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## Structure of an Oxonium Antimony(III) Sulphate, $(\text{H}_3\text{O})_2\text{Sb}_2(\text{SO}_4)_4$

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**Abstract.**  $M_r = 665.8$ , orthorhombic, space group  $Pbc2_1$ ,  $a = 11.085$  (2),  $b = 13.760$  (2),  $c = 8.919$  (3) Å,  $Z = 4$ ,  $V = 1360.4$  Å<sup>3</sup>,  $D_x = 3.25$  Mg m<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.71069$  Å,  $\mu = 4.7$  mm<sup>-1</sup>,  $T = 293$  K. Final  $R = 0.038$  for 896 independent reflections. The structure is polymeric with sheets in which  $-\text{Sb}-\text{O}-\text{S}-$  chains are linked together by  $\text{SO}_4$  groups; an unusual  $\text{SbO}_3E$  polyhedron is described with one strong axial  $\text{Sb}-\text{O}$  bond [2.012 (15) Å] and four equatorial  $\text{Sb}-\text{O}$  bonds [between 2.214 (12) and 2.263 (13) Å]. Oxonium cations lie between the layers and interact with them by strong hydrogen bonds (mean  $\text{O}\cdots\text{O}$  distance = 2.60 Å).

**Introduction.** This structure was examined as part of a systematic study of the influence of the lone pairs  $E$  in  $\text{SbO}_nE$  coordination. We hope to account for the differences between  $\text{SbO}_nE$  and  $\text{AsO}_nE$  polyhedra in similar 'sulphate' compounds in terms of ionic radii and the degree of covalency of the  $M-\text{O}$  bonds ( $M = \text{As}, \text{Sb}$ ). For arsenic(III) compounds such as  $\text{As}_2(\text{SO}_4)_3$  (Douglade & Mercier, 1982),  $\text{As}_2\text{O}(\text{SO}_4)_2$  (Mercier & Douglade, 1982*b*) and  $\text{As}_2\text{O}_2(\text{SO}_4)$  (Mercier & Douglade, 1982*a*) only  $\text{AsO}_3E$  tetrahedra have been observed. On the other hand, in antimony 'sulphates', the coordination number of Sb is greater, and  $\text{SbO}_4E$  polyhedra are often observed; e.g.  $\text{Sb}_2\text{O}(\text{SO}_4)_2$  (Mercier, Douglade & Theobald, 1975),  $\text{Sb}_2(\text{SO}_4)_3$  (Mercier, Douglade & Bernard, 1976),  $\text{Sb}_6\text{O}_7(\text{SO}_4)_2$  (Bovin, 1976), and  $\text{Sb}_2(\text{OH})_2(\text{SO}_4)_2 \cdot 2\text{H}_2\text{O}$  (Douglade, Mercier

& Vivier, 1978). Recently an unusual  $\text{SbO}_3E$  coordination has been described by us in  $\text{Sb}_4\text{O}_2(\text{OH})(\text{SO}_4)_4(\text{H}_5\text{O}_2) \cdot \text{H}_2\text{O}$  (Douglade & Mercier, 1980). In addition, such compounds may be good ionic proton conductors (Watelet, Picard, Baud, Besse & Chevalier, 1981), which could be of use in solid-state batteries. We also undertook this structural study to determine the composition and degree of hydration.

**Experimental.** Single crystals obtained at 293 K from a solution of  $\text{Sb}_2\text{O}_3$  (20 g l<sup>-1</sup>) dissolved in  $\text{H}_2\text{SO}_4$  (~17 *M*). Chemical analysis ( $\text{Sb}^{3+}$  and  $\text{SO}_4^{2-}$ ) of the mother liquor and the wet polycrystalline substrate only enabled us to show that the composition of the pure solid state lies between the 'limiting formulae'  $\text{Sb}_2\text{O}_3 \cdot 2\text{SO}_3$  and  $\text{Sb}_2\text{O}_3 \cdot 5\text{SO}_3 \cdot 4.5\text{H}_2\text{O}$ , since the new phase appears only in a sharp concentration range in strong sulphuric acid ( $1.40 < x < 1.52$  for  $\text{SO}_3 \cdot x\text{H}_2\text{O}$ ). On removal from the sulphuric acid solution, the crystals revert rapidly to the anhydrous compound  $\text{Sb}_2\text{O}(\text{SO}_4)_2$  and, because of this instability, the specific gravity was not determined.

