

The Crystal Structure of $\text{Sb}_4\text{O}_5(\text{OH})\text{ClO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$

JAN-OLOV BOVIN

Division of Inorganic Chemistry 2, Chemical Center, The Lund Institute of Technology, P. O. Box 740, S-220 07 Lund 7, Sweden

The crystal structure of the compound, $\text{Sb}_4\text{O}_5(\text{OH})\text{ClO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$, has been determined from three-dimensional X-ray data measured on an automatic diffractometer. The crystals are monoclinic (space group $I2/c$). The unit cell contains eight formula units and has the dimensions $a = 20.969(5)$, $b = 5.7051(8)$, $c = 17.872(4)$ and $\beta = 99.84(2)^\circ$. The structure was refined by a full-matrix least-squares technique using 1811 observed reflections to an unweighted R value of 0.037. It contains distorted trigonal bipyramidal SbO_4 - and tetrahedral SbO_3 -polyhedra, with the lone pairs of electrons of antimony at one of the equatorial corners of the bipyramids and at one corner of each tetrahedron, respectively. Four SbO_4 -polyhedra share edges with each other and form a short chain. In both ends of the chain an SbO_3 -polyhedron shares edges with a SbO_4 -polyhedron. The chain is then terminated in each end by an additional SbO_3 -polyhedron sharing corners. The short chains are linked, by sharing oxygen atoms with other chains, to infinite layers parallel to the bc -plane. The perchlorate ions and the water molecules are situated between the layers. The Sb—O bond distances vary between 1.952(9) and 2.378(9) Å.

During an investigation of the solubility of antimony(III) oxide (cubic and orthorhombic) in perchloric acid and nitric acid,¹ undertaken in order to elucidate which species of antimony(III) that exist in such solutions, it was found that the oxide phases were under certain conditions converted into different basic salts. The compositions of these solid phases in stable or metastable equilibrium with solutions of various acidities must be exactly known to make a correct interpretation of the solubility measurements possible. Complete determinations of their structures would have the added advantage that a comparison would be possible between the hydroxo complexes indicated in the solutions and the aggregates that can be discerned in the

solid phases. Such structural studies have therefore been started and the result of the first one concerning the nitrate, $\text{Sb}_4\text{O}_4(\text{OH})_2(\text{NO}_3)_2$,² has already been published. In this paper, the structure of a perchlorate, $\text{Sb}_4\text{O}_5(\text{OH})\text{ClO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$, is reported. This phase has previously been proposed and described by Jander and Hartmann³ as $4\text{Sb}_2\text{O}_3 \cdot \text{Cl}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$. Further studies completed or in progress include $\text{Sb}_2\text{O}_3(\text{ortho.})$,⁴ $\text{Sb}_2\text{O}_3(\text{cubic})$ and $\text{Sb}(\text{OH})_2\text{ClO}_4 \cdot 3\text{H}_2\text{O}$.

EXPERIMENTAL

Crystal preparation and analysis. Crystals of $\text{Sb}_4\text{O}_5(\text{OH})\text{ClO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$ were prepared by the following method: 5 M perchloric acid was heated in an Erlenmeyer flask to 110 °C and orthorhombic Sb_2O_3 was added until a saturated solution was obtained. The flask was stoppered and its temperature was decreased 5–10 °C per day to room-temperature. $\text{Sb}_4\text{O}_5(\text{OH})\text{ClO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$ crystallized as thin, colourless and transparent plates. The homogeneity of the sample was checked by X-ray Guinier-Hägg powder photographs. The crystals thus prepared were analysed titrimetrically for antimony(III) by a method according to Belcher.⁵ The perchlorate analysis was made according to Hoffman *et al.*⁶ and the water analysis according to a modification of the method of Fischer.^{7,8} The results of the analyses were in good agreement with the calculated values for $\text{Sb}_4\text{O}_5(\text{OH})\text{ClO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$. (Found: 70.3 % antimony(III), 14.9 % perchlorate, and 2.2 % water. Calc.: 70.3 %, 14.2 %, and 2.6 %).

Crystal data. Preliminary Weissenberg photographs showed the crystals to be monoclinic and the systematic absences found were: hkl with $h+k+l=2n+1$, $h0l$ with $l=2n+1$ which are characteristic of the space group $I2/c$. This space group is not given in the *International Tables*. The general point position:

$$\begin{aligned} &x, y, z; \bar{x}, \bar{y}, \bar{z}; \bar{x}, y, \frac{1}{2} - z; x, \bar{y}, \frac{1}{2} + z; \\ &\frac{1}{2} + x, \frac{1}{2} + y, \frac{1}{2} + z; \frac{1}{2} - x, \frac{1}{2} - y, \frac{1}{2} - z; \frac{1}{2} - x, \frac{1}{2} + y, z; \\ &\frac{1}{2} + x, \frac{1}{2} - y, z; \end{aligned}$$

