American Mineralogist, Volume 65, pages 931–935, 1980

The crystal structure of klebelsbergite, $Sb_4O_4(OH)_2SO_4$

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Abstract

Klebelsbergite is an antimony sulfate found at Felsöbánia, Hungary, and recently at Pereta, Tuscany, Italy. Crystal data are: $a = 5.766(2)$, $b = 11.274(2)$, $c = 14.887(2)$Å; space group $Pca2_1$; $Z = 4$. The atomic positions were determined by direct methods and refined by least-squares calculations to an R index of 0.045 for 1111 observed reflections.

The basic structural units are the Sb^{III}–O polyhedra and the SO_4 tetrahedron. Antimony polyhedra show, as usual, intermediate features between the SbO_3E tetrahedron and the SbO_4E trigonal bipyramid, where E indicates the unshared lone pair of electrons. These polyhedra are connected to each other by edge sharing to form Sb–O sheets parallel to (001). Adjacent sheets are linked together by SO_4 tetrahedra and, indirectly, by H-bonds. Taking into account anions and lone pairs, the volume occupied by each anion is similar to that found in close-packed structures. A marked pseudosymmetry (towards the centric group *Pcan*) is present in the Sb–O sheet.

Introduction

Klebelsbergite from Felsöbánia, Hungary, was first described by Zsivny (1929); however, the first complete description of the mineral is by Nakai and Appleman (1980). A second occurrence of klebelsbergite, at Pereta mine (Tuscany, Italy), is reported by Cipriani *et al.* (1980a). A synthetic compound equivalent to klebelsbergite was prepared by Nakai and Appleman by boiling Sb_2O_3 with sulfuric acid. The same compound was also obtained by researchers of the Laboratoire de Chimie-Physique, Besançon, France (Douglade, personal communication).

In recent years several Sb^{3+}–O compounds have been structurally studied and much attention has been directed towards the stereochemistry of elements with one unshared electron pair. Our work was undertaken in order to contribute to the crystal-chemistry knowledge of these compounds. Another question was the full knowledge of the chemical composition of klebelsbergite and if the true crystal-chemical formula was $Sb_4O_4(OH)_2SO_4$ or $Sb_4O_5SO_4 \cdot H_2O$.

Experimental

For our study a small (approx. $0.1 \times 0.1 \times 0.5$ mm) colorless crystal was chosen from a sample we collected at Pereta. Crystal data are: $a = 5.766(2)$, $b = 11.274(2)$, $c = 14.887(2)$Å, $V = 967.7$Å^3; $Z = 4$, $D_x = 4.67$ g cm^{-3}, formula weight 681.1. The space group, determined from the extinctions, is *Pcam* or $Pca2_1$. The latter is the correct one on the basis of the structure determination.

Intensities were collected with a Philips *PW 1100* four-circle computer-controlled diffractometer (Centro di Cristallografia Strutturale del C.N.R., Pavia, Italy), with Mo$K\alpha$ radiation and the ω–2θ scan technique. A total of 1469 independent reflections, in the range $2 < \theta < 30°$ were measured; only 1111 were considered to be actually observed according to the criterion $F_o > 5\sigma(F_o)$. Intensities were corrected for Lorentz-polarization effects; an absorption correction was carried out on the basis of the semiempirical method proposed by North *et al.* (1968).

Structure determination and refinement

As statistical tests did not give a clear indication on the absence of the symmetry center, the first attempts to solve the crystal structure of klebelsbergite were performed in the centric space group *Pcam*, which was later found to be incorrect. Other difficulties were presented by the incomplete knowledge of the chemical composition. The structure was solved by direct methods, using MULTAN (Main *et al.*, 1974). However, many successive three-dimensional Fou-

