

**MRÁZEKITE, $\text{Bi}_2\text{Cu}_3(\text{OH})_2\text{O}_2(\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$,
A NEW MINERAL SPECIES AND ITS CRYSTAL STRUCTURE**

TOMÁŠ ŘÍDKOŠIL

Institute of Geological Sciences, Charles University, Albertov 6, 120 00 Praha 2, Czechoslovakia

VLADIMÍR ŠREIN

*Institute of Geology and Geotechnics, Czechoslovak Academy of Sciences,
V. Holesovických 2, 180 00 Praha 8, Czechoslovakia*

JAN FÁBRY AND JIŘÍ HYBLER

Institute of Physics, Czechoslovak Academy of Sciences, Na Slovance 2, 180 40 Praha 8, Czechoslovakia

BORIS A. MAXIMOV

Institute of Crystallography, Academy of Sciences, Leninsky Prospekt 59, Moscow, Russia

ABSTRACT

Mrázekite, ideally $\text{Bi}_2\text{Cu}_3(\text{OH})_2\text{O}_2(\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$, monoclinic, $C2/m$, a 12.359(6), b 6.331(4), c 9.060(4) Å, β 122.71(4)°, V 596.55 Å³, $Z = 2$, occurs in the weathering zone of the copper deposit at Ľubietová (Libethen), central Slovakia, Czechoslovakia. It forms tiny translucent blue acicular crystals that are tabular along the cleavage plane $\{20\bar{1}\}$. Measured density is 4.90(2) g/cm³, and the calculated density is 5.013 g/cm³. The crystals are biaxial negative, $X \parallel b$, $Y \approx a$, $Z \approx c$. The indices of refraction are between 1.8 and 1.9; the average index $n_m = 1.89(5)$. The angle measured between the optic axes is 68(2)°. An electron-microprobe analysis yielded (in wt. %): CuO 26.14, Bi₂O₃ 51.97, P₂O₅ 15.89, As₂O₅ 0.11, H₂O 5.90 (calc.). The structure analysis converged to an R of 0.0511 for 567 observed reflections. Copper atoms located in two independent positions are octahedrally coordinated by O atoms (or OH groups or water molecules). These deformed, edge- and corner-sharing octahedra and PO₄ tetrahedra form strongly bonded infinite sheets parallel to the $(20\bar{1})$ plane, and connected to each other by Bi atoms and hydrogen bonds. The latter are suggested by the short distance (2.62 Å) between the OH group and one of the O atoms of the PO₄ group. The presence of the OH groups and H₂O was proved independently by infrared absorption spectroscopy. The five most intense powder-diffraction maxima [d in Å(1)(hkl)] are: 3.041(100)(310), 2.924(83)(021), 7.623(78)(001), 3.014(63)(203), and 5.200(52)(200). The name honors the late Zdenek Mrázek, discoverer of the species.

Keywords: mrázekite, new mineral species, crystal structure, infrared absorption spectrum, powder diffraction, optical properties, phosphate of Bi and Cu, oxy-hydroxyphosphate, Czechoslovakia.

SOMMAIRE

La mrázekite, de composition idéale $\text{Bi}_2\text{Cu}_3(\text{OH})_2\text{O}_2(\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$, est monoclinique, $C2/m$, a 12.359(6), b 6.331(4), c 9.060(4) Å, β 122.71(4)°, V 596.55 Å³, $Z = 2$. On la trouve dans une zone d'altération du gisement de cuivre à Ľubietová (Libethen), en Slovaquie centrale (Czechoslovaquie), en petits cristaux aciculaires translucides bleus; ils sont tabulaires parallèle au plan de clivage $\{20\bar{1}\}$. La densité mesurée est 4.90(2), et la densité calculée, 5.013. Les cristaux sont biaxes négatifs, $X \parallel b$, $Y \approx a$, $Z \approx c$; leurs indices de réfraction sont entre 1.8 et 1.9; $n_m = 1.89(5)$. L'angle $2V_m$ entre les axes optiques est 68(2)°. Une analyse à la microsonde électronique a donné 26.14% CuO (en poids), 51.97% Bi₂O₃, 15.89% P₂O₅, 0.11% As₂O₅, 5.90% H₂O (calc.). L'analyse de sa structure cristalline a abouti à un indice R de 0.0511 pour 567 réflexions observées. Le Cu occupe deux positions indépendantes; il est entouré, en coordination octaédrique, par des atomes de O (ou des groupes OH ou des molécules d'eau). Les octaèdres difformes, à arêtes et coins partagés, et les tétraèdres PO₄ sont les éléments de feuillettes à liaisons fortes parallèles au plan $(20\bar{1})$. Ces feuillettes sont liés par des atomes de Bi et par une liaison hydrogène, à laquelle nous attribuons la courte distance (2.62 Å) entre le groupe OH et un des atomes d'oxygène du groupe PO₄. La présence des groupes OH et de H₂O a été prouvée indépendamment par spectroscopie d'absorption dans l'infra-rouge. Les cinq raies les plus intenses du cliché de diffraction obtenu par la méthode des poudres [d en Å(1)(hkl)] sont: 3.041(100)(310), 2.924(83)(021), 7.623(78)(001), 3.014(63)(203), and 5.200(52)(200). Le nom rappelle Zdenek Mrázek, qui en a fait la découverte.

(Traduit par la Rédaction)

Mots-clés: mrázekite, nouvelle espèce minérale, structure

crystalline, spectre d'absorption infra-rouge, diffraction X (méthode des poudres), propriétés optiques, phosphate de Bi et Cu, oxy-hydroxyphosphate, Czechoslovaquie.

