

Slavikite—Revision of chemical composition and crystal structure

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ABSTRACT

Given its abundant occurrence at Wieściszowice, SW Poland, we have carried out a revision of the chemical composition and crystal structure of the sulfate mineral slavikite. Slavikite crystallizes in the trigonal space group $R\bar{3}$. The unit-cell parameters, determined using single-crystal X-ray diffraction ($R_1 = 0.0356$) at 100 K, are $a = 12.1347(6)$ Å, $c = 34.706(3)$ Å, and $V = 4425.9(5)$ Å³. The results of chemical analyses reported in the literature and made on material from Wieściszowice unequivocally show that Na is not an essential component of slavikite, at odds with the generally accepted Süsser formula and model of the crystal structure. Our chemical analyses and structure determination lead us to propose a new, more adequate, formula for slavikite: $(\text{H}_3\text{O}^+)_3\text{Mg}_6\text{Fe}_{15}(\text{SO}_4)_{21}(\text{OH})_{18} \cdot 98\text{H}_2\text{O}$. The crystal structure consists of infinite layers of Fe-hydroxy-sulfate linked with $[\text{Mg}(\text{H}_2\text{O})_6]^{2+}$ octahedra, forming a honeycomb-like structure. These layers are perpendicular to the Z axis and are built up from two types of SO_4^{2-} tetrahedra and two types of Fe octahedra (Fe1 with O and OH, and Fe2 with O, OH, and H_2O ligands attached, respectively).

Compared to previous studies, the main skeleton of the slavikite structure, i.e., the layers of Fe^{3+} -hydroxy-sulfate, $[\text{Mg}(\text{H}_2\text{O})_6]^{2+}$ octahedra and disordered isolated sulfate ions, remains unchanged. However, on the basis of careful chemical analysis and single-crystal X-ray diffraction studies, we conclude that Na cations are absent from the structure of slavikite and their positions are occupied by disordered protonated water clusters balancing the excess of negative charge in the structure. These protonated water clusters are located at the inversion centers on the $\bar{3}$ axes of symmetry between two $[\text{Mg}(\text{H}_2\text{O})_6]^{2+}$ cations also lying on such axes (but not at the inversion centers). This structure also contains another disordered moiety—an isolated sulfate anion located at the inversion center of the $\bar{3}$ axis. This SO_4^{2-} anion is disordered in such a way that each oxygen atom partially occupies 5 positions resulting from 5 different orientations of the anion. This complex anion is linked by hydrogen bonds with the O atoms of ordered water molecules. In consequence, the disordered sulfate anion is surrounded by 12 ordered water molecules, thus forming a spherical water environment around the sulfate.

Keywords: Slavikite, weathering sulfate, chemical composition, crystal structure

INTRODUCTION

Secondary sulfate minerals resulting from sulfide oxidation are currently recognized as sensitive environmental indicators and play an important role in the acid drainage mobilization of metals and the monitoring of water quality (Alpers et al. 2000). One of these minerals is slavikite, the subject of this paper. Slavikite forms as a product of pyrite weathering, especially in shales and slates containing chlorite or other magnesian minerals.

Slavikite has generally been recognized as a rare mineral, but is known from many localities. It has been found in Valachov Hill (type locality), Luka near Medník, Vrané, Štěchovice, Jarov, Troja, and Mandát, all Bohemia, Czech Republic (Van Tassel 1972); Smolník and Medzev, Slovakia (Makovický and Streško 1967); Pöham, Salzburg, St. Peter ob. Rehnweg, Kärnten, and Aigen, Steiermark, Austria; Franquénies, Brabant, Stavelot, and Val-Dieu, Liège, Belgium; St. Cyprien-sur-Dourdou and Aveyron, Kaymar, France (after Van Tassel 1972); Wieściszowice, Rudawy Janowickie, Poland (Parafiniuk 1991, 1996); Quebrada

de la Alcaparrosa, Argentina (Gordon 1941); Galena Hill near Porcupine Creek, Yukon Territory, Canada (Van Tassel 1972); and Alum Cave Bluff, Tennessee (Coskren and Lauf 2000; Hammarstrom et al. 2005). Slavikite has been reported also from Germany, Greece, Hungary, Italy, and Norway.

