Acta Chemica Scandinavica A 28 (1974) 267—274

The Crystal Structure of $Sb_4O_4(OH)_2(NO_3)_2$

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The crystal structure of the compound $Sb_4O_4(OH)_2(NO_3)_2$ has been determined by conventional methods from three-dimensional X-ray intensity data measured on an automatic diffractometer. The crystals are monoclinic (space group $P2_1/c$). The unit cell contains two formula units and has the dimensions $a = 11.020(2)$ Å, $b = 5.5355(5)$ Å, $c = 10.270(1)$ Å and $\beta = 123.71(1)°$. The structure was refined by a full matrix-least-squares technique, using 1084 observed reflections, to an R value of 0.046. It contains distorted trigonal bipyramidal SbO_4- and tetrahedral SbO_3-polyhedra, with the lone pair of electrons at one of the equatorial corners of the bipyramids and at one corner of each tetrahedron, respectively. Each SbO_4-polyhedron shares two edges with other SbO_4-units and two corners with SbO_3-polyhedra. Since each SbO_3-unit shares oxygens with two SbO_4-units infinite layers parallel to the bc-plane are formed. The nitrate ions are situated between these layers. The Sb—O distances in SbO_3 are 1.942(7), 2.052(6), and 2.067(6) Å and in SbO_4 2.019(6), 2.020(6), 2.236(6), and 2.265(6) Å, respectively.

The investigation of the crystal structure of $Sb_4O_4(OH)_2(NO_3)_2$ is a part of several studies on the chemistry of antimony(III) in solid state as well as in solution. The crystal structures of the following compounds have already been determined or are worked upon in this laboratory, *viz.* Sb_2O_3 (*orth.*).[1] SbOF,[2,3] $Sb_4O_5Cl_2$,[4,5] $SbPO_4$,[6] $SbO(H_2PO_4).H_2O$,[7] $Sb_4O_5(OH)ClO_4.\frac{1}{2}H_2O$,[8] and $Sb(OH)_2ClO_4.H_2O$. The hydroxo complexes of antimony(III) existing in solutions of perchloric and nitric acid has been investigated by Ahrland and Bovin,[9] applying solubility measurements. It was essential during that work to know the structure and composition of this solid phase, which has previously been described as $Sb_4O_5(NO_3)_2.H_2O$ in Gmelins Handbuch[10] and by Jander and Hartmann.[11] The formula is written $Sb_4O_4(OH)_2(NO_3)_2$ instead of $Sb_2O_2OHNO_3$.

EXPERIMENTAL

Crystal preparation and analysis. Crystals of $Sb_4O_4(OH)_2(NO_3)_2$ were prepared in perchloric acid according to the method described by Jander and Hartmann.[11] Since these were too small for a single crystal study the following method was evolved: 6 M nitric acid was heated to 110°C in an Erlenmeyer flask and orthorhombic Sb_2O_3 was added until a saturated solution was obtained. A little more Sb_2O_3 was then added so that some of the solid phase persisted. The flask was stoppered and its temperature was decreased by 5—10°C per day to roomtemperature. $Sb_4O_4(OH)_2(NO_3)_2$ crystallized as thin, colourless transparent plates. The homogeneity of the sample was confirmed by Guinier-Hägg X-ray powder photographs.

The material thus prepared was analysed for antimony(III) by the methods of Belcher[12] and Elkind *et al.*[13] Nitrogen analysis was made according to Dumas[14] and for the water analysis a modification of the method of Fischer[15,16] was employed. The results were 68.8 % antimony(III), 3.8 % nitrogen and 2.2 % water. Calc. for $Sb_4O_4(OH)_2(NO_3)_2$: 68.69, 3.95, and 2.5 %.

Crystal data. Preliminary Weissenberg photographs showed the crystals to be monoclinic with systematic absences $h0l$ with $l = 2n+1$ and $0k0$ with $k = 2n+1$. These are characteristic of the space group $P2_1/c$ (No. 14).

The unit cell dimensions were determined by least-squares refinement using as data the diffraction angles of 28 lines on the Cu$K\alpha_1$ ($\lambda = 1.5405$ Å) powder pattern made at room temperature in a Guinier-Hägg focusing camera equipped with a quartz monochromator and using KCl (cubic, $a = 6.2929$ Å) as internal standard, *cf.* Table 1. The density determined by measuring the loss of weight in benzene was in good agreement with the calculated value for two formula units of $Sb_4O_4(OH)_2(NO_3)_2$ per unit cell. Some crystal data are presented in Table 2.

