Preisingerite, Bi₃O(OH)(AsO₄)₂, a new species from San Juan Province, Argentina: its description and crystal structure[1]

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Abstract

Preisingerite, ideally $Bi_3O(OH)(AsO_4)_2$, triclinic, $P\bar{1}$, $a = 9.993(3)$, $b = 7.404(3)$, $c = 6.937(3)$Å, $\alpha = 87.82(2)$, $\beta = 115.01(2)$, $\gamma = 111.07(2)°$, $Z = 2$, was heretofore known as an unnamed species, for which only qualitative chemical composition and unindexed X-ray powder patterns had been reported. The mineral described here occurs in the weathering zones of the Bi–As–Cu deposits of San Francisco de Los Andes and Cerro Negro de la Aguadita, Department of Calingasta, San Juan Province, Argentina, as poorly developed tiny translucent grayish white crystals which are tabular parallel to (010) with a rhomboidal shape. Electron microprobe analysis yields Bi 68%, As 15%, P 0.3% and Pb < 0.5%. The calculated density is 7.24 g/cm³. The crystals are biaxial with $\alpha = 2.130$, $\beta = 2.16$ and $\gamma = 2.195$ ($\lambda = 589$ nm) derived from reflectivity measurements and from 2V, which is close to 90° as determined with a polarizing microscope.

The structure analysis, which converged to $R = 0.046$ for 1440 observed reflections, reveals clusters of six Bi atoms which are connected by two oxygens and two OH groups. These $Bi_6O_2(OH)_2$ groups are linked into a framework via the AsO_4 tetrahedra. The three different Bi atoms have one-sided coordinations, each with four oxygens at distances of 2.11–2.46Å (average 2.28Å). These coordinations are supplemented by five additional oxygens at distances of 2.57–3.36Å. Bonds within the AsO_4 tetrahedra measure 1.66–1.71Å (average 1.682Å). A hydrogen bond between the OH oxygen and an arsenate oxygen is indicated by $O \cdots O = 2.72$Å.

Introduction

In the late 1960's Dr. E. J. Llambías and Dr. L. Malvicini studied two Bi–As–Cu mineralized deposits in the San Juan Province, Argentina and observed two bismuth arsenate minerals, one of which was later identified as rooseveltite, $BiAsO_4$ (Bedlivy *et al.*, 1969, 1972). The second unnamed mineral was considered to be a new species because the X-ray powder pattern (Bedlivy *et al.*, 1969) did not match those of other bismuth arsenate minerals (atelestite, arsenobismite, walpurgite, mixite), although a powder pattern of an unnamed bismuth arsenate mentioned by Frondel (1943) showed some

resemblance. The problem of better characterizing the mineral from Argentina remained unresolved until recently, when samples were first studied by modern X-ray single crystal methods. These allowed the successful solution of the structure and also revealed the chemical formula. Then, with calculated and measured powder diagrams at hand, it became apparent that the new mineral was most likely identical to the unnamed bismuth arsenate of unknown composition detected by Frondel (1943) in samples from Utah (USA), Bolivia and Germany.

The mineral was named in honor of Anton Preisinger, professor of Mineralogy, Crystallography and Structural Chemistry at the University of Technology in Vienna. The mineral and its name have been approved by the Commission on New Minerals and Mineral Names of the International Mineralogical Association. Holotype material from Argentina is deposited at the Museum of Natural History in Vienna.

Occurrence and paragenesis

The mineral described in this paper was found in the weathering zones of the deposits of San Francisco de Los Andes and Cerro Negro de la Aguadita (Lat. 30° 45'S, Long. 69° 30'W) in the Department of Calingasta, San Juan Province, Argentina. The geology and mineralogy of these deposits have been described by Llambías and Malvicini (1966, 1969).

The San Francisco de los Andes mine is a breccia-pipe deposit, related to granodioritic plutons, with tourmaline, quartz and a complex Fe–Bi–Cu–Zn–Pb–Au–As–S mineralization. The most abundant primary ore minerals are pyrite, arsenopyrite, bismuthinite, chalcopyrite, digenite and tetrahedrite. The deposit once contained a substantial weathering zone with many arsenate minerals which originated from the decomposition of arsenopyrite: scorodite, beudantite, olivenite, conicalcite, clinoclase, rooseveltite and the new mineral (Bedlivy and Llambías, 1969; Bedlivy *et al.*; 1969, 1972).

At Cerro Negro de la Aguadita, which is only a trench in the weathering zone of a deposit of the same type as San Francisco de los Andes, three bismuth arsenates, rooseveltite, the new mineral and mixite, were found (Llambías and Malvicini, 1966).