As a rule, slavikite occurs with other secondary sulfates in the crusts or efflorescences on the surface of weathered pyrite-bearing rocks. It may be associated with halotrichite, pickeringite, fibroferrite, botryogen, copiapite, jarosite, natrojarosite, epsomite, gypsum, and sometimes also melanterite, szomolnokite, alunogen, alums, and other minerals (Van Tassel 1972).

The history of the study of slavikite is quite complicated and well summarized by Van Tassel (1972). It was first described by Jirkovský and Ulrich (1926) from an occurrence in the oxidation zone of pyritic shales on Valachov Hill near Skřiváň, Bohemia. The mineral was named in honor of the Czech mineralogist František Slavík (1876–1957), professor at Charles University in Prague. Rost (1941) proved that the same mineral had been described earlier, in 1882 by J. Klvaňa as paracoquimbite. Rost (1941) suggested that despite the priority rule, the name slavikite should be kept as it was better known in the literature. The name

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paracoquimbite was more appropriate for the trigonal polymorph of coquimbite. The lack of access to scientific papers during World War II was responsible for a duplicate description of slavikite by Van Tassel (1944) from Franquénies, Brabant, Belgium, under the name franquenite. The author himself later withdrew the proposal and accepted the priority of slavikite.

Slavikite is accepted as a valid mineral species, but it still remains poorly examined. Doubts have arisen even over such issues as the chemical formula (see Table 1) and crystal structure. The formula of Süssé (1975), based on a crystal structure determination, and most commonly applied in handbooks and mineral registers, has not been confirmed by any published chemical analysis. An appropriate solution to the problem of the mineral composition may lie in the slavikite occurrence at Wieściszowice, SW Poland.

OCCURRENCE

Wieściszowice is located in the Rudawy Janowickie unit, composed mainly of metamorphic rocks that belong to the eastern envelope of the Variscan Karkonosze granitoid massif, one of the main geologic units of the Western Sudetes in SW Poland. The metamorphic series is of Early Paleozoic age and includes a sericite-chlorite schist belt with dispersed pyrite mineralization. The richest parts of the pyrite-bearing schists were exploited near the village of Wieściszowice from 1793 to 1925. Large open pits and waste dumps are reminders of the mining work. Weathered pyrite-bearing schists excavated in the abandoned mine still produce an acid mine drainage (AMD) collected in the small Purple Pond with rusty-colored water filling the bottom of the open pit and a well-developed assemblage of sulfate minerals. The AMD has a pH of 2.6–2.8 and mineralization ranges from 3.0 to 5.5 g/L. The essential components of the AMD are (in mg/L): Fe 380–600, Ca 200–300, Mg 150–250, Al 90–170, and sulfate ion 2.500–4.300. Sodium and potassium contents are very low (5–5.5

and 0.1–0.5 mg/L, respectively). The assemblage of sulfate minerals formed in the weathering zone reflects the chemistry of the AMD solutions. This assemblage comprises magnesio- and aluminocopiapite, fibroferrite, pickeringite, slavikite, gypsum, epsomite, melanterite, and alunogen (Parafiniuk 1996).

Slavikite occurs at Wieściszowice as fine-grained encrustations and efflorescences on the surface of the pyrite-bearing schists. It may be the dominant component of sulfate crusts of ca. 10–20 cm² and up to few centimeters thick. The mineral practically never forms monomineralic aggregates, as it is invariably accompanied by a few percent of pickeringite, gypsum, or fibroferrite. Slavikite also occurs as an admixture in aggregates of fibroferrite, pickeringite, and other sulfate minerals. Slavikite aggregates easily mechanically desintegrate into individual euhedral to subhedral crystals smaller than 0.1 mm with tabular, hexagonal habit (Fig. 1). The crystals are flattened on the basal pinacoid and rimmed by small rhombohedral faces. Slavikite aggregates are green with a yellowish tint; under the microscope, crystals are yellow-greenish. Some crystals display a perfect cleavage parallel to the basal pinacoid. Slavikite dissolves slowly in cold water but quickly upon warming. It is stable under ambient conditions. Kept under ambient conditions for at least 10 years, slavikite samples do not reveal any sign of transformation or dehydration except for some splitting along cleavage planes and a little bending of dried cleavage flakes (Fig. 1).

