Table 6. *Structure types found in* R–Rh *alloys* (*up to* 50 *at.* % Rh) *together with their characteristic rare-earth polyhedra*

Large R	Fe₃C	Th₇Fe₃	La₅Rh₃	Nd₄Rh₃	CrB
	Trigonal prisms	Trigonal prisms	?	?	Trigonal prisms
Small R	Fe₃C	Th₇Fe₃	Mn₅Si₃	Y₃Rh₂	CsCl
	Trigonal prisms	Trigonal prisms	Archimedian antiprisms	All types of polyhedra	Cubes

type (Dwight, Conner & Downey, 1965). The compounds with Y_3Rh_2 structure type occur with the small rare-earth elements from Gd to Er and thus the formation of a structure with only R_6Rh trigonal prisms seems unlikely. As shown above one finds all the different coordination polyhedra in Y_3Rh_2: trigonal prisms, Archimedian antiprisms and cubes.

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The Crystal Structure of the Antimony(III) Oxide Sulphate Sb₆O₇(SO₄)₂

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The structure of $Sb_6O_7(SO_4)_2$ has been determined from intensities collected on a linear diffractometer with Mo $K\alpha$ radiation, and refined to an R of 0·041 for 1148 intensities. The crystals are orthorhombic, space group $Ccc2$, with $a = 12·073$ (2), $b = 19·023$ (4), $c = 5·876$ (1) Å, $Z = 4$. All three Sb^{III} atoms can be considered as three-coordinated and the coordination polyhedra are distorted tetrahedra, with the lone pair of electrons of Sb at one of the corners. The Sb–O distances within the tetrahedra vary between 1·994 (17) and 2·207 (18) Å. The three different SbO_3 polyhedra share corners and edges forming a cylindrical unit parallel to c. Each sulphate tetrahedron is situated between the cylindrical units.

Introduction

A compound of the composition $3Sb_2O_3 . 2SO_3$ has been reported to exist in equilibrium with 4·3–6·9 M sulphuric acid solutions (Hintermann & Venuto, 1968). Contrary to this result the compound was earlier described as containing water, with composition $3Sb_2O_3 . 2SO_3 . H_2O$ (Jander & Hartmann, 1965).

In nitric acid and perchloric acid solutions $Sb_4O_4(OH)_2(NO_3)_2$ and $Sb_4O_5(OH)ClO_4 . \frac{1}{2}H_2O$ (Ahr-

land & Bovin, 1974) exist as stable phases. Both compounds contain distorted hexagonally close-packed sheets of Sb and O atoms (Bovin, 1974a, b, 1975). Earlier published structures of $SbPO_4$ (Kindberger, 1970) and $SbO(H_2PO_4) . H_2O$ (Särnstrand, 1974), show however that, unlike the nitrate and perchlorate, these compounds are not built up of sheets.

The aim of the present work was to determine whether any water or hydroxide group exists in Sb^{III} oxide sulphate and to find out if the structure shows

any relationships to those of the earlier reported Sb^{III} oxide salts.

Experimental

Single crystals of $Sb_6O_7(SO_4)_3$ were first prepared in $6M$ perchloric acid solution (Jander & Hartmann, 1965). Single crystals were also obtained from $6M$ sulphuric acid solutions (Hintermann & Venuto, 1968). The compound formed in both cases as colourless, transparent crystals with prismatic habit and usually in acicular, radiating groups. Both methods gave the same compound judged from Weissenberg and Guinier–Hägg powder photographs. The crystals were analysed for Sb^{III} (Belcher, 1949; Elkind, Gayer & Boltz, 1953). The sulphate content was determined as $BaSO_4$ by the standard method. The water analysis was made according to a modification of the method of Fischer (Karlsson, 1972). The results are presented in Table 1.

Table 1. *Chemistry and crystallography of* $Sb_6O_7(SO_4)_2$

Data from the present investigation are compared with the results of Hintermann & Venuto (1968).

