Synthesis and Crystal Structure of Sr\textsubscript{10}[Sb\textsubscript{7}O\textsubscript{13}(OH)]\textsubscript{2}[SbSe\textsubscript{3}]\textsubscript{2}Se \cdot 2H\textsubscript{2}O

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INTRODUCTION

Very few oxoselenoantimonates with trivalent antimony are known. However, a few alkali oxoselenoantimonates are reported that are isostructural with the rare mineral cetineite(1). A noteworthy example is K\textsubscript{6}[Sb\textsubscript{12}O\textsubscript{18}][SbSe\textsubscript{3}] \cdot 6H\textsubscript{2}O, the structure of which was recently reported. This compound shows photoconductive properties (2, 3). The structure contains remarkable one-dimensional [Sb\textsubscript{12}O\textsubscript{18}] tubes with aperture ca. 7 Å (4). The water molecules contained within the tubes can be reversibly removed at room temperature. The tube walls are built up from [SbO\textsubscript{3}] pyramids and the space between the tubes is occupied by isolated [SbSe\textsubscript{3}] pyramids. The alkali cations within the tubes can be replaced by divalent cations with simultaneous replacement of Sr–O bonds into layers with composition [Sr\textsubscript{8}Sb\textsubscript{16}O\textsubscript{32}(OH)]\textsuperscript{4+}. The interlayer spaces are occupied by [SbSe\textsubscript{3}] pyramids and isolated Se\textsubscript{2} \textsuperscript{2−} anions. Both the [Sb\textsubscript{12}O\textsubscript{18}(OH)] single branched six-rings and the [SbSe\textsubscript{3}] pyramids can be considered as building blocks of the known structure K\textsubscript{6}[Sb\textsubscript{12}O\textsubscript{18}][SbSe\textsubscript{3}]\textsubscript{2} \cdot 6H\textsubscript{2}O. © 1998 Academic Press

A new strontium oxoselenoantimonate(III), Sr\textsubscript{10}[Sb\textsubscript{7}O\textsubscript{13}(OH)]\textsubscript{2}[SbSe\textsubscript{3}]\textsubscript{2} \cdot 2H\textsubscript{2}O, has been hydrothermally synthesized and characterized by single crystal structure determination. It crystallizes in the monoclinic system, space group P\textsubscript{2}\textsubscript{1}/n, with a = 11.4013(6) Å, b = 18.417(1) Å, c = 13.0568(7) Å, \( \beta = 108.51(1)^{\circ} \), \( V = 2599.9(2) \text{ Å}^3 \), measured at 223 K. In the structure [SbO\textsubscript{3}] pyramids share oxygen atoms to form [Sb\textsubscript{2}O\textsubscript{6}(OH)] single branched six-rings that are interconnected by Sr–O bonds into layers with composition [Sr\textsubscript{5}Sb\textsubscript{7}O\textsubscript{13}(OH)]\textsuperscript{4−}. The interlayer spaces are occupied by [SbSe\textsubscript{3}] pyramids and isolated Se\textsubscript{2} \textsuperscript{2−} anions. Both the [Sb\textsubscript{2}O\textsubscript{6}(OH)] single branched six-rings and the [SbSe\textsubscript{3}] pyramids can be considered as building blocks of the known structure K\textsubscript{6}[Sb\textsubscript{12}O\textsubscript{18}][SbSe\textsubscript{3}]\textsubscript{2} \cdot 6H\textsubscript{2}O.

During the synthesis of the cetineite type phase Sr\textsubscript{6}[Sb\textsubscript{12}O\textsubscript{18}][SbSe\textsubscript{3}]\textsubscript{2}(OH)\textsubscript{6} (5) a novel strontium oxoselenoantimonate, Sr\textsubscript{10}[Sb\textsubscript{7}O\textsubscript{13}(OH)]\textsubscript{2}[SbSe\textsubscript{3}]\textsubscript{2} \cdot 2H\textsubscript{2}O (1), was obtained. In the crystal structure of 1, determined from single crystal X-ray diffraction data, seven [SbO\textsubscript{3}] pyramids form a unique [Sb\textsubscript{2}O\textsubscript{6}(OH)] single branched six-ring that can be considered as a building block of the infinite [Sb\textsubscript{12}O\textsubscript{18}]\textsubscript{2} tubes found in the cetineite type structure. The isolated [SbSe\textsubscript{3}] pyramids in 1 are similar to those in the cetineite phases.

