Preparation and Crystal Structure of $(Sb_4O_5)(ReO_4)_2$ with Cationic Antimony Oxide Layers

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Received April 3, 1997

Introduction

Antimony(III) ions prefer low coordination numbers like 3 and 4 and have stereochemically active lone-pair electrons. These features prevent antimony(III) ions from building dense three-dimensional structures, and antimony(III) oxides with additional anions normally have low-dimensional structures. For example, $Sb_6O_7(SO_4)_2$[1] consists of linear chains, and $Sb_4O_5Cl_2$,[2] $Sb_4O_4(OH)_2(NO_3)_2$,[3] and $Sb_4O_5(OH)(ClO_4)(H_2O)_{0.5}$[4] have layered structures. Although cation-exchange reactions of compounds with anionic layers have been studied extensively, compounds with anionic layers are very rare, and their chemical functions like anion exchange have not been well explored. The combination of antimony(III) and oxygen is a good candidate for new cationic layered compounds with some chemical functions.

In the course of a study for new ternary oxides of rhenium, we reacted antimony(III) oxide with perrhenic acid. In this reaction, we had expected oxidation of antimony(III) by rhenium(VII). However, the redox reaction did not occur at all, and we found a compound having new $(Sb_4O_5)^{2+}$ layers after the product was heated.

Experimental

Materials. The starting compound Re_2O_7 was prepared by the reaction of rhenium metal powder (99.9%, Aldrich) with oxygen gas. Antimony trioxide (99.9%, Wako) was used as received.

Preparation of $(Sb_4O_5)(ReO_4)_2$. For the preparation of $(Sb_4O_5)(ReO_4)_2$, a hydrate compound $SbOReO_4{\cdot}2H_2O$ was used as an intermediate. The hydrate compound was originally obtained by a hydrothermal reaction,[5] but we found that a powder sample could be easily prepared under ambient pressure. To an aqueous solution of perrhenic acid (2.9 mmol in 1 mL) was added antimony trioxide powder (365 mg, 2.5 mmol of Sb), and the suspension was stirred to become viscous. After 20 cm^3 of water was added, the suspension was further stirred and the supernatant was decanted. Drying of the precipitate gave a white powder, which was identified by X-ray powder diffraction to be $SbOReO_4{\cdot}2H_2O$. The hydrate (0.435 g) was pressed into a disk (1.5 kbar) and heated in an evacuated silica tube (outer diameter, 12 mm; length, 15 cm) at 500 °C for 6 days to yield colorless, transparent single crystals of $(Sb_4O_5)(ReO_4)_2$. The X-ray powder diffraction showed that the product was a mixture of $(Sb_4O_5)(ReO_4)_2$ and $SbOReO_4{\cdot}2H_2O$. The possible destination of excess rhenium was hygroscopic perrhenic acid, which could not be detected by X-ray diffraction. Heating a mixture of $SbOReO_4{\cdot}2H_2O$ and Sb_2O_3 in a molar ratio of 2:1 under the same conditions gave a powder sample of $(Sb_4O_5)(ReO_4)_2$ in a single phase (identified by X-ray powder diffraction). The result was consistent with the single-crystal X-ray study showing the molar Sb:Re ratio to be 2. If the hydrate was heated under an oxygen flow, it decomposed into Re_2O_7, α-Sb_2O_4, and H_2O around 500 °C. The IR spectrum showed sharp absorptions around 900 cm^{-1} (854, 880, 918, 944, and 972 cm^{-1}), which indicated the existence of perrhenate ions.[6] **CAUTION!** The sealed-tube reaction described here may cause an explosion because the reaction yields gaseous water in a stoichiometric amount at the reaction temperature.

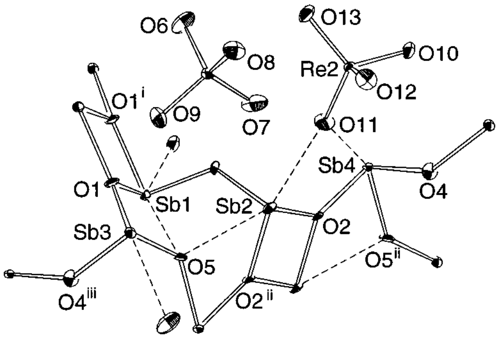

Figure 1. An ORTEP drawing of $Sb_4O_5(ReO_4)_2$ with 50% probability ellipsoids showing the coordination environments around metal atoms. The broken lines indicate long Sb−O bonds in the range 2.5−2.75 Å. Symmetry code: (i) $-x$, $-y$, $-z$; (ii) $1 - x$, $-y$, $-z$; (iii) $x - 1$, y, z;