	This work	Hintermann & Venuto (1968)
Space group	$Ccc2$	$Pmmn$
Unit-cell: a (Å)	12·073 (2)	12·03
b	19·023 (4)	18·89
c (Å³)	5·876 (1)	6·00
V (Å³)	1349·5	1363
Z	4	4
D_x (g cm^{-3})	5·09	5·16
D_m	5·01	
% Sb (obs.)	70·5	70·8
(calc.)	70·6	70·6
% SO_4 (obs.)	18·4	18·5
(calc.)	18·6	18·6
% H_2O (obs.)	0·1	
(calc.)	0	0
μ(Mo $K\alpha$) (cm^{-1})	126	–

Weissenberg photographs showed the crystals to be orthorhombic. The systematic absences were: hkl with $h+k=2n+1$, $0kl$ with $l=2n+1$ and $h0l$ with $l=2n+1$, characteristic of the space groups $Ccc2$ and $Cccm$. Hintermann & Venuto (1968) have suggested the space group $Pmmn$. Accurate cell dimensions were determined from a least-squares analysis of the θ values of 35 reflexions collected on a single-crystal four-circle diffractometer with graphite-monochromatized Mo $K\alpha$ radiation ($\lambda = 0.71069$ Å). The density was determined from the loss of weight in benzene. Some crystallographic data are presented in Table 1 with data given by Hintermann & Venuto (1968).

X-ray data were collected with a Philips Pailred single-crystal diffractometer (equi-inclination Weissenberg geometry). A single crystal of the dimensions given in Table 2 was mounted along **c**. Mo $K\alpha$ radiation, monochromatized by reflexion off the (002) planes of a graphite crystal and a monochromator angle of 6·08°, was used. The reflexions $hk0–hk4$ were collected for the Cu range $\sin \theta/\lambda \le 0.76$ by the ω-scan technique with a scan rate of $1.0°$ min^{-1}. The scan range was 4·0° for all reflexions. The stationary background counts were measured for 40 s at each end of the scan interval. The intensities of two standard reflexions, 400 and 080, were measured at regular intervals. The variations of their intensities were random and less than 5%. 1807 reflexions were recorded ($h \ge 0$). 174 reflexions, for which the two measured background values differed by more than 3·09 times the e.s.d. of their difference, were omitted. 485 reflexions with $I \le 2.58\sigma(I)$ were considered unobserved, $\sigma(I)$ being based on counting statistics. The remaining 1148 reflexions were corrected for Lorentz, polarization and absorption effects. The transmission factors, evaluated by numerical integration, varied from 0·74 to 0·89.

Table 2. *Crystal dimensions*

Boundary planes and their distances from an internal origin.

Plane	d (cm)
(740)	0·00066
($\bar{7}$40)	0·00066
($\bar{1}$00)	0·0049
($\bar{7}$40)	0·00066
($7\bar{4}$0)	0·00066
($\bar{1}$01)	0·0065
(00$\bar{1}$)	0·0092

Structure determination and refinement

A Patterson summation was calculated with the data set uncorrected for absorption. The large maxima, due to Sb–Sb interatomic vectors, could not be interpreted in the space group $Cccm$, but could be explained by those in the acentric $Ccc2$. A least-squares refinement based on Sb(1), Sb(2) and Sb(3) and a subsequent difference synthesis revealed the positions of the S and all O atoms. All atoms occupy the general eightfold position $8(d)$ except one O atom which occupies the fourfold position $4(a)$. A preliminary least-squares refinement with isotropic temperature factors for all atoms gave an R of 0·052 ($R = \sum ||F_o| - |F_c||/\sum F_o$) with the data uncorrected for absorption. After introduction of an absorption correction the isotropic refinement was repeated and R fell to 0·049. The collected data consisted of both reflexions hkl and $h\bar{k}l$, identical by symmetry. No averaging of these reflexions was, however, performed. The final full-matrix least-squares refinement, minimizing $\sum w_i(|F_o| - |F_c|)^2$ with weights $w_i = [\sigma^2(F_o) + a|F_o|^2 + b]^{-1}$, was extended to include anisotropic thermal parameters for the Sb atoms. The values of a and b were chosen so as to give the most constant averages of $w_i(|F_o| - |F_c|)^2$ over different F and $\sin \theta$ intervals. The values $a = 0.0001$ and $b = 1.5$ were used and R converged to 0·041 and R_w to 0·044,

where $R_w = [w_i(|F_o| - |F_c|)^2 / \sum w_i|F_o|^2]^{1/2}$. The value of $S = [\sum w_i(|F_o| - |F_c|)^2/(m-n)]^{1/2}$, where m and n are the number of observations and parameters varied, respectively, was 1·00. A final difference synthesis showed that the highest remaining peak had a height of 3·5 e Å^{-3}. The scattering factors were those of Cromer & Waber (1965) for neutral Sb and of Hanson, Herman, Lea & Skillman (1964) for neutral S and O. The final positional and thermal parameters are given in Table 3.* Selected interatomic distances and angles are presented in Table 4.