In both deposits preisingerite usually occurs together with rooseveltite. Both are the most abundant bismuth minerals in the weathering zone, while bismuthite and mixite are infrequent. Preisingerite usually forms porous aggregates of tiny tabular crystals. Rooseveltite, which is otherwise very similar in appearance, was found only in grayish white microcrystalline masses. Both minerals are frequently pseudomorphous after bismuthinite, which indicates that they were formed *in situ* and lacked mobility in the weathering zone, due probably to their extreme insolubility (Bedlivy *et al.*, 1972). Preisingerite occasionally was found as pulverulent masses impregnated by small quantities of beudantite or bismuthite.

The unnamed mineral described by Frondel (1943), which seems to be identical to preisingerite, has been found on samples originating from strongly oxidized parts of bismuth- and arsenic-bearing sulfide deposits. At Mammoth Mine, Tintic District, Utah, U.S.A., the mineral was reported to occur abundantly in pulverulent masses in association with arsenobismite, while at Schneeberg, Saxony, Germany, which is the type locality of two other bismuth arsenates, atelestite and walpurgite, it was observed on a specimen of pucherite.[3] The Bi–Sn deposit of Tazna, Bolivia, which Frondel (1943) mentioned as a third occurrence of the mineral, included an extended weathering zone containing bismoclite and bismuth arsenates (Ahlfeld, 1954).

Description and properties

Our most abundant and best samples of the mineral are from the San Francisco de Los Andes mine. These were used for the subsequent studies.

Preisingerite is translucent white to grayish white in color. The luster is subadamantine to adamantine, the streak white. The mineral is brittle, exhibits conchoidal fracture and seems to possess an indistinct cleavage. The Mohs' hardness is between 3 and 4. Attempts to determine the specific gravity by pyknometry yielded maximum values of ~6 g/cm^3; the computed density is 7.24 g/cm^3.

Preisingerite is triclinic. Most crystals are plates of rhomboidal shape up to 0.2 mm in maximum dimension. They are usually approximately 1/5 as thick as they are long. The crystals tend to be poorly developed with rounded faces and edges. Therefore, they could not be studied on an optical goniometer. On the X-ray four-circle diffractometer (for cell dimensions see Table 1, other details below) it was observed that the crystals are dominated by the {010} faces; the next most important faces are of the type {0*kl*} and {*hk*0}, but could not be precisely indexed. A scanning electron microscope view of some comparatively well-developed crystals is shown in Figure 1.

The crystals were analyzed with an ARL-SEMQ electron microprobe at 20 kV and 15 nA sample current using a beam about 20 μ in diameter.

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[3] Pucherite from this site was recently found to be accompanied not by preisingerite itself, but by the isostructural vanadate (Prof. K. Walenta, 1982, written communication and our own results).

Table 1. Preisingerite. Crystallographic data.

Triclinic, Space Group P$\bar{1}$			
a = 9.993(3) Å		α =	87.82(2)°
b = 7.404(3)		β =	115.01(2)
c = 6.937(3)		γ =	111.07(2)
Z = 2 $Bi_3O(OH)(AsO_4)_2$ *		V =	430.05 Å³
D_{calc} = 7.24 g·cm^{-3}			

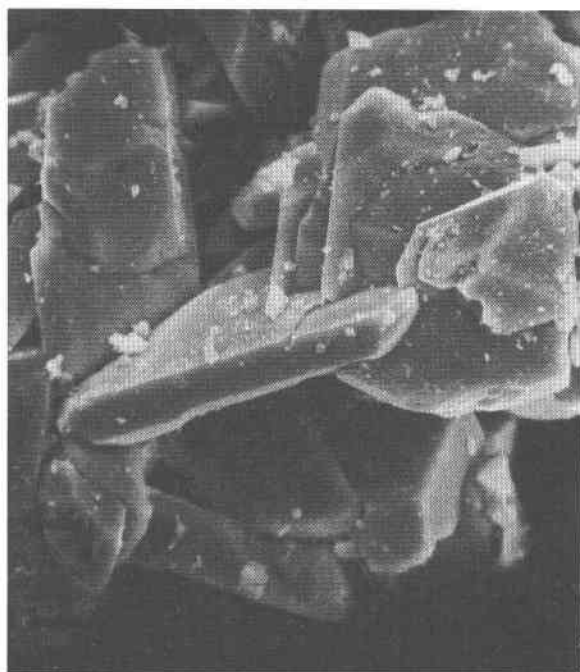* With minor replacement of AsO_4 by PO_4.

Fig. 1. Scanning electron microscope photo of preisingerite crystals. The crystals shown have maximum dimensions of about 0.02 mm.

Wavelength scans disclosed only Bi and As as main constituents with trace amounts of Pb and P. Quantitative measurements using Bi_2S_3, arsenopyrite, galenite and apatite as standards and the program of Weinke *et al.* (1974) for data correction, resulted in 68% Bi, 15% As, 0.3% P and less than 0.5% Pb. The idealized formula $Bi_3O(OH)(AsO_4)_2$, derived from the crystal structure analysis (see below), requires 66.85% Bi, 15.98% As, 17.06% O and 0.11% H (74.53% Bi_2O_3, 24.51% As_2O_5 and 0.96% H_2O). Pb and P can be assumed to replace Bi and As at mole percentages of <0.75 and ~5%, respectively.