INTRODUCTION

Mrázekite, a new mineral species, was discovered by the late Zdenek Mrázek (15.2. 1952 – 15.4. 1984) in the course of a detailed mineralogical investigation with the first author in ancient copper mine near Ľubietová (formerly Libethen), in Czechoslovakia. He also suggested that the material might be a new mineral species, and the following investigation confirmed his suggestion. We have named this new mineral in his honor. The problem of better characterizing the mineral from Ľubietová remained unresolved until recently, when samples were first studied by single-crystal methods. This approach led to the successful solution of the structure and also revealed the chemical formula. The mineral and its name were approved by the Commission on New Minerals and Mineral Names of the IMA. The type material is deposited in the Faculty of Science, Charles University, Prague, and in the National Museum in Prague (catalogue number P1N 88529).

OCCURRENCE

Mrázekite occurs in a secondary assemblage at the Reineria mine at Ľubietová, located in the western part of the Slovenské Rudohorie Mountains, approximately 15 km east of Banská Bystrica, Slovakia. The old copper deposit at Ľubietová is known mainly for two minerals first discovered there, libethenite by Breithaupt in 1823 (Hintze 1933), and euchroite by Heideringer in 1825 (Hintze 1933). The geology and mineralogy of this deposit have been described by Beudant (1822),

Čillík *et al.* (1967) and Chovan (1990), among others. The Ľubietová zone is composed of a metamorphic complex of Ľubietová crystalline basement with a Permian sedimentary cover overlain by Mesozoic sedimentary rocks. The metamorphic rocks, belonging to the Jarabá Group, are cut by granitic porphyries of probable Permian age.

The Ľubietová crystalline complex has an anticlinal sliced structure that was formed mainly during an orogeny in Cretaceous time. The anticlinal structure is perturbed by various tectonic dislocations. A system of siderite veins, veinlets and impregnations dispersed in arkose and graywacke contain quartz, often vuggy, with chalcopyrite and tetrahedrite as the principal primary minerals. The deposit once contained a substantial weathering zone with many arsenate and phosphate minerals. These originated from the decomposition of chalcopyrite and tetrahedrite. Faults and fracture zones have provided later access to groundwater, which brought about oxidation of the primary minerals. The oxidation resulted in formation of an assemblage of Cu arsenates and phosphates, such as libethenite, pseudomalachite and euchroite. The youngest secondary mineral are malachite, azurite, brochantite, langite (Provondra & Řídkošil 1989) and cyanotrichite (Čech & Láznička 1965).

The crystals of mrázekite occur in part as slender needles isolated or loosely grouped as small rosettes in a quartz matrix.

Tetrahedrite and an unidentified sulfosalt of Bi are considered to have provided the Cu, Bi and As for the formation of mrázekite. The phosphorus originated by the breakdown of pseudomalachite or apatite from the host rocks.

PHYSICAL PROPERTIES

The mrázekite crystals are bright or cerulean

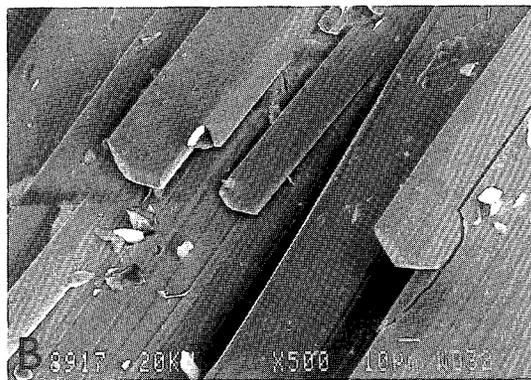
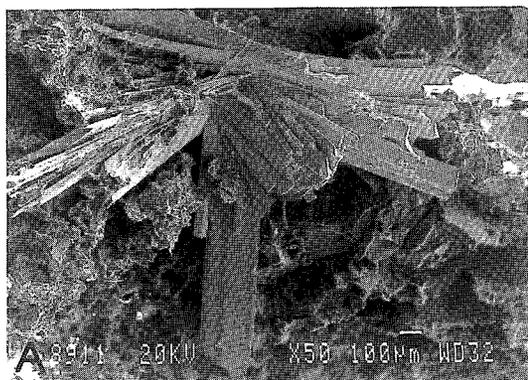


FIG. 1. A. The scanning electron photograph of aggregates of single crystals of mrázekite. B. Details of single crystals.

TABLE 1. X-RAY POWDER-DIFFRACTION DATA ON MRÁZEKITE

I/I_0	d_{obs} [Å]	d_{calc} [Å]	hkl
78	7.625	7.623	001
23	6.096	6.094	20-1
43	5.410	5.408	110
52	5.200	5.200	200
45	5.145	5.145	11-1
27	4.416	4.416	20-2
23	3.813	3.812	002
31	3.633	3.633	11-2
31	3.441	3.441	31-1
37	3.166	3.166	020
11	3.047	3.047	40-2
100	3.040	3.041	310
63	3.014	3.014	20-3
17	3.003	3.007	40-1
83	2.924	2.924	021
1	2.810	2.809	22-1
17	2.771	2.770	112
14	2.680	2.680	40-3
13	2.598	2.598	11-3
27	2.573	2.573	22-2
14	2.497	2.497	202
16	2.452	2.452	311
35	2.349	2.349	221
18	2.294	2.303	51-2
12	2.218	2.218	20-4
15	2.208	2.208	51-1
20	2.201	2.201	51-3
22	2.195	2.195	42-2
7	2.183	2.183	22-3
7	2.180	2.180	42-1
7	2.133	2.133	31-4
22	2.085	2.085	113
7	2.053	2.053	13-1
12	2.046	2.045	42-3
11	2.009	2.009	420
18	1.966	1.9658	51-4
3	1.911	1.9116	203
8	1.886	1.8864	60-4
23	1.876	1.8762	33-1
14	1.817	1.8166	22-4
15	1.803	1.8026	330
4	1.733	1.7332	600
17	1.731	1.7307	31-5
8	1.711	1.7112	511
8	1.701	1.7013	51-5
3	1.696	1.6958	13-3
8	1.653	1.6532	331
7	1.636	1.6364	223
7	1.586	1.5828	040
7	1.569	1.5692	53-3
7	1.526	1.5258	133
7	1.520	1.5202	620
9	1.484	1.4843	62-5
8	1.401	1.4013	24-3
6	1.400	1.4005	44-1
6	1.397	1.3877	82-3

Conditions: Guinier - de Wolff camera, $CuK\alpha$ radiation ($\lambda = 1.54178 \text{ \AA}$), calibrated with NaCl ($a = 5.6404 \text{ \AA}$).