Table 3. *Final positional and thermal parameters of* $Sb_6O_7(SO_4)_2$

Estimated standard deviations are in parentheses. The anisotropic thermal parameters are based on the expression $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$. The β_{ij} values are multiplied by 10^5.

	x	y	z	B (Å^2)
Sb(1)	0·10783 (11)	0·06606 (6)	0	–
Sb(2)	0·68785 (8)	0·06510 (6)	0·11354 (38)	–
Sb(3)	0·09265 (9)	0·20691 (5)	0·63163 (41)	–
O(1)	0	0	−0·1548 (38)	1·2 (3)
O(2)	0·2423 (8)	−0·0009 (10)	−0·1129 (30)	1·1 (2)
O(3)	0·8470 (9)	0·1010 (5)	0·1700 (22)	0·9 (2)
O(4)	0·0071 (15)	0·1652 (5)	0·8930 (27)	1·2 (2)
S	0·3665 (3)	0·1554 (2)	0·1589 (11)	1·2 (1)
O(5)	0·3085 (15)	0·1675 (9)	0·9396 (34)	3·1 (3)
O(6)	0·2847 (11)	0·1547 (7)	0·3500 (27)	1·3 (2)
O(7)	0·4456 (15)	0·2124 (9)	0·2011 (30)	3·7 (4)
O(8)	0·4237 (11)	0·0878 (7)	0·1627 (31)	2·3 (3)

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Sb(1)	153 (6)	77 (2)	556 (41)	−4 (3)	−2 (18)	−51 (13)
Sb(2)	110 (6)	72 (2)	845 (41)	22 (3)	−14 (19)	−73 (17)
Sb(3)	192 (6)	75 (2)	523 (43)	−47 (3)	−13 (22)	−1 (11)

Description and discussion of the structure

The Sb atoms of all Sb^{III}–O compounds studied so far have been found to have stereochemically active lone pairs of electrons. This is also the case for the Sb atoms in the present compound. Andersson, Åström, Galy & Meunier (1973) have shown that the structures of many oxides, fluorides and oxide fluorides of elements having lone pairs of electrons, among them Sb^{III}, can be described in an obvious way by assuming that the lone pair occupies a volume of the same size as that of an anion. The structures could in this way be considered as more or less close packed. In a cubic or hexagonal close-packed arrangement of anions and lone pairs of electrons, Sb (or other ns^2-elements) has three possible types of coordination polyhedra. The most unusual polyhedron of Sb^{III}, although common for other ns^2-elements, is the square pyramid with the lone pair of electrons at its apex.

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31589 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 4. *Interatomic distances* (Å) *and angles* (°) *in* $Sb_6O_7(SO_4)_2$

The superscripts refer to atoms at the following equivalent positions: x,y,z; (i) $-x, -y, z$; (ii) $-x, y, \frac{1}{2}+z$; (iii) $x, -y, \frac{1}{2}+z$; (iv) $\frac{1}{2}+x, \frac{1}{2}+y, z$; (v) $\frac{1}{2}-x, \frac{1}{2}-y, z$; (vi) $\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}+z$; (vii) $\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}+z$, where x,y,z refer to the coordinates listed in Table 3. Standard deviations are given in parentheses.

The Sb(1)–O polyhedron

Sb(1)–O(1)	2·025 (10)
Sb(1)–O(3^{ii})	2·122 (12)
Sb(1)–O(2)	2·167 (15)
Sb(1)–O(4)	2·331 (13)
O(1)—O(3^{ii})	2·858 (13)
O(1)—O(2)	2·936 (9)
O(1)—O(4)	3·156 (10)
O(3^{ii})–O(2)	2·558 (21)
O(3^{ii})–O(14)	2·513 (19)
O(2)—O(4)	4·248 (21)

O(1)—Sb(1)–O(3^{ii})	87·1 (6)
O(2)—Sb(1)–O(4)	141·6 (6)
O(1)—Sb(1)–O(2)	88·8 (5)
O(3^{ii})–Sb(1)–O(2)	73·2 (6)
O(1)—Sb(1)–O(4)	92·6 (4)
O(3^{ii})–Sb(1)–O(4)	68·5 (5)

