

Medenbachite, $\text{Bi}_2\text{Fe}(\text{Cu,Fe})(\text{O,OH})_2(\text{OH})_2(\text{AsO}_4)_2$, a new mineral species: Its description and crystal structure

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ABSTRACT

Medenbachite occurs in association with mixite, preisingerite, alunite, goethite, reichenbachite, and malachite in a silicified barite vein from Reichenbach near Bensheim, Odenwald, Hesse, Germany. It forms aggregates of small tabular crystals. No cleavage was observed; fracture is conchoidal and Mohs hardness is 4.5. The color varies from yellow to brown-yellow; the luster is vitreous to adamantine. Medenbachite is biaxial negative, $2V = 43(3)^\circ$, dispersion $r > v$, $\alpha = 2.03(2)$, $\beta = 2.09$ (calc.), and $\gamma = 2.10(2)^\circ$. Observed crystal forms are $\{001\}$, $\{\bar{1}01\}$, $\{101\}$, $\{\bar{1}10\}$, $\{0\bar{1}1\}$, and $\{13\bar{1}\}$. Medenbachite is triclinic, space group $P\bar{1}$, with $a = 4.570(1)$, $b = 6.162(1)$, $c = 8.993(1)$ Å, $\alpha = 94.56(1)$, $\beta = 99.69(1)$, $\gamma = 94.28(1)^\circ$, $V = 247.9$ Å³, $Z = 1$, $D_{\text{calc}} = 5.90$ g/cm³. The six strongest lines of the powder diffraction pattern are [$d(\text{Å})$, (I/I_0), (hkl)]: 8.823(62)(001), 3.749(100)(0 $\bar{1}2$,101), 3.596(77)($\bar{1}11$), 3.468(58)(110,1 $\bar{1}\bar{1}$), 2.903(69)(102), and 2.810(51)(021). Electron microprobe analyses gave Bi_2O_3 53.36, Fe_2O_3 8.99, FeO 1.00 (calc.), CuO 7.85, As_2O_5 25.32, H_2O (calc.) 3.07%, sum 99.59%. Microchemical tests indicate the presence of both Fe^{3+} and Fe^{2+} ions. On the basis of crystal-chemical considerations, the Fe^{3+} - Fe^{2+} distribution was calculated from the total iron content to achieve equal numbers of Fe^{3+} and $(\text{Cu}^{2+} + \text{Fe}^{2+})$ ions, for two crystallographically different positions. This yields the empirical formula $\text{Bi}_{2.04}\text{Fe}_{1.00}^{3+}(\text{Cu}_{0.88}\text{Fe}_{0.12}^{2+})_{21.00}\text{O}_{1.11}(\text{OH})_{3.03}(\text{AsO}_4)_{1.96}$, or ideally $\text{Bi}_2\text{Fe}^{3+}(\text{Cu,Fe}^{2+})(\text{O,OH})_2(\text{OH})_2(\text{AsO}_4)_2$. The structure refinement converged at $R = 0.079$ for 1124 unique reflections. Edge-sharing octahedra with an ordered occupation of alternating Fe^{3+} and $(\text{Cu}^{2+}, \text{Fe}^{2+})$ ions form columns parallel to $[010]$, which are linked parallel to (001) by arsenate tetrahedra. The Bi^{3+} is probably distributed over two sites, which are 0.463(5) Å apart. Refinement of the site-occupancy factors indicates 50% probability for the location of Bi^{3+} on each position.

INTRODUCTION

Weathering of small ore impregnations in a silicified barite vein near Reichenbach, Odenwald, Hesse, Germany, led to the formation of numerous secondary minerals. Among them, a brown-yellow bismuth-iron-copper-arsenate was found in very small amounts by K.P. in 1984. From preliminary X-ray and chemical data it was clearly evident that this material represents a new mineral, although a complete characterization was only recently successful. Medenbachite is the first known bismuth-iron-copper-arsenate; chemically related minerals are paulkellerite, $\text{Bi}_2\text{Fe}(\text{PO}_4)_2(\text{OH})_2$ (Dunn et al. 1988), mrázekite, $\text{Bi}_2\text{Cu}_3(\text{OH})_2\text{O}_2(\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ (Řídkošil et al. 1992), zairite, $\text{BiFe}_3(\text{OH})_6(\text{PO}_4)_2$ (Van Wambeke 1975), and mixite, $\text{BiCu}_6(\text{OH})_6(\text{AsO}_4)_3 \cdot 3\text{H}_2\text{O}$ (Mereiter and Preisinger 1986), but there are only slight structural relationships. The new mineral was named in honor of Olaf Medenbach, mineralogist at the University of Bochum,

Germany, for his contributions in various fields of mineralogy. Cotype material is preserved in the collection of the Institut für Mineralogie, Ruhr-Universität Bochum, Germany. Both the mineral and mineral name have been approved by the IMA Commission on New Minerals and Mineral Names (no. 93-048).

DESCRIPTION AND OCCURRENCE

The silicified barite vein of Reichenbach near Bensheim, Odenwald, Hesse, Germany, is the largest of several similar silicified veins occurring in the crystalline rocks of the northwestern Odenwald area. Small isolated grains of ore minerals (e.g., galena, chalcopyrite, tetrahedrite, tennantite, emplectite, wittichenite) occur inside the vein material. Weathering of these primary ore minerals leads to many secondary minerals, predominantly phosphates, arsenates, and vanadates of copper, lead, and bismuth. More detailed descriptions of the locality were given by Sieber et al. (1987) and Krause et al. (1993).