0003–004X/80/0910–0931$02.00

Table 1. Klebelsbergite: fractional atomic coordinates and thermal parameters

Atom	x	y	z	B eq.*	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Sb(1)	0.4789(2)	0.3596(2)	0.25	1.18	59(3)	29(1)	14(1)	5(2)	4(1)	1(1)
Sb(2)	0.3917(2)	0.0874(2)	0.0914(2)	0.86	60(3)	19(1)	9(1)	4(2)	0(1)	0(1)
Sb(3)	0.1526(2)	0.4078(2)	0.4322(2)	0.84	56(3)	20(1)	9(1)	5(2)	-2(1)	1(1)
Sb(4)	0.0483(2)	0.1412(2)	0.2673(1)	1.13	71(3)	26(1)	13(1)	8(2)	6(1)	-2(1)
S	0.6780(7)	0.2595(8)	0.5083(7)	1.18	64(12)	34(4)	11(2)	-1(7)	-7(6)	2(2)
O(1)	0.8525(25)	0.2505(14)	0.4312(14)	2.13	191(47)	65(16)	6(6)	4(22)	15(17)	13(10)
O(2)	0.6400(27)	0.3877(12)	0.5285(10)	2.27	288(57)	17(12)	24(8)	-2(21)	-32(17)	-1(7)
O(3)	0.4627(26)	0.2026(19)	0.4849(11)	3.87	137(47)	149(25)	25(8)	-106(29)	2(15)	-35(11)
O(4)	0.7742(25)	0.2015(15)	0.5899(13)	2.94	128(45)	125(18)	9(8)	77(22)	15(17)	28(12)
O(5)	0.2856(30)	0.4627(15)	0.1823(15)	1.50	166(53)	20(13)	15(9)	44(20)	1(17)	6(8)
O(6)	0.3077(24)	0.2026(17)	0.1821(12)	1.02	77(46)	26(13)	8(8)	-17(19)	22(14)	1(8)
O(7)	0.4238(30)	0.4919(18)	0.3657(13)	1.42	53(42)	61(16)	5(7)	-41(22)	13(16)	-12(8)
O(8)	0.1178(24)	0.0069(16)	0.1642(14)	0.73	26(40)	18(13)	10(8)	6(18)	-13(13)	5(8)
O(9)	0.2723(34)	0.0515(16)	0.3413(16)	2.22	268(59)	36(13)	14(10)	-26(23)	-58(18)	1(9)
O(10)	0.1994(26)	0.3088(15)	0.3213(12)	1.04	98(45)	16(12)	11(8)	-19(18)	21(13)	-13(8)
H(1)	0.301	0.513	0.129	4.00						
H(2)	0.337	0.101	0.389	4.00						

*Equivalent isotropic B (Å^2) calculated from anisotropic temperature factors, except for H(1) and H(2) where B was not refined.

Form of anisotropic temperature factors (x10^4): $\exp -(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+2\beta_{12}hk+2\beta_{13}hl+2\beta_{23}kl)$

rier syntheses were necessary to locate all non-hydrogen atoms. Some cycles of isotropic full-matrix least-squares refinement led to $R = 0.07$. A weight $W = 1/\sigma^2(F_o)$ with σ derived from counting statistics was given to all observed reflections. Two more least-squares cycles with the introduction of anisotropic thermal parameters were carried out. A difference Fourier synthesis at this stage did not give sure indication for H atoms. The latter were therefore located on the basis of crystal-chemical considerations, along the donor–acceptor alignment at about 1.0Å from the donor oxygen atom. The positional and thermal parameters of hydrogens were not refined. The final R value was 0.045 for the observed reflections and 0.071 including "less thans." Seven reflections were considered to be affected by secondary extinction and therefore excluded from least-squares calculations. Scattering-factor curves for all atoms and the anomalous dispersion coefficient for heavy atoms were taken from *International Tables for X-ray Crystallography* (1974, p. 99–101, 148–151).

The atomic positional and thermal parameters are listed in Table 1, and a list of observed and calculated structure factors appears in Table 2.[1]

Discussion

The basic structural units of klebelsbergite are the Sb^{3+}–O polyhedra and the SO_4 tetrahedron.