The Sb(2)–O polyhedron

Sb(2)–O(2^i)	1·994 (17)
Sb(2)–O(3)	2·066 (11)
Sb(2)–O(2^{ii})	2·207 (18)
Sb(2)–O(6^{ii})	2·327 (14)
O(2^i)–O(3)	2·749 (21)
O(2^i)–O(2^{ii})	2·938 (1)
O(2^i)–O(6^{ii})	2·947 (23)
O(3)—O(2^{ii})	2·558 (21)
O(3)—O(6^{ii})	2·666 (19)
O(2^{ii})–O(6^{ii})	4·357 (23)

O(2^i)–Sb(2)–O(3)	85·2 (5)
O(2^{ii})–Sb(2)–O(6^{ii})	147·9 (5)
O(2^i)–Sb(2)–O(2^{ii})	85·2 (5)
O(2^i)–Sb(2)–O(6^{ii})	86·8 (7)
O(3)—Sb(2)–O(2^{ii})	73·5 (5)
O(3)—Sb(2)–O(6^{ii})	74·5 (5)

The Sb(3)–O polyhedron

Sb(3)–O(4^{ii})	2·011 (16)
Sb(3)–O(4)	2·014 (16)
Sb(3)–O(3^{ii})	2·154 (10)
Sb(3)–O(7^{vii})	2·382 (18)
O(4^{ii})–O(4)	2·943 (2)
O(4^{ii})–O(3^{ii})	2·806 (20)
O(4^{ii})–O(7^{vii})	7·005 (22)
O(4)—O(3^{ii})	2·513 (19)
O(4)—O(7^{vii})	2·692 (21)
O(3^{ii})–O(7^{vii})	4·348 (21)

O(4^{ii})–Sb(3)–O(4)	94·0 (2)
O(3^{ii})–Sb(3)–O(7^{vii})	146·8 (5)
O(4^{ii})–Sb(3)–O(3^{ii})	84·7 (5)
O(4^{ii})–Sb(3)–O(7^{vii})	85·9 (6)
O(4)—Sb(3)–O(3^{ii})	74·1 (5)
O(4)—Sb(3)–O(7^{vii})	75·0 (6)

The sulphate tetrahedron

S——O(5)	1·484 (20)
O(6)	1·495 (16)
O(7)	1·466 (19)
O(8)	1·460 (14)
O(5)–O(6)	2·441 (25)
O(5)–O(7)	2·415 (26)
O(5)–O(8)	2·438 (24)
O(6)–O(7)	2·396 (23)
O(6)–O(8)	2·376 (20)
O(7)–O(8)	2·394 (22)

O(5)–S–O(6)	110 (1)
O(5)–S–O(7)	110 (1)
O(5)–S–O(8)	112 (1)
O(6)–S–O(7)	108 (1)
O(6)–S–O(8)	107 (1)
O(7)–S–O(8)	110 (1)

Antimony–antimony distances

Sb(1)–Sb(3)	3·449 (2)
Sb(1)–Sb(2^i)	3·571 (2)
Sb(1)–Sb(1^i)	3·619 (3)
Sb(2)–Sb(1^{ii})	3·353 (2)
Sb(2)–Sb(3^{ii})	3·783 (2)
Sb(2)–Sb(2^{iii})	3·843 (2)
Sb(3)–Sb(1^{ii})	3·693 (2)
Sb(3)–Sb(3^{ii})	3·693 (1)

These square pyramids fit perfectly in a cubic or hexagonal close-packing of anions and lone pairs. The only Sb^{III} compound which probably has this coordination is PbSbO$_2$Cl (Sillén & Melander, 1941).