Table 1. Guinier powder pattern of $Sb_4O_4(OH)_2(NO_3)_2$ using Cu$K\alpha$ radiation.

$h\,k\,l$	$10^5\sin^2\theta$ obs	$10^5\sin^2\theta$ calc	I obs
1 0 0	708	706	vs
1 1 0	2 647	2 642	v
0 1 1	2 751	2 749	vw
$\bar{2}$ 1 2	4 647	4 648	w
2 1 0	4 766	4 760	vw
0 1 2	5 196	5 187	m
$\bar{3}$ 0 0	6 360	6 353	w
$\bar{3}$ 1 2	6 498	6 496	s
1 1 2	7 577	7 575	w
0 2 0	7 750	7 745	vs
3 1 0	8 290	8 289	vw
$\bar{1}$ 2 0	8 446	8 451	w
$\bar{2}$ 0 4	9 105	9 103	vs
$\bar{3}$ 0 4	9 264	9 270	w
4 1 0	13 233	13 231	m
$\bar{3}$ 2 0	14 105	14 098	w
$\bar{2}$ 2 4	16 847	16 848	s
$\bar{3}$ 2 4	17 006	17 014	m
4 2 0	19 052	19 039	vw
5 2 2	20 230	20 237	vw
$\bar{0}$ 2 4	20 745	20 749	vw
$\bar{5}$ 2 1	21 987	21 999	vw
$\bar{3}$ 3 2		21 986	vw
3 2 2	22 387	22 393	vw
$\bar{1}$ 3 2	23 059	23 064	vw
$\bar{5}$ 1 6	23 625	23 624	w
$\bar{6}$ 1 6	26 351	26 345	vw
$\bar{0}$ 4 0	30 972	30 979	vw
$\bar{1}$ 4 2	33 257	33 255	vw
7 1 0	36 508	36 525	vw

Table 2. Crystallographic data for $Sb_4O_4(OH)_2(NO_3)_2$.

Unit cell:	$a = 11.020(2)$ Å
	$b = 5.5355(5)$ Å
	$c = 10.270(1)$ Å
	$\beta = 123.71(1)°$
	$V = 521.2$ Å^3
	$Z = 2$
Formula weight:	$M = 709.12$
Density, 20 °C.	$D_m = 4.45$ g cm^{-3}
	$D_x = 4.52$ g cm^{-3}

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 Mo$K\alpha$ radiation ($\lambda = 0.71069$ Å). The intensities were recorded at a take-off angle of 5°. The $\omega - 2\theta$ scan technique was used with an ω range of $(0.9 + 0.5 \text{ tg } \theta)°$. A minimum net count of 3000 for each reflection was attained within the maximum measuring time of 5 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 $(\sin\theta)/\lambda = 0.65$ Å^{-1} were examined. Of the 1265 reflections measured, 14 were considered to be below background since they gave counts of less than 10 in the fast (9 s) pre-scan, and 167 were rejected as being 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 remaining 1084 reflections were corrected for Lorentz, polarisation and absorption (*cf.* Table 3) effects using the program DATAPC [17] as modified by Christer Svensson of this Institute.

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

Plane	d (cm)
(1$\bar{0}$0)	0.00245
($\bar{1}$00)	0.00245
(0$\bar{1}$0)	0.01220
(010)	0.01220
(10$\bar{2}$)	0.00070
($\bar{1}$02)	0.00070

Crystal volume: 0.17×10^{-3} mm^3.

The linear absorption coefficient [18] for Mo$K\alpha$ radiation is 105 cm^{-1}. The transmission factors were in the range 0.60 – 0.86. Two standard reflections, 132 and 402, were measured with 90 min intervals to check for crystal decomposition and radiation stability. A mean decrease of 10 % in their intensities was found during the course of data collection. 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 eight antimony atoms were found to occupy two sets of fourfold positions 4(*e*) in $P2_1/c$. A least-squares refinement of these positions was performed. A subsequent three-dimensional difference electron density synthesis revealed the positions of all other non-hydrogen atoms, which also were in the general equivalent positions 4(*e*). A preliminary full matrix least-squares refinement was now performed refining the atomic coordinates and isotropic temperature factors for all atoms, and a scale factor.

The refinement converged to an R-value ($R = \sum||F_o| - |F_c||/\sum|F_o|$) of 0.086.