Table 1. Guinier-Hägg powder photograph of $\text{Sb}_4\text{O}_6(\text{OH})\text{ClO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$ using $\text{CuK}\alpha_1$ radiation.

hkl	$10^5 \sin^2 \theta$ obs	$10^5 \sin^2 \theta$ calc	I obs
2 0 0	553	556	m
2 0 2	1 537	1 544	vvw
1 1 0	1 962	1 962	vvw
2 1 1	2 458	2 459	m
4 0 2	2 538	2 543	vvw
1 1 2	2 613	2 616	vvw
1 1 2	2 833	2 839	vvw
4 1 1	4 005	4 015	vw
2 1 3	4 430	4 435	vvw
1 1 4	4 793	4 800	w
4 1 3	5 102	5 100	vw
6 0 2			
1 1 4	5 243	5 246	vw
5 1 2	5 500	5 505	m
4 1 3	6 443	6 438	w
6 0 2			
2 1 5	6 604	6 605	vw
0 1 5			
3 1 4	6 807	6 804	m
0 2 0	7 291	7 291	vs
1 2 1	7 563	7 566	vw
4 0 6	7 780	7 774	m
2 2 0	7 847	7 847	w
7 1 0	8 625	8 633	w
1 2 3	9 001	8 985	w
4 2 0	9 523	9 515	vvw
6 0 6	9 878	9 884	vw
7 1 2	10 187	10 179	vw
5 1 6	10 527	10 513	vw
0 0 8	12 256	12 245	vw
6 2 2	12 404	12 391	vvw
6 2 2	13 711	13 729	s
4 2 6	15 060	15 065	m
6 2 6	17 157	17 176	vvw
4 3 1	18 586	18 589	w
10 0 4	19 204	19 191	vw
1 3 4	19 839	19 829	m
5 3 2	20 104	20 090	vw
1 1 10	20 527	20 538	m
8 2 4	21 025	21 032	w
5 3 2	21 193	21 203	vw
3 3 4	21 398	21 387	vvw
10 0 8	21 962	21 684	vvw

Space group $I2/c$ was chosen instead of $C2/c$ because the unit cell dimensions were more suitable in $I2/c$.

The unit cell dimensions were determined by least-squares refinement using as data the diffraction angles of 40 lines on the $\text{CuK}\alpha_1$ ($\lambda = 1.54051 \text{ \AA}$) powder pattern collected at room temperature in a Guinier-Hägg focusing camera equipped with a quartz monochromator and using KCl (cubic, $a = 6.2929 \text{ \AA}$) as internal standard, cf. Table 1. The density determined by measuring the loss of weight in benzene was in good

Table 2. Crystallographic data for $\text{Sb}_4\text{O}_6(\text{OH})\text{ClO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$.

Unit cell:	$a = 20.969(5) \text{ \AA}$
	$b = 5.7051(8) \text{ \AA}$
	$c = 17.872(4) \text{ \AA}$
	$\beta = 99.84(2)^\circ$
	$V = 2106.9 \text{ \AA}^3$
	$Z = 8$
Formula weight:	$M = 692.46$
Density, 20 °C:	$D_m = 4.28 \text{ g cm}^{-3}$
	$D_x = 4.39 \text{ g cm}^{-3}$
Space group:	$I2/c$

agreement with the calculated value for eight formula units $\text{Sb}_4\text{O}_6(\text{OH})\text{ClO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$ per unit cell. Some crystallographic data are presented in Table 2.

Collection of intensity data. Three-dimensional intensity data from a single crystal (cf. Table 3) were collected on an Enraf-Nonius computer controlled four-circle diffractometer, CAD4, using graphite monochromatized $\text{MoK}\alpha$ radiation ($\lambda = 0.71069 \text{ \AA}$). The intensities were recorded at a take off angle of 5° . The $\omega - 2\theta$ scan technique was used with an ω range of $(0.9 + 0.5 \text{ tg}\theta)^\circ$. A minimum net count of 2000 for each reflection was attained within the maximum measuring time of 3 min. The scan speed thus required was calculated from the net intensity after a fast pre-scan. Two octants of the reciprocal space out to $(\sin \lambda)/\theta = 0.65 \text{ \AA}^{-1}$ were examined. The total number of reflections was 2496 of which 33 were considered not above background by giving net counts less than 10 in the fast pre-scan of totally 9 seconds and another 652 were rejected as being considered unobserved since their intensities were less than $3\sigma(I)$, where $\sigma(I)$ is the standard deviation of the intensity estimated from counting statistics. The intensities of the remaining 1811 reflections were corrected for Lorentz, polarization and absorption (cf. Table 3) effects. The linear absorption coefficient⁹ for the compound with $\text{MoK}\alpha$ is 108 cm^{-1} . The transmission factors

Table 3. Crystal dimensions. Boundary planes and their distances from an internal origin.