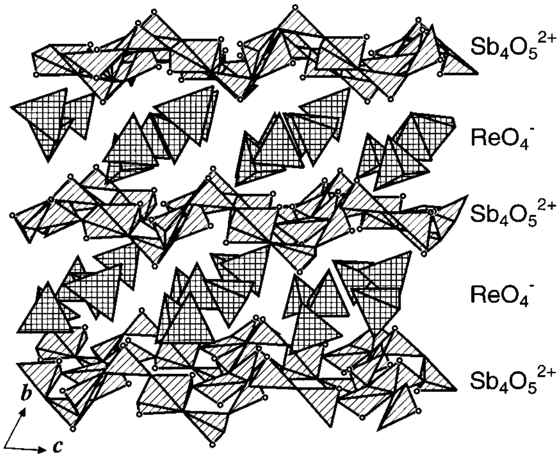

Figure 2. The structure of $Sb_4O_5(ReO_4)_2$ projected along the *a*-axis. The cross-hatched tetrahedra show ReO_4 anions, and the hatched trigonal pyramids are SbO_3 units. The small circles on the SbO_3 pyramids indicate the positions of antimony atoms.

Table 1. Summary of the Crystallographic Data for $Sb_4O_5(ReO_4)_2$

empirical formula	$O_{13}Re_2Sb_4$	formula weight	1067.4
a	9.938(2) Å	space group	$P\bar{1}$ (No. 2)
b	9.430(2) Å	*T*	295 K
c	7.688(2) Å	λ	0.7107 Å
α	114.95(2)°	ρ_{calc}	5.92 g/cm^3
β	111.16(4)°	μ	291 cm^{-1}
γ	90.12(2)°	$R(F_o)^a$	0.035^a
V	598.9(3) Å^3	$R_w(F_o)^b$	0.034^b
Z	2		

[a] $R(F_o) = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w(F_o) = \sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2$, $w = 1/\sigma(F_o)^2$.

Structure Determination. X-ray measurements were made on a Rigaku AFC6S diffractometer with graphite-monochromated Mo Kα (K-L) radiation. The size of the crystal used was 0.02 × 0.02 × 0.01 mm. Intensity data of all reflections with $l \geq 0$ were measured within the 2θ range of 5−60°. An empirical absorption correction was applied by the ψ-scan method (relative transmission factor, 0.78−0.99).[7] Positions of metal atoms were determined by the direct method (SHELXS86),[8] and oxygen atoms were located by the Fourier method (SHELXS76).[9] The structure was anisotropically refined by the full-

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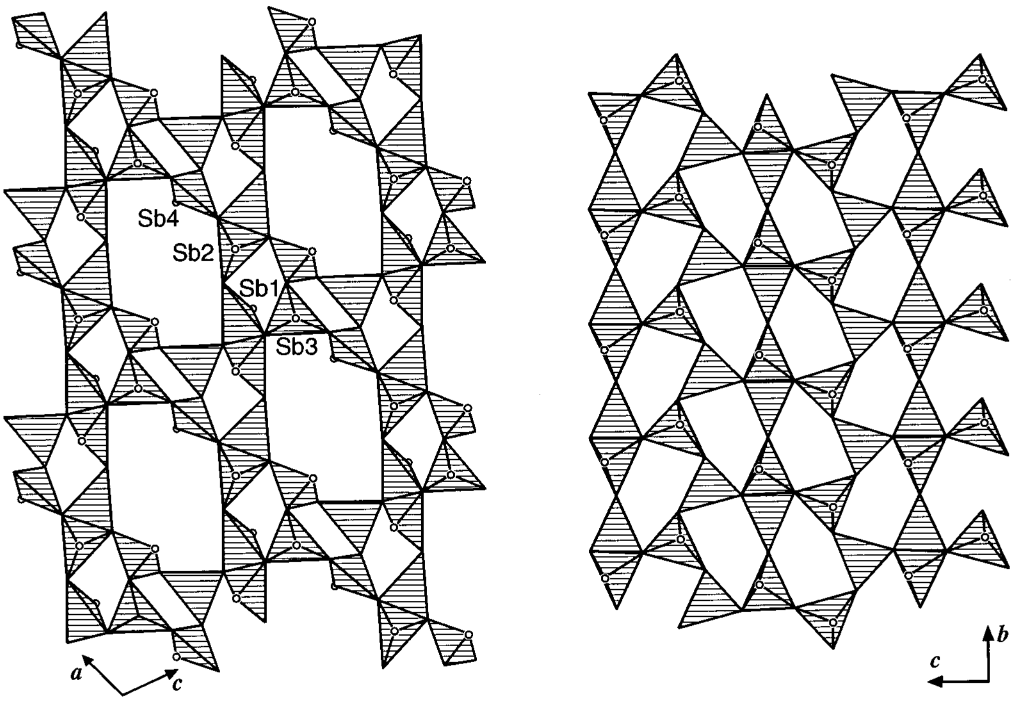

(a) (b)

Figure 3. The $(Sb_4O_5)^{2+}$ layer (a) in $Sb_4O_5(ReO_4)_2$ and (b) in $Sb_4O_5Cl_2$. The trigonal pyramids show SbO_3 units, and the small circles on apices indicate the positions of antimony atoms.

