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PERTLIKITE, A NEW TETRAGONAL Mg-RICH MEMBER OF THE VOLTAITE GROUP FROM MADENI ZAKH, IRAN

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ABSTRACT

Pertlikite, a new member of the voltaite group, is the tetragonal Mg-dominant analogue of the isometric phases voltaite and zincovoltaite. At its type locality, Madeni Zakh, Iran, the mineral occurs in a pyrite-bearing trachytic eruptive rock, and probably formed after the decomposition of pyrite. Pertlikite forms single crystals up to 1 cm; the phase is associated with metavoltine, botryogen, pyrite and alunite. In contrast to voltaite and zincovoltaite, the optical properties and the single-crystal study of the structure ($R1 = 0.022$) confirm the tetragonal symmetry, $\omega = 1.590(2)$, $\varepsilon = 1.586(2)$, space group $I4_1/acd$, a 19.2080(3), c 27.2158(7) Å, V 10041.2(6) Å^3, and $Z = 8$. The results of the chemical analysis, in combination with the Mössbauer data and the crystal-structure refinement, give the formula $(K_{1.98}Na_{0.01})_{\Sigma 1.99}$ $^{M2}(Fe^{2+}_{1.13}Mg_{0.49}Mn^{2+}_{0.27}Fe^{3+}_{0.10}Zn_{0.01})_{\Sigma 2.00}$ $^{M3}(Mg_{2.52}Fe^{3+}_{1.49})$ $_{\Sigma 4.01}$ $^{M1}Fe^{3+}_{2.00}$ $Al_{1.00}$ $(SO_4)_{12.00}\cdot 18\ H_2O$, which can be simplified to an ideal formula: K_2 $^{M2}(Fe^{2+},Mg)_2$ $^{M3}(Mg,Fe^{3+})_4$ $^{M1}Fe^{3+}_2$ Al $(SO_4)_{12}\cdot 18\ H_2O$. The strongest eight lines of the powder pattern [d in Å$(I)(hkl)$] are: 5.543(28)(132), 3.396(100)(440), 3.136(21) (345), 3.038(39)(444), 2.848(31)(361), 2.534(21)(273), 2.078(29)(567) and 1.601(21)(6$\underline{10}$4). The unit-cell parameters refined from the powder data (Cu$K\alpha$ radiation) are a 19.2167(2), c 27.1976(4) Å. The tetragonal structure of pertlikite results from Mg,Fe order at the $Fe2$ site. Relative to the isometric voltaite and zincovoltaite, the $Fe2$ site splits to create a site that is predominantly Mg ($Mg3$) and another that is dominantly Fe ($Fe2$) in pertlikite. For the three metal sites, the results of the refinement are $Fe1$: $\approx$ Fe; $Fe2$: Fe >> Mg; $Mg3$: Mg >> Fe. The H$_2$O molecules that bond to the Al atom are extensively disordered, as has been observed in the isometric phases. The measured density is 2.59(3) g/cm^3 (by pycnometer), and the calculated density is 2.56(1) g/cm^3. The name honors Franz Pertlik, Professor of Mineralogy and Crystallography, University of Vienna, Austria, in recognition of his extensive work on the crystal chemistry of minerals.

Keywords: pertlikite, voltaite group, crystal structure, chemical analyses, Madeni Zakh, Iran.

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SOMMAIRE

Nous décrivons la pertlikite, nouveau membre du groupe de la voltaïte; il s'agit de l'analogue tétragonal à dominance de Mg de la voltaïte et de la zincovoltaïte, isométriques. A sa localité type, Madeni Zakh, en Iran, on trouve le minéral dans une roche éruptive trachytique, dans laquelle elle serait le produit de décomposition de la pyrite. La pertlikite forme des monocristaux atteignant 1 cm; lui sont associées métavoltine, botryogène, pyrite et alunite. En contraste avec la voltaïte et la zincovoltaïte, les propriétés optiques et l'ébauche de la structure effectuée sur monocristal ($R1 = 0.022$) confirment la symétrie tétragonale, $\omega = 1.590(2)$, $\varepsilon = 1.586(2)$, groupe spatial $I4_1/acd$, a 19.2080(3), c 27.2158(7) Å, V 10041.2(6) Å^3, et $Z = 8$. Les résultats de l'analyse chimique, en combinaison avec les données de Mössbauer et l'affinement de la structure cristalline, mènent à la formule $(K_{1.98}Na_{0.01})_{\Sigma1.99} {}^{M2}(Fe^{2+}{}_{1.13}Mg_{0.49}Mn^{2+}{}_{0.27}Fe^{3+}{}_{0.10}Zn_{0.01})_{\Sigma2.00} {}^{M3}(Mg_{2.52}Fe^{3+}{}_{1.49})_{\Sigma4.01} {}^{M1}Fe^{3+}{}_{2.00} Al_{1.00} (SO_4)_{12.00}•18 H_2O$ ou, de façon idéale, $K_2 {}^{M2}(Fe^{2+},Mg)_2 {}^{M3}(Mg,Fe^{3+})_4 {}^{M1}Fe^{3+}{}_2 Al (SO_4)_{12}•18 H_2O$. Les huit raies les plus intenses du spectre de diffraction, méthode des poudres [d en Å(I)(hkl)] sont: 5.543(28)(132), 3.396(100)(440), 3.136(21)(345), 3.038(39)(444), 2.848(31) (361), 2.534(21)(273), 2.078(29)(567) et 1.601(21)(6$\overline{10}$4). Les paramètres de la maille élémentaire affinés à partir des données obtenues sur poudre (rayonnement Cu$K\alpha$) sont a 19.$\overline{21}$67(2), c 27.1976(4) Å. La structure tétragonale de la pertlikite résulte de la mise en ordre de Mg,Fe au site $Fe2$. Par rapport à la voltaïte et à la zincovoltaïte, le site $Fe2$ est subdivisé pour créer un site à dominance de Mg ($Mg3$) et un autre à dominance de Fe ($Fe2$). Pour les trois sites occupés par des métaux, les affinements ont donné $Fe1$: ≈ Fe; $Fe2$: Fe >> Mg; $Mg3$: Mg >> Fe. Les molécules de H$_2$O liées à l'atome Al sont largement désordonnées, tout comme dans les phases isométriques. La densité mesurée avec un pycnomètre est 2.59(3) g/cm^3, tandis que la densité calculée est 2.56(1) g/cm^3. Le nom honore Franz Pertlik, professeur de minéralogie et de cristallographie, Université de Vienne, en Autriche, en reconnaissance de ses travaux importants portant sur la cristallochimie des minéraux.