A common coordination polyhedron of Sb^{III} is the trigonal bipyramid with one of the equatorial corners occupied by the lone pair of electrons (E) [Fig. 1(a)]. Another common coordination polyhedron is the tetrahedron with the lone pair at one corner [Fig. 1(b)]. Galy, Meunier, Andersson & Åström (1975) have pointed out, as illustrated in Fig. 1, that only a slight displacement of the Sb atom out of the equatorial plane is necessary to change four- to three-coordination. It has been shown (Bovin, Svensson & Särnstrand,

1974) that, with only one exception, all known Sb^{III}–O polyhedra are intermediate between these two extremes (Fig. 1). This can be seen in Table 5, where four Sb–O distances are' given for each Sb environment. The table is arranged with the most typical trigonal bipyramids at the top and the most typical tetrahedra at the bottom, judged from the lengths of the fourth Sb–O distance. It is possible to calculate the theoretical Sb–O distances and angles for the trigonal bipyramids (Galy et al., 1975). The equatorial Sb–O distances should then be 2·00 and the axial 2·27 Å. The corresponding angles are 92·2 and 151·5°. The mean of the equatorial distances (Sb–1, Sb–2) given in Table 5 is 2·01 Å and the mean of the axial distances (Sb–3, Sb–4) for the seven first trigonal bipyramids is 2·22 Å. The corresponding angles have means of 92·0 and 148°. From these means it is clear that the experimentally found polyhedra closely correspond to the theoretically derived model. The trigonal bipyramid is one of the polyhedra which fits perfectly in a hexagonal close-packing arrangement. The tetrahedron could be found in both cubic and hexagonal close-packing arrangements.

An exception to this description is the pentagonal bipyramid found in $Sb(oxalate)_3^{3-}$ where the lone pair occupies one of the axial positions (Poore & Russell, 1971).

The three different polyhedra of Sb which exist in $Sb_6O_7(SO_4)_2$ are intermediate between the trigonal bipyramidal and the tetrahedral, i.e. the Sb atom is situated somewhat above the equatorial plane (Fig. 1). In the following description of $Sb_6O_7(SO_4)_2$ the tetrahedral model is arbitrarily used. According to Galy et al. (1975) it is possible to calculate the theoretical position of the centre of the lone pair of electrons, supposing the lone pair to occupy one of the corners of the tetrahedron. In Fig. 2 the calculated positions are drawn together with the positions of the atoms found within one unit cell. The linkage of the SbO_3 tetrahedra is illustrated in Fig. 3.

Andersson & Hyde (1974) and Hyde, Bagshaw, Andersson & O'Keeffe (1974) introduced chemical twinning on the unit-cell level for deriving a number of structures from a few parent ones. Chemical twinning is achieved in the same way as macroscopic twinning, with the same definition of twinning plane and twinning axis (Bruhns & Ramdohr, 1965; Dictionary of Geological Terms, 1962). Among minerals not only are twinnings well-known but also trillings and fourlings are found and this is also the case at unit-cell level. Thus Ru_7B_3 contains a chemical trilling (Hyde et al., 1974). A chemical fourling at unit-cell level is achieved when two twinning planes are perpendicular to each other, thus giving rise to four parts of the structure. These parts are then related to some other known structure or close packing of anions (Andersson & Bovin, 1976). A twinning plane is any plane which bears the same relation to the lattices of both parts of a twin and in this way the perpendicular c-glide planes
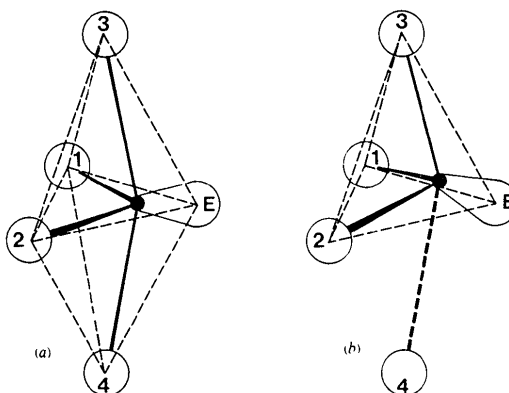

Fig. 1. The coordination polyhedra of antimony(III). (a) and (b) show idealized fourfold and threefold coordination, respectively. The notation is the same as in Table 5.
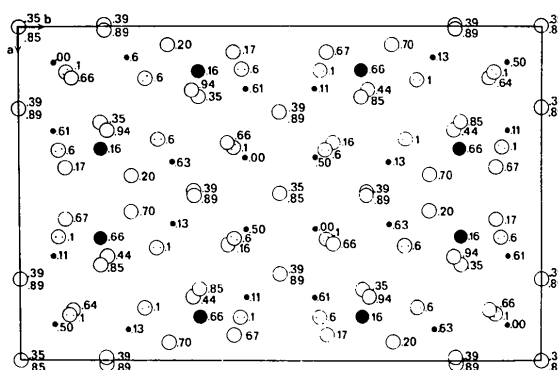