Table 2. Atomic Parameters for $Sb_4O_5(ReO_4)_2$

atom	x/a	y/b	z/c	U_{eq}
Re1	0.21761(6)	0.45518(6)	0.13796(8)	0.0111(2)
Re2	0.63240(5)	0.33099(6)	0.17643(8)	0.0082(2)
Sb1	0.10933(9)	−0.09649(11)	0.11734(14)	0.0111(3)
Sb2	0.44161(9)	0.15621(10)	0.45598(13)	0.0097(3)
Sb3	0.03874(9)	0.26612(9)	0.47249(13)	0.0081(3)
Sb4	0.73369(9)	−0.04046(10)	0.28669(12)	0.0081(3)
O1	−0.0046(9)	0.0948(11)	0.1683(13)	0.012(3)
O2	0.5923(9)	0.0067(10)	0.4323(13)	0.008(3)
O3	0.2934(9)	0.0226(11)	0.1768(13)	0.015(3)
O4	0.8898(10)	0.1463(11)	0.4871(14)	0.017(3)
O5	0.1942(9)	0.1357(11)	0.5167(14)	0.012(3)
O6	0.1508(12)	0.3473(13)	−0.133(2)	0.029(4)
O7	0.3629(13)	0.3764(15)	0.235(2)	0.034(5)
O8	0.2705(12)	0.6524(12)	0.216(2)	0.026(4)
O9	0.0855(12)	0.434(2)	0.223(2)	0.033(5)
O10	0.7985(10)	0.2980(12)	0.1578(15)	0.018(3)
O11	0.5823(11)	0.1909(12)	0.245(2)	0.024(4)
O12	0.6625(12)	0.5206(12)	0.362(2)	0.025(4)
O13	0.5052(10)	0.3046(12)	−0.065(2)	0.020(3)

matrix least-squares method (ANYBLK),[10] where 3011 observed reflections ($|F_o| > 3\sigma(|F_o|)$) were used. An empirical extinction correction was included in the refinements and the refined extinction parameter (rT) was $4.92(6) \times 10^{-8}$ cm^2.[11] Table 1 shows a summary of the crystallographic data and the structure determination.

Results and Discussion

Table 3. Interatomic Distances (Å) and Angles (deg) for $Sb_4O_5(ReO_4)_2$[a]

	Distances		
Sb1−O1	2.103(9)	$Sb1-O1^i$	2.070(8)
Sb1−O3	1.941(9)	Sb1−O5	2.717(9)
$Sb1-O10^i$	2.635(10)	Sb2−O2	2.063(8)
$Sb2-O2^i$	2.128(8)	Sb2−O3	1.948(8)
Sb2−O5	2.684(9)	Sb2−O11	2.600(11)
Sb3−O1	2.085(9)	Sb3−O4	1.924(9)
Sb3−O5	1.999(8)	Sb3−O6	2.574(10)
Sb4−O2	2.035(9)	Sb4−O4	1.963(8)
$Sb4-O5^i$	1.993(8)	Sb4−O11	2.717(10)
Re1−O6	1.739(10)	Re1−O7	1.699(11)
Re1−O8	1.710(10)	Re1−O9	1.711(11)
Re2−O10	1.725(9)	Re2−O11	1.747(10)
Re2−O12	1.690(10)	Re2−O13	1.736(9)
	Angles		
$O1-Sb1-O1^i$	73.0(4)	O1−Sb1−O3	96.7(4)
$O1^i-Sb1-O3$	93.3(4)	$O2-Sb2-O2^i$	71.2(4)
O2−Sb2−O3	95.0(4)	$O2^i-Sb2-O3$	92.2(3)
O1−Sb3−O4	91.1(4)	O1−Sb3−O5	77.4(3)
O4−Sb3−O5	97.8(4)	O2−Sb4−O4	99.1(4)
$O2-Sb4-O5^i$	77.2(3)	$O4-Sb4-O5^i$	88.9(4)

[a] Symmetry code: (i) $-x, -y, -z$.