The density, $4.90(2) \text{ g/cm}^3$, was determined by the pycnometric method (xylene). The difference between the measured density and the calculated value obtained from the structure determination (5.013 g/cm^3) is probably due to the presence of quartz, which is intergrown with the sample. The hardness is between 2 and 3 on the Mohs scale.

Both the observed and the calculated (Yvon *et al.* 1977) powder-diffraction patterns are reported in Table 1. The experimental data were obtained on a Guinier - de Wolff camera ($2R = 114.59 \text{ mm}$, $CuK\alpha$ 1.54178 \AA , 34 kV , 24 mA , exposure 24 hours); they were calibrated by linear interpolation using five lines of NaCl. The average difference between standard and observed 4θ values was 0.01° , and the maximum difference was 0.02° . The $4\theta_{calc}$ values were obtained by least-squares refinement (Burnham 1962). Integrated intensities were determined by densitometer measurement.

CHEMICAL COMPOSITION

The crystals of mrázekite were polished, coated with carbon and analyzed with a JEOL JXA 50A electron microprobe (operating voltage 15 kV , sample current $0.025 \mu\text{A}$, beam diameter about $15 \mu\text{m}$), which can reveal elements with an atomic number higher than 8. The measurements were carried out at six different points using a wavelength-dispersion scan. Such scans revealed only Bi, P and Cu as main constituents, with trace amounts of As. We used the following standards: synthetic Bi and eulytite (Bi), clinoclasite from Novoveská Huta ($CuK\alpha$ line, As) and apatite (P). The data were corrected by a version of the program based on conventional ZAF methods of Duncumb & Reed (1968) and Philibert (1963). The results are given in Table 2.

The formula of mrázekite scaled to 14 oxygen atoms is $Bi_{2.011}Cu_{2.962}P_{2.019}As_{0.008}O_{11.046} \bullet 1.954 H_2O$. This is in accordance with the idealized formula obtained as a result of the crystal-structure analysis: $Bi_2Cu_3(OH)_2O_2(PO_4) \bullet 2H_2O$.

blue, translucent, and possess a vitreous luster. Their hue is similar to that of linarite and azurite.

Mrázekite crystallizes as needles or plates elongated along the b axis and parallel to $\{201\}$. No crystals longer than 2 mm were found. A SEM photograph of mrázekite crystals (Fig. 1) shows their typical habit.

The orientation of the optical indicatrix is $X|b$, $Y \approx a$, $Z \approx c$, $ZAc = 16^\circ$; the indices of refraction are between 1.8 and 1.9, $n_m = 1.89(5)$. The angle between the optic axes is $68(2)^\circ$. The optical investigations were hampered by high indices of refraction and by rapid reaction of crystals with the immersion fluid (C.D West).

TABLE 2. CHEMICAL COMPOSITION OF MRÁZEKITE

	average	e. s. d.	min. value	max. value
CuO	26.14	0.09	25.95	26.23
Bi_2O_3	51.97	0.28	51.58	52.36
P_2O_5	15.89	0.29	15.44	16.18
As_2O_5	0.11	0.02	0.08	0.12
H_2O, OH^- *	5.90	0.41	6.34	5.48
Total:	100.00			

* Calculated, to insure charge balance. Results (in wt.%) represent an average of 6 point-analyses obtained with an electron microprobe.

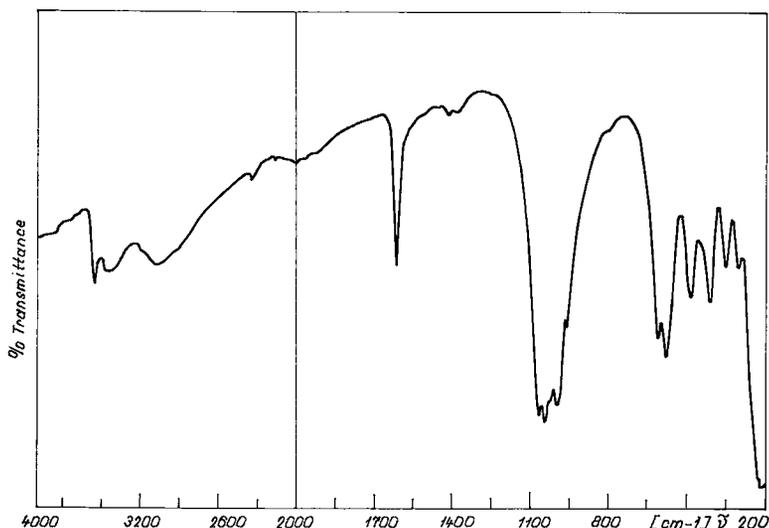


FIG. 2. The infrared absorption spectrum of mrázekite.