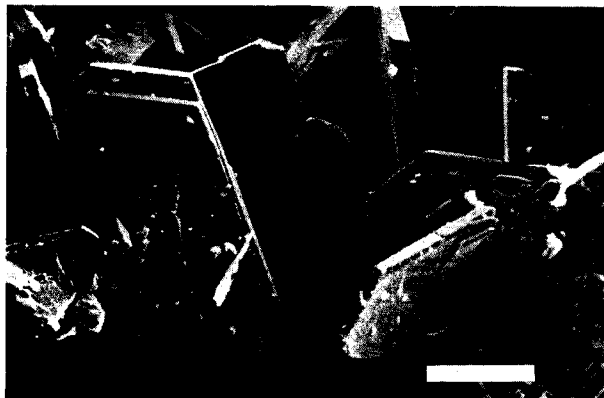


FIGURE 1. SEM micrograph of medenbachite. Scale bar is 20 μm .

Medenbachite was found in a quarry near the Borstein cliff, about 1 km east of the town of Reichenbach (latitude 49°42'49" N, longitude 8°41'00" E). Only two discoveries were made, in 1984 and 1989, and therefore the mineral is regarded as very rare; the total quantity of material found is only a few milligrams. Two samples were used in the study. Sample 8.0.137 (found in 1984) was used for determination of the physical properties and for the X-ray powder diffraction pattern, and sample 8.0.376 (found in 1989) was used for crystal-structure investigations and optical and morphological studies; electron microprobe analyses were performed on both samples. Those specimens used to determine quantitative data were assigned cotype status, and part of this material, including the crystal used for the investigation of the crystal structure, is deposited in the collection of the Institut für Mineralogie, Ruhr-Universität Bochum, Germany.

Medenbachite occurs as very small, intergrown, tabular crystals up to 0.2 mm in length, often forming aggregates of parallel intergrowths, which crystallize within cavernous quartz (Fig. 1). It may have been formed by weathering of Bi-bearing ore minerals like emplectite and wittichenite. Samples containing both primary and secondary minerals within the same specimen were not found. Associated minerals are (in order of decreasing frequency) mixite, preisingerite, alunite, goethite, reichenbachite, and malachite.

PHYSICAL AND OPTICAL PROPERTIES

The color of medenbachite is yellow to brown-yellow, depending on grain size. Very small and thin crystals are transparent, whereas larger crystals are translucent. The luster is vitreous to adamantine, and there is no fluorescence in either long- or short-wave ultraviolet radiation. The fracture is conchoidal, and no cleavage was observed. Medenbachite is completely soluble in warm, dilute, hydrochloric acid without effervescence. The density could not be determined due to lack of material; the calculated density is 5.90 g/cm³. A Leitz microhardness tester was used to measure Vickers microhardness; consid-

ering only perfect indentations, a mean value of hardness of $VHN_{25} = 420 \text{ kg/mm}^2$ was found, which corresponds to 4.5 on the Mohs hardness scale.

The interfacial angles of several medenbachite crystals were measured by means of a two-circle optical goniometer. Because of poor crystal quality and the small size (about 0.1 mm), no precise measurements were possible. Nevertheless, the results were sufficient to determine the morphology. The crystals are tabular on $\{101\}$ and slightly elongated parallel to $[111]$. They exhibit two main zones: One is parallel to $[111]$ and includes $\{101\}$, $\{1\bar{1}0\}$, $\{0\bar{1}1\}$, and the other is parallel to $[010]$ and includes $\{101\}$, $\{101\}$, and $\{001\}$ (Fig. 2a). These results were confirmed on crystals oriented on an X-ray precession camera prior to the goniometric measurements.

Grain samples immersed in Cargille oils were used to determine the refractive indices α and γ . The index β was calculated; it could not be determined experimentally because of the small crystal size, a refractive index value >2.05 , and β orientation nearly perpendicular to (101) . The optical character and the orientation of the indicatrix were measured using a spindle stage and crystals immersed in methylene iodide. These measurements were repeated using a West solution, because of the high refractive indices of medenbachite, to minimize the deviations caused by total reflection. Medenbachite is biaxial negative, $2V_{\text{meas}} = 43(3)^\circ$ (from extinction curves), dispersion $r > v$, $\alpha = 2.03(2)$, $\beta = 2.09$ (calc.), and $\gamma = 2.10(2)$ (all measurements at 592 nm). No distinct pleochroism was found. For crystals lying on (101) , γ' shows an oblique extinction of 38° in reference to the crystal elongation $[111]$. The optical orientation (ϕ, ρ) is $X(-14^\circ, 74^\circ)$, $Y(-117^\circ, 52^\circ)$, and $Z(95^\circ, 43^\circ)$. All optical and morphological data are summarized in the stereographic projection in Figure 2b. Calculation of the Gladstone-Dale relationship using a mean refractive index of 2.073, the calculated density of 5.90 g/cm³, and the chemical composition of sample 8.0.376 (Table 1) reveals excellent agreement between chemical and physical data ($1 - K_p/K_c = -0.026$; Mandarino 1981).

CHEMICAL COMPOSITION

An electron microprobe (Cameca CAMEBAX, 20 kV, 10 nA, beam diameter of 5 μm) was used for chemical analyses. The standards used were synthetic Bi₂S₃ (Bi), mimetite (As), CuSrSi₄O₁₀ (Cu), and synthetic andradite glass (Fe). No other elements with atomic number greater than eight were detected. Direct determination of H₂O was not possible because of the small amount of material available and because most of the material could not be separated from adhering mixite. H₂O was calculated, assuming three OH groups, on the basis of charge-balance requirements and bond-valence calculations. The alternative formulation of three OH groups as OH⁻ + O²⁻ + H₂O could be excluded by IR spectroscopy. The investigation of several crystal aggregates using a Bruker Fourier-transform IR microscope gave absorption bands at 3475 (very strong; OH), 3405 (strong; OH), 1040 (strong;