Plane	d (cm)
(100)	0.00097
($\bar{1}00$)	0.00097
(101)	0.00395
($\bar{1}0\bar{1}$)	0.00395
(010)	0.01175
($\bar{0}10$)	0.01175

Crystal volume: $0.17 \times 10^{-3} \text{ mm}^3$.

Table 4. Final positional and thermal parameters in $\text{Sb}_4\text{O}_5(\text{OH})\text{ClO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$. The form of anisotropic temperature factor is $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$. Standard deviations are given within parentheses.

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Sb(1)	.21675(4)	.04352(16)	.07538(4)	.00095(2)	.00778(24)	.00091(2)	-.00018(5)	.00020(2)	-.00020(6)
Sb(2)	.29647(4)	.03243(16)	.29368(4)	.00077(2)	.00875(24)	.00101(2)	.00032(5)	.00023(2)	.00050(6)
Sb(3)	.14115(4)	-.04377(16)	.34515(4)	.00085(2)	.01087(25)	.00085(2)	.00052(6)	.00017(2)	.00040(6)
Sb(4)	.37048(4)	-.03307(16)	.02440(4)	.00074(2)	.00991(25)	.00089(2)	-.00046(5)	.00012(2)	-.00017(6)
O(1)	.3168(4)	.1269(15)	.4235(4)	.0011(2)	.0093(26)	.0004(2)	.0010(6)	.0000(2)	-.0002(6)
O(2)	.2447(4)	.1562(15)	.1872(5)	.0012(2)	.0069(25)	.0011(3)	.0013(6)	-.0002(2)	.0002(7)
O(3)	.1667(4)	-.1594(14)	.4514(4)	.0011(2)	.0071(24)	.0004(2)	-.0004(6)	.0000(2)	.0011(6)
O(4)	.3910(5)	-.1317(19)	.1669(5)	.0016(3)	.0151(32)	.0015(3)	-.0014(8)	.0000(2)	.0007(8)
O(5)	.2228(4)	-.1511(15)	.3141(5)	.0009(2)	.0068(24)	.0013(3)	.0007(6)	0.002(2)	-.0003(7)
O(6)	.2993(4)	.1555(15)	.0528(5)	.0009(2)	.0084(25)	.0013(3)	.0019(6)	0.003(2)	-.0001(7)
Cl	.0498(2)	.0461(10)	.6202(3)	.0012(1)	.0387(18)	.0032(2)	.0008(3)	.0006(1)	-.0004(5)
O(7)	.104(1)	.006(4)	.677(1)	.004(1)	.089(11)	.002(4)	.006(2)	-.0003(4)	-.001(2)
O(8)	.068(1)	.035(4)	.051(1)	.0028(5)	.103(12)	.0030(5)	-.005(2)	.0008(4)	.006(2)
O(9)	-.006(1)	-.046(5)	.637(2)	.0030(5)	.109(16)	.014(2)	.002(3)	.0053(8)	.008(4)
O(10)	.039(2)	.291(4)	.612(2)	.008(1)	.047(10)	.015(2)	.004(3)	.003(1)	.003(3)
O(11)	$\frac{1}{2}$.0660(29)	$\frac{1}{2}$.0016(4)	.018(5)	.0029(6)	0	-.0004(4)	0

Table 5. Coordination distances (Å) and angles (°) with standard deviations (in parentheses) in $\text{Sb}_4\text{O}_5(\text{OH})\text{ClO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$. Notations of the atoms, cf. Table 4.