EXPERIMENTAL METHODS

Ten samples of slavikite were separated under a stereomicroscope and verified by powder X-ray diffraction (PXRD). Next, ca. 250 mg samples were dissolved in warm water acidified with HCl, filtered, and the solutions analyzed by ICP-OES method using Parkin Elmer Optima 5300 DV apparatus. The standard uncertainty of a single ICP measurement is <1%, whereas the relative error of the whole ICP analysis is <5%. Insoluble residues were dried, weighed, and examined by PXRD. Water content was determined thermogravimetrically from separate samples using a LabSys TG-DTA/DSC with a standard uncertainty at the level of less than 2%.

Crystal structure determination

Due to the instability of the crystals at room temperature when subjected to the relatively high intensity of an X-ray beam produced by a rotating anode, the measurement was conducted at 100 K on a Bruker SMART APEX II diffractometer with graphite-monochromated MoK α radiation. An Oxford Cryosystem 600 cooling device was applied to perform data collection at 100 K. Both psi and omega type

TABLE 1. Chemical formulae of slavikite

(Na,K) ₂ Fe ₁₀ (SO ₄) ₁₃ (OH) ₆ ·63H ₂ O	Jirkovský and Ulrich (1926)
Fe(SO ₄ OH)·8H ₂ O	Rost (1941)
MgFe ₃ (SO ₄) ₄ (OH) ₃ ·18H ₂ O	Gordon (1941)
NaMg ₇ Fe ₃ (SO ₄) ₇ (OH) ₆ ·33H ₂ O	Süssé (1975)
(H ₃ O ⁺) ₃ Mg ₆ Fe ₁₅ (SO ₄) ₂₁ (OH) ₁₈ ·98H ₂ O	This work

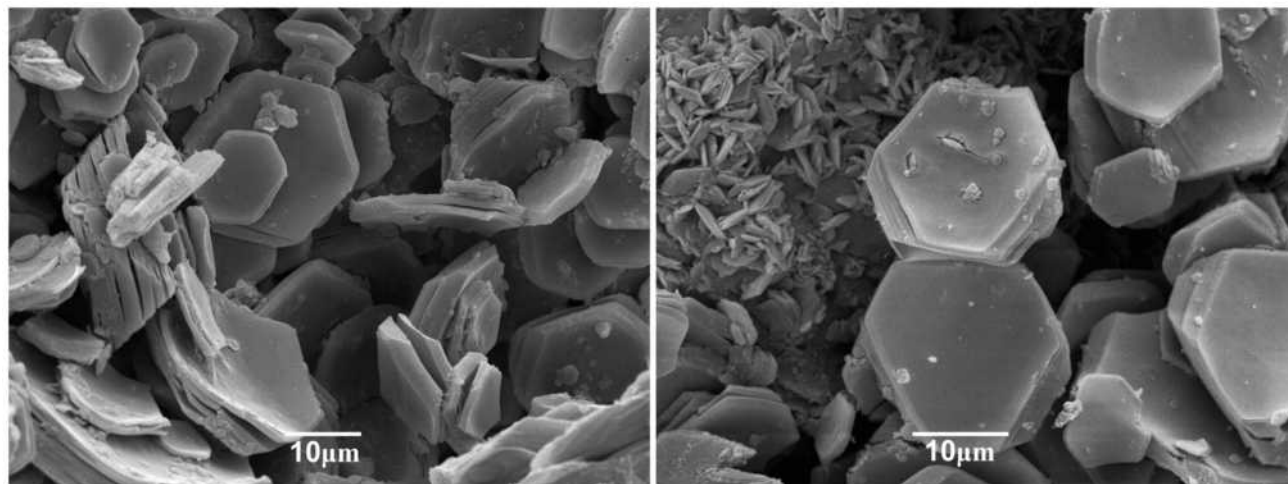


FIGURE 1. SEM images of slavikite crystals from Wieściszowice.

scans were used during data collection. The data were corrected for Lorentz and polarization effects. An empirical correction for absorption was applied (Bruker 2004a). Data collection, cell refinement, and data reduction were carried out with the Bruker suite of programs (Bruker 2004b, 2004c).