A thermogravimetric analysis of a 192.2 mg sample of preisingerite was carried out with a heating rate of 4°C per minute in a stream of dry nitrogen. Between 300 and 470°C the sample lost 2.2 mg in weight with an indistinct endothermic effect. Between 600 and 700°C a weight loss of 1.1 mg and a more pronounced but blurred endothermic effect was observed. Another sample of preisingerite was heated in steps to temperatures of 250°, 540°, and 800°C, and after each step an X-ray powder pattern was taken. The powder pattern of preisingerite heated to 250°C remained unchanged, but two unique powder patterns were obtained for samples heated to 540° and 800°C, thus showing that phase

transformations had taken place. From these observations it is likely that the mineral decomposes between 300 and 470°C by dehydration; the loss in weight observed by TGA (2.2 mg = 1.1%) is in good agreement with the loss to be expected from the formula (1.9 mg).

Preisingerite is colorless in transmitted light and optically biaxial with very high refringence and considerable birefringence. Optic axis figures obtained from several grains showed an almost straight isogyre indicating a 2V close to 90°. The reflectivity of about 25 polished grains of random orientations was measured in polarized light of $\lambda =$ 589 nm yielding minimum and maximum values of Rp = 13.0% and Rg = 14.0%, corresponding to indices of refraction of $\alpha = 2.130$ and $\gamma = 2.195$. From these figures and from the 2V of 90°, β was calculated as 2.16. The average index of refraction, $n = 2.14$, calculated using the Gladstone–Dale equation and the constants given by Mandarino (1976), is in excellent agreement with the refractive indices given above.

X-ray diffraction study

Single crystal X-ray investigations were carried out on a Philips PW 1100 four circle diffractometer with graphite monochromatized Mo$K\alpha$ radiation. Many crystals were tested and found to be unsuitable because of pronounced subparallel intergrowth which caused reflection half widths of about 5° in ω. After considerable effort a transparent brick-shaped fragment, tabular parallel to (010) and of approximate dimensions 0.02 × 0.06 × 0.08 mm, was found to be suitable for data collection. Cell dimensions were determined from least-squares refinement of the 2θ angles of about 160 reflections. The unit cell given in Table 1 was preferable to a reduced cell for reasons given below. The intensity data were measured by the ω-scan technique with a scan width of $\Delta\omega = 2°$ and measuring times of two minutes for the scan as well as the background. Of the 2524 independent reflections recorded in the range $2° < \theta < 30°$, 1440 with $I_{max} > 2\sigma(I_{backg})$ were used in the structure analysis. The data were corrected for 1/Lp and absorption. For this purpose the crystal shape was approximated by six faces, {010}, {3$\overline{1}$0} and {2$\overline{1}$8}. The transmission factors were calculated by Gaussian integration and ranged from 0.49 to 0.23.

The positions of the Bi atoms were found by direct methods using MULTAN-74 (Main *et al.*,

Table 2. Preisingerite. Atomic coordinates and temperature factors.

Atom	x	y	z	B_i ($\mathring{A}^2$)	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23} *
Bi(1)	0.52327(11)	0.41421(14)	0.75230(14)	1.04	1.09(3)	1.18(4)	0.94(3)	0.15(3)	0.59(3)	0.37(3)
Bi(2)	0.29838(11)	0.74044(14)	0.55549(14)	1.00	0.96(4)	0.88(4)	1.28(3)	0.21(3)	0.62(3)	0.34(3)
Bi(3)	0.07735(12)	0.16090(15)	0.28045(16)	1.40	1.09(4)	1.29(4)	1.67(3)	-0.04(3)	0.59(3)	0.32(3)
As(1)	0.6952(3)	0.0172(4)	0.9215(4)	1.08	0.92(9)	1.05(9)	1.25(8)	0.30(7)	0.52(6)	0.30(7)
As(2)	0.0961(3)	0.3720(4)	0.7862(4)	1.04	0.70(9)	0.87(10)	1.33(8)	-0.04(8)	0.43(7)	0.09(7)
O(1)	0.3777(22)	0.5382(27)	0.4759(27)	1.4(3)						
O(2)	0.3066(21)	0.1549(27)	0.5579(26)	1.3(3)						
O(3)	0.8590(21)	0.0275(27)	0.8943(26)	1.4(3)						
O(4)	0.5569(27)	-0.2084(33)	0.8602(33)	2.4(4)						
O(5)	0.6210(19)	0.1596(25)	0.7526(24)	1.0(3)						
O(6)	0.7684(22)	0.1052(27)	1.1811(27)	1.6(3)						
O(7)	0.2584(19)	0.5101(25)	0.7497(24)	1.0(3)						
O(8)	-0.0468(20)	-0.4637(25)	0.6902(25)	1.0(3)						
O(9)	0.0209(21)	0.1498(26)	0.6362(26)	1.2(3)						
O(10)	0.1695(22)	0.3727(27)	1.0506(27)	1.6(3)						

* The anisotropic temperature factor is in the form: $T = \exp[-1/4(B_{11}a^{*2}h^2 + \ldots + 2B_{23}b^*c^*kl)]$. B_i from the anisotropic values according to Hamilton.