Fig. 2. Projection of the unit cell into the (001) plane. The figures indicate the z coordinates. Large open circles are oxygen, large open circles with two dots are the antimony lone pair of electrons, small black circles are antimony and large black circles are sulphur.
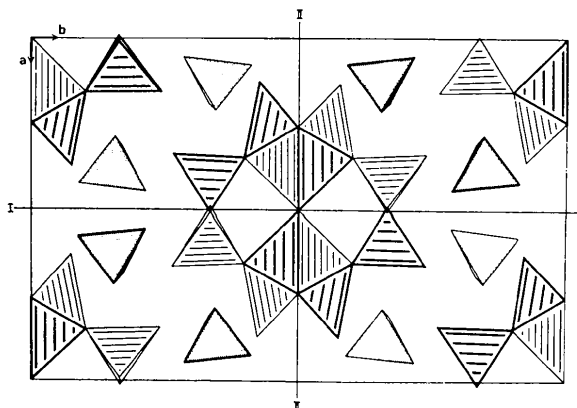

Fig. 3. The c axis projection of SbO_3 tetrahedra and the sulphate tetrahedra (shaded). The relative heights (cf. Fig. 2) of the different SbO_3 tetrahedra are indicated by the thickness of the lines. The c-glide planes I–I and II–II are also the twinning planes in the chemical fourling.

Table 5. *Distances and angles in different antimony(III)–oxygen(fluorine) coordination polyhedra*

Distances and angles are calculated from the atomic coordinates given in the references. The notation is in accordance with Fig. 1.