EXPERIMENTAL

In a typical synthesis, elemental Sb (0.37 g, 3.0 mmol) and Se (0.30 g, 3.8 mmol) and LiOH \cdot H\textsubscript{2}O (0.60 g, 14.2 mmol) were mixed with 2 ml water. Sr(OH)\textsubscript{2} \cdot 8H\textsubscript{2}O (0.57 g, 2.2 mmol) was subsequently added to the mixture. Finally the mixture was sealed in air in a Teflon-lined autoclave with 23 ml inner volume and heated at 220°C for four days. The product was washed with water, vacuum filtered, and dried in air. Brown prismatic crystals of the title compound crystallized together with a minor amount of Sr\textsubscript{6}[Sb\textsubscript{12}O\textsubscript{18}][SbSe\textsubscript{3}]\textsubscript{2}(OH)\textsubscript{6} in the form of tiny dark red crystals.

The composition of the title compound was determined using JEOL 8600 electron microscope operating at 15 keV with a 10-μm beam diameter and a beam current of 30 nA. For single crystal X-ray data, a fragment with approximate dimensions 0.50 × 0.24 × 0.20 mm was cut off from a large crystal and mounted on a glass fiber using silicon sealant. Intensities were measured on a SMART platform diffractometer equipped with a 1 K CCD area detector using graphite-monochromatized MoK\textsubscript{α} radiation at –50°C. A hemisphere of data (1271 frames at detector distance 5 cm) was collected using a narrow-frame method with scan widths of 0.30° in \( \omega \) and an exposure time of 30 s/frame. The first 50 frames were remeasured at the end of the data collection to monitor instrument and crystal stability, and the maximum correction applied on the intensities was \( <1\% \). The data were integrated using the Siemens SAINT program (6), with the intensities corrected for Lorentz factor, polarization, air absorption, and absorption due to variation in the path length through the detector.

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faceplate. Final cell constants were refined using 6762 reflections having I > 10σ(I). An absorption correction was first made using the program SADABS (7) based on equivalent reflections. After solving the structure, a further absorption correction was applied using the program DIFABS (8).

The structure was solved by direct methods and refined using SHELXTL (9). All nonhydrogen positions were derived by direct methods and refined anisotropically in the final refinements. The hydrogen atoms were located from difference maps and refined isotropically with atom distance constraints. Crystallographic and refinement details are summarized in Table 1. Atom positions are given in Table 2 and selected bond lengths and bond angles in Table 3.

### STRUCTURE DESCRIPTION AND DISCUSSION

The local coordination environments of the antimony atoms are shown in Fig. 1. The Sb(1–7) atoms are each coordinated to three oxygen atoms to form trigonal pyramids with Sb–O bond length in the range 1.90–2.09 Å and O–Sb–O angles between 81.4° and 94.3°. The coordination environments of Sb(1–6) are further complemented by one or two Se atoms with weak Sb–Se interactions (3.18–3.37 Å). The Sb(8) atom is coordinated by three Se atoms to form an [SbSe3] pyramid with Sb–Se bond lengths 2.55–2.56 Å and Se–Sb–Se angles between 99.6° and 104.9°.

The Sr atoms are each coordinated both by Se atoms with Sr–Se bond lengths 3.30–3.48 Å and by O atoms including water oxygen with Sr–O bond lengths 2.40–2.96 Å. The coordination number of each of the five inequivalent Sr atoms is 7 with such bond length limits. The Sr coordination environments are shown in Fig. 2.