The Sb(1)–O-polyhedron			
Sb(1)–O(6)	1.952(9)	$\angle \text{O}(1)–\text{Sb}(1)–\text{O}(2)$	75.2(3)
Sb(1)–O(1)	2.009(9)	$\angle \text{O}(1)–\text{Sb}(1)–\text{O}(3)$	69.5(3)
Sb(1)–O(2)	2.085(9)	$\angle \text{O}(1)–\text{Sb}(1)–\text{O}(6)$	91.2(4)
Sb(1)–O(3)	2.378(8)	$\angle \text{O}(2)–\text{Sb}(1)–\text{O}(3)$	144.5(3)
O(1)–O(2)	2.498(12)	$\angle \text{O}(2)–\text{Sb}(1)–\text{O}(6)$	89.0(4)
O(1)–O(3)	2.517(11)	$\angle \text{O}(3)–\text{Sb}(1)–\text{O}(6)$	89.0(3)
O(1)–O(6)	2.829(12)		
O(2)–O(6)	2.832(12)		
O(3)–O(6)	3.049(12)		
The Sb(2)–O-polyhedron			
Sb(2)–O(5)	1.952(9)	$\angle \text{O}(2')–\text{Sb}(2)–\text{O}(2)$	72.3(4)
Sb(2)–O(2)	2.030(9)	$\angle \text{O}(1)–\text{Sb}(2)–\text{O}(2)$	69.1(3)
Sb(2)–O(2')	2.143(9)	$\angle \text{O}(2)–\text{Sb}(2)–\text{O}(5)$	93.7(4)
Sb(2)–O(1)	2.350(8)	$\angle \text{O}(1)–\text{Sb}(2)–\text{O}(2')$	141.3(3)
O(1)–O(2)	2.498(12)	$\angle \text{O}(2')–\text{Sb}(2)–\text{O}(5)$	92.7(4)
O(1)–O(5)	2.985(12)	$\angle \text{O}(1)–\text{Sb}(2)–\text{O}(5)$	87.4(3)
O(2)–O(2')	2.464(17)		
O(2)–O(5)	2.905(12)		
O(2')–O(5)	2.963(12)		
The Sb(3)–O-polyhedron			
Sb(3)–O(4)	1.969(11)	$\angle \text{O}(3)–\text{Sb}(3)–\text{O}(4)$	79.9(4)
Sb(3)–O(5)	1.985(9)	$\angle \text{O}(3)–\text{Sb}(3)–\text{O}(5)$	93.5(4)
Sb(3)–O(3)	1.995(8)	$\angle \text{O}(4)–\text{Sb}(3)–\text{O}(5)$	88.5(4)
O(3)–O(4)	2.545(13)		
O(3)–O(5)	2.898(12)		
O(4)–O(5)	2.760(14)		
The Sb(4)–O-polyhedron			
Sb(4)–O(6)	1.975(9)	$\angle \text{O}(1)–\text{Sb}(4)–\text{O}(3)$	77.5(3)
Sb(4)–O(3)	1.997(8)	$\angle \text{O}(3)–\text{Sb}(4)–\text{O}(6)$	94.8(4)
Sb(4)–O(1)	2.027(8)	$\angle \text{O}(1)–\text{Sb}(4)–\text{O}(6)$	92.5(4)
O(1)–O(3)	2.517(11)		
O(1)–O(6)	2.890(12)		
O(3)–O(6)	2.966(12)		
The perchlorate ion			
Cl–O(9)	1.36(2)	$\angle \text{O}(7)–\text{Cl}–\text{O}(8)$	106(1)
Cl–O(7)	1.40(2)	$\angle \text{O}(7)–\text{Cl}–\text{O}(9)$	113(1)
Cl–O(10)	1.42(3)	$\angle \text{O}(7)–\text{Cl}–\text{O}(10)$	109(2)
Cl–O(8)	1.44(2)	$\angle \text{O}(8)–\text{Cl}–\text{O}(9)$	116(1)
O(7)–O(8)	2.27(2)	$\angle \text{O}(8)–\text{Cl}–\text{O}(10)$	107(2)
O(7)–O(9)	2.30(3)	$\angle \text{O}(9)–\text{Cl}–\text{O}(10)$	106(2)
O(7)–O(10)	2.30(3)		
O(8)–O(9)	2.37(3)		
O(8)–O(10)	2.29(4)		
O(9)–O(10)	2.22(4)		
Possible hydrogen bonds			
O(11)⋯O(4)	2.75(1)	$\angle \text{O}(4) \cdots \text{O}(11) \cdots \text{O}(4')$	132(1)
O(11)⋯O(9)	2.98(3)	$\angle \text{O}(4) \cdots \text{O}(11) \cdots \text{O}(9)$	127(1)
		$\angle \text{O}(4) \cdots \text{O}(11) \cdots \text{O}(9')$	90(1)
		$\angle \text{O}(9) \cdots \text{O}(11) \cdots \text{O}(9')$	84(1)
Sb–Sb distances			
Sb(1)–Sb(4)	3.353(1)		
Sb(1)–Sb(2)	3.410(1)		
Sb(1)–Sb(4)	3.524(1)		
Sb(2)–Sb(2)	3.370(2)		
Sb(2)–Sb(3)	3.559(1)		
Sb(3)–Sb(4)	3.394(1)		

were in the range 0.40–0.82. Two control reflections, 345 and 408, were measured with 90 min intervals to check for crystal decomposition and radiation stability. The mean decrease in intensity over the whole exposure time was 6% for both control reflections. All intensities were therefore scaled with a first-order polynomial determined by least-squares.

STRUCTURE DETERMINATION AND REFINEMENT

From a three-dimensional Patterson synthesis the antimony atoms of the unit cell were found to occupy four eightfold positions in $I2/c$. A least-squares refinement was performed based on the deduced antimony atom positions. Subsequent three-dimensional electron density difference synthesis revealed the positions of all other non-hydrogen atoms. All atoms occupy eightfold point positions except the water oxygens which occupy a fourfold point position.