TABLE 3. INFRARED ABSORPTION SPECTRUM OF MRÁZEKITE

Frequency [cm ⁻¹]	Tentative assignment	
303	w	sp
348	m	sp
410	m	sp
482	m	sp
580	s	sp
608	s	sp
800	vw	sh
960	vs	sh
996	vs	sp
1042	vs	sp
1068	vs	sp
1200	vw	sh
1386	vw	sp
1418	vw	sp
1543	vw	sh
1614	s	sp
1910	vw	sh
2000	vw	b
2165	vw	b
2330	w	sp
3076	m	b
3460	m	b
3556	m	sh

Intensity scale: s strong, m medium, w weak, vw very weak. Character of absorption maxima: sp sharp, sh shoulder, b broad.

THE INFRARED-ABSORPTION SPECTRUM

The infrared absorption spectrum (Fig. 2, Table 3) was recorded on a Philips PU 9512 spectrometer in the region (200–4000 cm⁻¹) using the KBr pellet method.

The spectrum proves the presence of H₂O and OH⁻ in the structure, and reinforces the findings of the X-ray analysis (see below). The bands at 3556, 3460, and 3076 cm⁻¹ belong to the stretching vibrations of the hydroxyl groups of H₂O and the OH⁻ group itself. The bands at 1386 and 1418 cm⁻¹

were assigned to in-plane bending vibrations of the OH group. The bands in the region 2000 – 2600 cm⁻¹ are combination bands (Pechkovskiy *et al.* 1981). The sharp peak at 1614 cm⁻¹ belongs to δ H₂O of the water molecule.

The X-ray structure analysis revealed the existence of a hydrogen bond [2.62(2) Å] between the oxygen bonded to two copper atoms and the phosphate oxygen. The stereochemical considerations given below imply that the oxygen bonded to two copper atoms is the hydrogen-bond donor atom, and the phosphate oxygen is the hydrogen-bond acceptor atom. If a [HPO₄]²⁻ group were present in the structure, then bands in the region 860 – 915 cm⁻¹ [ν PO(H)] and in the region 700 – 900 cm⁻¹ [γ (POH)] should be observed. Except for a peak of very low intensity at 800 cm⁻¹, no bands were observed in this region.

The bands at 1068 and 960 cm⁻¹ are asymmetrical and symmetrical stretching vibrations of PO₄, respectively (Povarennykh 1978). The relatively moderate splitting of the composite band in the region 960–1068 cm⁻¹ and the two peaks at 580 and 608 cm⁻¹ also support the proposal that [PO₄]³⁻ is present rather than [HPO₄]²⁻ (Pechkovskiy *et al.* 1981).

DETERMINATION OF THE CRYSTAL STRUCTURE

The single crystals chosen for this experiment did not exceed 0.2 mm in length. Laue photographs indicate the poor quality of most of the crystals. Nevertheless, the precession photographs of a small plate gave rough cell-parameters and indicated as

possible space-groups $C2$, Cm , or $C2/m$. A small chip of irregular shape, with approximate dimensions $0.1 \times 0.09 \times 0.05$ mm, was finally chosen for diffractometer measurements.

The data were collected using an Enraf-Nonius CAD-4F diffractometer, operated at 50 kV and 40 mA, with graphite-monochromatized $MoK\alpha$ radiation. The unit-cell parameters [a 12.359(6), b 6.331(4), c 9.060(4) Å, β 122.71(4)°] were refined by least squares with 25 reflections in the range $9.90^\circ < \theta < 17.52^\circ$. The intensities of 1838 reflections, of which 1155 were considered observed [$I > 1.96\sigma(I)$], were measured by the ω -scan mode to a θ_{\max} of 30° within the range ($-17 < h < 17$, $-8 < k < 8$, $0 < l < 12$).

The ω -scan angle and the horizontal detector aperture were set equal to $(2.00 + 0.35 \tan \theta)^\circ$ and $(2.00 + 1.05 \tan \theta)^\circ$, respectively; the vertical detector aperture was set at 4 mm. The intensity-standard reflection (514) was monitored every 3600 seconds; its intensity variation was $\pm 5\%$ during the collection of the data. The prescan speed was $10.06^\circ/\text{min}$. The final scan was not applied for reflections whose ratio $\sigma(I)/I$ determined after the prescan lay outside the interval (0.05, 1). The final scan speeds ranged from 2.87 to $10.06^\circ/\text{min}$.

Intensities were corrected for the variation of the standard reflection by linear interpolation, and the LP-correction was applied. The estimated R -factors from the counting statistics were found to equal 0.044 and 0.099 for observed and all reflections, respectively.

Scattering factors (including anomalous dispersion) were taken from Cromer & Mann (1968) and from the International Tables for X-ray Crystallography (1974). The presence of As was neglected in the calculations. The positions of non-hydrogen atoms were determined by Patterson and Fourier methods. After the isotropic refinement had converged ($R = 0.2158$), the values of observed structure-factors were corrected for absorption by the program DIFABS (Walker & Stuart 1983). The minimum and maximum correction-coefficients were 0.562 and 2.249 for reflections (-17 - 1.8) and (-6 - 8.0), respectively. The value of the absorption factor μ is 349.44 cm^{-1} . All other calculations were performed by the SDS program system for X-ray structure analysis (Petříček & Maly 1988). The isotropic refinement was then repeated in order to get a more precise model. The original uncorrected observed structure-factors were corrected by DIFABS again. After that, the symmetrically equivalent reflections were averaged. This resulted in 942 unique reflections, of which 567 were observed [$I > 1.96 \sigma(I)$].