It is well known from the literature that anions linked to an Sb^{3+} atom are arranged all to one side of the cation so that it is out of the center of its coordination polyhedron. This usually happens for ns^2-elements which have one unshared electron pair. Two ideal coordination polyhedra for Sb^{3+} are the tetrahedron and the trigonal bipyramid. In both instances a vertex is supposed to be occupied by the lone pair of electrons (E) which has the same volume as that of

[1] To receive a copy of Table 2, order Document AM-80-138 from the Business Office, Mineralogical Society of America, 2000 Florida Avenue, N.W., Washington, D.C. 20009. Please remit $1.00 in advance for the microfiche.

an anion (Galy *et al.*, 1975). Taking into consideration anions and lone pairs, the structures of many oxides and fluorides of ns^2-elements can be considered as close packed. In the SbO_3E model (tetrahedron) there are three strong Sb–O bonds with distances of 2.0Å. In the SbO_4E model (trigonal bipyramid) there are two equatorial and two axial Sb–O bonds. According to Galy *et al.* (1975) the theoretical distances are 2.0 and 2.27Å respectively, while the corresponding theoretical angles are 92.2 and 151.5°. According to the same authors it is also possible to calculate the theoretical position of the center of the lone pair *E*, which should be approximately 1.1Å distant from the Sb atom.

Bovin (1976) has collected the experimental Sb–O distances found in 28 compounds; the analysis of these values and of others found in subsequently solved structures shows that the experimentally found polyhedra show intermediate features between the tetrahedron and the trigonal bipyramid. Indeed only a slight displacement of the Sb atom out of the equatorial plane of the trigonal bipyramid is necessary to change four- to three-coordination.

Selected interatomic distances and angles in klebelsbergite are reported in Table 3. As also shown in Figure 1, each of the four independent Sb atoms is bound to four O atoms with distances ranging from 1.90 to 2.48Å. The four polyhedra have very similar Sb–O mean distances (from 2.10 to 2.14Å), and all exhibit arrangements intermediate between the SbO_3E and SbO_4E models. However, the Sb(3) polyhedron resembles more a distorted tetrahedron than a trigonal bipyramid, while the contrary happens for the other three polyhedra. Two of the shortest distances (1.90 and 1.98Å) are related to the hydroxyl oxygens O(5) and O(9) which are linked to only one Sb atom. Within the upper limit of 3.0Å there are few other Sb–O distances, not so far taken into consideration: however, they are very long and likely refer to very weak bonds.

The Sb–O polyhedra are tightly connected to each other by edge sharing so as to form layers parallel to (001). The values of the Sb–Sb distances between contacting polyhedra, 3.5Å or less, are similar to those found in other structures, *e.g.* in $Sb_6O_7(SO_4)_2$ (Bovin, 1976). In the unit cell there are two parallel Sb–O sheets connected by means of SO_4 tetrahedra, and indirectly by means of H-bonds. Oxygens belonging to the SO_4 group are of two kinds: O(1) and O(4) are linked also to an Sb atom, while O(2) and O(3) are acceptors of a H-bond. Consequently, S–O(1) and S–O(4) distances should be longer than S–

Table 3. Klebelsbergite: selected interatomic distances (Å) and angles (°)