A preliminary full matrix least-squares refinement was now performed with isotropic temperature factors for all atoms. The refinement converged to an R -value of 0.102 ($R = \sum ||F_o| - |F_c|| / \sum |F_o|$). When the isotropic refinement was repeated with the data corrected for absorption effects the R -value was 0.060. Then anisotropic temperature factors were introduced for all atoms and the positional and thermal parameters were refined together with an overall scale factor. The R -value was now reduced to 0.045. Correction was then made for isotropic secondary extinction with the full matrix least-squares program *LINUS*.¹⁰ The function minimized was $\sum w_i (|F_o| - |F_c|)^2$, where the weights, w_i , were calculated from the expression $w_i^{-1} = \sigma^2(F_o^2) / 4F_o^2 + cF_o^2 + d$. The values of the constants c and d were chosen so as to give the

most constant averages of $w_i (|F_o| - |F_c|)^2$ over ranges of F and $\sin\theta$. The values $c = 0.0003$ and $d = 0.55$ were used in the last refinement, which converged to $R = 0.037$ and $R_w = 0.051$, where $R_w = [\sum w_i (|F_o| - |F_c|)^2 / \sum w_i |F_o|^2]^{1/2}$. The atomic scattering factors used were those given by Hansen *et al.*¹¹ The final value of the isotropic extinction parameter g was $0.08(2) \times 10^4$. The value of S defined by $S = [\sum w_i (|F_o| - |F_c|)^2 / (m - n)]^{1/2}$, where m and n are the number of observations and parameters varied, respectively, was 1.009. The final positional and thermal parameters are given in Table 4. Lists of observed and calculated structure amplitudes are available by request to the author. Selected interatomic distances and angles are presented in Table 5. The drawings (Figs. 1–5) were obtained with the program ORTEP.¹²

DESCRIPTION AND DISCUSSION OF THE STRUCTURE

The $\text{Sb}_4\text{O}_5(\text{OH})\text{ClO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$ structure contains distorted SbO_4 - and SbO_3 -polyhedra. The coordination spheres of Sb(1) and Sb(2) (notations of the atoms, *cf.* Table 4) could be described as trigonal bipyramids with the lone pair of electrons of antimony in one of the equatorial corners (*cf.* Fig. 1). The SbO_3 -polyhedra of Sb(3) and Sb(4) are tetrahedral with the lone pair in one of the corners (*cf.* Fig. 1).

Four SbO_4 -polyhedra share edges and build up a short chain (the coordination polyhedra around the atoms Sb(1) and Sb(2) in Fig. 1). In both ends of the chain an Sb(4)O_3 -polyhedron shares edges with an SbO_4 -polyhedron. The chains are terminated in both ends by one Sb(3)O_3 -polyhedron sharing corners. The chains are linked to each other, by sharing the oxygen

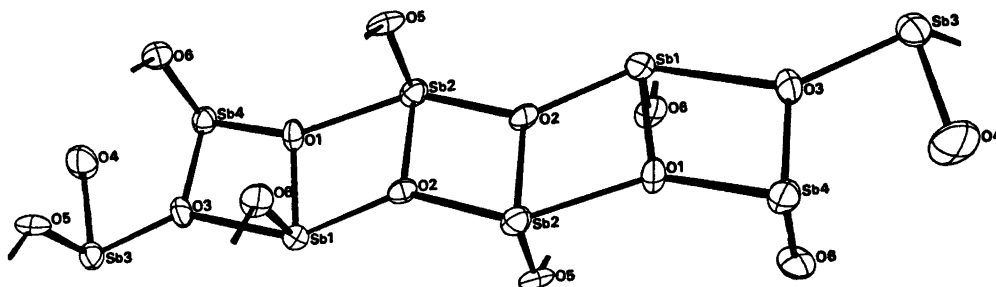


Fig. 1. The short chain of Sb–O polyhedra.

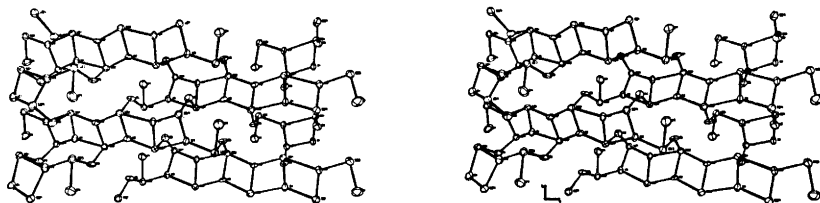


Fig. 2. Stereoview of the infinite layers of Sb-O.