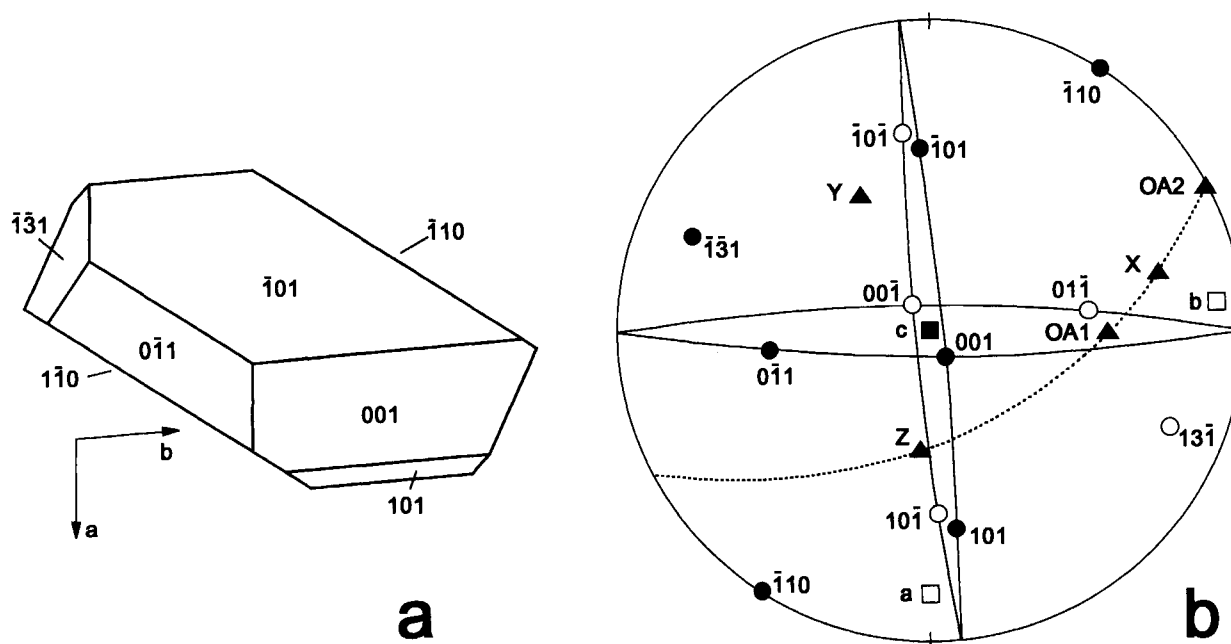


FIGURE 2. Morphology of medenbachite viewed parallel to [001] (a), and stereographic projection (b), including morphology and optical orientation. Solid symbols = upper hemisphere, open symbols = lower hemisphere; a , b , c = crystallographic axes; X , Y , Z = optic indicatrix orientation; OA1, OA2 = optic axes; dotted line = optic axial plane; solid lines = [100], [010], [001].

arsenate), and $900\text{--}750\text{ cm}^{-1}$ (very strong, broad; arsenate). The absence of absorption bands in the $1600\text{--}1650\text{ cm}^{-1}$ region suggests the presence of OH^- rather than H_2O in medenbachite.

The microprobe data (Table 1) show that the ratio Bi:(Fe + Cu):As is 1:1:1; furthermore, variations in the Fe and Cu values indicate a partial solid solution, ranging from approximately 1:1 to 1.5:0.5 for the Fe:Cu ratio. The complete microprobe data, including the results of 33 analyzed spots, are reported in Table 2.¹ Microchemical tests gave strong evidence for Fe^{3+} [as iron-(III)-thiocyanate complex (Feigl 1960)] and weak indication of Fe^{2+} [as a red complex with 2,2' dipyridyl (Feigl 1960)]. Mössbauer spectroscopic study and quantitative determination of Fe^{2+} by wet-chemical methods were impossible because of the lack of material. The crystal-structure analysis revealed two sites with Fe^{3+} ordered in M1, and M2 probably occupied jointly by Cu^{2+} and Fe^{2+} . This investigation could not determine to what extent small amounts of Fe^{3+} participate in the occupation of the M2 site; all calculations throughout the paper were made on the assumption that no Fe^{3+} is present in the M2 site (for details see Discussion). Consequently, the Fe^{3+} - Fe^{2+} distribution was calculated from the microprobe data to

achieve an equal occupation of the M1 and M2 sites. From the microprobe data it is evident that the occupation of the M2 site may vary between nearly exclusive occupation by Cu^{2+} ($\text{Cu}_{0.96}\text{Fe}_{0.04}^{2+}$, microprobe spot analysis with the highest Cu^{2+} content of sample 8.0.376) and subequal occupation by Cu^{2+} and Fe^{2+} ions ($\text{Cu}_{0.51}\text{Fe}_{0.49}^{2+}$, microprobe spot analysis with the highest Fe content of

TABLE 1. Microprobe analyses of medenbachite (in weight percent)

Oxide	Sample 8.0.376		Sample 8.0.137	
	Mean*	Calculated	Mean**	Calculated
Bi_2O_3	53.36	52.87	53.37	52.98
$\text{Fe}_2\text{O}_3^\dagger$	8.99	9.06	8.67	9.08
FeO^\dagger	1.00	0.98	2.90	2.86
CuO	7.85	7.94	5.82	5.88
As_2O_5	25.32	26.08	26.41	26.13
H_2O (calc.)	3.07	3.07	3.07	3.07
Sum	99.59	100.00	100.24	100.00
Number of ions on the basis of 12 O atoms				
Bi^{3+}	2.04	2.00	2.02	2.00
Fe^{3+}	1.00	1.00	0.96	1.00
Fe^{2+}	0.12	0.12	0.31	0.35
Cu^{2+}	0.88	0.88	0.65	0.65
O^{2-}	1.11	1.00	0.88	1.00
OH^-	3.03	3.00	3.01	3.00
AsO_4^{3-}	1.96	2.00	2.03	2.00

* Mean of 16 analyses.

** Mean of 17 analyses.

† The $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratio was calculated to achieve equal occupation of the M1 (Fe^{3+}) and the M2 ($\text{Cu}^{2+} + \text{Fe}^{2+}$) sites.

¹ A copy of Tables 2 and 7 may be ordered as Document AM-96-609 from the Business Office, Mineralogical Society of America, 1015 Eighteenth Street NW, Suite 601, Washington, DC 20036, U.S.A. Please remit \$5.00 in advance for the microfiche.