Anisotropic temperature factors were then introduced for all atoms and again the positional and thermal parameters were refined together with an overall scale factor. The R-value was now reduced to 0.056. When the anisotropic refinement was repeated with data corrected for absorption effects the R-value was 0.048. Corrections were then made for isotropic secondary extinction with the full matrix least-squares program LINUS.[19] The function minimized was $\sum w_i(|F_o| - |F_c|)^2$, where the weights, w_i, were calculated from the expression $w_i^{-1} = \sigma^2(F_o^2)/4F_o^2 + cF_o^2$. The value of the constant c was chosen so as to give the most constant averages of $w_i(|F_o| - |F_c|)^2$ over ranges of F and sin θ. A value of $c = 0.001$ was used in the last refinement. The R-value converged to 0.046 and the R_w-value to 0.058 where $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$. The final value of S defined by $S = [\sum w(|F_o| - |F_c|)^2/(m-n)]^{1/2}$ where m and n are the number of observations and parameters varied, respectively, was 1.52. The atomic scattering factors used were those given by Hanson *et al.*[20]

The final value of the isotropic extinction parameter g was $0.07(4) \times 10^4$. In the last cycle of refinement the shifts for all parameters were less than 0.01 times their corresponding standard deviations. The final positional and thermal parameters are given in Table 4, and observed and calculated structure amplitudes are compared in Table 5. Interatomic distances and bond angles presented in Table 6 were calculated with the program DISTAN, written by A. Zalkin. The drawings (Figs. 1 and 2) were obtained with the program ORTEP.[21]

DESCRIPTION AND DISCUSSION OF THE STRUCTURE

The fundamental structural elements of the structure of $Sb_4O_4(OH)_2(NO_3)_2$ are distorted SbO_4- and SbO_3-polyhedra. The SbO_4-polyhedron is trigonal pyramidal with the lone electron pair in one of the equatorial corners (Fig. 1). The SbO_3-polyhedron is tetrahedral with the lone pair in one of the corners (Fig. 1). The SbO_4-polyhedra each share two edges and thus build up infinite chains parallel to b. These chains are linked by two corners of each SbO_3-polyhedron to form infinite layers parallel to the bc-plane (*cf.* Fig. 1).

Table 4. Final positional and thermal parameters in $Sb_4O_4(OH)_2(NO_3)_2$. The form of the anisotropic temperature factor is exp $[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2\,hk\beta_{12} + 2\,hl\beta_{13} + 2\,kl\beta_{23})]$. Standard deviations are given within parentheses.

Atom	x	y	z	Atom	x	y	z
Sb(1)	0.17601(6)	0.20160(11)	0.35476(7)	O(4)	0.2845(11)	0.2689(17)	0.1680(11)
Sb(2)	0.11237(7)	0.74852(11)	0.06549(7)	O(5)	0.4655(9)	0.2371(15)	0.4074(10)
O(1)	0.0326(6)	0.0720(12)	0.1328(6)	O(6)	0.5050(11)	0.2725(16)	0.2223(11)
O(2)	0.0307(6)	0.0705(12)	0.4049(6)	N	0.4228(10)	0.2641(16)	0.2676(12)
O(3)	0.7557(7)	0.1305(13)	0.6048(7)				

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Sb(1)	0.00469(9)	0.01077(23)	0.00315(9)	−0.00074(8)	0.00267(7)	−0.00062(8)
Sb(2)	0.00409(9)	0.01283(24)	0.00343(10)	0.00010(8)	0.00228(7)	0.00176(9)
O(1)	0.0049(7)	0.0094(19)	0.0020(7)	0.0006(9)	0.0023(6)	0.0004(9)
O(2)	0.0042(7)	0.0102(19)	0.0025(7)	−0.0001(9)	0.0026(6)	−0.0005(9)
O(3)	0.0060(8)	0.0115(21)	0.0052(9)	0.0009(11)	0.0030(7)	0.0004(11)
O(4)	0.0068(10)	0.0367(40)	0.0064(11)	0.0030(15)	0.0020(9)	−0.0012(15)
O(5)	0.0061(10)	0.0283(34)	0.0054(11)	0.0032(13)	0.0022(9)	0.0005(13)
O(6)	0.0109(12)	0.0237(32)	0.0111(14)	0.0013(14)	0.0084(11)	0.0024(15)
N	0.0038(9)	0.0186(30)	0.0078(13)	0.0002(12)	0.0031(10)	0.0005(14)