(Traduit par la Rédaction)

Mots-clés: pertlikite, groupe de la voltaïte, structure cristalline, analyses chimiques, Madeni Zakh, Iran.

INTRODUCTION

Voltaite is a sulfate that is found in the oxidation zone of some sulfide deposits and also in fumaroles (Mereiter 1972a); it has been known for over a century and a half. The formula of voltaite was given by Strunz (1970) as $K_2Fe^{2+}{}_5Fe^{3+}{}_4(SO_4)_{12}•18H_2O$, whereas Back & Mandarino (2008) quoted the formula as $K_2Fe^{2+}{}_5Fe^{3+}{}_3Al(SO_4)_{12}•18H_2O$. Blaas (1883) reported the chemical composition and morphological aspects of a sample of voltaite from a pyrite-bearing trachytic eruptive rock from Madeni Zakh, Iran. Its composition is enriched in Mg with respect to the holotype material. He noted that these crystals are up to 1 cm in size, and that they are in some cases associated with metavoltine. Blaas (1881) also noted that these sulfates enclose small crystals of pyrite and that they probably originated from decomposed pyrite. The hand specimen with the new tetragonal Mg-rich member of the voltaite group (in association with metavoltine, botryogen, pyrite, and alunite), which was found in the collection of the former "Mineralogisches Museum der Universität Wien", now Institut für Mineralogie und Kristallographie, University of Vienna, Austria, was acquired in the year 1886 (Figs. 1, 2). The new mineral is named pertlikite, to honor Franz Pertlik (born 1943), Professor of Mineralogy and Crystallography, University of Vienna, Austria, in recognition of his extensive work on the crystal chemistry of minerals. Pertlikite was approved by the IMA Commission on New Minerals and Mineral Names (no. 2005–055) prior to publication. Type material is deposited at the Institut für Mineralogie und Kristallographie, Geozentrum, Universität Wien,

Vienna, Austria, catalogue number 7813 (type material, acquisition year: 1886). Holotype material (the crystal chosen for structure refinement) is deposited at the Smithsonian Institution, National Museum of Natural History, Washington D.C., catalogue number NMNH174370, and type material is also deposited at the Harvard Museum of Natural History, Cambridge, Massachusetts, catalogue number 135547.
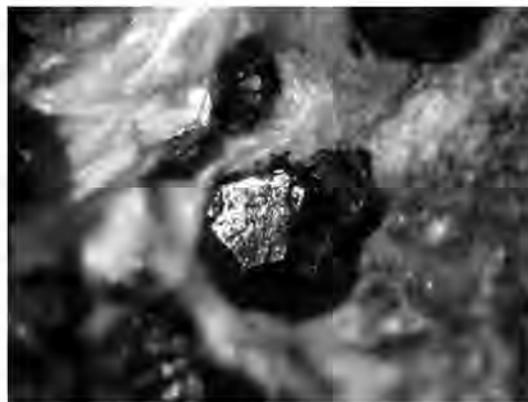

FIG. 1. Dark olive green to black crystal of pertlikite (~2 mm in diameter) from the type material, which is deposited at the Institut für Mineralogie und Kristallographie, Geozentrum, Universität Wien, Vienna, Austria, catalogue number 7813 (acquisition year: 1886).

Previous Work

The crystal structure of synthetic voltaite, with the formula K_2 $^{M2}(Fe^{2+}_5Fe^{3+})$ $^{M1}Fe^{3+}_2$ $Al(SO_4)_{12} \cdot 18H_2O$, space group $Fd3c$, a 27.254(8) Å, was determined by Mereiter (1972a) from photographic X-ray methods ($R =$ 0.033 for 726 observed F_{hkl}). He described the dominant structural feature as a continuous framework composed of $[Fe^{3+}O_6]$ octahedra, $[Fe^{2+}_{5/6}Fe^{3+}_{1/6}O_4(H_2O)_2]$ octahedra and $[K^TO_{12}]$ polyhedra linked by SO_4 tetrahedra. The arrangement gave rise to "cages" occupied by disordered $[Al(H_2O)_6]$ octahedra (Mereiter 1971, 1972a, b).

Gossner & Arm (1930) published a chemical and X-ray (Laue photographs) investigation on synthetic voltaite, Al-free "K–Mn-voltaite", and "Co-voltaite". Gossner & Fell (1932) cited lattice parameters, chemical composition, density, optical data and morphological aspects for synthetic "Tl–Fe^{2+}-voltaite", "Tl–Mg-voltaite", "Tl–Cd-voltaite", "Rb–Cd-voltaite", and "(NH)$_4$–Mg-voltaite". They also described lattice parameters for synthetic "Tl–Mn-voltaite", "Rb–Fe^{2+}-voltaite", "K–Cd-voltaite", and "(NH)$_4$–Cd-voltaite". They gave the general formula for compositions of the voltaite series as $(SO_4)_{12}$ Fe$^{III}_4$ Me^{II}_5 $Me^I_2 \cdot 16$–18 H_2O. Gossner & Drexler (1933) gave the chemistry, optical data, lattice parameters, and morphological aspects of synthetic Al-free "Rb–Mn-voltaite", Al-bearing "(NH)$_4$–Zn-voltaite", "Rb–Zn-voltaite", and "Tl–Zn-voltaite". They further described synthetic Al-free "(NH)$_4$–Mn-voltaite" and Al-free "Tl–Mn-voltaite", and compiled the lattice parameters of the synthetic compositions of the voltaite series. Gossner & Drexler (1933) found that synthetic "Fe^{2+}-voltaites", contrary to "Mn-voltaites", always need a significant quantity of Al_2O_3 for crystallization. A single isotropic EPR line of Fe^{3+} in synthetic "Cd–Fe^{3+}-voltaite" with the formula $(NH_4)_2Cd_5Fe^{3+}_3Al(SO_4)_{12} \cdot 18$ H_2O, was observed in a temperature range from 295 to 1.57 K by Nazarian et al. (1977). Schwarte & Fischer (1989) described the chemistry and crystal structure of a synthetic Al-free, cubic "K–Mg–Fe^{3+}-voltaite" with the formula K_2 $^{M2}(Mg_5Fe^{3+})$ $^{M1}Fe^{3+}_2$ Fe^{3+} $(SO_4)_{12} \cdot 18$ H_2O, and with $a =$ 27.225(1) Å (ICSD #56365). Li et al. (1989) described zincovoltaite, a new cubic member of the voltaite group, with the formula K_2 Zn_5 Fe^{3+}_3 $Al(SO_4)_{12} \cdot 18H_2O$.