1974). Statistical tests indicated centrosymmetry and hence space group $P\bar{1}$. The phase determination process was based on 150 E_{hkl} with E > 1.8, 1120 Σ_2 relationships, three origin-defining phases, one Σ_1 determined phase and four multisolution phases. An E-map computed with the most promising of the phase sets (combined figure of merit 2.97) revealed three Bi atoms. Two As and ten O atoms were subsequently located by difference Fourier maps. The structure was then refined by full-matrix least-squares with the program SHELX-76 (Sheldrick, 1976) using anisotropic temperature factors for Bi and As, and isotropic ones for O. The final refinement converged to R = 0.046 and R_w = 0.047 with weighting function w = $(1/\sigma^2(F_o) + 0.0016 \times F_o^2)$. A concluding difference map showed no unusual features. Neutral atom scattering functions and corrections for anomalous dispersion were taken from the *International Tables for X-ray Crystallography* (1974). Final atomic coordinates and temperature factors are given in Table 2, observed and calculated structure factors in Table 3[4].

Table 4 lists the data from a calculated X-ray powder pattern and from a sample measured on a powder diffractometer with CuKα radiation. The calculated intensities are integrated while the measured intensities are peak heights. The agreement between the two patterns is satisfactory. Due to the large number of independent reflections (254 within 2θ = 10–60°) line overlap is serious and the appear-

ance of the measured powder pattern depends somewhat on the angular resolution of the diffractometer. Also given in Table 4 are the X-ray powder patterns of Bedlivy et al.[5] (1969) (pattern 3) and of Frondel's (1943) unnamed mineral (pattern 4). When comparing Frondel's powder pattern with ours one has to take into account that his was recorded by the Debye–Scherrer method and has poor resolution relative to those obtained by diffractometry. After allowing for some systematic shifts of the *d*-values given by Frondel, and after taking into account that his intensity values were probably not corrected for absorption, the agreement with our present powder patterns is good. Thus, there is little doubt that Frondel's unnamed mineral is identical to the new mineral preisingerite from Argentina.

Powder patterns of preisingerite heated to 540 and 800°C are given in Table 5[4]. The pattern obtained after heating to 540°C could be indexed based on a triclinic cell with a = 9.92 (1), b = 7.16 (1), c = 6.97 (1)Å, α = 87.79 (5), β = 115.25(5), γ = 110.29 (5)° and V = 416Å^3. These cell dimensions do not differ very much from those of unheated preisingerite (Table 1; note the decrease in b) which indicates that structural changes caused by heating and loss of structural water are probably small.

Structure

The structure determination reveals that the mineral is an oxo-hydroxy arsenate of trivalent bismuth which has the chemical formula $Bi_3O(OH)(AsO_4)_2$.

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[4] Tables 3 and 5 of observed and calculated structure factors and powder patterns of heated preisingerite may be obtained by ordering document AM-82-202 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.

[5] Due to a typographical error in Table 1 of this paper pattern 1 corresponds to the strongest reflections of preisingerite, while pattern 2 corresponds to rooseveltite.

Table 4. X-ray powder diffraction data for preisingerite

Table 4. (continued)