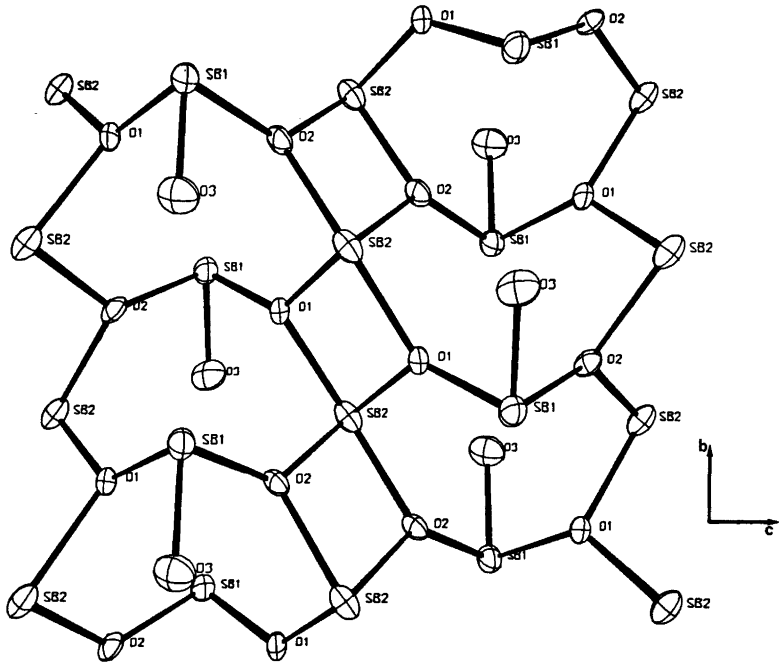

Fig. 1. The antimony-oxygen coordination within a layer. Projection along the *a*-axis.

The three oxygen atoms O(4), O(5), O(6) (*cf.* Table 4) and the nitrogen atoms form the planar NO_3^--ion. The distances N–O and the angles O–N–O (*cf.* Table 5) are normal (*cf. International Tables*,[18] Luzzati,[22] Taylor *et al.*[23]). The nitrate ions are situated between the layers described above (*cf.* Fig. 2). For the interpretation of the solubility function of Sb(III) in nitric acid with $Sb_4O_4(OH)_2(NO_3)_2$ 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-} and OH^--ions from each other. In order to establish the nature of the oxygen atoms O(1), O(2), O(3), a procedure due to Donnay *et al.*[24] was used. It is based on the principle of local neutralization of charge and makes it possible to recognize O^{2-}, OH^-, and H_2O in crystal structures derived by X-ray

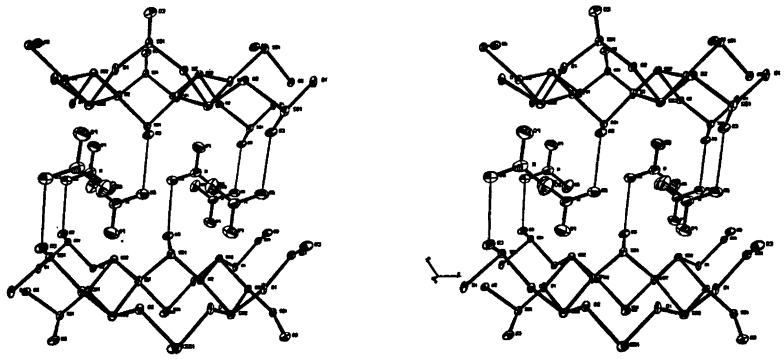

Fig. 2. Stereoview down the *b*-axis. Possible hydrogen bonds are marked with thin lines.

Table 5. Observed and calculated structureamplitudes. The columns list l, $|F_o|$ and $|F_c|$.