Experimental Details

Sample selection

Parts of a single crystal ~2 mm in diameter were broken off and used for optical characterization and chemical analyses, whereas another piece, about ~150 μm in size, was used for a determination of the crystal structure.

Crystal structure

The pertlikite crystal was mounted on a Bruker Apex CCD diffractometer equipped with graphite-monochromated $MoK\alpha$ radiation. Refined cell-parameters and other crystal data are listed in Table 1. Redundant data were collected for an approximate sphere of reciprocal space, and were integrated and corrected for Lorentz and polarization factors using the Bruker program SAINTPLUS (Bruker AXS Inc. 2001).

Upon reducing the data and determining the space group, it was clear that pertlikite, unlike other voltaite-group compounds, is tetragonal, and the space group was routinely determined from the structure data. The tetragonal structure was solved using direct methods as implemented in the Bruker SHELXTL v. 6.10 package of programs. The structure was refined with neutral-atom scattering factors and terms for anomalous dispersion. The refinement was performed with anisotropic thermal parameters for all non-hydrogen atoms. In Table 1, we list details of the refinement, in Table 2, we list the atom
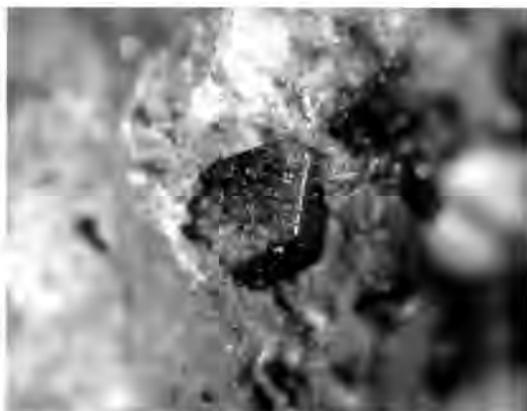

FIG. 2. Dark olive green to black crystal of pertlikite (~1 mm in diameter) from the type material, which is deposited at the Institut für Mineralogie und Kristallographie, Geozentrum, Universität Wien, Vienna, Austria, catalogue number 7813 (acquisition year: 1886).

TABLE 1. CRYSTAL DATA AND RESULTS OF STRUCTURE REFINEMENT OF PERTLIKITE FROM MADENI ZAKH, IRAN

Space group	$I4_1/acd$	Z	8
Unit-cell parameters (Å)			
a	19.2080(3)	c	27.2158(7)
Unit-cell volume (Å³)	10041.2(6)		
Frame width, scan time	0.20°, 15 s	Number of frames	4500
Detector distance	5 cm		
Measured reflections, full sphere	110,831		
R_{int} before absorption correction*	0.0485		
R_{int} after absorption correction*	0.0230		
Unique reflections in $I4_1/acd$	3,644	Refined parameters	295
$R1$, $I > 4\sigma_I$	0.022	$wR2$	0.0622
Difference peaks (+,-), e⁻/Å³	0.55, 0.33	Goodness-of-fit	1.137

* The absorption correction was done by evaluation of multiple scans.

coordinates, equivalent-isotropic displacement parameters, and site occupancies, and in Table 3, we present selected interatomic distances. Structure factors and anisotropic displacement factors for selected atoms may be obtained from the Depository of Unpublished Data, MAC website [document Pertlikite cm46_661].

The X-ray powder-diffraction (XRD) data for pertlikite (a greyish green powder) were collected on a PW 3710 Philips diffractometer using Cu$K\alpha$ radiation (40 kV, 40 mA). The irradiated sample-area was kept at 12 × 12 mm² (automatic divergence-slits gave a constant area for each 2θ angle). The pertlikite powder was prepared on a round zero-background silicon holder and dispersed in a few drops of acetone and allowed to dry. The XRD data were collected at 295(1)K over the 2θ range of 5–100° using 0.02° steps and a counting time of 12 s/step. The powder-diffraction data are presented in Table 4, with indices for peaks $d > 1.30$ Å.

Chemical analyses

The crystal was prepared as a polished section for chemical analysis. All elements except H and C were determined with a wavelength-dispersive ARL SEMQ electron microprobe at the Mineralogisch–Petrographische Abteilung, Naturhistorisches Museum, Vienna, Austria. The operating conditions were 15 kV accelerating voltage, sample current 15 nA (on benitoite), and spot size 10 μm. Natural silicates and oxides were used as standards (orthoclase: K$K\alpha$, jadeite: Na$K\alpha$, Al$K\alpha$, almandine: Fe$K\alpha$, gahnite: Zn$K\alpha$, olivine: Mg$K\alpha$, tephroite: Mn$K\alpha$, anhydrite: S$K\alpha$). Under the conditions described, analytical errors on all analyses are ±1% relative for major elements and ±5% relative for minor elements.

Additional grains of pertlikite were picked for "bulk" H and C analysis with a 2400 CHN Elemental Analyzer (Perkin Elmer). The analyzer operates by flash combustion of the specimen encapsulated in tin cups or disks whereby the specimen is completely combusted at a temperature of 1760°C. The resulting gases are chemically scrubbed of the halogens and are separated in a gas chromatographic column. Detection is assured by a thermal conductivity detector (TCD). Errors on H_2O are estimated at ±10% relative based on replications.

Mössbauer spectroscopy

Approximately 20 mg of sample were gently crushed under acetone and subsequently mixed with a sugar-acetone solution to form sugar coatings around each grain and prevent preferred orientation. Grains were gently heaped in a sample holder confined by kapton tape. Mössbauer spectra were acquired at temperatures between 4 and 295 K using a source of 100–60 mCi ^{57}Co in Rh on a WEB Research Co. model WT302