TABLE 3. X-ray powder diffraction data of medenbachite*

l_{obs}	d_{obs}	l_{calc}^{**}	d_{calc}	hkl
62	8.823	35	8.826	001
17	6.118	11	6.118	010
44	5.264	30	5.264	011
7	4.822	3	4.821	011
4	4.480	2	4.487	100
9	4.414	3	4.413	002
28	4.317	21	4.317	101
32	3.780	29	3.783	110
100	3.749	{ 84	3.750	012
77	3.596	{ 8	3.744	101
		{ 100	3.596	111
58	3.468	{ 59	3.473	110
		{ 34	3.465	111
36	3.430	{ 26	3.430	012
23	3.059	{ 18	3.059	020
		{ 4	3.042	111
		{ 3	3.020	112
10	3.009	{ 10	3.009	112
3	2.939	{ 3	2.942	003
69	2.903	73	2.902	102
51	2.810	50	2.810	021
23	2.754	21	2.754	013
48	2.685	34	2.686	103
18	2.632	22	2.632	022
44	2.558	{ 35	2.559	013
		{ 9	2.545	121
19	2.514	23	2.514	121
7	2.488	10	2.489	113
5	2.430	6	2.428	120
6	2.411	3	2.411	022
12	2.297	{ 22	2.298	122
		{ 4	2.288	122
22	2.271	{ 21	2.272	201
16	2.243	{ 9	2.244	122
		{ 3	2.244	200
11	2.228	{ 7	2.227	113
		{ 4	2.227	023
4	2.207	3	2.207	004
4	2.171	4	2.170	210
8	2.158	6	2.159	202
8	2.133	6	2.134	104
6	2.088	{ 5	2.089	201
		{ 3	2.085	211
		{ 3	2.045	114
18	2.043	{ 18	2.044	211
		{ 4	2.039	030
13	2.029	{ 8	2.029	031
		{ 5	2.028	023
4	2.017	2	2.016	014
6	1.989	{ 9	1.990	122
		{ 3	1.987	123
4	1.948	4	1.947	031
8	1.921	{ 7	1.921	032
		{ 7	1.916	211
		{ 6	1.884	131
13	1.875	{ 14	1.875	024
		{ 11	1.873	131
		{ 4	1.856	213
5	1.852	{ 3	1.850	212
10	1.836	13	1.836	114
5	1.817	4	1.817	221
10	1.798	{ 23	1.798	222
		{ 7	1.797	130
13	1.765	{ 19	1.765	005
		{ 6	1.761	132
7	1.755	{ 8	1.754	132
		{ 3	1.740	015
		{ 6	1.737	220
11	1.734	{ 6	1.735	212
		{ 13	1.734	123
		{ 6	1.732	204
		{ 7	1.721	114
13	1.713	{ 17	1.712	124
		{ 4	1.711	131
		{ 5	1.709	115

TABLE 3.—Continued

l_{obs}	d_{obs}	l_{calc}^{**}	d_{calc}	hkl
5	1.675	7	1.675	124
5	1.666	{ 5	1.669	214
		{ 6	1.665	214
3	1.657	3	1.658	115
3	1.638	11	1.637	223
3	1.619	4	1.619	133
2	1.607	5	1.607	033
2	1.580	5	1.581	230
2	1.573	5	1.573	034
2	1.557	7	1.559	125
3	1.545	{ 3	1.547	115
		{ 6	1.543	231
14	1.531	{ 13	1.531	041
		{ 13	1.530	223

* Sample 8.0.137; transmission powder diffractometer STOE STADI P; $\text{CuK}\alpha$, radiation; external standard: Si.

** Calculated with the program LAZY PULVERIX (Yvon et al. 1977); reflections with $l_{\text{calc}} \geq 3$ are listed.

sample 8.0.137). The chemical formula of medenbachite was derived on the basis of 12 O atoms, equal occupation of the M1 and M2 sites, and H_2O calculated from the ideal composition given in Table 1. It can be written (for sample 8.0.376) as $\text{Bi}_{2.04}\text{Fe}_{1.00}^{3+}(\text{Cu}_{0.88}\text{Fe}_{0.12}^{2+})_{\Sigma 1.00}\text{O}_{1.11}(\text{OH})_{3.03}(\text{AsO}_4)_{1.96}$, or ideally as $\text{Bi}_2\text{Fe}^{3+}(\text{Cu,Fe}^{2+})(\text{O,OH})_2(\text{OH})_2(\text{AsO}_4)_2$. The formulation of the OH groups as $(\text{O,OH})_2$ and $(\text{OH})_2$ refers to crystallographic sites O5 and O2, respectively.

X-RAY DIFFRACTION STUDY

Single-crystal X-ray precession and diffractometer studies show medenbachite to be triclinic, space group $P1$ or $P\bar{1}$; crystal-structure refinement confirmed the space group $P\bar{1}$. The observed powder pattern (Table 3) is in good agreement with the pattern calculated from the crystal structure. Similarities with the pattern of other bismuth arsenates or phosphates are not recognizable. Unit-cell dimensions refined from X-ray powder diffraction data of two different samples are given in Table 4.

A tabular crystal of dimensions $0.20 \times 0.10 \times 0.06$ mm was used for crystal-structure determination. A total of 2607 unique reflections were recorded (ω -scan, with 96 profile steps and variable scan speed between 1.2 and $29.3^\circ/\text{min}$) in the range $h = \pm 7$, $k = \pm 10$, and $l = -5$ to 15 up to $2\theta = 75^\circ$ on a Syntex R3 four-circle diffrac-

TABLE 4. Unit-cell parameters of medenbachite

Cell parameter	Sample 8.0.137	Sample 8.0.376
a (Å)	4.570(1)	4.581(1)
b (Å)	6.162(1)	6.178(1)
c (Å)	8.993(1)	8.969(2)
α (°)	94.56(1)	94.29(2)
β (°)	99.69(1)	99.93(2)
γ (°)	94.28(1)	94.85(3)
V (Å ³)	247.9(1)	248.1(1)

Note: Parameters refined from X-ray powder diffraction data.