Sb(1)		**Sb(3)**	
Sb(1)-O(5)	1.90(2)	Sb(3)-O(7)	2.08(2)
Sb(1)-O(6)	2.26(2)	Sb(3)-O(10)	2.01(2)
Sb(1)-O(7)	2.30(2)	Sb(3)-O(1,2)	2.48(2)
Sb(1)-O(10)	2.01(2)	Sb(3)-O(7,9)	2.00(2)
average	2.12	average	2.14
Sb(1)-O(5,7)	2.86(2)*	Sb(3)-O(2,9)	2.72(1)*
O(5)-O(6)	2.94(3)	O(7)-O(10)	2.52(3)
O(5)-O(7)	2.86(3)	O(7)-O(1,2)	4.38(3)
O(5)-O(10)	2.75(3)	O(7)-O(7,9)	2.89(2)
O(6)-O(7)	4.31(3)	O(10)-O(1,2)	2.67(2)
O(6)-O(10)	2.47(3)	O(10)-O(7,9)	2.83(3)
O(7)-O(10)	2.52(3)	O(1,2)-O(7,9)	3.09(2)
O(5)-Sb(1)-O(6)	89.2(7)	O(7)-Sb(3)-O(10)	76.2(7)
O(5)-Sb(1)-O(7)	85.4(8)	O(7)-Sb(3)-O(1,2)	148.1(7)
O(5)-Sb(1)-O(10)	89.1(7)	O(7)-Sb(3)-O(7,9)	90.2(7)
O(6)-Sb(1)-O(7)	141.3(6)	O(10)-Sb(3)-O(1,2)	72.0(6)
O(6)-Sb(1)-O(10)	70.4(6)	O(10)-Sb(3)-O(7,9)	89.8(7)
O(7)-Sb(1)-O(10)	71.2(7)	O(1,2)-Sb(3)-O(7,9)	86.6(7)
Sb(2)		**Sb(4)**	
Sb(2)-O(6)	1.94(2)	Sb(4)-O(6)	2.08(2)
Sb(2)-O(8)	2.12(2)	Sb(4)-O(8)	2.19(2)
Sb(2)-O(4,5)	2.32(2)	Sb(4)-O(9)	1.98(2)
Sb(2)-O(8,8)	2.00(2)	Sb(4)-O(10)	2.23(2)
average	2.10	average	2.12
Sb(2)-O(3,6)	2.89(2)*	Sb(4)-O(1,2)	2.96(2)*
		Sb(4)-O(9,10)	2.91(2)*
O(6)-O(8)	2.48(3)	O(6)-O(8)	2.48(3)
O(6)-O(4,5)	2.77(2)	O(6)-O(9)	2.93(3)
O(6)-O(8,8)	2.97(2)	O(6)-O(10)	2.47(3)
O(8)-O(4,5)	4.28(3)	O(8)-O(9)	2.83(3)
O(8)-O(8,8)	2.89(2)	O(8)-O(10)	4.16(3)
O(4,5)-O(8,8)	2.67(3)	O(9)-O(10)	2.95(2)
O(6)-Sb(2)-O(8)	75.2(7)	O(6)-Sb(4)-O(8)	70.8(7)
O(6)-Sb(2)-O(4,5)	80.9(6)	O(6)-Sb(4)-O(9)	92.3(8)
O(6)-Sb(2)-O(8,8)	98.1(8)	O(6)-Sb(4)-O(10)	70.0(7)
O(8)-Sb(2)-O(4,5)	149.6(7)	O(8)-Sb(4)-O(9)	85.2(8)
O(8)-Sb(2)-O(8,8)	88.9(7)	O(8)-Sb(4)-O(10)	140.0(6)
O(4,5)-Sb(2)-O(8,8)	76.0(6)	O(9)-Sb(4)-O(10)	88.7(7)
Hydroxyls		**S**	
O(5)-O(2,3)	2.88(3)	S-O(1)	1.53(2)
O(5)-H(1)	0.98	S-O(2)	1.49(2)
H(1)...O(2,3)	1.90	S-O(3)	1.44(2)
		S-O(4)	1.49(2)
O(9)-O(3)	2.95(3)	average	1.49
O(9)-H(2)	0.98		
H(2)...O(3)	1.97	O(1)-O(2)	2.45(2)
		O(1)-O(3)	2.45(2)
		O(1)-O(4)	2.47(3)
		O(2)-O(3)	2.41(2)
		O(2)-O(4)	2.42(2)
		O(3)-O(4)	2.38(2)
Cation-cation distances (<3.8 Å)			
Sb(1)-Sb(3)	3.35(2)	O(1)-S-O(2)	108.2(9)
Sb(1)-Sb(4)	3.51(2)	O(1)-S-O(3)	110.9(9)
Sb(2)-Sb(4)	3.34(3)	O(1)-S-O(4)	109.8(9)
Sb(2)-Sb(2,8)	3.49(3)	O(2)-S-O(3)	110.7(9)
Sb(2)-Sb(4,8)	3.78(3)	O(2)-S-O(4)	108.4(9)
Sb(3)-Sb(3,7)	3.56(2)	O(3)-S-O(4)	108.8(9)
S-Sb(2,4)	3.38(2)		
S-Sb(3,1)	3.40(2)		
S-Sb(3)	3.64(2)		

The equivalent positions (referred to Table 1) are designated by the second number in parentheses and are (1) = 1+x,y,z; (2)=-1+x,y,z; (3)=1-x,1-y,-1/2+z; (4)=3/2-x,y,1/2+z; (5)=3/2-x,y,-1/2+z; (6)=1/2-x,y,-1/2+z; (7)=1/2+x,1-y,z; (8)=1/2+x,-y,z; (9)=-1/2+x,1-y,z; (10)=-1/2+x,-y,z.