Structure. Tables 2 and 3 give the results of the X-ray structure determination of $(Sb_4O_5)(ReO_4)_2$, and Figure 1 shows the ORTEP drawing of the structure. The compound consists of cationic layers of composition $(Sb^{III}{}_4O_5)^{2+}$ and perrhenate ions between the layers as illustrated in Figure 2. The antimony atoms are connected with three oxygen atoms to form SbO_3 trigonal pyramids. As shown in Figure 3a, half of the SbO_3 pyramids merge with another pyramid to make Sb_2O_4 units by sharing an edge. The Sb_2O_4 units are connected with each other through apices to make an infinite linear chain running along the [101] direction. These chains are further connected with Sb_4O_8 rings, which are made of four SbO_3 pyramids, to form a two-dimensional layer of $(Sb^{III}{}_4O_5)^{2+}$.

The present compound $(Sb_4O_5)(ReO_4)_2$ is unique in the chemistry of antimony(III) oxide compounds with oxo anions. Antimony oxide sulfate $Sb_6O_7(SO_4)_2$[1] has columns containing both antimony(III) and sulfur(VI). On the other hand, phosphate

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and arsenate ions are incorporated in the antimony oxide layer to make $SbPO_4$ and $SbAsO_4$ layers. Perchlorate ions and nitrate ions are the only oxo anions so far reported to make layered compounds with antimony(III) oxide. However, the compounds with these oxo anions, $Sb_4O_5(OH)(ClO_4)(H_2O)_{0.5}$[4] and $Sb_4O_4(OH)_2(NO_3)_2$,[3] contain antimony atoms coordinated by four oxygen atoms along with those coordinated by three, and the Sb:O ratios of the antimony oxide layers in them are 4:6 instead of 4:5 as found in $(Sb_4O_5)(ReO_4)_2$. Furthermore, hydrogen bonds give the three-dimensional character to these compounds, and they are structurally very different from $(Sb_4O_5)(ReO_4)_2$. The compound that has the closest similarity with $(Sb_4O_5)(ReO_4)_2$ is antimony chloride oxide $Sb_4O_5Cl_2$. It has layers of the same composition of $(Sb_4O_5)^{2+}$ (Figure 3b).[2] The layers in $Sb_4O_5Cl_2$ have similar chains of Sb_2O_4 units. However, the chains in $Sb_4O_5Cl_2$ are not linked with Sb_4O_8 groups but with zigzag chains of corner-sharing trigonal pyramids of SbO_3. While the $(Sb_4O_5)^{2+}$ layer in $Sb_4O_5(ReO_4)_2$ has large holes surrounded by eight SbO_3 pyramids, the holes in the layer of $Sb_4O_5Cl_2$ are much smaller. The difference in the structure of $(Sb_4O_5)^{2+}$ layers between $Sb_4O_5(ReO_4)_2$ and $Sb_4O_5Cl_2$ suggests that the structure of the cationic layer is strongly influenced by the anions between the layers.

The Sb−O bond distances in the SbO_3 trigonal pyramids are between 1.923(9) and 2.128(8) Å (average 2.021 Å). However, the list of interatomic distances shows many Sb−O distances that are a little longer than 2.5 Å (Table 3). Although the distribution of the Sb−O distances is continuous, we define the long Sb−O bonds as those between 2.5 and 2.75 Å. Then, the Sb1 and Sb2 atoms have two of them, and the others have one. Two of the long bonds make additional oxygen bridges between the antimony atoms in a $(Sb_2O_5)^{2+}$ layer. Each antimony atom is connected with a perrhenate ion through a long Sb−O bond to make a three-dimensional framework. The existence of these long bonds explains why the structure of the $(Sb_4O_5)^{2+}$ layer in $Sb_4O_5Cl_2$ is different from that in $Sb_4O_5(ReO_4)_2$. Observed splitting of the ν_{Re-O} absorption in the IR spectrum (Experimental Section) also suggests that the long Sb−O bonds are strong enough to change the force constants of some of the Re−O bonds and to lower the symmetry of the perrhenate ion.

Chemical Properties. The structure of $(Sb_4O_5)(ReO_4)_2$ suggests the possibility of the topotactic exchange reaction of the perrhenate ions with other anions. However, the compound is easily decomposed by water into antimony trioxide and perrhenic acid, and anion-exchange reactions are not possible in aqueous systems. The facile decomposition of $(Sb_4O_5)^{2+}$ layers in water indicates that the long bonds connecting antimony atoms and perrhenate ions discussed above are essential to stabilize the layered structure of $(Sb_4O_5)(ReO_4)_2$.

Acknowledgment. This research was supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science, Sports, and Culture of Japan (No. 07804040).

Supporting Information Available: Listings of crystallographic information in CIF format are available. Access information is given on any current masthead page.

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