TABLE 5. Positional and isotropic atomic displacement parameters of medenbachite*

Atom	x	y	z	U_{eq}
Bi1**	0.1589(7)	0.2996(8)	0.3953(6)	0.0253(8)
Bi2**	0.2541(7)	0.3223(8)	0.3883(6)	0.0234(8)
M1†	0	0	0	0.0233(14)
M2†	0	1/2	0	0.0214(12)
As	0.5411(6)	0.7998(4)	0.2178(3)	0.0224(7)
O1	0.314(4)	0.565(3)	0.198(2)	0.024(5)
O2	0.145(4)	0.742(3)	0.899(2)	0.025(5)
O3	0.338(4)	0.012(3)	0.182(2)	0.029(5)
O4	0.245(4)	0.224(3)	0.916(2)	0.023(5)
O5	0.277(4)	0.617(3)	0.541(3)	0.034(6)
O6	0.246(5)	0.139(3)	0.611(2)	0.033(6)

* Sample 8.0.376.

** For Bi, single-atom model yields $x = 0.2077(5)$, $y = 0.3114(3)$, $z = 0.3917(2)$, $U_{eq} = 0.0480(5)$.† M1 = Fe^{3+} , M2 = $Cu^{2+} + Fe^{2+}$.**TABLE 8.** Interatomic distances (Å) and angles (°) in medenbachite

BiO ₆ polyhedron	Bi2O ₆ polyhedron	AsO ₄ tetrahedron
Bi1-O6 = 2.23(2)	Bi2-O5 = 2.12(2)	As-O6 = 1.67(2)
Bi1-O5 = 2.24(2)	Bi2-O5 = 2.18(2)	As-O4 = 1.68(2)
Bi1-O5 = 2.26(2)	Bi2-O6 = 2.37(2)	As-O1 = 1.69(2)
Bi1-O5 = 2.55(2)	Bi2-O1 = 2.39(2)	As-O3 = 1.69(2)
Bi1-O1 = 2.64(2)	Bi2-O3 = 2.67(2)	mean 1.68
Bi1-O2 = 2.74(2)	Bi2-O5 = 2.67(2)	O1-As-O3 = 110.1(8)
Bi1-O3 = 2.79(2)	Bi2-O2 = 2.87(2)	O1-As-O4 = 106.4(8)
		O1-As-O6 = 115.2(9)
M1O ₆ octahedron*	M2O ₆ octahedron*	O3-As-O4 = 107.6(9)
M1-O4 = 1.98(2) × 2	M2-O2 = 1.94(2) × 2	O3-As-O6 = 107.0(9)
M1-O2 = 2.00(2) × 2	M2-O1 = 2.08(2) × 2	O4-As-O6 = 110.3(9)
M1-O3 = 2.04(2) × 2	M2-O4 = 2.27(2) × 2	mean 109.4°
O3-M1-O2 = 88.5(7)	O1-M2-O2 = 84.0(7)	
O3-M1-O4 = 87.9(7)	O1-M2-O4 = 88.3(6)	
O2-M1-O4 = 83.7(7)	O2-M2-O4 = 77.7(7)	

* M1 = Fe^{3+} , M2 = $Cu^{2+} + Fe^{2+}$.

tometer using MoK α radiation (graphite monochromator). X-ray precession photographs showed additional weak intensity, which obviously stems from intergrown small crystallites. All computations were made using the SHELXTL package of programs (Sheldrick 1990) and its empirical absorption correction. The positions of the cations were found by Patterson synthesis, and the positions of the O atoms were obtained from difference-Fourier maps. For the least-squares refinement, only the most significant 1124 unique reflections with intensity greater than $6\sigma(F_o)$ were used to avoid contamination of the data set with the additional intensity caused by intergrown small crystallites. Complex scattering factors for fully ionized atoms were taken from the *International Tables for X-ray Crystallography*, volume IV (Ibers and Hamilton 1974).

Refinement of positional and individual atomic displacement parameters (Table 5) in space group $P\bar{1}$ using unit weights gave $R = 0.093$, leaving some residual electron density in the vicinity of the Bi³⁺ ions. In addition, the U_{11} parameter of Bi³⁺ was about three times larger than the U_{22} and U_{33} parameters (Table 6). Split-site re-

finement for the Bi³⁺ ion resulted in $R = 0.079$. The split positions are separated by a distance of 0.463(5) Å. Refinement of the site-occupancy factors indicates a 50% probability for the location of Bi³⁺ on each position. For the split-atom model, the isotropic displacement factors of Bi³⁺ are reduced by about 50% in comparison with the single-atom model, and the anisotropic displacement ellipsoids are almost spherical (Tables 5 and 6). A similar effect has been noted for isoelectronic Pb²⁺ in magnetoplumbite, PbFe₁₂O₁₉ (Moore et al. 1989), pseudoboleite, Pb₃₁Cu₂₄Cl₆₂(OH)₄₈ (Giuseppetti et al. 1992), and nealite, Pb₃Fe(AsO₃)₂Cl₄·2H₂O (Giuseppetti et al. 1993). Refinement in space group $P1$ was attempted but did not yield a significantly lower R value in spite of more variables. Observed and calculated structure-factor amplitudes are reported in Table 7.¹ The data given in Tables 5–9 refer to the split-atom model with a site-occupancy factor of 50% on each position.