The structure was solved by direct methods (Sheldrick 1990) and refined using SHELXL (Sheldrick 1993). The refinement was based on F^2 for all reflections except those with very negative F^2 . Weighted R factors, wR , and all goodness-of-fit S values are based on F^2 . Conventional R factors are based on F with F set to zero for negative F^2 . The $F_o^2 > 2\sigma(F_o^2)$ criterion was used only for calculating R factors and is not relevant to the choice of reflections for the refinement. The R factors based on F^2 are about twice as large as those based on F . Scattering factors were taken from Tables 6.1.1.4 and 4.2.4.2 in the *International Tables for Crystallography*, Vol. C (Wilson 1992).

All ordered non-H atoms were refined with anisotropic temperature factors. In the case of the disordered, isolated sulfate anion, the central S2, oxygen atoms O9 and O11 were treated anisotropically, and atoms O10A and O10B O were refined isotropically. Because of the location of the sulfate on the $\bar{3}$ axis of symmetry, the sum of occupancies of all O atoms was set to be equal to 2/3. The O10A and O10B distances to S2 were set to be similar as in an ordered sulfate tetrahedron. Molecules forming the protonated cluster of water were assigned partial occupancy. The O14 and O15 atoms were refined with anisotropic thermal parameters while O16 was treated isotropically. The unit cell contains the following O atoms associated with water molecules: O6-O8 and O12-O13, which are fully occupied at the 18-fold symmetry sites in the crystal lattice, thus giving a total of 90 H₂O, O14 (sixfold with occupancy 1/3) and the partially occupied 18-fold sites O15-O16, which adds another 11 water molecules to make a total of 101, and out of these, 3 are protonated to [H₃O]⁺ to keep electroneutrality of the unit cell.

All H atoms of the ordered water molecules or hydroxyl groups were located geometrically and their positions and temperature factors were refined with constraints (DFIX instructions causing the O...H distance to be close to 1 Å, and the H...O...H angle in the water molecule close to 105°).

RESULTS AND DISCUSSION

Chemical composition

An assessment of the true chemical composition of slavikite was and is plagued by uncertainties and contradictions. The controversy started with the paper of Jirkovský and Ulrich (1926) whose analysis showed significant amounts of alkalis, especially Na, but did not find Mg (Table 2). Their analysis and mineral formula seem to be incorrect as they have never been confirmed. The results of the chemical analyses of Rost (1941), Gordon (1941), Van Tassel (1944), and Makovický and Streško (1967), performed by wet classical methods (Table 2), proved Mg as an essential component of slavikite, whereas Na and K were subordinate. These results are generally in good agreement with the Gordon (1941) formula: $\text{MgFe}_3(\text{SO}_4)_4(\text{OH})_3 \cdot 18\text{H}_2\text{O}$. However, as a result of his structural study, Süssé (1975) returned to the idea of the inclusion of Na in the slavikite composition. His crystal structure determination was made on material from La Alcaparrosa, Argentina, but his paper (Süssé 1975) does not contain a chemical analysis of slavikite. Nevertheless, the Süssé formula: $\text{NaMg}_2\text{Fe}_3(\text{SO}_4)_4(\text{OH})_6 \cdot 33\text{H}_2\text{O}$ is currently in common use. According to this formula, slavikite should contain 1.80 wt% Na₂O. We know of no published chemical analysis of slavikite with such a high Na content, and thus consistent with the Süssé (1975) formula. Furthermore, the absence of Na in slavikite was reported recently by Parafiniuk (1996) and Hammarstrom et al. (2005).