Compound	Sb–O(F) bond distances (Å)				Angles		Remarks	References
	Sb–1	Sb–2	Sb–3	Sb–4	1–Sb–2	3–Sb–4		
L-SbOF	1·956 (18)	1·993 (17)	2·162 (5)	2·162 (5)	96·1 (7)	142·9 (8)	1 = F⁻	Åström & Andersson (1973)
SbPO₄	1·983 (10)	2·035 (12)	2·181 (10)	2·181 (10)	87·9 (5)	164·8 (5)		Kindberger (1970)
β-Sb₂O₄	2·032 (9)	2·032 (9)	2·218 (9)	2·218 (9)	87·9 (4)	148·1 (4)		Rogers & Skapski (1964)
Sb(pyrogallate).H₂O	2·021 (8)	2·021 (8)	2·244 (4)	2·244 (4)	91·9 (5)	149·1 (1)		Särnstrand (1976b)
α-Sb₂O₄	2·011 (33)	2·043 (38)	2·209 (42)	2·259 (33)	88 (1)	148 (1)		Gopalakrishnan & Manohar (1975)
Sb₄O₄(OH)₂(NO₃)₂	2·019 (6)	2·020 (6)	2·236 (6)	2·265 (6)	98·3 (2)	141·6 (2)		Bovin (1974a)
SbO(H₂PO₄).H₂O	1·970 (8)	1·977 (8)	2·145 (9)	2·291 (10)	94·4 (3)	156·3 (3)		Särnstrand (1974)
M-SbOF	2·006 (13)	2·012 (13)	2·038 (13)	2·304 (15)	98·4 (5)	146·2 (4)	3 = F⁻	Åström & Andersson (1971)
Sb₆O₇(SO₄)₂	1·994 (17)	2·066 (11)	2·207 (18)	2·327 (14)	85·2 (5)	147·9 (5)		This work
SbNbO₄	2·008 (9)	2·035 (9)	2·134 (9)	2·331 (13)	92·1 (4)	150·7 (4)		Skapski & Rogers (1965)
Sb₆O₇(SO₄)₂	2·025 (10)	2·128 (12)	2·167 (15)	2·331 (13)	87·1 (7)	141·1 (6)		This work
Sb₃O₃(OH)ClO₄.¼H₂O	1·952 (9)	2·030 (9)	2·145 (9)	2·350 (9)	93·7 (4)	141·3 (3)		Bovin (1974b)
M-SbOF	1·952 (12)	1·987 (15)	2·062 (12)	2·364 (13)	89·9 (6)	144·0 (6)	1 = F⁻	Åström & Andersson (1971)
Sb₄O₅(OH)ClO₄.½H₂O	1·952 (9)	2·009 (9)	2·085 (9)	2·378 (8)	91·2 (4)	144·5 (3)		Bovin (1974b)
Sb₂O₇(SO₄)₂	2·011 (16)	2·014 (17)	2·154 (10)	2·382 (19)	94·0 (2)	146·8 (5)		This work
Sb₄O₅Cl₂	1·902 (1)	2·061 (5)	2·144 (6)	2·469 (6)	91·8 (2)	139·0 (2)		Edstrand (1947), Särnstrand (1976a)
Sb₂O₃.2SO₃	1·894 (5)	2·122 (10)	2·161 (10)	2·490 (11)	91·3 (4)	156·0 (3)		Mercier et al. (1975)
Sb₄O₅(OH)ClO₄.½H₂O	1·975 (9)	1·997 (8)	2·027 (8)	2·572 (10)	94·8 (4)	142·8 (3)		Bovin (1974b)
Sb₂O₃ (orthorhombic)	1·977 (7)	2·023 (4)	2·019 (6)	2·619 (6)	98·1 (2)	139·3 (2)		Svensson (1974)
Sb₅O₇I	1·935 (19)	1·978 (18)	2·091 (15)	2·782 (19)	94·6 (8)	148·0 (6)		Krämer (1975)
Sb₄O₄(OH)₂(NO₃)₂	1·942 (7)	2·067 (6)	2·052 (6)	2·745 (9)	82·9 (3)	152·7 (3)		Bovin (1974a)
Sb₅O₇I	1·955 (17)	1·965 (18)	2·063 (14)	2·794 (17)	91·3 (7)	150·2 (6)		Krämer (1975)
Sb₄O₅Cl₂	1·931 (6)	2·015 (5)	2·080 (6)	2·905 (3)	94·8 (3)	153·9 (2)	4 = Cl⁻	Edstrand (1947), Särnstrand (1976a)
Fe₄Ti₃SbO₁₃(OH)	2·006 (3)	2·009 (4)	2·006 (3)	2·918 (3)	92·5 (1)	155·4 (1)		Moore & Araki (1976)
Sb₂O₃ (cubic)	1·977 (1)	1·977 (1)	1·977 (1)	2·918 (2)	96·0 (3)	160·9 (9)		Svensson (1975)
Sb₅O₇I	1·962 (19)	1·988 (16)	2·001 (18)	2·988 (16)	94·1 (7)	134·3 (6)		Krämer (1975)
Sb₅O₇I	1·959 (16)	1·961 (17)	2·024 (16)	3·042 (18)	89·4 (7)	149·2 (6)		Krämer (1975)
Sb₅O₇I	1·949 (17)	2·000 (19)	2·016 (17)	3·086 (17)	89·5 (7)	146·8 (6)		Krämer (1975)

of $Sb_6O_7(SO_4)_2$ could be considered as twinning planes. Fig. 3 shows how these two twinning planes I–I and II–II divide the unit cell of $Sb_6O_7(SO_4)_2$ into four parts. Each fourth of the unit cell consists in its turn of a left and a right half, containing distorted hexagonally close-packed O and a lone pair of electrons. The structure of $Sb_6O_7(SO_4)_2$ could thus be considered as a chemical fourling.

In almost all compounds containing twins at the unit-cell level, the twinning plane has polyhedra which are different from those found in the parent structure. This is also the case in the present structure, where the line intersecting the twinning plane contains a special point position, O(1), not fitting into the hexagonally close-packed pattern. Therefore the tetrahedron of Sb(1) has rather long Sb–O distances.

The hexagonally close-packed part in each fourth of the unit cell is repeated at the centre by the symmetry of the two twinning planes, to form a cylindrical unit. This unit has a much shorter radius than that found in $K_3SbS_3.3Sb_2O_3$ (Graf & Schäfer, 1975). Contrary to the present structure that cylindrical unit is large enough to contain six cations.

O(5), O(6), O(7) and O(8) and the S atom form the tetrahedral SO_4^{2-} ion. The distances and O–S–O angles (Table 4) are normal (*International Tables for X-ray Crystallography*, 1962). In the sulphate tetrahedra O(6) and O(7) are weakly bonded to Sb(2) and Sb(3), respectively (Fig. 4). O(5) and O(8) are not bonded to Sb.