h	k	l	d_{cal}	I_{cal}	d_{obs} (2)	I_{obs} (2)	d_{obs} (3)	I_{obs} (3)	d_{obs} (4)	I_{obs} (4)
1	0	0	8.379	2	8.402	1			8.488	10
0	1	0	6.846	3	6.835	4	6.80	10		
-1	1	1	6.688	10	6.691	8	6.66	14		
-1	0	1	6.565	4	6.567	4				
0	0	1	6.229	17	6.231	17	6.21	15	6.226	10
0	-1	1	4.951	9	4.955	6	4.92	7		
1	1	0	4.527	38 }	4.524	35	4.50	50	4.545	20
-2	0	1	4.512	5 }						
-2	1	0	4.391	12	4.395	10	4.38	13		
2	0	0	4.190	3	4.190	3			4.191	10
1	-1	1	4.130	10	4.128	8	4.12	8		
-1	2	0	3.698	1	3.693	1				
0	2	0	3.423	1	3.436	6	3.41	10		
-2	2	0	3.344	3	3.344	3				
-2	0	2	3.283	100	3.281	100	3.28	72	3.280	100
-2	2	1	3.258	93 }	3.263	97	3.25	90		
-1	2	1	3.249	4 }						
1	1	1	3.199	47 }						
0	-2	1	3.187	85 }	3.194	87	3.18	100	3.200	90
-2	1	2	3.157	4 }						
1	-2	1	3.115	5 }						
0	0	2	3.115	14 }	3.113	13				
-1	1	2	3.094	17 }						
2	1	0	3.090	49	3.091	74	3.08	76	3.108	90
2	-1	1	3.087	32 }						
-3	1	0	3.017	49	3.016	38	3.01	37	3.026	40
-3	2	1	2.861	12 }	2.859	13	2.85	16	2.866	20
-1	-2	1	2.859	5 }						
0	2	1	2.843	2 }	2.843	3				
-3	1	2	2.832	2 }						
1	2	0	2.817	4	2.817	3			2.825	10
-2	-1	2	2.796	8	2.796	4				
-3	0	2	2.769	2	2.768	1				
2	-2	1	2.710	4 }	2.703	15	2.69	14	2.717	20
0	1	2	2.701	13 }						
1	-1	2	2.613	28	2.612	18	2.61	18	2.621	40
1	0	2	2.574	6	2.575	8	2.57	6	2.591	10
-3	-1	1	2.514	14	2.512	9	2.51	10		
-4	1	1	2.491	19	2.489	15	2.49	13	2.500	30
-1	2	2	2.441	2	2.440	1				
-2	3	0	2.428	2	2.428	3				
-3	-1	2	2.365	3	2.368	4			2.392	10
-2	0	3	2.306	3	2.305	3				
-1	3	1	2.267	13 }	2.265	15			2.282	20
-3	3	1	2.262	4 }						
-4	2	2	2.229	5	2.229	3				
3	0	1	2.212	14	2.211	14			2.223	30
-1	-1	3	2.175	6	2.176	5			2.191	10
-2	-1	3	2.147	3	2.147	1				
-1	1	3	2.118	12	2.118	9			2.128	20
2	0	2	2.097	4	2.096	4				
0	-1	3	2.066	4 }						
-1	-3	1	2.059	7 }	2.057	15			2.073	30
0	3	1	2.055	11 }						
-4	3	1	2.047	4 }	2.035	8				
-3	3	2	2.036	1 }						
1	3	0	2.016	4	2.016	4				
0	-3	2	1.9718	4 }						
-4	-1	2	1.9685	19 }						
3	-3	1	1.9670	17 }	1.967	31			1.983	80
-5	1	1	1.9654	11 }						
-4	3	0	1.9565	6 }						
2	2	1	1.9343	5	1.935	3				
-3	-2	2	1.9252	3	1.928	3				
-1	3	2	1.9104	7 }	1.906	13			1.913	50
-4	2	3	1.9050	16 }						
0	-2	3	1.8919	6	1.892	3				
1	2	2	1.8632	3 }	1.863	9			1.874	20
-2	-2	3	1.8622	12 }						
-2	4	0	1.8487	11 }	1.849	14				
-1	2	3	1.8487	4 }						
3	2	0	1.8478	5 }						
1	0	3	1.8360	3 }	1.834	4			1.842	20
-5	0	1	1.8325	4 }						
-2	-3	1	1.8211	9	1.820	13				
-5	2	0	1.7984	5 }	1.794	10			1.804	50
-5	3	1	1.7948	8 }						
-5	2	3	1.7491	4	1.750	4			1.754	20
3	0	2	1.7351	8	1.735	3				
-3	3	3	1.7182	10	1.719	13			1.722	20
-3	1	4	1.7007	4	1.701	3				
0	2	3	1.6778	7 }	1.676	9			1.682	50
5	0	0	1.6758	11 }						
-1	-1	4	1.6471	5	1.647	1			1.654	10
-4	0	4	1.6413	6	1.642	4				
-4	4	2	1.6290	5	1.629	2			1.632	10
3	2	1	1.6185	6	1.619	3				
1	-3	3	1.5970	6 }	1.596	6			1.610	20
0	-4	2	1.5933	4 }						
-6	1	3	1.5752	6	1.575	4			1.576	70
-6	3	2	1.5694	5 }	1.570	9				
5	-2	1	1.5687	8 }						
2	-4	2	1.5573	2	1.558	4				
-5	4	2	1.5457	3 }	1.542	5			1.545	20
-4	-1	4	1.5427	3 }						

1   Calculated pattern. Integrated intensities evaluated with isotropic temperature factors and complex neutral atom scattering factors for all atoms. Lp-corrections for Cu/Ni radiation. 163 reflections with I_{cal}<3 and d_{cal}>1.5418 Å were omitted.

2   Pattern measured on a PHILIPS powder diffractometer with graphite monochromatized Cu Kα radiation and a beam divergence angle of 1°; scanned at 1/8° 2θ per minute. The intensities refer to peak heights.

3   Pattern reported by Bedlivy, Llambías and Astarloa (1969); d_{obs} and peak heights obtained by diffractometry with Cu/Ni radiation.

4   Pattern of the unnamed bismuth arsenate mineral recorded by Frondel (1943) with film methods and Cu/Ni radiation; a correction for absorption apparently has not been applied to the intensities.