H=	0 K=	0	-5	58	54	-5	72	68	-6	33	30	3	52	56	-5	97	90	-10	89	90	-6	124	123
-10	97	97	-3	42	40	-4	55	51	-5	48	42	4	56	59	-3	54	56	-9	32	31	-5	25	26
-8	30	28	-2	42	42	-3	59	55	-4	139	128	5	17	18	-2	107	107	-7	69	68	-4	77	77
-6	37	36	-1	58	54	-1	52	50	-3	112	107	6	32	30	-1	62	67	-6	150	147	-3	81	81
-4	199	184	0	65	66	0	31	34	-2	62	62	7	45	46	0	114	125	-5	77	77	-2	71	71
-2	47	41	1	50	54	1	74	77	-1	20	19	8	65	63	1	73	77	-4	99	101	-1	18	16
2	47	41	2	43	42	2	84	81	1	93	99				2	74	75	-3	44	44	0	69	71
4	198	186	3	41	40	4	60	56	2	28	30	H=	3 K=	4	3	26	25	-2	16	16	1	49	51
6	36	36	5	57	54	5	64	61	3	43	42	-9	53	54	4	107	111	-1	71	76	2	28	29
8	28	28	6	56	52	7	34	33	4	82	81	-8	26	23	5	54	53	2	46	48	3	40	42
10	97	97							5	55	54	-7	13	12	6	37	37	3	54	56	4	45	45
			H=	0 K=	7	H=	1 K=	6	6	88	86	-6	69	66	7	14	16	4	119	123	5	17	18
H=	0 K=	1	-1	32	30	-6	24	25	7	46	44	-5	93	89				5	25	25			
-10	40	38	1	28	30	-5	16	16	8	15	17	-4	114	111	H=	4 K=	4	6	13	11	H=	6 K=	6
-8	49	48				-4	25	23				-3	46	46	-10	24	24				-11	66	68
-7	18	16	H=	1 K=	0	-3	48	47	H=	2 K=	5	-2	24	25	-8	75	73	H=	5 K=	6	-10	47	46
-5	21	21	-10	127	129	-2	89	86	-8	47	51	-1	97	97	-7	74	69	-10	34	34	-9	45	43
-4	115	107	-8	111	108	-1	73	70	-7	37	38	0	89	97	-6	64	60	-9	51	52	-8	40	39
-3	40	39	-6	127	115	0	43	43	-6	69	68	1	61	65	-5	41	41	-8	104	99	-7	41	41
-2	288	265	-4	123	115	3	70	67	-5	75	70	2	61	64	-4	36	35	-7	40	39	-5	75	73
-1	70	59	-4	16	19	4	37	36	-4	16	15	3	50	53	-3	56	53	-6	37	36	-4	89	91
1	42	59	-2	43	39				-3	24	24	4	39	37	-1	86	88	-5	57	53	-2	84	89
2	244	265	2	180	185	H=	1 K=	7	-2	45	44	5	69	70	0	90	98	-4	52	51	-1	63	69
3	41	39	4	224	224	-5	22	25	-1	82	80	6	19	19	1	19	22	-3	65	66	1	31	34
4	112	107	6	142	140	-1	18	15	0	71	77				2	99	106	-2	55	60	2	22	26
5	21	21	8	20	19	0	56	57	1	22	25	H=	3 K=	5	3	69	72	0	65	68	3	34	35
7	16	16				1	42	44	2	54	55	-9	37	38	6	39	39	1	68	72	4	21	23
8	48	48	H=	1 K=	1	2	32	30	3	55	55	-8	47	49				2	51	52			
10	39	38	-10	79	78				4	19	17	-7	54	52	H=	4 K=	5	3	26	27	H=	6 K=	7
			-9	24	23	H=	2 K=	0	5	51	50	-6	27	26	-9	46	47	4	28	28	-9	39	38
H=	0 K=	2	-8	128	125	-10	32	33	6	39	39	-4	26	29	-8	19	19	5	48	48	-8	33	35
-10	89	87	-6	188	175	-8	130	128				-3	77	75	-6	25	27				-7	44	45
-9	46	45	-5	33	31	-6	58	53	H=	2 K=	6	-2	87	86	-5	69	68	H=	5 K=	5	-6	68	70
-8	51	50	-4	59	56	-4	362	304	-9	39	41	-1	60	60	-4	40	40	-9	27	26	-4	62	61
-7	27	26	-3	53	44	-2	28	27	-8	18	14	0	56	60	-3	51	52	-7	53	52	-3	71	71
-6	73	69	-2	17	17	0	14	16	-7	26	22	1	57	61	-2	63	66	-6	44	45	-2	20	20
-4	90	93	-1	38	34	2	32	34	-6	37	35	3	53	54	-1	63	66	-5	69	69	-1	26	25