Wet single crystals sealed in Lindemann tubes employed for X-ray measurement, systematic absences ( $0kl \rightarrow k = 2n + 1$ ;  $h0l \rightarrow l = 2n + 1$ ) in the orthorhombic system indicated space group  $Pbcm$  or  $Pbc2_1$ , crystal approximately  $0.2 \times 0.2 \times 0.25$  mm used for data collection, automated Nonius CAD-4 four-circle diffractometer of the Lyon-1 University, graphite monochromator,  $\text{Mo } K\alpha$  radiation, cell dimensions

obtained by least squares from setting angles of 25 reflections ( $15 < \theta < 25^\circ$ ); intensities of 1652 independent reflections with  $2\theta < 64^\circ$  determined,  $\omega$ - $2\theta$  scan technique, intensity of one standard reflection measured every 100 min of X-ray exposure varied by no more than 2% about its mean, Lp corrections applied but no absorption correction made ( $\mu R \sim 0.5$ ), 896 with  $I > 2\sigma(I)$  considered observed and used in structure refinement.

In oxide derivatives with lone pairs  $E$ , the space is filled by compact stacking of  $\text{O}^{2-}$  and  $E$  pairs both of which occupy mean volumes of about  $16 \text{ \AA}^3$  (Galy, Meunier, Andersson & Astrom, 1975). The number of Sb atoms per cell, based on the possible formulae, should be between 8 and 16. Unsuccessful attempts in  $Pbcm$  led us to attempt the structure solution in the non-centrosymmetric space group  $Pbc2_1$ .

Two Sb atoms located from Patterson map, successive Fourier syntheses revealed S and O atoms but no further heavy atoms; full-matrix refinement with *SHELX* 76 (Sheldrick, 1976) with anisotropic Sb and S atoms and isotropic O atoms and an empirical extinction correction [ $F_e = F_c(1 - xF_c^2/\sin\theta)$ ] with  $x = 4.2 \times 10^{-4}$  led to a final  $R_w^* = \sum w^{1/2} |F_o| - |F_c| / \sum w^{1/2} F_o = 0.034$ , weighting scheme  $w = 0.8973 / [\sum \sigma^2(F_o) + 0.0007 F_o^2]$ , no H atoms clearly evident in final difference Fourier synthesis, highest residual electron density being  $1.0 \text{ e \AA}^{-3}$ ,  $F(000) = 1264$ , scattering factors of neutral Sb, S and O atoms taken from Cromer & Mann (1968), anomalous-dispersion terms included (Cromer & Liberman, 1970).

**Discussion.** Final positional parameters are given in Table 1.

The structure consists of sheets related by an  $a$  translation. The (100) projection of the structure (Fig. 1) shows one sheet. The skeleton of these sheets consists of alternating Sb—O—S atoms,  $b/4$  apart, running parallel to the [001] axis. These chains are linked together by O—S—O bridges [S(1) and S(4)]; the Sb(2) lie at  $x \sim 0$ , while on each side, the Sb(1) chains are alternately at  $x \sim -\frac{1}{4}$  and  $x \sim \frac{1}{4}$ . As the  $x$  axis is long ( $11.085 \text{ \AA}$ ), no direct interactions between two sheets can occur; the oxonium O atoms, however, occupy the space between layers and play an important role in stabilizing the structure.

The sulphate ions have an almost regular tetrahedral shape (Table 2); three of the four independent ones (1, 3 and 4) have terminal  $\text{SO}_2$  groups with a mean S—O length of  $1.45 \text{ \AA}$ ; the bridging O—S—O group is characterized by somewhat longer bonds ( $\sim 1.49 \text{ \AA}$ ); this small difference also occurs in several 'antimony

sulphates' quoted in the *Introduction*. The S(2) sulphate is tridentate.