DESCRIPTION OF THE CRYSTAL STRUCTURE

The crystal structure consists of chains of edge-sharing octahedra of $Fe^{3+}O_4(OH)_2$ and $(Cu^{2+}, Fe^{2+})O_4(OH)_2$ run-

TABLE 6. Anisotropic atomic displacement parameters of medenbachite

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Bi1*	0.0221(15)	0.0249(14)	0.0257(12)	0.0044(9)	-0.0060(14)	0.0028(14)
Bi2*	0.0190(14)	0.0208(12)	0.0274(13)	0.0063(8)	-0.0054(15)	0.0006(13)
M1**	0.0197(25)	0.0205(21)	0.0297(25)	0.0095(18)	0.0019(19)	0.0009(18)
M2**	0.0202(21)	0.0179(17)	0.0262(20)	0.0102(14)	0.0012(16)	0.0008(15)
As	0.0205(12)	0.0209(10)	0.0254(12)	0.0096(8)	0.0006(9)	0.0006(9)
O1	0.0207(86)	0.0196(71)	0.0305(85)	0.0123(62)	0.0022(68)	-0.0042(62)
O2	0.0090(71)	0.0283(77)	0.0343(93)	0.0130(69)	-0.0031(65)	-0.0054(60)
O3	0.0251(96)	0.0195(72)	0.0370(97)	0.0036(66)	-0.0080(75)	0.0017(66)
O4	0.0190(86)	0.0211(72)	0.0312(87)	0.0038(62)	0.0098(69)	0.0021(61)
O5	0.0179(88)	0.0321(94)	0.0454(116)	-0.0081(80)	-0.0022(80)	-0.0006(74)
O6	0.0326(111)	0.0388(104)	0.0251(87)	0.0094(77)	-0.0063(77)	0.0005(85)

Note: Atomic displacement parameters in the form $\exp(-2\pi^2 \sum \sum U_{ij} h_i h_j a_i^* a_j^*)$.* For Bi, single-atom model yields U_{11} 0.0815(12), U_{22} 0.0287(5), U_{33} 0.0275(6), U_{23} 0.0023(4), U_{13} -0.0152(6), and U_{12} 0.0213(6).** M1 = Fe^{3+} , M2 = $Cu^{2+} + Fe^{2+}$.

TABLE 9. Bond-valence values for medenbachite (H atoms excluded)

	O1	O2	O3	O4	O5	O6	ΣV
Bi1*	0.11	0.09	0.08		0.79	0.34	1.41
Bi2*	0.22	0.06	0.10		0.95	0.23	1.56
M1**		0.52 ^{x2} →	0.47 ^{x2} →	0.55 ^{x2} →			3.08
M2**	0.34 ^{x2} →	0.49 ^{x2} →		0.20 ^{x2} →			2.06
As	1.22		1.24	1.25		1.30	5.01
ΣV	1.89	1.16	1.89	2.00	1.74	1.87	

Note: Calculated from the parameters of Brese and O'Keeffe (1991).

* Because of the 50% site-occupancy factor of Bi1 and Bi2, the bond-valence sums must be added [$\Sigma V(\text{Bi}) = 2.97$].

** Based on M1 = Fe³⁺ and M2 = Cu²⁺.

ning along [010] (Fig. 3). The chains of octahedra are corner linked by As³⁺O₄ tetrahedra to form Fe³⁺(Cu, Fe²⁺)(OH)₂(AsO₄)₂ layers parallel to (001) (Fig. 4). The Bi atoms are asymmetrically coordinated by seven O atoms with Bi-O distances of 2.12–2.87 Å (Table 8); these are in the expected range of Bi-O bond lengths, as determined on chemically related minerals like paulkellerite and mrázekite (Grice and Groat 1988, Effenberger et al. 1994). The irregular Bi³⁺O₇ coordination polyhedra are joined by O5 atoms to form zigzag bands arranged in (001) and running parallel to [100]. They connect the Fe³⁺(Cu, Fe²⁺)(OH)₂(AsO₄)₂ layers across (001). On the basis of bond-valence calculations (Table 9), O2 [1.16 vu, ideal 1.0 for (OH)] and O5 [1.74 vu, ideal 1.5 for (O, OH)] are probably OH.

DISCUSSION

Fe atoms in oxysalt minerals are often sixfold coordinated by O atoms in more or less distorted octahedra with mean Fe³⁺-O markedly smaller than Fe²⁺-O. Typical values estimated from the data of Brese and O'Keeffe (1991) are 2.01 and 2.14 Å for Fe³⁺-O and Fe²⁺-O, respectively. Therefore, the smaller and less distorted M1O₆ octahedron (mean M1-O = 2.01 Å) is believed to be occupied by Fe³⁺. The bond distances vary between 1.98 and 2.04 Å, resulting in negligible distortion of the M1O₆ octahedron (Table 8). Nearly identical Fe³⁺-O bond distances (1.987, 1.991, and 2.041 Å; mean Fe-O = 2.006) were found in the chemically related mineral paulkellerite (Grice and Groat 1988).

The environment of ⁶³Cu atoms is usually the tetragonal dipyramid (4 + 2 coordination). Octahedrally coordinated Cu²⁺ spontaneously induces a local distortion caused by the Jahn-Teller effect. The resulting elongated octahedra exhibit a strong bimodal distribution of Cu-O distances with equatorial bond lengths mainly between 1.90 and 2.10 Å (maximum at 1.97) and axial bond lengths between 2.20 and 2.80 Å (maximum at 2.45) (Eby and Hawthorne 1993). In medenbachite, the larger and more distorted octahedron M2O₆ (mean M2-O = 2.09 Å) shows equatorial bond lengths of 1.94 (M2-O2) and 2.08 Å (M2-O1), and distinct elongation of the axial M2-O4 bonds