*Largest Sb-O distances (<3 Å).

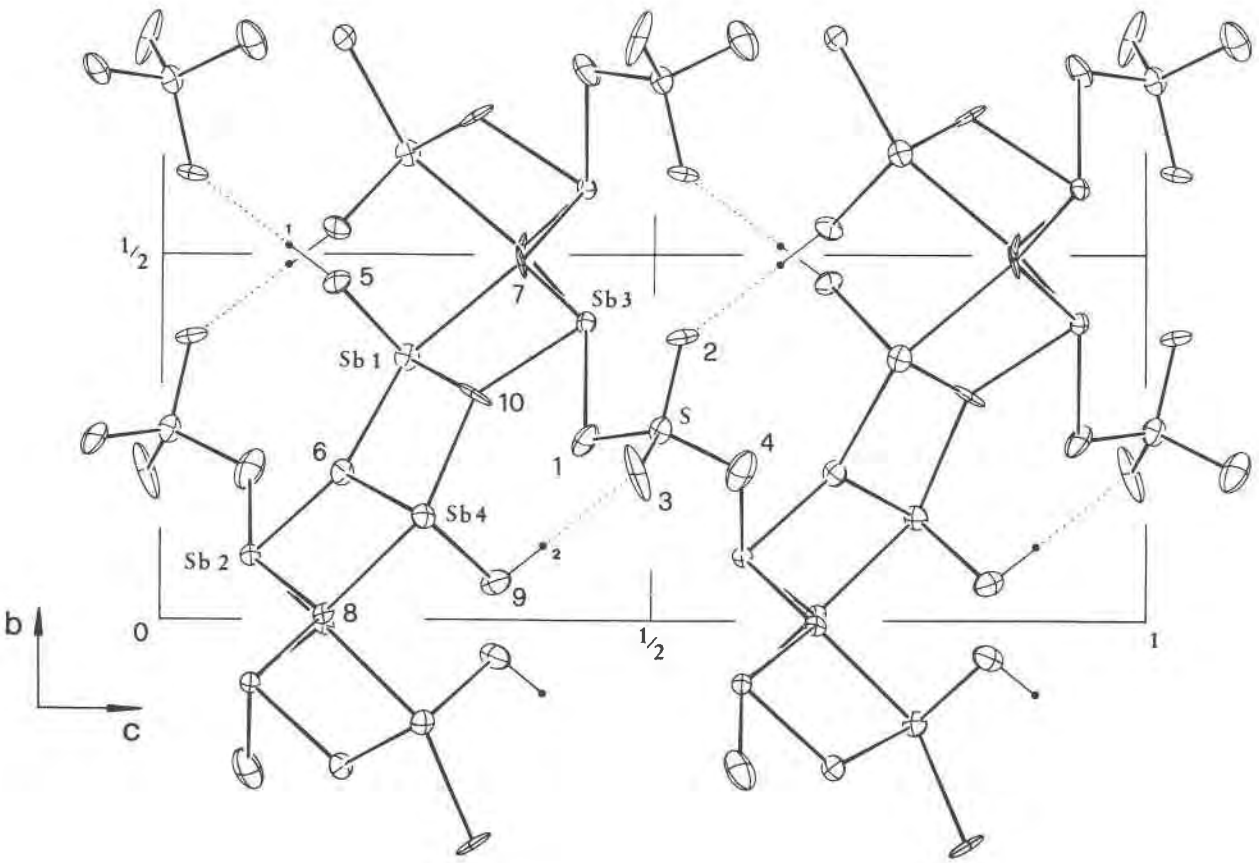

Fig. 1. Klebelsbergite: a projection of the structure down the *a* axis.