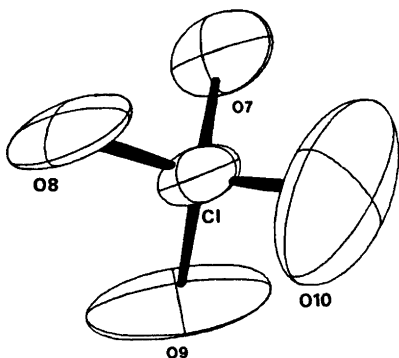


Fig. 3. The perchlorate ion. The thermal ellipsoids are drawn to enclose a 50 % probability.

atoms O(5) and O(6), to infinite layers parallel to the bc -plane (cf. Fig. 2). The four oxygen atoms O(7), O(8), O(9), O(10) and the chlorine atoms form the tetrahedral ClO_4^- -ion (cf. Fig. 3). The distances Cl-O and angles O-Cl-O (cf. Table 5) are normal (cf. International Tables,⁹ Lee and Carpenter,¹³ Nordman,¹⁴ and Almlöf¹⁵). The oxygen atoms in the ClO_4^- -ion have large thermal motions, however. The r.m.s.-components (R1,R2,R3) of the thermal vibrations for O(7), O(8), O(9), and O(10) are (0.41, 0.16, 0.24), (0.44, 0.13, 0.24), (0.55, 0.11, 0.42) and (0.54, 0.22, 0.41).

The perchlorate ions and the water molecules are situated between the layers described above (cf. Fig 4).

For the interpretation of the solubility function of Sb(III) in perchloric acid with $\text{Sb}_2\text{O}_3 \cdot (\text{OH})\text{ClO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$ as solid phase it was necessary to verify the existence of the OH^- -ion in the structure. Since the hydrogen atoms could not be located from the available X-ray data it was difficult to distinguish O^{2-} , OH^- , and water from each other. In order to establish the nature of the oxygen atoms O(1), O(2), O(3), O(4), O(5), O(6), and O(11) a procedure based on the principle of local neutralization of charge was used, according to Donnay *et al.*¹⁶ A calculation of cation to anion distances and associated bond valences leads to valence sums $\sum \nu$ for the oxygen atoms. For O^{2-} , OH^- , and H_2O $\sum \nu$ is approximately 2.0, 1.0, and 0.0, respectively. The calculated values of $\sum \nu$ varied between 1.8 and 2.4 for the atoms O(1), O(2), O(3), O(5), O(6), indicating that these are oxide ions. $\sum \nu$ for O(4) and O(11) was 1.0 and 0.0. Thus O(4) should be an OH^- -ion and O(11) a water molecule. The distance O(4)-O(11) between hydroxide and water is 2.74 Å (cf. Table 5) which agrees very well with previously determined hydroxide to water distances in the mineral Colemanit, $\text{CaB}_2\text{O}_4(\text{OH})_3 \cdot \text{H}_2\text{O}$ (2.76 ± 0.03 Å)¹⁷ and in $\text{Zn}_3(\text{OH})_6\text{Cl}_2 \cdot \text{H}_2\text{O}$ ¹⁸ (2.79 Å). It

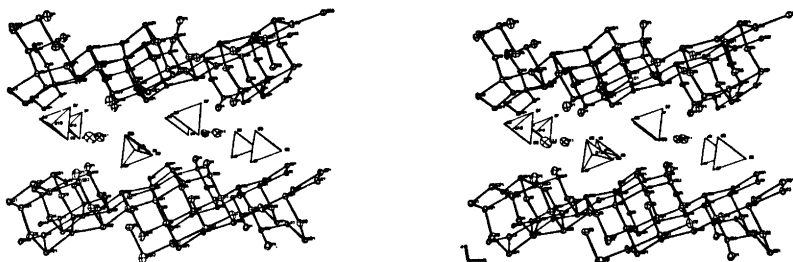


Fig. 4. Stereoview down the b -axis. The perchlorate ions are drawn with tetrahedra.

also agrees well with hydrogen bond distances in inorganic solids given in the International Tables.⁹ The water molecules are thus hydrogen bonded to two different Sb—O-layers (cf. Fig. 4). Possible hydrogen bonds also exist between the water molecule and two perchlorate ions (cf. Table 5). The distance O(11)—O(9), 2.98 Å, is in agreement with that which Lee *et al.*¹³ found in perchloric acid monohydrate, where hydrogen bonds have been certainly proved. The angle O(9)—O(11)—O(9) (cf. Fig. 5, Table 5) differs from the angle in water, but according to Hamilton and Ibers¹⁹ the distribution of the O—O—O angles could be from 80° to 150° in hydrogen bonded hydrates.

A knowledge of the crystal structures of oxide salts can be useful for deducing the coordination of the complexes in solution, as has been shown in many instances. Thus, the dimeric $\text{Th}(\text{OH})_2\text{Th}$ has been identified both in solution and solid state by X-ray investigations by Johansson.^{20–21} Olin and Söderquist²² found the complex $\text{Pb}_6\text{O}(\text{OH})_6^{4+}$ as discrete groups in the oxide salt $\beta\text{-}[\text{Pb}_6\text{O}(\text{OH})_6](\text{ClO}_4)_4 \cdot \text{H}_2\text{O}$ and Hong and Olin^{23,24} has identified the complex $\text{Pb}_4(\text{OH})_4^{4+}$ in the oxide salts $\text{Pb}_4(\text{OH})_4(\text{ClO}_4)_4 \cdot 2\text{H}_2\text{O}$ and $[\text{Pb}_4(\text{OH})_4]_3(\text{CO}_3)(\text{ClO}_4)_{10} \cdot 6\text{H}_2\text{O}$.