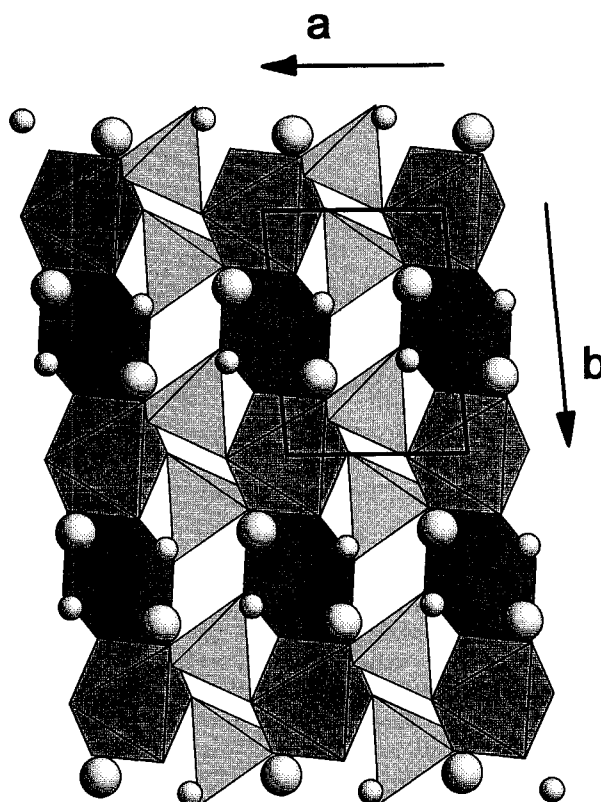


FIGURE 3. Polyhedral model of medenbachite viewed along [001]; large spheres represent Bi atoms, small spheres are O5 atoms; the M2 octahedron (Cu²⁺, Fe²⁺) is slightly darker than the M1 octahedron (Fe³⁺).

(2.27 Å). Therefore, the M2 site is believed to be occupied mainly by Cu²⁺ and minor amounts of Fe²⁺ present in medenbachite. This is in agreement with the distortion of the coordination octahedron expected from the Jahn-Teller effect and is also confirmed by the bond-valence sums, which are close to the expected values for trivalent cations on the M1 site and divalent cations on the M2 site (Table 9).

The partial solid solution of Cu and Fe, indicated by the microprobe data, is probably limited to the M2 site. From the literature, several examples of a Cu²⁺ ↔ Fe²⁺ substitution are known, such as poitevinite-szomolnokite [(Cu,Fe)SO₄·H₂O; Giester et al. 1994], siderotile-chalcantite [(Fe,Cu)SO₄·5H₂O; Jambor and Trail 1963], melanterite-boothite [(Fe,Cu)SO₄·7H₂O; Keating and Berry 1953], and possibly Cu-bearing vesuvianite [Ca₁₉Al₄(Cu,Fe)(Al,Mg,Zn)₈Si₁₈O₆₈(OH,F)₁₀; Fitzgerald et al. 1986], whereas proven cases of solid solution involving Cu²⁺ and Fe³⁺ are unknown. Consequently, we assume that the M1 site is always completely occupied by Fe³⁺, whereas occupation of the M2 site may vary between nearly complete occupation by Cu²⁺ to subequal

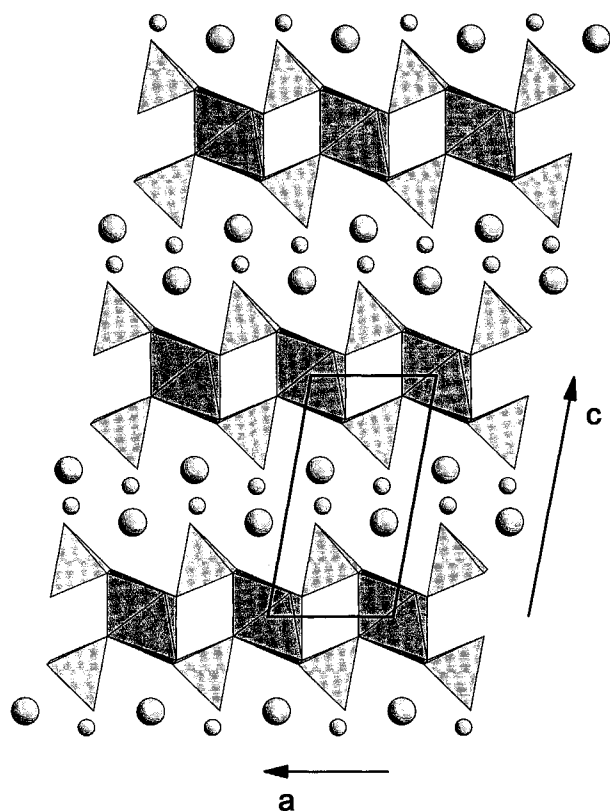


FIGURE 4. Polyhedral model of medenbachite viewed along [010] showing the $\text{Fe}^{3+}(\text{Cu},\text{Fe}^{2+})(\text{OH})_2(\text{AsO}_4)_2$ layers connected by BiO_5 zigzag bands; large spheres represent Bi atoms, small spheres are O5 atoms.

occupation by Cu^{2+} and Fe^{2+} ions. The present data do not allow an unequivocal conclusion regarding the occupation of the M2 site with either Cu^{2+} - Fe^{2+} or Cu^{2+} - Fe^{2+} - Fe^{3+} . If Fe^{3+} is introduced in the M2 site, it would also contribute to the Cu-Fe solid-solution series. Charge balance could then be achieved by changing the O/OH ratio of the crystallographic position O5, being 1 with only divalent cations on the M2 site and >1 with the introduction of Fe^{3+} . Therefore, the general chemical formula of medenbachite can be written as $\text{Bi}_2\text{Fe}^{3+}(\text{Cu},\text{Fe}^{2+},\text{Fe}^{3+})(\text{O},\text{OH})_2(\text{OH})_2(\text{AsO}_4)_2$.

The unit-cell parameters may vary slightly with the Fe:Cu ratio. For increasing Cu content the c parameter decreases, whereas a and b increase; the unit-cell volume remains nearly constant. The values of Table 4 (based on measurements with a STOE STADI P transmission powder diffractometer) were confirmed by measurements on additional samples using a Philips PW1710 powder diffractometer. In comparison with Cu^{2+} (0.73 Å), the ionic radius of Fe^{3+} (0.64 Å) is distinctly smaller and that of Fe^{2+} (0.77 Å) is only slightly greater (Shannon and Prewitt 1969). The effect of a $\text{Cu}^{2+} \leftrightarrow \text{Fe}^{2+}$ substitution should

be clearer with respect to the variation of the M2-O distances. The crystal used for the structure determination was taken from sample 8.0.376 with an Fe/Cu ratio near 1.1:0.9, and therefore only a small amount of Fe^{2+} would be expected in the M2 site. Unfortunately, a crystal with higher Fe content suitable for structure determination could not be found.