The structure consists of clusters of six Bi atoms which are connected by two oxygens and two OH groups. These $Bi_6O_2(OH)_2$ groups are linked by the AsO_4 tetrahedra to form a framework. Figures 2 and 3 show projections of the structure, Table 6 gives interatomic distances and angles.

The coordination polyhedra of the three independent Bi atoms (Fig. 4) are clearly controlled by the stereochemically active electron lone pair of trivalent Bi (Galy et al., 1975). Each Bi atom exhibits a one-sided coordination by four nearest-neighbor oxygen atoms at distances less than 2.5Å. This coordination is supplemented by five additional oxygen atoms which are arranged around the electron lone pair side of each Bi at Bi–O distances of 2.5–3.4Å. The coordination polyhedra defined by the four oxygens next to each Bi can be described as distorted trigonal bipyramids, where two oxygens occupy the axial corners while two other oxygens and the electron lone pair occupy the three equatorial corners. The trigonal bipyramidal shape is most closely approached in the case of Bi(2). For Bi(3) the trigonal bipyramid is considerably distorted because the axial oxygen O(10) is slightly displaced by another weakly bonded oxygen, O(1) with Bi–O = 3.08Å. In the case of Bi(1) the coordination polyhedron is a cross between a trigonal bipyramid and a tetragonal pyramid. The O–Bi–O angles between the equatorial oxygens are in the range of 75–96° and those between the axial oxygens are in the range of 151–130°. For each of the three different Bi atoms the bonds to the equatorial oxygens are shorter (2.11–2.30Å) than the bonds to the axial oxygens (2.26–2.45Å). The mean values of the two axial and two equatorial Bi–O bond lengths are quite close for all three Bi atoms (between
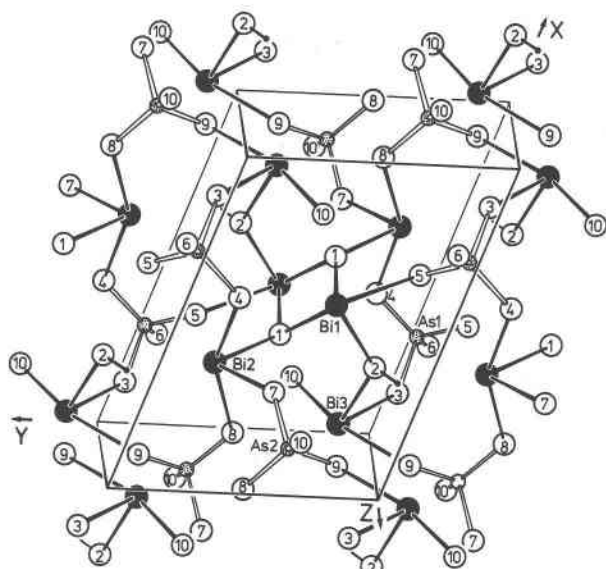
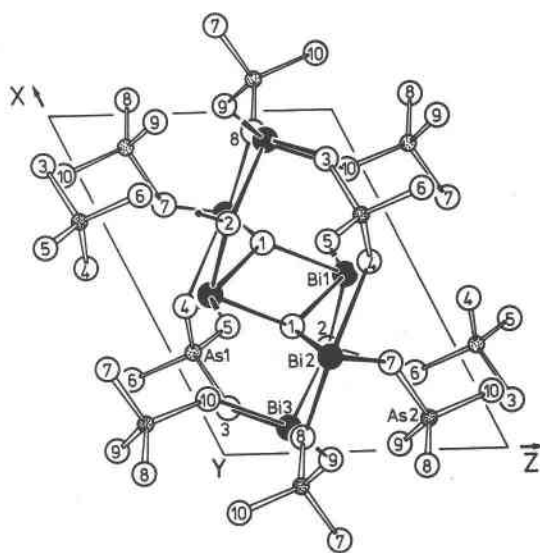Fig. 2. The structure of preisingerite viewed approximately parallel -c^*. Only Bi–O bonds less than 2.5Å are shown.

Fig. 3. The structure of preisingerite in a projection along the b axis. Only Bi–O bonds less than 2.5Å are shown.