Charge neutrality involves the existence of six 'protons' in the asymmetric unit. None of the 16 O atoms of  $\text{SO}_4$  groups can be bonded to H atoms because of their high valency number  $\nu$  (between 1.5 and 2.1) calculated with the formulations of Donnay & Allman (1970) and of Brown & Shannon (1973); a value of about 1.0 would be appropriate for OH groups. Moreover, an S—O bond length greater than about  $1.55 \text{ \AA}$  is expected for S—OH groups (Gustafsson, Lundgren & Olovsson, 1977). Thus the free O(1) and O(2) atoms (with  $\nu = 0$ ) must be protonated. Their environment is very typical of  $\text{H}_3\text{O}^+$

Table 1. Atomic coordinates ( $\times 10^4$ ) and isotropic thermal parameters ( $\text{\AA}^2 \times 10^4$ )

	$x$	$y$	$z$	$U$
Sb(1)	-2485 (1)	-2191 (1)	-8320	137 (5)*
Sb(2)	143 (1)	-102 (1)	-6667 (3)	150 (5)*
S(1)	56 (4)	-2213 (3)	-5184 (8)	156 (25)*
S(2)	-2241 (4)	83 (3)	-8984 (7)	143 (31)*
S(3)	-4645 (4)	-2683 (3)	-10842 (8)	143 (25)*
S(4)	2345 (5)	325 (3)	-8998 (7)	136 (34)*
O(1)	-4975 (10)	-4874 (8)	-6776 (26)	254 (28)
O(2)	2823 (10)	-2310 (9)	-8594 (20)	210 (32)
O(11)	-1103 (10)	-2740 (8)	-5184 (20)	210 (28)
O(12)	54 (10)	-1576 (7)	-6589 (26)	222 (26)
O(13)	101 (11)	-1594 (9)	-3879 (18)	223 (29)
O(14)	1050 (11)	-2896 (9)	-5292 (21)	257 (32)
O(21)	-3121 (11)	-742 (8)	-9054 (18)	186 (29)
O(22)	-1074 (9)	-372 (7)	-8379 (24)	164 (24)
O(23)	-2002 (10)	448 (9)	-10495 (18)	175 (26)
O(24)	-2661 (10)	846 (8)	-7979 (18)	224 (32)
O(31)	-3376 (11)	-2548 (9)	-10206 (18)	211 (29)
O(32)	-5166 (11)	-3553 (9)	-10194 (19)	241 (30)
O(33)	-4394 (12)	-2769 (10)	-12494 (20)	233 (33)
O(34)	-5367 (11)	-1832 (8)	-10568 (19)	198 (29)
O(41)	2391 (10)	1186 (8)	-7979 (16)	168 (27)
O(42)	1294 (10)	-299 (8)	-8421 (26)	223 (28)
O(43)	3451 (11)	-242 (8)	-8863 (17)	185 (31)
O(44)	2034 (11)	600 (9)	-10533 (19)	214 (28)

$$* U_{\text{eq}} = (U_{11}U_{22}U_{33})^{1/3}.$$

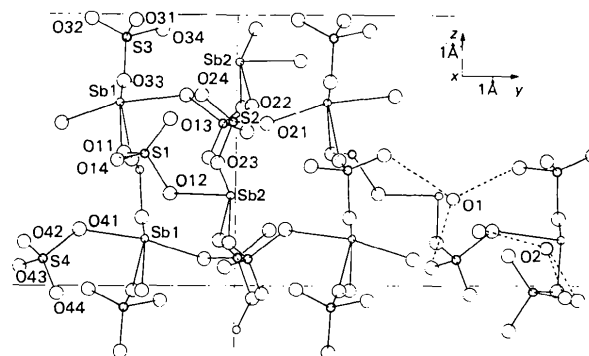


Fig. 1. Projection of the structure of  $(\text{H}_3\text{O})_2\text{Sb}_2(\text{SO}_4)_4$  along [100]. The two  $\text{H}_3\text{O}^+$  [O(1) and O(2)] cations appear near Sb(2) and Sb(1) atoms respectively, but shifted from  $a/2$ . We have put them only on the right side of the picture to show their coordination by strong O—H...O hydrogen bonds indicated by broken lines.

\* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38197 (6 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. Bond lengths (Å) and angles (°) in the SO<sub>4</sub> tetrahedra with their e.s.d.'s

S(1)O <sub>4</sub>		S(2)O <sub>4</sub>		S(3)O <sub>4</sub>		S(4)O <sub>4</sub>	
S(1)—O(11)	1.475 (12)*	S(2)—O(21)	1.498 (12)*	S(3)—O(31)	1.528 (13)*	S(4)—O(41)	1.494 (13)*
S(1)—O(12)	1.529 (20)*	S(2)—O(22)	1.535 (12)*	S(3)—O(33)	1.504 (18)*	S(4)—O(42)	1.536 (14)*
S(1)—O(13)	1.443 (15)	S(2)—O(23)	1.462 (16)*	S(3)—O(32)	1.449 (14)	S(4)—O(43)	1.458 (12)
S(1)—O(14)	1.451 (12)	S(2)—O(24)	1.457 (14)	S(3)—O(34)	1.439 (13)	S(4)—O(44)	1.462 (17)
O(11)—S(1)—O(12)	106.3 (9)*	O(21)—S(2)—O(22)	104.7 (7)*	O(31)—S(3)—O(32)	108.6 (9)	O(41)—S(4)—O(42)	105.4 (9)*
O(11)—S(1)—O(13)	108.7 (9)	O(21)—S(2)—O(23)	109.9 (9)*	O(31)—S(3)—O(33)	101.7 (8)*	O(41)—S(4)—O(43)	110.2 (8)
O(11)—S(1)—O(14)	110.0 (7)	O(21)—S(2)—O(24)	111.3 (8)	O(31)—S(3)—O(34)	110.5 (8)	O(41)—S(4)—O(44)	111.9 (8)
O(12)—S(1)—O(13)	108.8 (7)	O(22)—S(2)—O(23)	108.1 (9)*	O(32)—S(3)—O(33)	113.5 (1.0)	O(42)—S(4)—O(43)	108.1 (7)
O(12)—S(1)—O(14)	108.5 (9)	O(22)—S(2)—O(24)	110.3 (9)	O(32)—S(3)—O(34)	112.5 (8)	O(42)—S(4)—O(44)	106.2 (1.0)
O(13)—S(1)—O(14)	114.2 (9)	O(23)—S(2)—O(24)	112.2 (8)	O(33)—S(3)—O(34)	109.5 (1.0)	O(43)—S(4)—O(44)	114.5 (9)

\* These bonds belong to S—O—Sb bridges while the other ones which are shorter are terminal bonds.

oxonium cations (Fig. 1, Table 3). Both are coordinated to three O atoms at a mean distance of 2.60 Å and with the three O...O...O angles lying between 100 and 126°. This angular distribution, along with the short O...O distances, implies that each central oxygen O(1) and O(2) corresponds to an H<sub>3</sub>O<sup>+</sup> species. For typical H<sub>3</sub>O<sup>+</sup> ions in crystal structures, O...O is about 2.57 Å with a mean O...O...O angle of 109.3° (Lundgren & Olovsson, 1976). These oxonium ions interact by strong hydrogen bonds with each of two layers, stabilizing the structure. The appreciable distance (4.42 Å) between two neighbouring H<sub>3</sub>O<sup>+</sup> species does not favour proton diffusion in this structure.

Galy *et al.* (1975) have shown that the lone pairs *E* in numerous oxide compounds (As<sup>III</sup>, Sb<sup>III</sup>, Pb<sup>II</sup>, Sn<sup>II</sup>) fill a mean volume of about 16 Å<sup>3</sup> which is identical to that filled by an O<sup>2-</sup> ion, so that many structures can be described in terms of close packing (cubic or hexagonal) of O<sup>2-</sup> and *E* pairs, the metals lying either in O<sub>3</sub>*E* tetrahedra or in O<sub>4</sub>*E* trigonal bipyramids at a distance of about 1 Å from the theoretical *E* location. In the structure reported here, the mean volume is 17 Å<sup>3</sup> and two different SbO<sub>4</sub>*E* polyhedra are involved (Table 4). The Sb(2) atom is surrounded by two equatorial O atoms (Sb—O ~ 2.035 Å) while the two others are respectively at 2.071 (17) and 2.359 (19) Å; this configuration is intermediate between SbO<sub>3</sub>*E* and SbO<sub>4</sub>*E*.