-3	51	49	0	54	65	4	109	109	-5	62	62	4	32	33	0	24	23	-4	83	83	0	55	57
-2	39	33	1	70	69	6	188	191	-4	66	63	6	44	43	1	73	77	-3	26	26	1	47	48
-1	86	70	2	254	271	8	60	58	-3	35	34				2	34	34	-2	23	24	2	56	53
0	276	345	3	30	28				-2	57	50	H=	3 K=	6	3	20	20	-1	70	73	3	45	45
1	70	70	4	154	151	H=	2 K=	1	2	50	52	-7	25	25	4	41	40	0	38	41			
2	34	33	5	42	42	-11	27	27	3	38	36	-6	63	61	5	55	56	1	21	17	H=	6 K=	8
3	50	49	6	101	99	-10	47	49	4	61	61	-5	57	57				2	51	56	-7	19	18
4	86	83	8	61	59	-9	16	14				-4	29	31	H=	4 K=	6	3	58	60	-6	24	27
5	72	69				-8	98	98	H=	2 K=	7	-3	58	59	-7	69	70	4	44	43	-5	55	55
6	25	24	H=	1 K=	7	-7	31	30	-1	43	43	1	30	31	-6	45	42				-4	41	43
8	51	50	-11	29	31	-6	243	220	0	70	71	2	45	48	-5	19	19	H=	5 K=	6	-2	37	37
9	45	45	-10	114	115	-5	54	48	1	22	20	3	28	30	-4	17	14	-7	43	44	-1	49	51
10	58	57	-8	120	114	-4	12	11				4	59	58	-3	51	53	-6	21	21	0	33	34
			-7	51	48	-3	22	19	H=	3 K=	0				-2	37	37	-5	47	48			
H=	0 K=	3	-6	98	88	-2	144	158	-12	64	60	H=	3 K=	7	-1	48	48	-4	53	55	H=	7 K=	0
-10	31	30	-5	38	34	-1	78	78	-10	54	57	-2	23	22	0	41	42	-3	53	56	-12	134	144
-9	20	19	-4	98	83	0	60	68	-8	12	11	-1	27	27	1	21	24	-1	18	18	-10	30	31
-8	29	28	-3	40	36	1	15	17	-6	11	14				2	36	35	0	58	58	-8	30	27
-7	68	68	-2	64	58	2	91	91	-4	256	234	H=	4 K=	0	3	43	43	1	49	50	-6	93	93
-6	17	16	-1	98	96	3	58	57	-2	125	126	-12	99	107							-4	184	184
-4	91	85	0	80	92	4	141	142	0	187	242	-10	88	92	H=	5 K=	0	H=	6 K=	0	0	44	44
-3	108	94	1	28	26	5	24	25	2	107	112	-8	186	183	-12	51	54	-12	61	65	2	146	146
-2	212	178	2	105	107	6	87	86	4	14	13	-6	24	20	-10	29	32	-8	83	81	4	39	39
-1	94	82	3	90	86	7	29	29	6	38	40	-4	51	43	-8	275	266	-6	86	83			
1	86	82	4	151	152	8	145	146				-2	119	127	-6	98	95	-4	189	195	H=	7 K=	1
2	185	178	5	29	28	9	15	17	H=	3 K=	1	0	95	101	-4	234	231	-2	195	199	-13	15	19
3	101	94	6	109	107				-12	75	81	2	246	244	-2	74	74	0	51	52	-12	13	14
4	87	85	7	45	47	H=	2 K=	2	-11	24	29	4	32	33	0	28	32	2	46	45	-11	15	17
5	16	16	9	35	35	-10	39	40	-10	73	77	6	78	76	2	99	110	6	82	83	-10	116	114
7	47	48				-9	18	17	-9	13	15				4	25	24				-9	34	35
8	28	29	H=	1 K=	3	-8	121	117	-7	45	43	H=	4 K=	1	6	127	128	H=	6 K=	1	-8	58	58
9	21	19	-10	58	57	-7	25	24	-6	104	100	-12	73	81				-13	20	24	-5	38	37
10	31	30	-9	58	57	-6	40	56	-5	52	50	-10	135	140	H=	5 K=	1	-12	16	19	-4	114	116
			-8	100	95	-5	19	17	-2	299	321	-9	37	38	-12	18	18	-11	14	14	-3	24	27
H=	0 K=	4	-7	42	41	-4	319	277	-1	27	29	-8	35	31	-11	17	19	-10	27	28	-2	86	90
-9	56	55	-6	122	113	-3	33	33	0	105	123	-6	94	87	-10	121	124	-9	25	24	-1	31	32
