 19–24. (b) Sykora, R. E.; King, J. E.; Illies, A. J.; Albrecht-Schmitt, T. E. *J. Solid State Chem.* **2004**, *177*, 1717–1722.

(12) $[Sb_6O_7][(SO_4)_2]$ (SLUG-34): colorless, needlelike, crystal dimens 0.245 × 0.035 × 0.030 mm, orthorhombic, space group *Ccc*2, $a$ = 12.0329(6) Å, $b$ = 18.9371(10) Å, $c$ = 5.8595(3) Å, $V$ = 1335.19(12) Å$^3$, $Z$ = 4, $T$ = 296(2) K, $\lambda$(Mo K$\alpha$) = 0.71073 Å, $\mu$(Mo K$\alpha$) = 12.364 mm$^{-1}$, 7481 reflections collected, 6647 reflections collected, 1479 unique ($R_{\text{int}}$ = 0.0263), giving R1 = 0.0115, wR2 = 0.0278 for 1471 data with $[I > 2\sigma(I)]$ and R1 = 0.0116, wR2 = 0.0279 for all 1479 data.

(13) *Cambridge Structural Database:* A covalent Sb–O bond length is generally between 1.9 and 2.1 Å, while 90.8% Sb–O bonds have bond lengths of less than 2.27 Å.

(14) (a) Fei, H.; Paw, L. U.; Rogow, D. L.; Bresler, M. R.; Abdollahian, Y. A.; Oliver, S. R. J. *Chem. Mater.* **2010**, *22*, 2027–2032. (b) Fei, H.; Rogow, D. L.; Oliver, S. R. J. *J. Am. Chem. Soc.* **2010**, *132*, 7202–7209. (c) Zhao, X.; Wu, T.; Zheng, S. T.; Wang, L.; Bu, X.; Feng, P. *Chem. Commun.* **2011**, *47*, 5536–5538. (d) Choi, H. J.; Dinca, M.; Long, J. R. *J. Am. Chem. Soc.* **2008**, *130*, 7848.