Table 6. Preisingerite. Interatomic distances and angles*

Bi(1)		Bi(2)		Bi(3)	
Bi(1) – O(1)	2.154 Å	Bi(2) – O(1)	2.112 Å	Bi(3) – O(3)	2.289 Å
– O(2)	2.221	– O(7)	2.162	– O(2)	2.301
– O(1')	2.259	– O(8)	2.313	– O(9)	2.312
– O(5)	2.414	– O(4)	2.455	– O(10)	2.421
mean value	2.262	mean value	2.261	mean value	2.331
Bi(1) – O(10)	2.630	Bi(2) – O(5)	2.583	Bi(3) – O(3)	2.573
– O(4)	2.784	– O(6)	2.613	– O(6)	2.736
– O(7)	2.970	– O(2)	3.041	– O(9')	2.747
– O(7')	3.147	– O(9)	3.287	– O(8)	2.927
– O(4')	3.290	– O(5')	3.361	– O(1)	3.077
O(1) – Bi(1) – O(2)	96.2°	O(1) – Bi(2) – O(7)	75.0°	O(3) – Bi(3) – O(2)	80.1°
– O(1')	71.7	– O(8)	85.3	– O(9)	75.4
– O(5)	71.9	– O(4)	74.8	– O(10)	75.9
O(2) – Bi(1) – O(1')	76.3	O(7) – Bi(2) – O(8)	81.9	O(2) – Bi(3) – O(9)	80.1
– O(5)	75.3	– O(4)	72.7	– O(10)	104.5
O(1')– Bi(1) – O(5)	130.4	O(8) – Bi(2) – O(4)	150.9	O(9) – Bi(3) – O(10)	149.7

As(1)		As(2)		Hydrogen bond	
As(1) – O(3)	1.700 Å	As(2) – O(7)	1.696 Å	O(2) ⟶ O(6)	2.719 Å
– O(4)	1.667	– O(8)	1.674		
– O(5)	1.664	– O(9)	1.713		
– O(6)	1.684	– O(10)	1.662		
mean value	1.679	mean value	1.686		
O(3) – As(1) – O(4)	112.7°	O(7) – As(2) – O(8)	111.8°		
– O(5)	105.8	– O(9)	105.9		
– O(6)	103.8	– O(10)	103.3		
O(4) – As(1) – O(5)	109.4	O(8) – As(2) – O(9)	107.0		
– O(6)	111.8	– O(10)	112.9		
O(5) – As(1) – O(6)	113.1	O(9) – As(2) – O(10)	115.9		

* All Bi–O distances below 3.5 Å are given. The shortest Bi–As distance is Bi(3)–As(1)=3.340 Å, the shortest Bi–Bi distance is Bi(1)–Bi(1)=3.577 Å

Standard deviations for Bi–O and As–O 0.015–0.023 Å (average = 0.017 Å), for O–O 0.03 Å, for O–Bi–O 0.6°, and for O–As–O 0.9°.
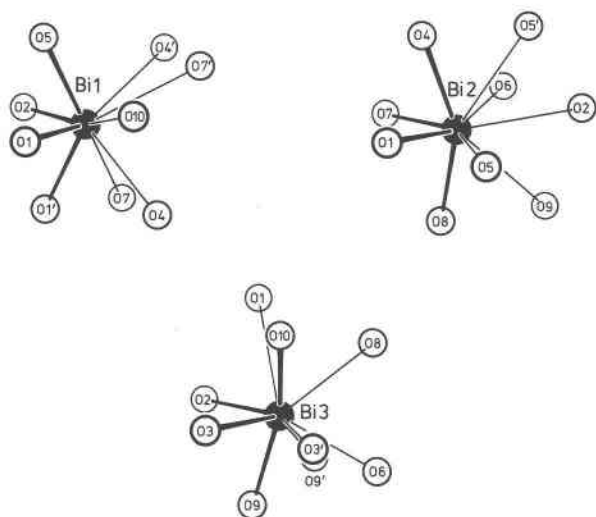
Fig. 4. Bismuth–oxygen coordination in preisingerite viewed normal to the line bisecting the bond direction of the pair of equatorial oxygens. Bi–O bonds under 2.5Å are shown as heavy lines, those between 2.5 and 3.5Å as thin lines.
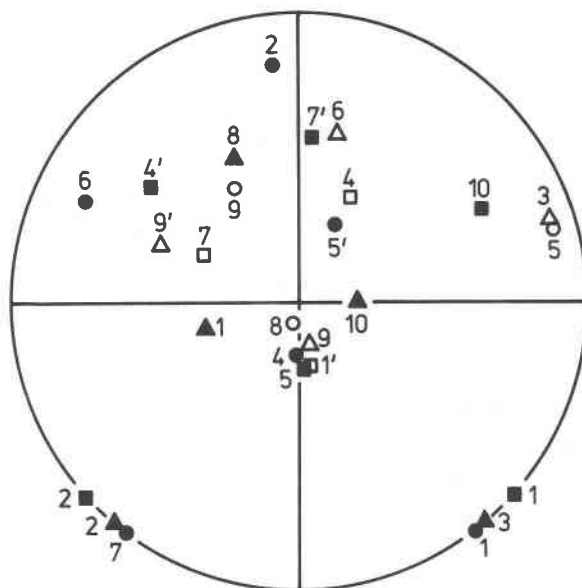

Fig. 5. Stereographic projection of the Bi–O bond directions in preisingerite following the orientation convention of Zemann (1971). Squares, circles and triangles represent bonds to Bi(1), Bi(2) and Bi(3), respectively. Solid symbols indicate pole angles $\leq 90°$, lined ones pole angles $> 90°$.