-8	59	54	-5	82	76	-2	37	36	1	23	27	-5	53	48	-9	17	14	-8	31	28	0	195	210
-7	24	22	-3	94	80	-1	29	26	2	117	119	-4	15	13	-7	44	40	-7	36	35	1	28	30
-6	63	60	-2	20	18	0	67	67	3	38	39	-2	158	165	-6	226	214	-6	195	192	2	18	22
-5	79	71	-1	52	49	1	44	47	4	25	26	-1	23	26	-5	34	32	-5	24	24	3	15	14
-4	21	21	0	10	11	3	47	48	7	31	31	0	149	174	-4	138	134	-4	135	136	4	85	89
-3	33	31	1	98	101	4	85	85	8	109	109	1	13	15	-3	49	44	-3	55	56	5	15	18
-2	50	42	2	175	173	5	35	34				2	125	133	-2	65	62	-2	137	145			
-1	80	56	4	99	94	6	151	154	H=	3 K=	2	4	134	137	-1	15	17	-1	14	12	H=	7 K=	2
0	152	158	5	73	72	7	46	46	-11	42	45	5	13	15	1	16	16	0	115	124	-12	123	130
1	57	56	6	57	55	8	29	29	-10	25	28	6	13	13	2	37	38	1	33	35	-11	26	28
2	44	42	7	26	25	9	14	16	-9	35	34	7	18	18	3	13	7	4	36	37	-10	17	17
3	31	31	8	38	40				-7	43	39				4	147	164	6	30	32	-8	75	73
4	22	21	9	27	26	H=	2 K=	3	-6	54	52	H=	4 K=	2	6	15	14				-7	46	41
5	72	71				-11	38	41	-5	50	47	-12	75	78				H=	6 K=	2	-5	26	26
6	41	40	H=	1 K=	4	-9	34	32	-4	247	231	-11	65	68	H=	5 K=	2	-12	66	71	-4	72	73
7	22	22	-8	77	75	-8	83	82	-3	49	71	-10	53	55	-12	27	27	-11	26	28	-3	44	44
8	47	46	-7	91	95	-7	45	44	-1	40	42	-8	126	123	-10	20	20	-10	13	10	-2	144	139
9	43	55	-6	19	16	-6	141	149	0	190	228	-7	80	75	-9	40	39	-9	36	34	-1	49	51
			-5	41	38	-5	107	92	1	41	45	-6	31	29	-8	100	103	-8	50	48	0	38	36
H=	0 K=	5	-4	64	58	-3	96	84	2	89	93	-5	20	21	-7	61	54	-6	65	64	1	31	34
-8	15	16	-3	100	91	-2	121	117	3	24	26	-4	35	35	-6	42	59	-5	72	70	2	121	126
-7	65	65	-2	97	89	-1	115	113	5	55	58	-3	66	64	-5	46	45	-4	136	139	3	38	38
-6	37	36	-1	87	82	0	92	90	6	34	34	-2	64	67	-4	130	127	-3	32	31	4	33	32
-4	89	82	0	64	69	1	18	19				-1	59	63	-3	83	84	-2	153	162			
-3	85	74	1	24	25	2	66	66	H=	3 K=	3	0	126	141	-2	64	69	-1	63	69	H=	7 K=	3
-2	74	69	2	26	27	3	76	73	-11	39	42	1	22	23	-1	15	16	0	26	26	-11	28	30
-1	40	56	3	80	76	4	56	55	-10	66	67	2	180	198	0	61	65	1	35	36	-10	80	87
1	54	56	4	89	88	5	48	47	-9	35	34	3	55	56	1	70	75	2	37	38	-9	72	74
2	73	69	5	12	11	6	68	69	-8	33	32	4	33	34	2	91	97	3	31	33	-8	71	68
3	79	74	6	68	66	7	35	34	-7	75	70	6	65	66	3	20	20	5	32	34	-5	66	65
4	87	82	7	46	45	8	85	85	-6	73	69	7	35	35	4	28	28	6	67	70	-4	32	32
6	37	36	8	19	19				-3	106	101				5	41	42				-3	27	28
7	47	45				H=	2 K=	4	-2	205	204	H=	4 K=	3	6	107	110	H=	6 K=	3	-2	66	67
8	20	16	H=	1 K=	5	-10	33	34	-1	40	42	-10	102	105	7	26	23	-11	30	32	-1	43	46
			-8	29	29	-9	46	47	0	115	129	-9	77	76				-10	20	21	0	109	113
H=	0 K=	6	-7	29	31	-7	50	49	1	72	78	-7	15	15	H=	5 K=	3	-9	49	47	1	45	46
-6	55	52	-6	71	69	-7	74	71	2	47	48	-6	66	63	-11	47	50	-7	57	56	2	29	27