The full-matrix least-squares refinement [Bi, Cu, P refined anisotropically, 41 parameters; the minimized function was $w(|F_o| - |F_c|)^2$, $w^{-1} =$

$[\sigma^2(F_o) + (0.03|F_o|)^2]$, where $\sigma^2(F_o)$ is derived from counting statistics] resulted in an R of 0.12 ($wR = 0.07$) for reflections including unobserved ones, and an R of 0.0511 ($wR = 0.0581$) for observed reflections only; $S = \Sigma |wF|^2 / (m-n) = 1.195$ (where m is the number of reflection and n the number of refined parameters), residual electron densities $\Delta\rho(\max) = 5.95 \text{ e}\text{\AA}^{-3}$, $\Delta\rho(\min) = -7.82 \text{ e}\text{\AA}^{-3}$, $(\Delta/\rho)_{\max} < 0.01$. The minimal density of electrons was in the region of Bi atom.

Lists of structure factors and anisotropic thermal parameters have been deposited with the Depository of Unpublished Data, CISTI, National Research Council of Canada, Ottawa, Ontario K1A 0S2.

DISCUSSION OF THE STRUCTURE

The structure determination reveals that the mineral is an oxo-hydroxo-phosphate of trivalent bismuth and divalent copper, with two water molecules. It has the chemical formula $\text{Bi}_2\text{Cu}_3(\text{OH})_2\text{O}_2(\text{PO}_4)_2 \cdot 2 \text{H}_2\text{O}$.

The projection along the monoclinic axis of the structure is shown in Figure 3 (ball-and-stick model), the coordinates and $B_{\text{eq}}/B_{\text{iso}}$ are given in Table 4, and the relevant distances and angles are listed in Table 5. The bond-valence table calculated according to Brown & Wu (1976) is shown in Table 6.

The X-ray structure analysis yielded the positions of all atoms except hydrogen. Since the presence of fluorine was excluded by the electron-microprobe analysis, all light atoms except H determined in the structure were unambiguously oxygen atoms. As a result, six negative charges per formula unit remained, which had to be compensated by six hydrogen atoms.

The oxygen atoms situated on the long axes of deformed coordination octahedra around copper atoms (the angles contained by the normals to the equatorial planes and by the intercepts O6-Cu1 and O6-Cu2 are 9.13° and 8.68° , respectively) are suspected to belong to water molecules. This contention is supported by the IR-spectrum and stereochemical considerations. It is likely that an uncharged water molecule would be more distant from a copper atom than an OH^- group. Moreover, the O6 atom is rather isolated, as it lies 2.73 \AA away from three Cu atoms and 3.1 \AA from the nearest oxygen atom. The former and the latter distances are the limiting ones both for the Cu-O covalent and O-O hydrogen bonds, respectively. The bond-valence sum of the O6 atom, equal to 0.186 (see Table 6), shows also clearly that this atom represents a water molecule.

Each of the remaining two hydrogen atoms in the formula unit is most likely involved in hydrogen

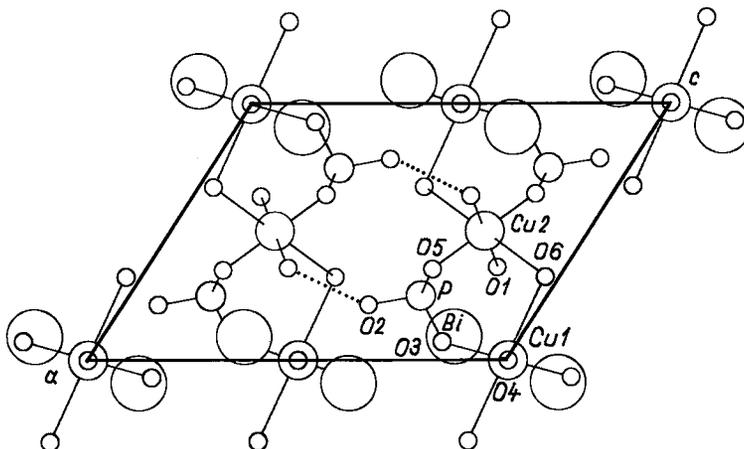


FIG. 3. The projection along the monoclinic axis of the structure of mrázekite by means of a ball-and-stick model. The O1 atom is part of the OH⁻ group, and the O6 atom represents the water molecule. Hydrogen bonds are represented by dotted lines.

TABLE 4. FRACTIONAL ATOMIC COORDINATES ($\times 10^4$), B_{eq} AND B_{iso} FOR NON-OXYGEN AND FOR OXYGEN ATOMS

$B_{eq} = 4/3 \sum_i \sum_j \beta_{ij} a_i a_j$					
atom site*	x	y	z	B_{eq}/B_{iso}	$[Å^2]$
Bi 4i	1595(1)	0	907(1)	1.54(3)	
Cu1 2b	0	5000	0	1.2(1)	
Cu2 4f	2500	2500	5000	1.75(9)	
P 4i	3061(5)	5000	2522(7)	1.1(2)	
O1 4i	1639(15)	0	3607(21)	1.9(3)	
O2 4i	856(15)	0	-2146(21)	2.0(3)	
O3 4i	1805(16)	5000	691(22)	2.2(3)	
O4 4g	0	2070(34)	0	2.2(3)	
O5 8g	3153(13)	3028(30)	3526(19)	3.3(3)	
O6 4i	366(19)	5000	3248(27)	3.1(4)	

* The site column is a combination of the multiplicity and of the Wyckoff symbol. Estimated standard deviation is shown in parentheses.

bonds connecting O1 and O2. In short hydrogen bonds like this one [the distance O1...O2 is 2.62(2) Å], the hydrogen atoms should be situated along the line connecting oxygen atoms (Brown 1976).

Stereochemical reasons exclude hydrogen bonds between the oxygen atoms situated in equatorial planes around copper atoms (O1, O3, O4, O5). The short O4...O4' distance (the primes indicate symmetrically equivalent atoms) in the latter case is caused by bonding these oxygen atoms to Bi. For example, in CuBi₂O₄ (Arpe & Müller-Buschbaum 1976), the oxygen atoms are separated by only 2.37 Å. Moreover, the hydrogen cannot be bonded to O4, since this oxygen atom is triagonally coordinated by two Bi atoms and the Cu1 atom.