O(2) and S–O(3). However, this is not entirely fulfilled, as S–O(2) and S–O(4) distances have the same length of 1.49Å, which correspond to the S–O mean value. On the other hand, other "very weak" bonds (distances greater than 2.7Å) are present between antimony and oxygen atoms. The analysis of O–S–O angles and of O–O edges shows some distortion in the SO_4 tetrahedron. On the basis of an IR spectrum Nakai and Appleman (1980) concluded that there are several kinds of S–O bonds in klebelsbergite and that the SO_4 tetrahedron is significantly distorted. This statement is in agreement with our structural results.

As mentioned above, the connection between the sheets is also achieved by means of H-bonds between the hydroxyl oxygens O(5) and O(9) and the sulfate oxygens O(2) and O(3) respectively. The O–O distances are 2.88 and 2.95Å, so they can be considered as weak H-bonds. The interlayer bonding should on the whole be strong enough to generate good cohesion also in this direction; in fact, the mineral has no distinct cleavage (Nakai and Appleman, 1980).

This structure can be also considered on the basis of the volume occupied by each anion. For this calculation, according to Andersson *et al.* (1973), the volume of the unit cell can be simply divided by the number of anions and lone pairs. The value found in klebelsbergite, 17.3Å^3, compares well with 16.6Å^3 found in orthorhombic Sb_2O_3 (Svensson, 1974), 16.8Å^3 in $Sb_2O_3 \cdot 2SO_3$ (Mercier *et al.*, 1975), and 16.3Å^3 in $Sb_2(OH)_2(SO_4)_2 \cdot 2H_2O$ (Douglade *et al.*, 1978). Therefore in klebelsbergite anions and lone pairs are close-packed.

The electrostatic valence balance (see Table 4), computed according to Brown and Kun Wu (1976), is not fully satisfactory, especially for O(1) and O(10), which appear to be underbonded and overbonded respectively.

Klebelsbergite and the new mineral peretaite, $CaSb_4O_4(OH)_2(SO_4)_2 \cdot 2H_2O$ (Cipriani *et al.*, 1980b) are the only naturally-occurring Sb sulfates. Among the synthetic compounds, at least three anhydrous and one hydrated Sb sulfates are structurally known. None of the above compounds, however, has an

Table 4. Klebelsbergite: electrostatic valence balance

Atom	Sb(1)	Sb(2)	Sb(3)	Sb(4)	S	H(1)	H(2)	Sum
O(1)			0.33	0.15	1.31			1.79
O(2)			0.22		1.47	0.18		1.87
O(3)		0.16			1.73		0.15	2.04
O(4)		0.43			1.49			1.92
O(5)	1.07 0.17					0.82		2.06
O(6)	0.49	0.96		0.71				2.16
O(7)	0.45		0.87 0.73					2.05
O(8)		0.82 0.63		0.56				2.01
O(9)				0.90 0.16			0.85	1.91
O(10)	0.82		0.85	0.52				2.19
Sum	3.00	3.00	3.00	3.00	6.00	1.00	1.00	

atomic arrangement which, on the whole, resembles the present structure. This point is discussed in the paper dealing with the structure of peretaite (Menchetti and Sabelli, 1980).

A final noteworthy point is the presence of a marked pseudosymmetry in the Sb–O sheet. The pseudosymmetry element is an inversion center (at approximately 1/4, 1/4, 1/4 in Fig. 1) which refers Sb(1) to Sb(4), Sb(2) to Sb(3), O(6) to O(10), and so on. It is interesting to compare some "symmetrical" distances or angles. The only atoms which do not obey this "symmetry" are the sulfate oxygens, especially O(2) and O(3). The pseudocenter, of course, implies a pseudo glide plane parallel to (001), with translation $1/2\ a + 1/2\ b$, located at $c = 0$ and $1/2$ in Figure 1. With these additional elements the symmetry should be the corresponding centrosymmetrical group *Pcan*. Actually the intensities of reflections $hk0$ with $h + k = 2n$ are stronger than the intensities of the reflections with $h + k = 2n + 1$. In conclusion, with the exception of a few oxygens, the structure of klebelsbergite can be regarded as centrosymmetrical. Should this structure be twinned, as generally occurs when such a pseudosymmetry is present, the (001) plane would be the twinning plane.

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Manuscript received, April 2, 1980;
accepted for publication, April 22, 1980.