The Sb(1) configuration is more interesting since we can describe it as an SbO<sub>5</sub>*E* octahedron with one Sb—O axial strong bond [2.012 (15) Å] and four equatorial bonds (mean value ~ 2.24 Å). This coordination has been demonstrated and discussed in a previous work (Douglade & Mercier, 1980) where two similar SbO<sub>5</sub>*E* octahedra shared one O(ax)—O(eq) edge. In this structure, this polyhedron is discrete: the Sb atom is positioned above the four equatorial atoms near the axial lone pair *E*. The octahedron O<sub>5</sub>*E* is distorted with axial—equatorial O...O lengths (2.70 Å) shorter than the equatorial distances (3.11 Å), as was previously found (Douglade & Mercier, 1980).

This structure determination allowed us first to determine the true chemical composition of these

unstable crystals and, secondly, to prove the existence of H<sub>3</sub>O<sup>+</sup> species which could not be assigned by chemical and spectroscopic analyses. One can consider that this new phase appears in strong sulphuric acid

Table 3. Environment of the H<sub>3</sub>O<sup>+</sup> ions

Distances in Å, angles in °.			
H <sub>3</sub> O(1) <sup>+</sup>		H <sub>3</sub> O(2) <sup>+</sup>	
O(1)...O(32)	2.59 (2)	O(2)...O(14)	2.50 (2)
O(1)...O(34)	2.62 (2)	O(2)...O(24)	2.60 (2)
O(1)...O(43)	2.56 (2)	O(2)...O(34)	2.75 (2)
O(32)—O(1)—O(34)	122 (2)	O(14)—O(2)—O(24)	101 (2)
O(32)—O(1)—O(43)	101 (2)	O(14)—O(2)—O(34)	99 (2)
O(34)—O(1)—O(43)	126 (2)	O(24)—O(2)—O(34)	115 (2)

Table 4. Bond lengths (Å) and angles (°) in the SbO<sub>4</sub> and SbO<sub>5</sub> polyhedra with their e.s.d.'s

Sb(1)O <sub>5</sub> <i>E</i>		Sb(2)O <sub>4</sub> <i>E</i>	
Sb—O(ax)		Sb—O(eq)	
Sb(1)—O(31)	2.012 (15)	Sb(2)—O(12)	2.032 (10)
		Sb(2)—O(42)	2.037 (19)
Sb—O(eq)		Sb—O(ax)	
Sb(1)—O(11)	2.263 (13)	Sb(2)—O(22)	2.071 (17)
Sb(1)—O(21)	2.214 (12)	Sb(2)—O(23)	2.359 (19)
Sb(1)—O(33)	2.241 (14)		
Sb(1)—O(41)	2.256 (14)	O(eq)—Sb(2)—O(eq)	
O(ax)—Sb(1)—O(eq)		O(12)—Sb(2)—O(42)	85.6 (6)
O(31)—Sb(1)—O(11)	73.0 (6)	O(eq)—Sb(2)—O(ax)	
O(31)—Sb(1)—O(21)	79.4 (5)	O(12)—Sb(2)—O(22)	79.3 (6)
O(31)—Sb(1)—O(33)	78.8 (6)	O(12)—Sb(2)—O(23)	80.0 (7)
O(31)—Sb(1)—O(33)	83.9 (6)	O(42)—Sb(2)—O(22)	79.5 (5)
O(31)—Sb(1)—O(41)	83.9 (6)	O(42)—Sb(2)—O(23)	76.5 (7)
O(ax)...O(eq)		O(ax)—Sb(2)—O(ax)	
O(31)...O(11)	2.55 (2)	O(22)—Sb(2)—O(23)	149.3 (8)
O(31)...O(21)	2.70 (2)		
O(31)...O(33)	2.70 (2)		
O(31)...O(41)	2.86 (2)		
Mean	2.70		
O(eq)...O(eq)			
O(11)...O(21)	3.22 (2)		
O(21)...O(33)	2.85 (2)		
O(33)...O(41)	3.14 (2)		
O(41)...O(11)	3.23 (2)		
Mean	3.11		

media in which the dissolution of  $\text{Sb}_2\text{O}_3$  breaks all the Sb—O—Sb bridges to give 'free'  $\text{Sb}^{3+}$  ions surrounded by  $\text{SO}_4^{2-}$  ions; on cooling, the crystallization involves the inclusion of  $\text{H}_3\text{O}^+$  ions between the polymeric layers.