2.26Å and 2.33Å). The arrangement of the oxygens which are located on the electron lone pair side of each Bi atom is quite irregular and differs considerably between the three Bi. This can be seen from Figure 5, where the bond directions around the Bi atoms are given in a stereographic projection as proposed by Zemann (1971) for Te(IV) compounds.

Each set of six Bi atoms is linked by two oxygens O(1) and two hydroxyl oxygens O(2) to form a cluster with $\bar{1}$ symmetry. The two oxygens O(1) define an edge-sharing link between a pair of Bi(1)O$_4$ polyhedra [O(1)–O(1) = 2.59Å, Bi(1)–Bi(1) = 3.577Å]; the remaining BiO$_4$ polyhedra are attached to this dimer via corner-sharing links. The oxygen O(1) has a tetrahedral coordination with three strongly bonded Bi atoms—two Bi(1) and one Bi(2) with Bi–O = 2.11, 2.15 and 2.26Å, average = 2.175Å—and one weakly bonded Bi(3) with Bi–O = 3.08Å. The Bi–O(1)–Bi angles subtended by the three strongly bonded bismuth atoms are 121.9, 116.4 and 108.3°. With respect to the three short Bi–O bonds, the coordination of O(1) compares well with that of the oxo-anions in bismuth basic nitrates (Lazarini, 1978, 1979a, 1979b; Sundvall, 1979), for which Bi–O bonds of 2.08–2.30Å with mean values of 2.14–2.19Å have been found. The hydroxyl oxygen O(2) has two strong Bi–O bonds of 2.22 and 2.30Å, and in addition a weak interaction with a third Bi at a distance of 3.04Å. This oxygen apparently forms a hydrogen bond to the arsenate oxygen O(6) with O $\cdots$ O = 2.72Å. The coordina-

tion of O(2) resembles closely that of OH(8) in [Bi$_6$O$_5$(OH)$_3$](NO$_3$)$_5 \cdot$3H$_2$O (Lazarini, 1978), for which Bi–O bonds of 2.22, 2.32 and 2.86Å and a hydrogen bond of 2.81Å have been found.

The two independent AsO$_4$ tetrahedra exhibit dimensions of As–O = 1.66–1.71Å and O–As–O = 103–116°. The mean bond lengths, 1.68Å for As(1) and 1.69Å for As(2), are in good agreement with the mean tetrahedral distance of 1.683(10)Å reported by Shannon & Calvo (1973) for 21 arsenates. Each of the eight AsO$_4$ oxygens, except O(6), is bonded to Bi atoms via one strong and one or two weak bonds with Bi–O distances of 2.26–2.45Å and 2.57–3.36Å, respectively. O(6), which accepts the hydrogen bond from O(2), forms only two weak Bi–O bonds

Table 7. Preisingerite. Bond valence sums according to Brown and Wu (1976)

	Bi^{3+} Bi–O<2.5 Å	Bi^{3+} Bi–O>2.5 Å	As^{5+}	H(d)/H(a)*	valence sum
O(1)	0.78, 0.71, 0.56	0.12			2.17
O(2)	0.61, 0.51	0.13		0.80	2.05
O(3)	0.53	0.29	1.18		2.00
O(4)	0.37	0.20, 0.09	1.32		1.98
O(5)	0.40	0.29, 0.08	1.34		2.11
O(6)		0.27, 0.21	1.24	0.20	1.92
O(7)	0.69	0.14, 0.11	1.19		2.13
O(8)	0.50	0.15	1.29		1.94
O(9)	0.50	0.21, 0.09	1.12		1.92
O(10)	0.39	0.26	1.35		2.00

* H(d) = hydrogen bond donor, H(a) = hydrogen bond acceptor.

of 2.61 and 2.74Å. When considering only Bi–O bonds less than 2.5Å, each $AsO_4(2)$ tetrahedron is bonded to four different $Bi_6O_2(OH)_2$ groups, while the $AsO_4(1)$ tetrahedron establishes a bridging link within one $Bi_6O_2(OH)_2$ group with two of its oxygens, and a link to a second $Bi_6O_2(OH)_2$ group with another oxygen.

Bond valence sums have been calculated using the empirical parameters of Brown and Wu (1976). The results are presented in Table 7. The valence sums show only the usual small deviations from the ideal values and confirm the given assignments of O(1) and O(2) to oxo-anion and OH group.

The structure of preisingerite closely resembles that of atelestite—$Bi_2O(OH)AsO_4$, space group $P2_1/a$, $a = 10.83$, $b = 7.43$, $c = 7.00$Å, $\beta = 107.08°$, z = 4—which recently was studied in this laboratory and will be reported in a forthcoming paper. Sections of the two structures, extending in both cases parallel to (100), are very similar with respect to atomic arrangement and bond lengths. The unit cell given in Table 1 accounts for this relationship and was therefore preferable to a reduced cell, which had originally been chosen for preisingerite. The transformation matrix for the present to the reduced cell is: $-1\ 0\ 0/0\ -1\ 0/-1\ 0\ 1$.

Acknowledgments

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