Table 5. Continued.

diffraction methods. A calculation of cation to anion distances and associated bond valences leads to valence sums for the oxygen atoms. The valence sum $\sum v$ is approximately equal to 2 for an O^{2-}-ion, 1 for an OH^--ion and 0 for a water molecule. $\sum v$ for O(1), O(2), and O(3) were calculated to 2.2, 2.2, and 1.1. In the present case the oxygen atom O(3) should thus be a hydroxide ion. This is also supported by the distance O(3)–O(5) of 2.74(1) Å (*cf.* Table 6), which is in good agreement with hydrogen bond distances in inorganic solids given in the *International Tables*.[18] The angle O(3)···O(5)–N of 114.°7(7) also agrees well with that found by Luzzati [22] in $HNO_3.3H_2O$. It has been shown by Andersson, Åström, Galy and Meunier [25] 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 about 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 $Sb_4O_4(OH)_2(NO_3)_2$, the result is 16.3 Å^3. This value compared with data from Andersson and Åström [26] indicated that the total struc-

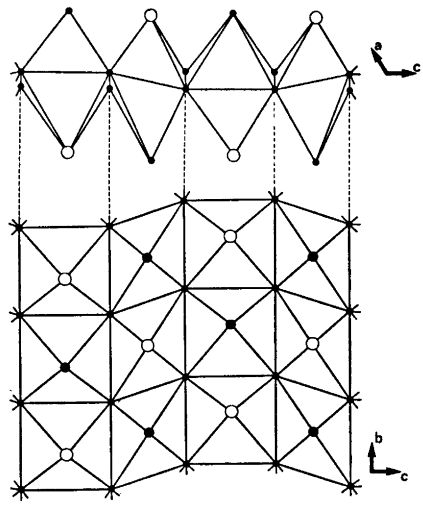

Fig. 3. The distorted cubic close packing of oxygen and lone pairs of electrons of antimony in the layer parallel to the *bc*-plane. The upper view is along the *b*-axis and the lower is perpendicular to the *bc*-plane.

Table 6. Coordination distances (Å) and angles (°) with standard deviations (in brackets) in $Sb_4O_4(OH)_2(NO_3)_2$. Notation of the atoms, *cf.* Table 4.

The SbO_3-polyhedron			
Sb(1) – O(3)	1.942(7)	∠O(1) – Sb(1) – O(2)	85.90(22)
Sb(1) – O(1)	2.052(6)	∠O(1) – Sb(1) – O(3)	82.79(26)
Sb(1) – O(2)	2.067(6)	∠O(2) – Sb(1) – O(3)	82.91(26)
O(1) – O(3)	2.642(9)		
O(2) – O(3)	2.656(9)		
O(1) – O(2)	2.807(8)		
The SbO_4-polyhedron			
Sb(2) – O(1)	2.019(6)	∠O(1′) – Sb(2) – O(1)	72.23(23)
Sb(2) – O(2)	2.020(6)	∠O(1′) – Sb(2) – O(2′)	141.60(20)
Sb(2) – O(2′)	2.236(6)	∠O(1′) – Sb(2) – O(2)	82.67(23)
Sb(2) – O(1′)	2.265(6)	∠O(1) – Sb(2) – O(2′)	82.84(23)
O(1′) – O(2′)	3.056(8)	∠O(1) – Sb(2) – O(2)	98.34(23)
O(1′) – O(2)	2.820(9)	∠O(2′) – Sb(2) – O(2)	72.39(24)
O(1′) – O(1)	2.533(11)		
O(2′) – O(2)	2.519(11)		
O(1) – O(2)	2.836(9)		
The nitrate ion			
N – O(6)	1.227(14)	∠O(4) – N – O(5)	116.3(9)
N – O(5)	1.247(13)	∠O(4) – N – O(6)	120(1)
N – O(4)	1.281(13)	∠O(5) – N – O(6)	124(1)
O(4) – O(5)	2.148(12)		
O(4) – O(6)	2.170(14)		
O(5) – O(6)	2.181(13)		
Possible hydrogen bond distance			
O(3)···O(5)	2.737(11)	∠O(3)···O(5) – N	114.7(7)

ture has an approximately close-packed arrangement of oxygens and lone pairs of electrons. If only the Sb – O layers and one oxygen atom, O(4), from the nitrate ion are considered the result is 15.6 Å³. The arrangement of these oxygen atoms and the electron pairs is approximately cubic close packed; (*cf.* Fig. 3).

Acknowledgements. The author thanks Professor Bengt Aurivillius for his introduction to the techniques of structure determination, his valuable discussions during this work and his stimulating and helpful interest. The author is also indebted to Professor Sten Ahrland, Dr. Karin Aurivillius and Dr. Sten Andersson for their kind interest in this work. Christer Svensson and Kerstin Renhult Aspelin are thanked for their assistance with the data collection.

This work received financial support from the Swedish Natural Science Research Council.

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Received January 2, 1974.