TABLE 2. PERTLIKITE: COORDINATES AND EQUIVALENT ISOTROPIC *U* OF ATOMS

Atom	x	y	z	U_{eq}	Occupancy
S1	0.961717(16)	0.013192(16)	0.881669(11)	0.01256(7)	S$_{1.00}$
S2	0.855855(16)	0.093187(16)	0.012190(11)	0.01247(7)	S$_{1.00}$
S3	0.106330(16)	0.130649(16)	0.974391(11)	0.01271(7)	S$_{1.00}$
Fe1	0	0	0	0.01297(7)	Fe$_{1.00}$
Fe2	0.794208(17)	0	¾	0.01341(11)	Fe$_{0.719(3)}$
Mg2	0.794208(17)	0	¾	0.01341(11)	Mg$_{0.281}$
Mg3	0.852518(17)	0.147397(17)	0.897173(12)	0.01346(12)	Mg$_{0.742(2)}$
Fe3	0.852518(17)	0.147395(17)	0.897173(12)	0.01346(12)	Fe$_{0.258}$
Al	0	¼	⅛	0.01185(14)	Al$_{1.00}$
K	0.00007(3)	0	¾	0.03164(13)	K$_{1.00}$
O1	0.94004(7)	-0.05104(6)	0.85726(5)	0.0293(3)	O$_{1.00}$
O2	0.00530(6)	0.05430(6)	0.84827(4)	0.0234(2)	O$_{1.00}$
O3	0.89868(6)	0.05176(6)	0.89558(4)	0.0230(2)	O$_{1.00}$
O4	0.00262(5)	-0.00378(5)	0.92639(4)	0.0193(2)	O$_{1.00}$
O5	0.85269(6)	0.13891(6)	0.05494(4)	0.0290(3)	O$_{1.00}$
O6	0.82315(6)	0.12712(6)	0.96982(4)	0.0229(2)	O$_{1.00}$
O7	0.81894(5)	0.02821(5)	0.02480(4)	0.0233(2)	O$_{1.00}$
O8	0.92949(5)	0.07699(6)	0.00033(4)	0.0190(2)	O$_{1.00}$
O9	0.08850(7)	0.19804(6)	0.99582(4)	0.0298(3)	O$_{1.00}$
O10	0.08053(6)	0.12894(6)	0.92374(4)	0.0239(2)	O$_{1.00}$
O11	0.18249(5)	0.12144(6)	0.97558(4)	0.0245(2)	O$_{1.00}$
O12	0.07354(5)	0.07388(5)	0.00326(4)	0.0192(2)	O$_{1.00}$
O13	0.94033(6)	0.19736(6)	0.92101(5)	0.0247(2)	O$_{1.00}$
H13A	0.9744(12)	0.1777(15)	0.9208(12)	0.065(9)	H$_{1.00}$
H13B	0.9316(16)	0.2257(14)	0.9413(9)	0.073(10)	H$_{1.00}$
O14	0.79926(7)	0.04325(6)	0.68084(4)	0.0252(2)	O$_{1.00}$
H14A	0.8389(10)	0.0467(17)	0.6716(12)	0.079(11)	H$_{1.00}$
H14B	0.7683(15)	0.0688(17)	0.6744(15)	0.106(14)	H$_{1.00}$
O15	0.75947(6)	0.10238(6)	0.87849(4)	0.0248(2)	O$_{1.00}$
H15A	0.7275(12)	0.1120(15)	0.8966(10)	0.064(9)	H$_{1.00}$
H15B	0.752(2)	0.096(2)	0.8505(8)	0.103(14)	H$_{1.00}$
OW1	-0.0137(2)	0.1927(2)	0.17896(16)	0.0198(15)	O$_{0.225(5)}$
OW2	-0.0190(3)	0.1585(2)	0.10342(18)	0.0210(15)	O$_{0.222(5)}$
OW3	-0.0759(2)	0.2820(3)	0.08946(16)	0.0227(15)	O$_{0.236(5)}$
OW4	0.0579(3)	0.2639(3)	0.17991(17)	0.0216(16)	O$_{0.221(5)}$
OW5	0.0898(2)	0.2685(2)	0.10361(17)	0.0213(15)	O$_{0.233(5)}$
OW6	-0.0332(3)	0.3269(2)	0.08894(17)	0.0218(15)	O$_{0.226(5)}$
OW7	0	¼	0.1946(4)	0.023(4)	O$_{0.129(7)}$
OW8	-0.0697(4)	0.3197(4)	⅛	0.024(4)	O$_{0.134(7)}$
OW9	0.0694(4)	0.3194(4)	⅛	0.023(4)	O$_{0.133(7)}$

TABLE 3. SELECTED INTERATOMIC DISTANCES (Å) IN PERTLIKITE FROM MADENI ZAKH, IRAN

S1-	O1	1.462(1)		S2-	O5	1.459(1)
	O2	1.466(1)			O6	1.466(1)
	O3	1.469(1)			O7	1.476(1)
	O4	1.485(1)			O8	1.484(1)
Mean		1.471		Mean		1.471
S3-	O9	1.460(1)		Fe1-	O12 (×2)	2.004(1)
	O10	1.465(1)			O8 (×2)	2.005(1)
	O11	1.474(1)			O4 (×2)	2.005(1)
	O12	1.484(1)		Mean		2.005
Mean		1.471				
				Mg3-	O10	2.040(1)
Fe2-	O7 (×2)	2.036(1)			O3	2.040(1)
	O14 (×2)	2.060(1)			O13	2.046(1)
	O11 (×2)	2.080(1)			O15	2.050(1)
Mean		2.059			O2	2.090(1)
					O6	2.093(1)
§ Al-	OW3	1.854(4)		Mean		2.060
	OW3	1.854(4)				
	OW3	1.854(4)		K-	O6 (×2)	2.866(1)
	OW3	1.854(4)			O11 (×2)	2.868(1)
	OW1	1.854(4)			O2 (×2)	2.873(1)
	OW1	1.854(4)			O9 (×2)	3.261(1)
	OW1	1.855(4)			O5 (×2)	3.267(1)
	OW1	1.855(4)			O1 (×2)	3.288(1)
	OW5	1.855(4)		Mean		3.071
	OW5	1.855(4)				
	OW5	1.855(4)				
	OW5	1.855(4)				
Mean		1.855				

§ The H_2O molecules bonded to the Al site exhibit extensive disorder, and are all partially occupied. Each Al atom bonds to six of the disordered molecules of H_2O.

spectrometer (Mount Holyoke College) and corrected to remove the fraction of the baseline due to the Compton scattering of 122 keV gammas by electrons inside the detector. Run time was 24 hours with 6.5 million baseline counts and 8% absorption. Spectra were collected in 2048 channels and corrected for nonlinearity. Data were modeled using an in-house program (Dist3e) from the University of Ghent, which uses model-independent, quadrupole-splitting distributions for which the subspectra consist of Lorentzian shaped lines. Peak areas were not corrected for differential recoil-free fractions for Fe^{2+} and Fe^{3+} because the appropriate correction-factors do not exist.

Optical properties

Optical data were collected on pertlikite to aid in determining its crystal system, as well as for the necessary requirements for characterization of a new mineral. The data species were collected on spindle-stage-equipped Leitz Ortholux polarizing light microscope with a variable slide monochromator and temperature-controlled heating oil-cell.