The [Sb(1)O2(OH)] and [Sb(2–6)O3] pyramids share oxygen atoms at their corners to form a [Sb6O13(OH)] six-ring that is attached to the [Sb(7)O3] pyramid as a single branch (Fig. 1). These [Sb6O13(OH)] single branched rings are packed parallel to (010) with the [Sb(7)O3] branches aligned along the [101] direction. An infinite row of these rings is formed through translation symmetry along [101]. Each two such rows are related by a glide plane.
n with Sr(2–4) atoms located between them and are interconnected by the Sr–O bonds into a [101] band. Within the band the Sb(7) atoms (ring branches) of one chain lie approximately over the centers of the rings of another chain. Neighboring bands are interconnected into [Sr5Sb7O13(OH)]4− oxide layers parallel to (010) by Sr(1,5)–O bonds and hydrogen bonds between O(8) and OH (d(O8–OH) = 2.61 Å) (Fig. 3). The layers are slightly wavy. H2O molecules are located at the wave troughs and complement the coordination sphere of the Sr(5) cations (Fig. 4). There is no hydrogen bonding between water oxygen and other atoms. The space between the oxide layers is occupied by [SbSe3]3− pyramids and isolated Se2− anions.
FIG. 2. Coordination environments of the Sr atoms. Thermal ellip-
soids are drawn with 95% probability.

(Fig. 4). The oxide layers are held together through ionic
Sr–Se bonds and weak interactions between the Sb atoms of
the rings and Se atoms. The shortest Sr–Se bonds are those
between the Sr(2) cations located near the centers of the
six-rings and the interlayer Se(4) anions. However, the ther-
mal ellipsoid of the Se(4) atom is considerably larger than
those of the Se(1–3) atoms, suggesting the presence of static
disorder probably due to the absence of strong covalent
bonds to Se(4) (Fig. 1, 5). Refinements in which the Se(4)
position was split between two sites were unstable. The
structure can be described as built up from alternating oxide
and selenide sheets.

Separation between the oxide and selenide units most
likely reflects the substantial size and electronegativity dif-
ferences between oxygen and selenium. Similar phenomenon
can be found in some oxothioantimonates. For example,
the structure of the mineral sarabauite CaSb$_{10}$O$_{10}$S$_{6}$ contains
[CaSb$_{6}$O$_{10}$] slabs sandwiching [Sb$_4$S$_6$] units (10). In the
cetineite-type compounds, infinite oxide tubes are sur-
rrounded by infinite columns of [Sb$_3$] or [SbSe$_3$] pyramids
(1, 5).

A far as we can ascertain, the [Sb$_6$O$_{12}$] six-rings are
found only in the [Sb$_{12}$O$_{18}$] tubes of the cetineite-type
structure. The tube can be considered as formed from the
[Sb$_6$O$_{12}$] six-rings in the way that each rings shares its six
terminal oxygen atoms with neighboring rings. In fact, the
[Sb$_7$O$_{13}$(OH)] group found in the title compound can also
be considered as a building block for the [Sb$_{12}$O$_{18}$] cetineite tubes. As shown in Fig. 6, two [Sb$_7$O$_{13}$(OH)]
groups can be connected to form a structural unit with three
six-rings. Three such units can be connected into a cetineite-
type tube. Since the cetineite phase Sr$_6$[Sb$_{12}$O$_{18}$]
[SbSe$_3$]$_2$(OH)$_6$ crystallized together with the title com-
 pound, the structural relationship suggests the possibility
that [Sb$_7$O$_{13}$(OH)] groups might be secondary building units present in solution during the crystallization of both phases. The yield of Sr$_6$[Sb$_{12}$O$_{18}$][SbSe$_3$]$_2$(OH)$_6$ can be slightly improved by lowering the Sr(OH)$_2$·8H$_2$O content of the reactant mixture, but the compound has not yet been synthesized as a single phase.

The bond valence sums calculated with empirical parameters (11) for Sb atoms range from 2.98 to 3.21 v.u. and confirm the trivalent nature of all 8 Sb cations that is indicated by the characteristic pyramidal coordination envrioms. The stereochemically active lone electron pairs (LEP) of the Sb atoms of the oxide layers all point into the interlayer spaces (the selenide sheets). Therefore, the Se$^{2-}$ anions are actually surrounded by the LEP of antimony cations. The structural similarities between the title compound and K$_6$[Sb$_{12}$O$_{18}$][SbSe$_3$])$_2$·6H$_2$O suggest that measurements of the photoconductivity of Sr$_{10}$[Sb$_7$O$_{13}$(OH)]$_2$[SbSe$_3$]$_2$·2H$_2$O would be of interest.
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