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REFERENCES CITED

- Breese, N.E., and O'Keeffe, M. (1991) Bond-valence parameters for solids. *Acta Crystallographica*, B47, 192-197.
- Dunn, P.J., Grice, J.D., Wicks, F.J., and Gault, R.A. (1988) Paulkellerite, a new bismuth iron phosphate mineral from Schneeberg, Germany. *American Mineralogist*, 73, 870-872.
- Eby, R.K., and Hawthorne, F.C. (1993) Structural relations in copper oxysalt minerals: I. Structural hierarchy. *Acta Crystallographica*, B49, 28-56.
- Effenberger, H., Krause, W., Belendorff, K., Bernhardt, H.-J., Medenbach, O., Hybler, J., and Petříček, V. (1994) Revision of the crystal structure of mrázekite, $\text{Bi}_2\text{Cu}_3(\text{OH})_2\text{O}_2(\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$. *Canadian Mineralogist*, 32, 365-372.
- Feigl, F. (1960) *Tüpfelanalyse*, Anorganischer Teil (4th edition), 594 p. Akademische Verlagsgesellschaft, Frankfurt on the Main, Germany.
- Fitzgerald, S., Rheingold, A.L., and Leavens, P.B. (1986) Crystal structure of Cu-bearing vesuvianite. *American Mineralogist*, 71, 1011-1014.
- Giester, G., Lengauer, C.L., and Redhammer, G. (1994) Characterization of the $\text{FeSO}_4 \cdot \text{H}_2\text{O}$ - $\text{CuSO}_4 \cdot \text{H}_2\text{O}$ solid-solution series, and the nature of poitevinite, $(\text{Cu},\text{Fe})\text{SO}_4 \cdot \text{H}_2\text{O}$. *Canadian Mineralogist*, 32, 873-884.
- Giuseppetti, G., Mazzi, F., and Tadini, C. (1992) The crystal structure of pseudoboleite: $\text{Pb}_3\text{Cu}_{24}\text{Cl}_{62}(\text{OH})_{48}$: Its relations with the structures of boleite and cumengeite. *Neues Jahrbuch für Mineralogie Monatshefte*, 113-126.
- (1993) The crystal structure of nealite: $\text{Pb}_2\text{Fe}(\text{AsO}_4)_2\text{Cl}_4 \cdot 2\text{H}_2\text{O}$. *Neues Jahrbuch für Mineralogie Monatshefte*, 278-288.
- Grice, J.D., and Groat, L.A. (1988) Crystal structure of paulkellerite. *American Mineralogist*, 73, 873-875.
- Ibers, J.A., and Hamilton, W.C., Eds. (1974) *International tables for X-ray crystallography*, vol. IV, p. 213-216. Kynoch, Birmingham, U.K.
- Jambor, J.L., and Traill, R.J. (1963) On rozenite and siderotil. *Canadian Mineralogist*, 7, 751-763.
- Keating, L.F., and Berry, L.G. (1953) Pisanite from Flin Flon, Manitoba. *American Mineralogist*, 38, 501-505.
- Krause, W., Belendorff, K., and Bernhardt, H.-J. (1993) Petitjeanite, $\text{Bi}_2\text{O}(\text{OH})(\text{PO}_4)_2$, a new mineral, and additional data for the corresponding arsenate and vanadate, preisingerite and schumacherite. *Neues Jahrbuch für Mineralogie Monatshefte*, 487-503.
- Mandarino, J.A. (1981) The Gladstone-Dale Relationship: Part IV. The compatibility concept and its application. *Canadian Mineralogist* 19, 441-450.
- Meier, K., and Preisinger, A. (1986) Kristallstrukturdaten der Wismutminerale Atelestite, Mixit und Pucherit. *Anzeiger der österreichischen Akademie der Wissenschaften, math.-naturwiss. Klasse*, 123, 79-81.
- Moore, P.B., Sen Gupta, P.K., and Le Page, Y. (1989) Magnetoplumbite, $\text{Pb}^{2+}\text{Fe}_2^{3+}\text{O}_{19}$: Refinement and lone-pair splitting. *American Mineralogist*, 74, 1186-1194.
- Rídkošil, T., Šrein, V., Fábry, J., Hybler, J., and Maximov, B.A. (1992)

- 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. *Canadian Mineralogist*, 30, 215–224.
- Shannon, R.D., and Prewitt, C.T. (1969) Effective ionic radii in oxides and fluorides. *Acta Crystallographica*, B25, 925–946.
- Sheldrick, G.M. (1990) SHELXTL: Program for crystal structure determination. Cambridge, U.K.
- Sieber, N.H.W., Tillmanns, E., and Medenbach, O. (1987) Hentschelite, $\text{CuFe}_2(\text{PO}_4)_2(\text{OH})_2$, a new member of the lazulite group, and reichenbachite, $\text{Cu}_3(\text{PO}_4)_2(\text{OH})_4$, a polymorph of pseudomalachite, two new copper phosphate minerals from Reichenbach, Germany. *American Mineralogist*, 72, 404–408.
- Van Wambeke, L. (1975) La zairite, un nouveau minéral appartenant à la série de la crandallite. *Bulletin de la Société française de Minéralogie et de Cristallographie*, 98, 351–353.
- Yvon, K., Jeitschko, W., and Parthé, E. (1977) LAZY PULVERIX, a computer program, for calculating X-ray and neutron diffraction powder patterns. *Journal of Applied Crystallography*, 10, 73–74.

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