RESULTS AND DISCUSSION

Mössbauer spectroscopy

The Mössbauer spectrum of pertlikite is shown in Figure 3, along with spectra of voltaite from Minas Rio Tinto, Huelva, Andalucia, Spain (NMNH 158795) and United Verde mine, Jerome, Arizona (NMNH 115034) for comparison. All the spectra are similar in appearance to those of Long et al. (1980), who unfortunately
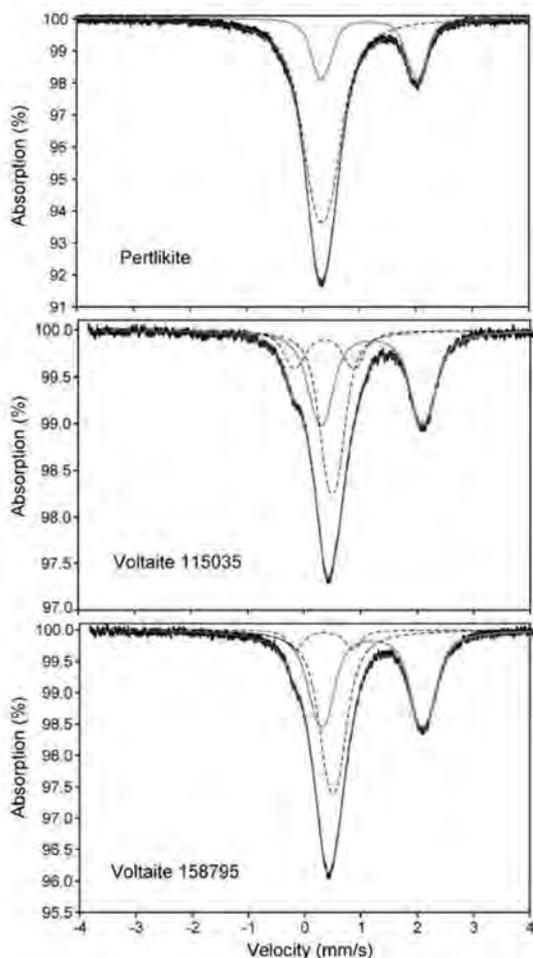

FIG. 3. Mössbauer spectra of voltaite group minerals, including pertlikite, measured at 295 K. Fe^{2+} doublets are shown as solid gray lines, Fe^{3+} as dashes. Data points are plotted as error bars.

TABLE 4. PERTLIKITE: X-RAY POWDER-DIFFRACTION DATA

I	d_{meas}	d_{calc}	h	k	l	I	d_{meas}	d_{calc}	h	k	l	I	d_{meas}
8	9.621	9.612	1	1	2	8	1.716	1.716	6	7	9	2	1.123
5	7.866	7.847	0	2	2	3	1.700	1.699	8	8	0	2	1.116
16	6.807	6.794	2	2	0	1	1.685	1.686	1	11	4	2	1.113
28	5.543	5.548	1	3	2	8	1.673	1.673	3	11	2	2	1.106
2	4.587	4.595	2	3	3	6	1.860	1.660	4	10	6	2	1.102
3	4.292	4.297	3	3	2	2	1.648	1.648	2	10	8	2	1.091
5	3.921	3.924	0	4	4	3	1.625	1.624	1	11	6	2	1.086
12	3.628	3.632	2	4	4	1	1.615	1.616	4	11	3	2	1.080
100	3.396	3.397	4	4	0	21	1.601	1.602	6	10	4	2	1.076
10	3.201	3.203	3	5	2	2	1.591	1.590	0	12	2	2	1.073
21	3.136	3.139	3	4	5	1	1.579	1.580	2	12	0	3	1.067
39	3.038	3.039	4	4	4	10	1.572	1.572	8	9	3	2	1.057
8	2.981	2.984	2	5	5	2	1.559	1.559	0	12	4	2	1.054
4	2.900	2.898	1	5	6	4	1.549	1.549	2	10	10	2	1.048
31	2.848	2.849	3	6	1	7	1.531	1.531	6	11	1	2	1.044
6	2.774	2.774	2	6	4	2	1.519	1.519	4	12	0	4	0.996
1	2.663	2.665	4	6	0	3	1.510	1.510	3	11	8	8	0.971
9	2.627	2.628	4	5	5	<1	1.500	1.501	8	10	0	2	0.970
7	2.616	2.616	0	6	6	2	1.493	1.492	2	12	6	1	0.953
21	2.534	2.534	2	7	3	2	1.483	1.483	6	10	8	2	0.948
2	2.523	2.524	1	7	4	2	1.476	1.476	8	9	7	2	0.938
9	2.480	2.481	3	7	2	7	1.465	1.465	8	10	4	2	0.926
8	2.402	2.403	4	4	8	3	1.460	1.459	7	8	11	2	0.923
5	2.366	2.366	3	5	8	6	1.448	1.449	2	10	12	2	0.919
1	2.330	2.331	5	5	6	2	1.441	1.441	4	12	6	2	0.912
3	2.308	2.305	1	8	3	3	1.433	1.432	9	9	8	1	0.909
16	2.264	2.265	6	6	0	7	1.427	1.427	6	11	7	2	0.899
3	2.241	2.242	3	8	1	2	1.411	1.411	8	11	1	1	0.896
1	2.204	2.204	5	7	2	3	1.402	1.402	7	11	6	2	0.895
14	2.183	2.183	4	7	5	1	1.372	1.373	5	13	2	2	0.878
1	2.147	2.149	4	8	0	8	1.368	1.367	1	14	1	1	0.871
4	2.123	2.122	4	8	2	1	1.352	1.352	2	14	2	1	0.862
29	2.078	2.079	5	6	7	1	1.341	1.341	9	10	7	1	0.844
6	2.048	2.049	4	8	4	9	1.333	1.333	6	10	12	1	0.820
2	2.028	2.027	2	6	10	2	1.328	1.328	4	13	7	1	0.753
2	2.025	2.026	1	9	4	2	1.320	1.320	6	12	8	<1	0.748
7	2.004	2.004	3	9	2	1	1.229					1	0.745
2	1.960	1.962	0	8	8	1	1.224					1	0.739
1	1.940	1.941	3	9	4	1	1.210					<1	0.731
4	1.921	1.922	6	8	0	1	1.192					<1	0.710
7	1.903	1.903	6	8	2	3	1.185					<1	0.702
8	1.885	1.885	6	6	8	2	1.180					1	0.698
4	1.867	1.867	2	10	4	2	1.173					2	0.671
7	1.818	1.816	2	10	4	1	1.168					1	0.658
4	1.804	1.804	3	10	3	2	1.156					1	0.653
8	1.773	1.773	6	9	1	2	1.139						
4	1.727	1.727	4	8	12	2	1.133						