From solubility measurements in perchloric acid solutions Ahrlund and Bovin¹ found that the complex $\text{Sb}_2(\text{OH})_2^{4+}$ exists in metastable equilibria with the solid phases orthorhombic or cubic Sb_2O_3 . After a few days of agitation the stable phase $\text{Sb}_4\text{O}_5(\text{OH})\text{ClO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$ is formed. If $\text{Sb}_4(\text{OH})_4^{4+}$ is a fragment in the Sb—O-layers of this compound it is reasonable to expect that the distance between the antimony atoms within the group is significantly shorter than any other Sb—Sb-distances in the structure. In the Sb—O-

layers Sb(2) is joined to Sb(2') by two oxygens O(2) with the longest Sb—O-distances 2.143(9) Å. The Sb(2)—Sb(2')-distance is 3.370(1) Å which is significantly shorter than the distance from Sb(2) to Sb(3) in an other short chain (cf. Fig. 2 and Table 5). Also Sb(1) and Sb(4) are joined over two oxygens O(3) and O(1) with the longest Sb—O-distance 2.378(8) Å. The Sb(1)—Sb(4)-distance is almost the same (3.343(1) Å) as in the other group. It seems possible that these groups are fragments of the complex $\text{Sb}_2(\text{OH})_2^{4+}$ found in solution. Also in other solid compounds of Sb(III), Bi(III) and Te(IV) the shortest metal to metal distance exists between metal atoms joined by two oxygens. In $\text{Sb}_4\text{O}_4(\text{OH})_2(\text{NO}_3)_2$ (Ref. 2) the two shortest Sb—Sb distances are 3.437(1) Å and 3.464(1) Å and $\text{Sb}_4\text{O}_5\text{Cl}_2$ ^{25,26} 3.418(1) Å. Aurivillius^{27,28} found in $\text{Bi}(\text{OH})\text{CrO}_4$ and $\text{Bi}(\text{OH})\text{SeO}_4 \cdot \text{H}_2\text{O}$ aggregates of the formula $\text{Bi}_2(\text{OH})_2^{4+}$ and the shortest Bi to Bi distances, 3.667(3) Å and 3.664(3) Å, respectively, are within these groups. In the structures of $\text{Te}_2\text{O}_3(\text{OH})\text{NO}_3$ ²⁹ and $\beta\text{-TeO}_2$ ³⁰ two Te(IV) are joined by two oxygens in the same way with the shortest Te to Te distances 3.270(2) Å and 3.17 ± 0.003 Å, respectively.

It has been shown by Andersson, Åström, Galy and Meunier³¹ that for many solid oxides, or oxide fluorides of Sb(III), Pb(II), Bi(III), and Te(IV), the volume of the lone pair and its cation is very nearly the same as that of an anion. If the volume of the unit cell is divided by the number of anions and lone pairs of antimony in $\text{Sb}_4\text{O}_5(\text{OH})\text{ClO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$, the result is 18.1 Å³. This value, compared with data (15.2–19.4 Å³) from Andersson and Åström,³² indicates that the total structure has an approximate closepacked arrangement of oxygens and lone pairs of electrons. The structure of $\text{Sb}_4\text{O}_4(\text{OH})_2(\text{NO}_3)_2$ (Ref. 2) is more effectively closepacked than $\text{Sb}_4\text{O}_5(\text{OH})\text{ClO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$ since the corresponding value is 16.3 Å³. In the structure of $\text{Sb}_4\text{O}_4(\text{OH})_2(\text{NO}_3)_2$ the oxygen and lone pairs of electrons in the Sb—O layers with one oxygen from the nitrate group was nearly cubic closepacked. If only the Sb—O layers and one oxygen atom, O(7), from the perchlorate ion are considered, the arrangement of oxygens and lone pairs of electrons has some similarity to the structure of $\text{Sb}_4\text{O}_4(\text{OH})_2(\text{NO}_3)_2$. If in $\text{Sb}_4\text{O}_5(\text{OH})\text{ClO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$ the infinite ribbons of octahedra, which are held together by tetrahedra

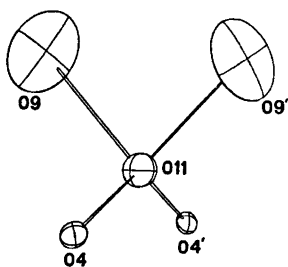


Fig. 5. Possible hydrogen bonds to the water oxygen. The thermal ellipsoids enclose areas with an atomic probability of 50 % (cf. Table 5).