$Sb_2O_3.2SO_3$ (Mercier, Douglade & Theobald, 1975) contains the complex $Sb_2O(SO_4)_2$ in an arrangement which shows no resemblance to the present structure.

The stoichiometry of $Sb_6O_7(SO_4)_2$ and the water analysis show that Jander & Hartmann (1965) probably made their investigation on an incompletely dried material and that Hintermann & Venuto (1968) were closer to the correct stoichiometry when they proposed the formula $3Sb_2O_3.2SO_3$.

Andersson *et al.* (1973) have shown that in compounds with a closed-packed arrangement of anions (*e.g.* O^{2-}, F^-) and lone pairs of electrons, the volume of the unit cell divided by the number of anions and lone pairs is between 15·2 and 19·4 Å³. The corresponding value for $Sb_6O_7(SO_4)_2$ is 16·1 Å³ which indicates that its anions and lone pairs are effectively close-packed.

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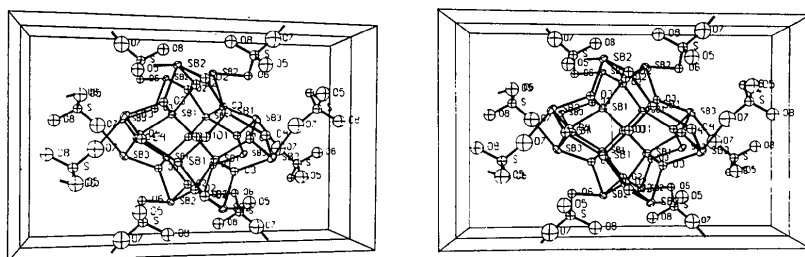
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Fig. 4. Stereo view down the c axis of the structure of $Sb_6O_7(SO_4)_2$.

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Charge Density Studies Below Liquid Nitrogen Temperature. II. Neutron Analysis of p-Nitropyridine N-Oxide at 30K and Comparison with X-ray Results

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The earlier 30K X-ray analysis of p-nitropyridine N-oxide has been complemented with a low-temperature neutron diffraction study. Analysis of the X–N deformation densities at different data cut-off values indicates an effect of series termination on lone-pair and also bond densities, which can be accounted for by a quantitative analysis within a single Gaussian approximation to the density peaks. The nitroxo group lone-pair densities are situated at right angles to the NO bond axis. Comparison with other X–N densities leads to differences in hybridization between NO and CO oxygen atoms, the former having a p σ-bonding orbital and non-hybridized s and p lone-pair orbitals. No bonding electrons are observed in the terminal NO bonds.

Introduction

The present study is a continuation of the charge density analysis of p-nitropyridine N-oxide described recently (Wang, Blessing, Ross & Coppens, 1976). To complement the earlier work, neutron data have been collected at the high-flux beam reactor of the Institut Laue–Langevin. Of special interest are the nature of the bonding in the nitroxo and nitro substituents, the resolution achievable and the magnitude of series termination effects in charge density studies at very low temperatures.

Data collection and refinement

Neutron data were collected on the four-circle diffractometer D10 located at a thermal neutron guide of the Institut Laue–Langevin high-flux beam reactor. Low temperature was achieved with a liquid He cryostat (Claudet, Tippe & Yelon, 1976) which has a tem-

perature stability of better than 0·5°. Cell dimensions were taken from the earlier X-ray analysis and are listed with other crystallographic information in Table 1.

Table 1. *Crystal data*

Numbers in parentheses here and under similar conditions throughout the paper are estimated standard deviations in units of the last digit.

Space group *Pnma*; $Z=4$; $\mu=1\cdot52$ (2) cm^{-1}; $\varrho_c=1\cdot637$ g cm^{-3}
$a=12\cdot498$ (6), $b=5\cdot814$ (2), $c=7\cdot824$ (2) Å

$(\sin \theta/\lambda)_{max}$: 0·55 Å^{-1}
Measurement temperature: 30K
Total number of reflexions: 1456
Number of unique reflexions: 451

A crystal 13·5 mm^3 showing the forms $\{111\}$, $\{100\}$ and the face (001) was used for data collection and oriented with **c** close to, but not coinciding with, the φ axis of the diffractometer. The construction of the cryostat prevents centring after cooling, but crystal orientation and measurements at both positive and

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