Note: d values in Å. The unit-cell parameters refined from the powder-diffraction data (CuKα radiation) are a 19.2167(2), c 27.1976(4) Å.

did not give doublet parameters for their doublets. Mössbauer parameters of the three samples are given in Table 5. The spectrum of pertlikite is the simplest of the three samples, with 76% of the total Fe as Fe^{3+} and 24% as Fe^{2+}. The Fe^{3+} parameters for pertlikite are δ = 0.41 mm/s and Δ = 0.16 mm/s, which are similar to those for other hydrous sulfates, particularly those in the hydration series $Fe_2(SO_4)_3 \cdot nH_2O$, which includes quenstedtite, coquimbite, paracoquimbite, kornelite, and lausenite. The Fe^{3+} doublets with the same parameters are also found in the two samples of voltaite studied for comparison (Table 5), and were assigned by Hermon *et al.* (1976) to the *M*1 site in voltaite. Voltaite also has a smaller Fe^{3+} doublet (6–16% of the total Fe), with δ = 0.35 mm/s and Δ in the range 1.06–1.18 mm/s, which Hermon *et al.* (1976) assigned to *M*2.

The Fe^{2+} parameters for pertlikite are δ = 1.24 mm/s and Δ = 1.66 mm/s, with 24% of the total area. These values are also very similar to those found for Fe^{2+} in voltaite (Table 5). It is notable that both samples of voltaite studied contain roughly half the Fe as Fe^{2+}, significantly less than the 63% Fe^{2+} in the ideal formula, and twice as much as the Fe^{2+} in pertlikite. This requires that some of the Fe^{3+} in voltaite is at the *M*2 site.

In summary, the Mössbauer data suggest that pertlikite contains 76% of the total iron as Fe^{3+} in octahedral coordination, and 24% of the total Fe as Fe^{2+}.

Optical properties

Initially, pertlikite was refined in the same isometric space-group as voltaite. Results of that refinement suggested that further examination of the space group was necessary. When a single crystal was observed in cross-polarized light, it was found to be optically aniso-tropic. An extinction dataset was then collected on this sample. The graphical output from the newest version of EXCALIBRW (Gunter *et al.* 2005) showed pertlikite to be uniaxial because one of its extinction curves plots as a great circle (Bloss 1981, Gunter *et al.* 2005). The pole

to this great circle is the optic axis (*i.e.*, the ε vibration direction). Thus the optic sign of the mineral can be readily determined by the use of an accessory plate, and pertlikite was shown to be optically (–).

Output from EXCALIBRW was also used to orient both ε and ω to determine the indices of refraction by use of the double variation method (Su *et al.* 1987). With this method, we found ε = 1.586(2), and ω = 1.590(2). Because pertlikite exhibits a very low birefringence, the determination of the optic sign as measured indices of refraction might yield an incorrect result; however, the optic sign was determined directly by use of an acces-sory plate, as discussed above. By using the cell param-eters (Table 1) and chemical composition (Table 6), the density of pertlikite was calculated to be 2.56 g/cm³. Given the density and the mean index of refraction [(ε + ω^2)/3 = 1.590], the Gladstone–Dale compatibility index was calculated to be –0.033. This index is used to determine the relationship between the measured index of refraction and crystal structure, and for pertlikite, it shows excellent agreement (Mandarino 1981).

Physical properties

Pertlikite forms crystals up to ~1 cm, dark olive green to black in color (Figs. 1, 2). No fluorescence was detected in either long- or short-wave ultraviolet radiation. The fracture in pertlikite is conchoidal, and no distinct cleavage was observed. The density of pertlikite measured by pycnometer, D_{meas}, is 2.59(3) g/cm³, and the calculated density, D_{calc}, is 2.56(1) g/cm³ (using the chemical data from Table 6). The H_2O content measured by elemental analysis (15.3 wt.% ± 10%) is within the uncertainty consistent with the result obtained by crystal-structure refinement (16.73 wt.%).

Crystal structure and chemical composition

Pertlikite is a member of the voltaite group, which includes the voltaite and zincovoltaite, isomorphous isometric phases that crystallize in space group $Fd3c$. The crystal structure of voltaite has been described (Mereiter 1972a), and we here describe the atomic

TABLE 5. MÖSSBAUER PARAMETER FOR VOLTAITE-GROUP MINERALS

	CS (mm/s)	QS (mm/s)	% Area
Pertlikite from Madeni Zakh, Iran			
*M*1+*M*3 Fe^{3+}	0.41	0.16	76
*M*2 Fe^{2+}	1.24	1.66	24
Voltaite, NMNH 158795			
*M*1+*M*2 Fe^{3+}	0.51	0.18	44
*M*2 Fe^{3+}	0.35	1.06	6
*M*2 Fe^{2+}	1.20	1.56	50
Voltaite, NMNH 115034			
*M*1+*M*2 Fe^{3+}	0.50	0.13	37
*M*2 Fe^{3+}	0.36	1.18	16
*M*2 Fe^{2+}	1.20	1.62	47

TABLE 6. COMPOSITION[1] OF PERTLIKITE FROM MADENI ZAKH, IRAN

K_2O wt.%	4.80(12)	Fe_2O_3*	14.78	SO_3	49.58(34)
Na_2O	0.02(1)	ZnO	0.04(1)	H_2O[2]	16.73
Al_2O_3	2.64(5)	MgO	6.26(69)		
FeO*	4.20	MnO	0.97(25)	Total	100.02

Note: Errors for oxides are the standard deviations of repeated analyses. [1] Average results of 10 electron-microprobe analyses. [2] Estimated by crystal-structure refinement. For the H_2O content, which was measured by elemental analysis (15.3 wt.%), the uncertainty was evaluated at 10%. The H_2O content measured by elemental analysis is within the uncertainty consistent with the result obtained by crystal-structure refinement (16.73 wt.%). CO_2 was sought by elemental analysis but is below detection limit (500 ppm for C). FeO_{total} = 17.50(86) wt%. FeO and Fe_2O_3 were calculated by Mössbauer spectroscopy (Table 5). The chemical analysis (in combination with results of the crystal-structure refinement) gives the following formula, calculated on the basis of 23 cations: $(K_{1.99}Na_{0.01})_{\Sigma1.99}$ $^{M2}(Fe^{2+}_{1.13}Mg_{0.49}$ $Mn^{2+}_{0.27}Fe^{3+}_{0.19}Zn_{0.01})_{\Sigma2.00}$ $^{M3}(Mg_{2.52}Fe^{3+}_{1.49})_{\Sigma4.01}$ $^{M1}Fe^{3+}_{2.00}$ $Al_{1.00}$ $(SO_4)_{12.00} \cdot 18H_2O$.

arrangement of the tetragonal phase pertlikite on the basis of the isometric isomorph voltaite.