Contrary to O4, the O1 atom is tetrahedrally bonded to two equally distant copper atoms

TABLE 5. RELEVANT INTERATOMIC DISTANCES [Å] AND BOND ANGLES [°]

Bi - O1	2.42(2)	O1 - Bi - O2	162.4(6)
Bi - O2	2.40(2)	O1 - Bi - O3	96.0(4)
Bi - O3	3.191(3)	O1 - Bi - O3d	145.4(5)
Bi - O3b	3.191(3)	O1 - Bi - O4	84.3(3)
Bi - O3d	3.02(2)	O1 - Bi - O5	61.4(5)
Bi - O4	2.13(1)	O2 - Bi - O3	85.5(4)
Bi - O4b	2.13(1)	O2 - Bi - O3d	52.1(5)
Bi - O5	2.84(2)	O2 - Bi - O4	81.9(4)
Bi - O5b	2.84(2)	O2 - Bi - O5	128.8(5)
Bi - Bif	3.353(1)	O3 - Bi - O3b	165.6(6)
Cu1 - O3	1.96(2)	O3b - Bi - O3d	82.8(4)
Cu1 - O4	1.85(2)	O3b - Bi - O4b	56.9(6)
Cu1 - O6	2.73(3)	O3b - Bi - O4	132.6(6)
Cu2 - O1	1.94(1)	O3 - Bi - O5	48.8(4)
Cu2 - O5	1.93(2)	O3 - Bi - O5b	132.8(4)
Cu2 - O6	2.73(2)	O4 - Bi - O4b	76.1(7)
P - O2d	1.55(2)	O4 - Bi - O5	88.6(5)
P - O3	1.54(1)	O4 - Bi - O5b	143.8(4)
P - O5	1.51(2)	O5 - Bi - O5b	84.9(5)
P - O5e	1.51(2)	O3 - Cu1 - O4	90.00(0)
O1 - O2f	2.62(2)	O3 - Cu1 - O6	99.1(7)
O1 - O4	3.06(2)	O4 - Cu1 - O6	90.00(0)
O1 - O4b	3.06(2)	O1 - Cu2 - O5	88.8(9)
O1 - O5	2.71(2)	O1 - Cu2 - O6	94.4(4)
O1 - O5b	2.71(2)	O5 - Cu2 - O6	97.6(7)
O1a - O5	2.77(3)	O2d - P - O3	104.5(1.1)
O1a - O5e	2.77(3)	O2d - P - O5	109.8(8)
O2 - O4	2.97(2)	O3 - P - O5	110.6(7)
O2 - O4b	2.97(2)	O5 - P - O5e	111.2(7)
O3 - O4	2.70(2)	Cu2 - O1 - Cu2b	109.0(6)
O3 - O4e	2.70(2)	Cu2 - O1a - Bi1a	111.2(7)
O3 - O6h	3.10(2)	Bi1a - O1a - Cu2e	111.2(7)
O4 - O4b	2.62(3)	Bi - O4 - Bif	104.0(9)
O4 - O6	3.30(2)	Bi - O4 - Cu1	128.0(5)
O5 - O6a	3.13(2)	Bif - O4 - Cu1	128.0(5)
		Cu1 - O6 - Cu2	99.9(8)
		Cu1 - O6 - Cu2e	99.9(8)
		Cu2 - O6 - Cu2e	70.8(5)
		Cu2e - O1a - O2g	114.2(7)
		Cu2 - O1a - O2g	114.2(7)
		Bi1a - O1a - O2g	96.4(6)
		Bi - O2 - Pd	114.7(7)
		P - O2d - O1i	144.(1.)

symmetry code:

a. -x+0.5, -y+0.5, -z+1

c. x-1, y, z-1

e. x, -y+1, z

g. x+0.5, y+0.5, z+1

i. x+0.5, y+0.5, z

b. x, -y, z

d. -x+0.5, -y+0.5, -z

f. -x, -y, -z

h. -x, y, -z

Estimated standard deviation is shown in parentheses.

TABLE 6. MRÁZEKITE, BOND-VALENCE TABLE

	Bi	Cu1	Cu2	P	Sum
O1	0.395		0.482 0.482		1.359
O2	0.413			1.215	1.628
O3	0.099 0.099 0.131	0.454 [0.454]		1.249	2.032
O4	0.748 0.748	0.641 [0.641]			2.137
O5	0.178 [0.178]		0.498 [0.498]	1.359 [1.359]	2.035
O6		0.062 [0.062]	0.062 0.062		0.186
Sum	2.989	2.314	2.084	5.182	

The parameters are taken from Brown & Wu (1976); for Bi, $R_1 = 2.010 \text{ \AA}$, $N = 5.0$; for Cu, $R_1 = 1.718 \text{ \AA}$, $N = 6.0$; for P, $R_1 = 1.622 \text{ \AA}$, $N = 4.29$. Terms in square brackets denote one cation bonded to two oxygen atoms, but each oxygen atom is bonded to only one cation.

[1.94(1) Å], to the Bi atom [2.42(2) Å] and to the supposed hydrogen atom (see below). The pertinent angles are: Bi–O1–Cu2, Bi–O1–Cu2' ($2 \times 111.2^\circ$) and Cu2–O1–Cu2' (109.0°). Thus the O1 atom is in the sp^3 state, just as O2 [the angle Bi–O2–P1 is 114.7°].