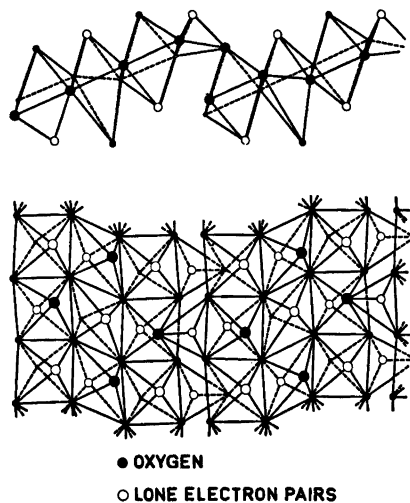


Fig. 6. The packing of oxygen atoms and lone pair of electrons of antimony in the layer parallel to the bc -plane. The upper view is along the b -axis and the lower is perpendicular to the bc -plane.

(cf. Fig. 6), are joined together by octahedral edge-sharing, infinite layers of octahedra are obtained similar to those in $Sb_2O_4(OH)_2(NO_3)_2$.

Acknowledgement. The author thanks Professor Bengt Aurivillius for his valuable help during this work. The author is also indebted to Professor Sten Arhland, Dr. Karin Aurivillius and Dr. Sten Andersson for their kind interest. Kerstin Renhult Aspelin and Christer Svensson are thanked for their assistance with the data collection. This work received financial support from the Swedish Natural Science Research Council.

REFERENCES

- Ahrland, S. and Bovin, J.-O. *Acta Chem. Scand. A*. *In press*.
- Bovin, J.-O. *Acta Chem. Scand. A* 28 (1974) 267.
- Jander, G. and Hartmann, H.-J. *Z. Anorg. Chem.* 339 (1965) 239.
- Svensson, C. *Acta Crystallogr. B* 30 (1974) 458.
- Belcher, R. *Anal. Chim. Acta* 3 (1949) 578.
- Hoffman, K. A., Metzler, A. and Höbold, K. *Ber. Deut. Chem. Ges.* 43 (1910) 1080.
- Vogel, A. T. *A Textbook of Quantitative Inorganic Analysis*, 3rd Ed., Longmans, London 1961, p. 944.
- Karlsson, R. *Talanta* 19 (1972) 1639.
- International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham 1962, Vol. III.
- Coppens, P. and Hamilton, W. *Acta Crystallogr. A* 26 (1970) 71.
- Hansen, H. P., Herman, F., Lea, I. D. and Skillmans, S. *Acta Crystallogr.* 17 (1964) 1040.
- Johnson, C. K. *A Fortran Thermal-Ellipsoid Plot-Program for Crystal Structure Illustration*, Oak Ridge National Laboratory, Chemistry Division, Oak Ridge, Tennessee 1965.
- Lee, F. S. and Carpenter, G. B. *J. Phys. Chem.* 63 (1959) 279.
- Nordman, C. E. *Acta Crystallogr.* 15 (1962) 18.
- Almlöf, J. *Chem. Scr.* 3 (1973) 73.
- Donnay, G. and Allman, R. *Amer. Mineral.* 55 (1970) 1003.
- Christ, C. L., Clark, J. R. and Evands, H. T. *Acta Crystallogr.* 11 (1958) 761.
- Nowacki, W. and Silverman, J. *Acta Crystallogr.* 10 (1957) 787.
- Hamilton, W. C. and Ibers, J. A. *Hydrogen Bonding in Solids*, Benjamin, New York 1969, p. 213.
- Johansson, G. *Acta Chem. Scand.* 22 (1968) 389.
- Johansson, G. *Acta Chem. Scand.* 22 (1968) 399.
- Olin, Å. and Söderquist, R. *Acta Chem. Scand.* 26 (1972) 3505.
- Hong, S.-H. and Olin, Å. *Acta Chem. Scand.* 27 (1973) 2309.
- Hong, S.-H. and Olin, Å. *Acta Chem. Scand. A* 28 (1974) 233.
- Edstrand, M. *Acta Chem. Scand.* 1 (1947) 178.
- Särnstrand, C. *Private communications*.
- Aurivillius, B. and Löwenhielm, A. *Acta Chem. Scand.* 18 (1964) 1937.
- Aurivillius, B. *Acta Chem. Scand.* 18 (1964) 2375.
- Swink, L. N. and Carpenter, G. B. *Acta Crystallogr.* 21 (1966) 578.
- Beyer, H. *Z. Kristallogr.* 124 (1967) 228.
- Andersson, S., Åström, A., Galy, J. and Meunier, G. *J. Solid. State Chem.* 6 (1973) 187.
- Andersson, S. and Åström, A. *NBS Special Publication 364, Solid State Chemistry*, Proceedings of 5th Materials Research Symposium, issued July 1972.

Received April 5, 1974.