Although demonstrably tetragonal by optical methods and crystal structure, the deviations of pertlikite from isometricity are subtle. A preliminary refinement of pertlikite in $Fd3c$ gave a final R value of 3.45% as compared to 2.22% for the final refinement in the correct space-group, $I4_1/acd$. Voltaite crystallizes in $Fd3c$, in the setting with the origin at $\bar{3}$ (with coordinates of Mereiter 1972a), with $Z = 16$ and $V \approx 20,200$ Å^3. The tetragonal phase pertlikite crystallizes in $I4_1/acd$, in the setting with the origin at $\bar{1}$, with $Z = 8$ and $V \approx 10,041$ Å^3. In pertlikite, the c axis corresponds to the isometric c, but the a_1 and a_2 tetragonal axes form the second-order pyramid, thus $a_{1,2(vlt)} \approx \sqrt{2}\, a_{(prt)}$.

The reasonable refinement of the atomic arrangement of pertlikite in the isometric space-group of voltaite demonstrates the similarity of the structures. As noted below, the symmetry breaking from isometric to tetragonal occurs because of cation ordering. The atomic arrangement of pertlikite is shown in Figure 4. As noted in the atomic arrangement of voltaite, the structure is formed of a continuous framework composed of $[\text{Mg,Fe}^{3+}\text{–O}_6]$ octahedra, $[\text{Mg,Fe}^{2+},\text{Fe}^{3+}\text{–O}_4(\text{H}_2\text{O})_2]$ octahedra and $[\text{K}^+\text{O}_{12}]$ polyhedra linked by SO_4 tetrahedra. The arrangement gives rise to "cages" occupied by disordered $[\text{Al}(\text{H}_2\text{O})_6]$ octahedra (Mereiter 1971, 1972a, b). Figure 4 shows the cages in the atomic arrangement as illustrated in the [001] projection of the continuous framework.

Table 7 displays the relationship of atomic positions in voltaite and in pertlikite, and illustrates the reason for the symmetry-breaking in the tetragonal phase pertlikite. In voltaite, the metal atoms, dominantly Fe, are contained in two sites, Fe1 and Fe2. In pertlikite, the tetragonal equivalent of the voltaite Fe1 site exists (= Fe1$_{prt}$), but the voltaite Fe2 equivalent is split into two sites, the Fe2$_{prt}$ site, occupied by $\text{Fe}_{0.719(3)}\text{Mg}_{0.281}$, and

the Mg3$_{prt}$ site, occupied by $\text{Mg}_{0.742(2)}\text{Fe}_{0.258}$. The break in symmetry in pertlikite thus results from the splitting that occurs by creating sites to accommodate Fe (Fe2) and Mg (Mg3) in the tetragonal pertlikite, as compared to the single Fe-bearing site in voltaite.

Twelve of the H_2O molecules in the formula unit of pertlikite form part of the coordination polyhedra of Fe2 and Mg3. The other six H_2O molecules form the $\text{Al}(\text{H}_2\text{O})_6$ octahedron centered at 0,1/4,1/8. The orientation of this octahedron is disordered. This orientational disorder has been modeled by nine oxygen positions (OW1 through OW9, Table 2).

It is possible to subdivide these refined positions of oxygen into groups of six oxygen atoms that form regular octahedral coordination of the aluminum atom. Figure 5a shows these partially occupied positions of oxygen that surround the aluminum atom. At any given aluminum site, only one of these orientations would be occupied, and Figure 5b shows a selected $\text{Al}(\text{H}_2\text{O})_6$ octahedron and the distances of the O–H...O bonds that would be formed. It was not possible to locate the hydrogen atoms, given this positional disorder. The ability to independently refine partially occupied oxygen atoms with reasonable displacement-parameters indicates that the orientation of the $\text{Al}(\text{H}_2\text{O})_6$ is limited to these specific positions and not completely disordered.

The results of the chemical analysis (Table 6), in combination with the Mössbauer data (Table 5) and the crystal-structure refinement (Tables 1–3), give the pertlikite formula $(\text{K}_{1.98}\text{Na}_{0.01})_{\Sigma 1.99}\ ^{M2}(\text{Fe}^{2+}_{1.13}\text{Mg}_{0.49}\text{Mn}^{2+}_{0.27}\text{Fe}^{3+}_{0.10}\text{Zn}_{0.01})_{\Sigma 2.00}\ ^{M3}(\text{Mg}_{2.52}\text{Fe}^{3+}_{1.49})_{\Sigma 4.01}\ ^{M1}\text{Fe}^{3+}_{2.00}\ \text{Al}_{1.00}\ (\text{SO}_4)_{12.00}\bullet 18\ \text{H}_2\text{O}$, which can be simplified to an ideal formula of $\text{K}_2\ ^{M2}(\text{Fe}^{2+},\text{Mg})_2\ ^{M3}(\text{Mg},\text{Fe}^{3+})_4\ ^{M1}\text{Fe}^{3+}_2\ \text{Al}\ (\text{SO}_4)_{12}\bullet 18\ \text{H}_2\text{O}$. In Table 8, the relations among chemistry, lattice parameters, crystal systems, space groups, the strongest lines in the powder pattern, and optical data of voltaite-group minerals are given.