With regard to Brown's method, the dilemma as to which of the oxygen atoms, O1 or O2, is the hydrogen-bond donor or the acceptor may be solved: the angles Cu2–O1–O2, Cu2–O1–O2' ($2 \times 114.2^\circ$) and Bi–O1–O2' (96.4°) indicate that the hydrogen atom is bonded to O1 because the direction O1–H, which must conform to the sp^3 state of O1, is roughly the same as the direction O1–O2. The hydrogen atom should thus be located in the symmetry plane that is also occupied by O1 and O2 atoms. The same reasoning excludes O2 from being a hydrogen-bond donor atom because the angle P'–O2'–O1 (144.2°) is too different from the expected value close to the tetrahedral angle.

The other possible site for placing the remaining hydrogen atoms has not yet been mentioned. The O2...O4 distance [2.97(2) Å] corresponds to the weak hydrogen bond. Then the O2 would inevitably have to be the hydrogen-bond donor atom because of planar coordination of O4. However, the infrared absorption spectrum indicates the presence of the phosphate group rather than the $[\text{HPO}_4]_a^{2-}$ group in the structure. It is also reasonable to expect that owing to the shorter O1...O2 distance, these atoms are more likely connected by the hydrogen bond than the atoms O2...O4.

The further confirmation of the proposed assignment of hydrogen atoms to oxygen atoms yield bond valences calculated according to Brown & Altermatt (1985) and Brown & Wu (1976) (see Table 6). The sums of bond valences are 2.137 for

O4, 1.628 for O2 and 1.359 for O1. On the contrary, the bond-valence sum of O4 is slightly excessive (2.137), so that this atom cannot be involved in any hydrogen bonding.

The geometry of the phosphate molecule is normal. The P–O2 and P–O3 bond distances are somewhat longer than the other P–O bond lengths. All oxygen atoms in the phosphate group except O2 are coordinated to Cu atoms, O2 to Bi atom. The coordination polyhedron of the Bi atom is shown in Figure 4.

The deformed coordination octahedra of Cu and the PO_4 tetrahedra polymerize to form infinite strongly bonded sheets parallel with the cleavage plane $\{20\bar{1}\}$. Shown in Figure 5 is the projection of the structure along the monoclinic axis expanded over several unit cells, with Cu-bearing octahedra, P-bearing tetrahedra and bismuth atoms represented by circles. The internal structure of these sheets is shown in Figure 6. These sheets are composed of infinite chains of edge-sharing Cu2 octahedra parallel to b , cross-linked to each other by Cu1 octahedra sharing two corners with Cu2 octahedra. This construction is reinforced by PO_4 tetrahedra sharing two corners with Cu2 octahedra and one corner with the Cu1 octahedron. The adjacent sheets are separated by less densely bonded layers represented by Bi–O bonds and hydrogen bonding.

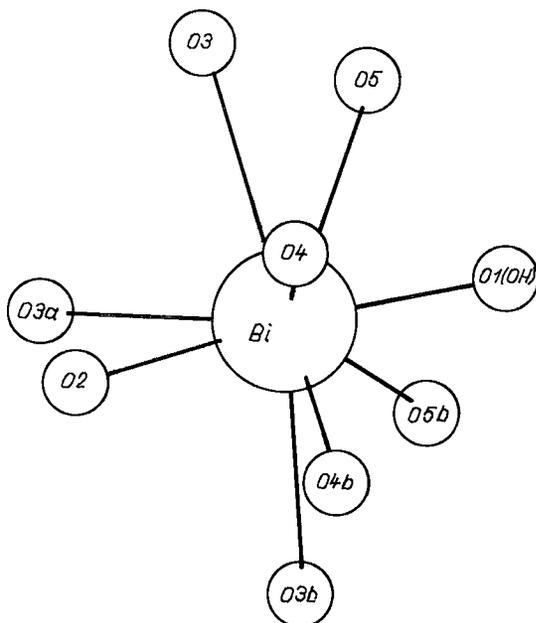


FIG. 4. The coordination of the Bi atom by oxygen atoms.