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## Eisen(II,III)germaniumoxid $\text{Fe}_{3,2}\text{Ge}_{1,8}\text{O}_8$

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**Abstract.**  $M_r = 437.4$ , monoclinic,  $P2_1/c$ ,  $a = 8.479$  (9),  $b = 8.333$  (3),  $c = 9.196$  (15) Å,  $\beta = 117.7$  (1)°,  $V = 575$  (1) Å<sup>3</sup>,  $Z = 4$ ,  $D_m = 5.04$  (5),  $D_x = 5.05$  Mg m<sup>-3</sup>,  $\lambda$  (Mo  $K\alpha$ ) = 0.71069 Å,  $\mu = 16.7$  mm<sup>-1</sup>. The structure was determined with 3191 X-ray diffraction intensities and refined to  $R = 0.046$ . The O atoms form an arrangement similar to the cubic closest packing of spheres; the Fe atoms occupy octahedral sites and the Ge atoms tetrahedral ones forming  $\text{Ge}_2\text{O}_7$  groups. One of the tetrahedral sites is partly occupied by Fe atoms.

**Einleitung.** Nach Takayama, Kimizuka, Kato, Yamamura & Haneda (1981), Takayama & Kimizuka (1981) sowie Takayama, Kimizuka, Kato & Yamamoto (1982) existieren im Dreistoffsystem  $\text{GeO}_2$ – $\text{FeO}$ – $\text{Fe}_2\text{O}_3$  bei 1273 K fünf ternäre Verbindungen. Eine von ihnen,  $\text{Fe}_{3-x}\text{Ge}_x\text{O}_4$  ( $0 \leq x \leq 1$ ), bildet eine kontinuierliche Mischkristallreihe mit Spinell- bzw. Magnetitstruktur. Eine andere,  $\text{Fe}_{1,07}\text{Ge}_{0,93}\text{O}_3$ , kristallisiert in einer orthorhombischen Struktur des Pyroxentyps.  $\text{Fe}_{15}\text{Ge}_8\text{O}_{36}$  kristallisiert triklin in einer Struktur, in der die O-Atome nach der Art der kubisch dichten Kugelpackung angeordnet sind (Kato, Takayama,

Kimizuka, Haneda & Yamamura, 1983). Für  $\text{Fe}_{3,2}\text{Ge}_{1,8}\text{O}_8$  liegt ein vorläufiger Strukturvorschlag vor (Kato, Takayama & Kimizuka, 1979), dem die seinerzeit angenommene Zusammensetzung  $\text{Fe}_3\text{Ge}_2\text{O}_8$  zugrunde gelegt wurde.  $\text{Fe}_{5,33}\text{Ge}_{2,67}\text{O}_{12}$  [in unserer früheren Arbeit (Takayama, Kimizuka, Kato, Yamamura & Haneda, 1981):  $\text{Fe}_4\text{Ge}_2\text{O}_8$ ] weist Satellitenreflexe auf, die sich nicht ganzzahlig indizieren lassen. Seine Struktur wird zur Zeit im hiesigen Institut untersucht. Im Rahmen der vorliegenden Arbeit wird das Ergebnis einer Strukturverfeinerung von  $\text{Fe}_{3,2}\text{Ge}_{1,8}\text{O}_8$  mitgeteilt und erörtert

**Experimentelles.** Der vorliegenden Strukturverfeinerung wurden dieselben Kristalldaten und Intensitätsdaten zugrunde gelegt, die von Kato, Takayama & Kimizuka (1979) für die Strukturbestimmung von 'Fe<sub>3</sub>Ge<sub>2</sub>O<sub>8</sub>' benutzt worden waren. Die von ihnen seinerzeit nicht mitgeteilten experimentellen Einzelheiten werden im folgenden kurz angegeben.

Kristallgestalt dreieckiges Plättchen mit abgestumpften Ecken, 0,10 × 0,08 × 0,03 mm, Gitterkonstanten aus 10  $2\theta$ -Werten gemessen auf einem Einkristalldiffraktometer (Fa. Rigaku), Intensitäten von 9779 Reflexe gemessen durch  $\omega$ -Abtastung für  $2\theta <$

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