TABLE 7. RELATIONS OF ATOM POSITIONS IN VOLTAITE AND PERTLIKITE

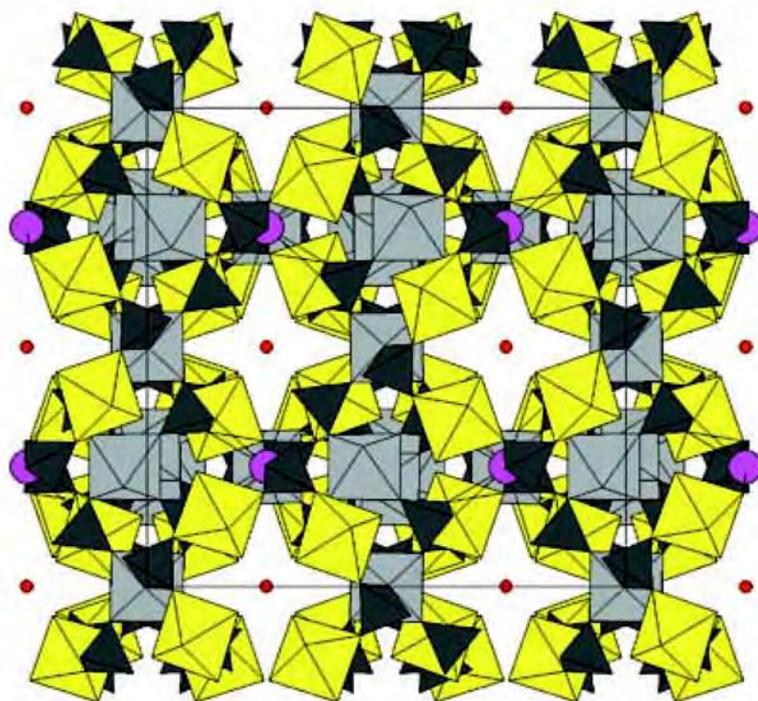| Voltaite $Fd3c$	Pertlikite $I4_1/acd$
K (32b)	K (16e)
Al (16a)	Al (8b)
S (192h)	S1 (32g)
	S2 (32g)
	S3 (32g)
Fe1 (32c)	Fe1(16c)
Fe2 (96g)	Fe2 (16e)
	Mg3 (32g)

FIG. 4.   A [001] projection of the atomic arrangement of pertlikite, with the unit cell outlined. The Al atoms are shown in red, occupying the channels in the pertlikite atomic arrangement. Gray octahedra are $Fe1O_6$ and $Fe2O_6$ octahedra, and the yellow octahedron is $Mg3O_6$; the sulfate tetrahedron is shown in dark gray, and the potassium atom is shown in purple. The H_2O molecules that bond to Al atoms are not shown (see Fig. 5).
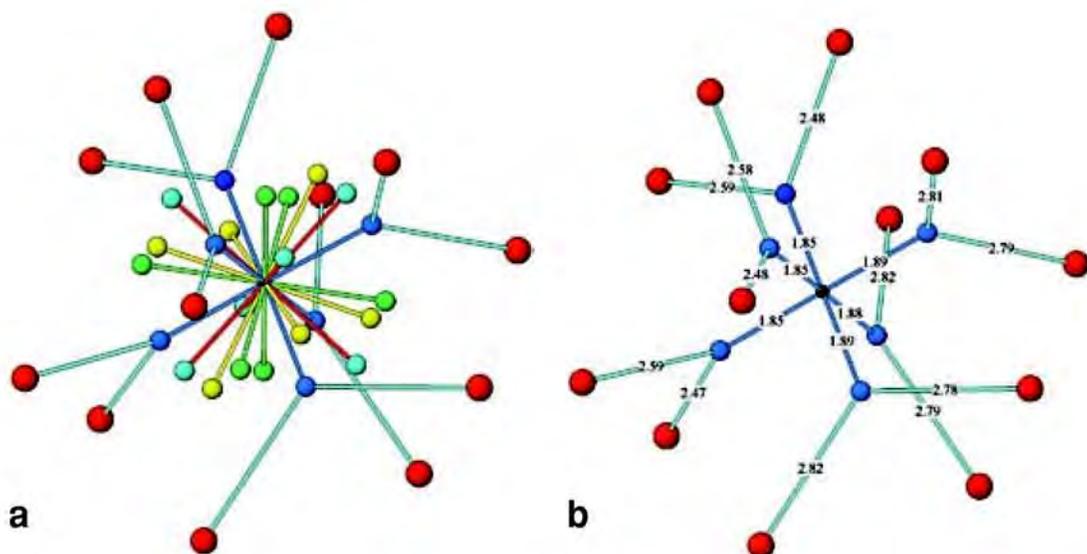

a   **b**

FIG. 5.   a. The disordered $Al(H_2O)_6$ octahedral position. Different orientations of octahedra are indicated by different colors. The hydrogen bonds (light blue) are formed with other oxygen atoms of the structure (red). Only one octahedron orientation (dark blue) has hydrogen bonds indicated. b. One orientation of the $Al(H_2O)_6$ octahedron (blue) and the distances to neighboring oxygen atoms to which hydrogen bonds form (light blue). Distances are in ångström units.

TABLE 8. RELATIONS OF VOLTAITE-GROUP MINERALS

	pertlikite	voltaite[1]	zincovoltaite[2]
Strunz–Nickel grouping	-	7.CC.25	7.CC.25
formula	$K_2 (Fe^{2+},Mg)_2$	$K_2 Fe^{2+}_5$	$K_2 Zn_5$
	$(Mg,Fe^{3+})_4 Fe^{3+}_2$	$Fe^{3+}_3 Al$	$Fe^{3+}_3 Al$
	$Al (SO_4)_{12} \cdot 18H_2O$	$(SO_4)_{12} \cdot 18H_2O$	$(SO_4)_{12} \cdot 18H_2O$
crystal system	tetragonal	cubic	cubic
space group	$I4_1/acd$	$Fd3c$	$Fd3c$
lattice parameter a (Å)	19.2167(2)[3]	27.178(1)	27.180(1)
lattice parameter c (Å)	27.1976(4)[3]	-	-
cell volume (Å³)	10043.6(3)	20075(2)	20079(2)
strongest lines	5.543(28)	5.55(60)	5.53(48)
in the powder pattern	6.807(16)	6.80(30)	4.24(28)
	3.628(12)	3.54(80)	3.54(67)
	3.396(100)	3.40(100)	3.39(100)
	3.136(21)	3.14(25)	3.13(39)
	3.038(39)	3.03(45)	3.03(28)
	2.848(31)	2.85(35)	2.84(32)
	2.534(21)	2.53(20)	-
	2.078(29)	2.08(30)	-
	1.601(21)	1.60(20)	-
Optical data	$n(\omega) = 1.590(2)$	n = 1.593–1.608	n = 1.605(3)
	$n(\varepsilon) = 1.586(2)$	-	-

Note: [1] PDF 20–1388, Mineral Powder Diffraction File Databook (1993). [2] Li et al. (1987). [3]The cell parameters of pertlikite differ from those derived from the single-crystal refinement of the structure. These parameters were derived by using CuKα radiation and were calculated with the program PC-RIETVELD PLUS (Fischer et al. 1993). Although the powder-derived cell parameters differ from those derived from the single-crystal determination of the structure beyond the reported precision, the parameters are adequately similar.

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