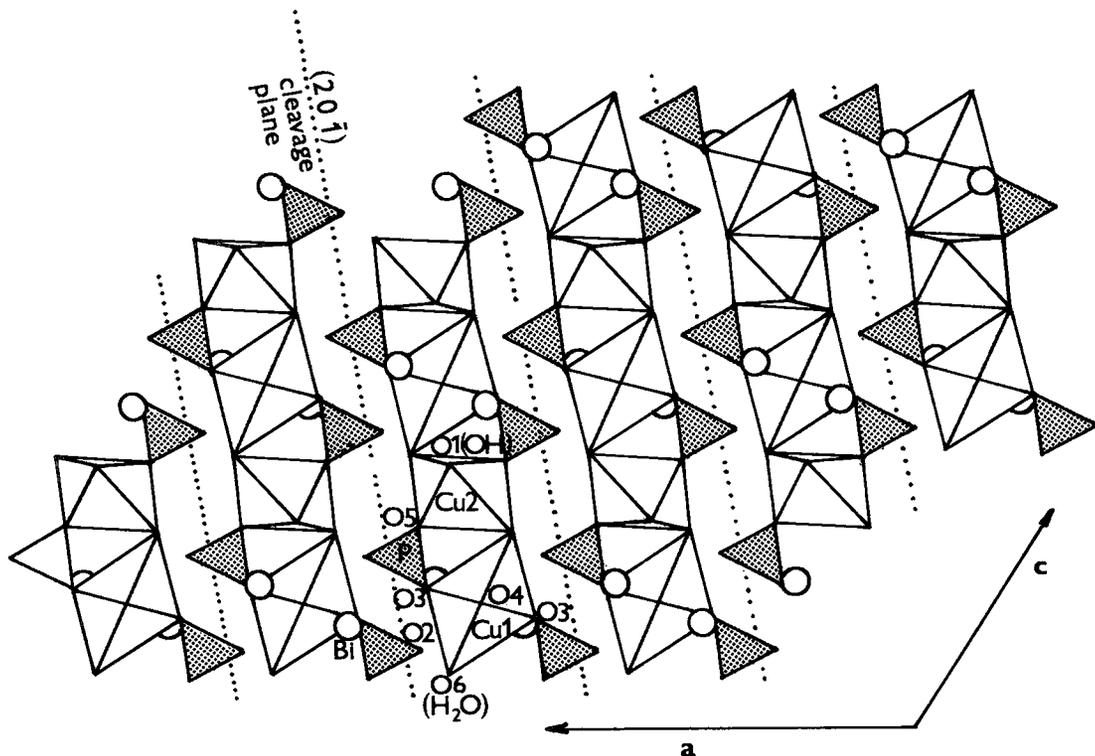


FIG. 5. The expanded projection along the monoclinic axis in the form of coordination polyhedra, *i.e.*, Cu1 and Cu2 octahedra and P tetrahedra. Bismuth atoms are represented by circles. The densely bonded sheets parallel with the cleavage plane $\{20\bar{1}\}$ are visible in sections.

The sums of bond valences of O4 (2.137) and of Cu1 (2.314) (see Table 6) are somewhat higher than expected, perhaps owing to the contraction of Cu1 octahedra along the *b* axis. This causes a shorter Cu1–O4 distance (1.85 Å).

The recent comprehensive work of Hawthorne (1990) enabled us to compare mrázekite with some similar structures. The isolated infinite chain or edge-sharing Cu octahedra with adjacent corner-sharing S tetrahedra appears in the structure of the mineral linarite $\text{PbCuSO}_4(\text{OH})_2$ (Bachmann & Zemmann 1961). These chains can be cross-linked by the tetrahedra to form the infinite sheets such as in tsumcorite $\text{Pb}[(\text{Zn}, \text{Fe}^{3+})(\text{AsO}_4)(\text{H}_2\text{O}, \text{OH})_2]$ (Zn and Fe^{3+} octahedra, As tetrahedra (Tillmanns & Gebert 1973) and bermanite $\text{Mn}^{2+}[\text{Mn}^{3+}(\text{PO}_4)(\text{OH})_2](\text{H}_2\text{O})_4$ (Mn^{3+} octahedra, P tetrahedra) (Kampf & Moore 1976). In mrázekite, similar sheets are formed from these chains cross-linked by the P tetrahedra and by the additional corner-sharing Cu1 octahedra. The same chain of octahedra appears also as a building block of framework structures, *e.g.*, of melonjosephite $\text{Ca}[(\text{Fe}^{2+}\text{Fe}^{3+})(\text{PO}_4)_2(\text{OH})]$, (chain of edge-sharing Fe octahedra, cross-link by edge- and corner-shar-

ing Fe octahedra and P tetrahedra), (Kampf & Moore 1977), lawsonite $\text{Ca}[\text{Al}_2(\text{Si}_2\text{O}_7)(\text{OH})_2](\text{H}_2\text{O})$, (Al octahedra and Si_2O_7 groups of Si tetrahedra), (Baur 1978), and descloizite $\text{Pb}[\text{Zn}(\text{VO}_4)(\text{OH})]$, (Zn octahedra, V tetrahedra), (Hawthorne & Faggiani 1979).

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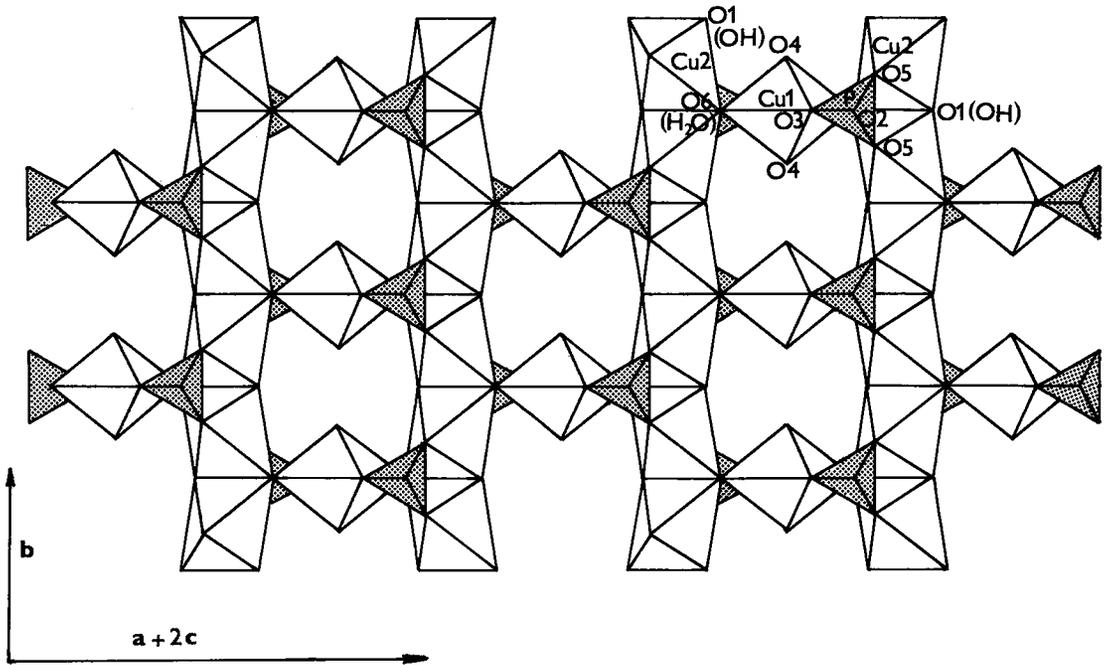


FIG. 6. The internal structure of densely bonded sheets. The bismuth atoms are omitted for clarity.

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