Problems with determining the true composition of slavikite result from its mode of occurrence. Aggregates of very fine slavikite crystals always contain admixtures of other minerals, which are practically impossible to extract. Hydrated slavikite crystals

TABLE 2. Chemical composition of slavikite compiled from the literature

	1	2	3	4	5	6	7	8	9	10	11
Na ₂ O	1.63	0.68	0.28	0.53	0.29	—	—	—	—	—	—
K ₂ O	0.57	0.26	0.13	0.16	—	—	—	—	—	—	—
MgO	—	4.40	4.54	4.63	4.40	4.23	3.90	3.63	3.63	2.86	4.84
CaO	0.01	0.42	2.38	0.87	—	—	0.41	0.42	0.02	0.43	0.44
MnO	—	—	—	—	—	—	0.89	0.04	—	—	—
FeO	—	0.00	0.82	0.65	—	1.0	—	—	0.62	0.86	0.48
Fe ₂ O ₃	20.08	19.08	18.75	16.94	23.93	14.84	22.98	17.45	17.89	20.17	16.10
Al ₂ O ₃	4.29	2.79	1.77	3.52	—	5.51	0.59	1.56	2.41	1.79	2.94
SO ₃	34.06	34.70	34.61	34.23	34.62	32.77	31.87	31.20	30.15	30.93	31.80
H ₂ O	38.76	36.65	36.58	38.46	37.21	40.7	35.72	35.74	37.12	34.00	38.98
Insoluble	0.52	—	—	—	—	—	4.08	10.50	7.92	7.40	5.62
Total	99.92	98.98	99.86	99.99	100.45	99.05	100.44	100.54	99.76	98.44	101.20

Notes: (1) Valachov, Czech Republic = Jirkovský and Ulrich 1926; (2) Luka pod Mednikem = Rost 1941 (16.22% insol. residue); (3) Jarov = Rost 1941 (4.65% insol. residue); (4) Jarov = Rost 1941 (2.20% insol. residue); (5) Quebrada de la Alcaparrosa, Argentina = Gordon 1941; (6) Franquénies, Belgium = Van Tassel 1944; (7–8) Medzev, Slovakia = Makovický and Streško 1967; (9–11) Wieściszowice, Poland = Parafiniuk 1991.

are very unstable under the electron beam, limiting the application of the electron microprobe. Since the weathering zone at Wieściszowice is practically free of alkalis, the slavikite samples from there are suitable for solving the problem of the presence or absence of Na in this material. The slavikite samples under study do contain a minor admixture of other sulfates, especially gypsum and pickeringite, but are free of natrojarosite and other Na minerals. Bulk chemical analysis can help to explicitly solve the problem of Na presence in slavikite, pivotal to verifying the mineral formula and structure. Loss of water in the temperature interval 20–540 °C was also taken into account (see Fig. 2). The results of the chemical analysis of the Wieściszowice slavikite are shown in Table 3.

The results unequivocally indicate that Na is not an essential component of slavikite from this locality because Na contents are ≤0.01 wt%. Variable, although in many cases significant, amounts of Ca and Al were detected in the analyses. They are caused by the presence of sulfate admixtures that were detected by PXRD (see above). We assume that Ca and Al do not enter into the structure of slavikite in appreciable amounts, as noted by Makovický and Streško (1967) on the basis of their optical and XRD observations. This assumption is also confirmed by results of thermal parameters and the amount of electron density associated with the peaks we found on electron density maps (see description of crystal structure). After the extraction of gypsum and pickeringite contents calculated from the amounts of CaO and Al₂O₃, respectively, one can obtain a chemical formula for slavikite close to the formula found by X-ray structure determination (see next paragraph): $(\text{H}_3\text{O}^+)_3\text{Mg}_6\text{Fe}_{15}(\text{SO}_4)_{21}(\text{OH})_{18} \cdot 98\text{H}_2\text{O}$. Thus, we propose this new formula as correct for slavikite, rather than the Süssé version. The redefinition of slavikite as a Na-free mineral has been approved by CNMNC IMA (Nomenclature Voting Proposal 08-D).

Crystal structure and its properties

The crystallographic data together with the refinement parameters are collected in the Table 4. The list of coordinates of atoms of slavikite together with their occupancies and equivalent isotropic temperature factors (U_{eq}) is presented in Table 5. All tensor elements describing anisotropic thermal parameters for

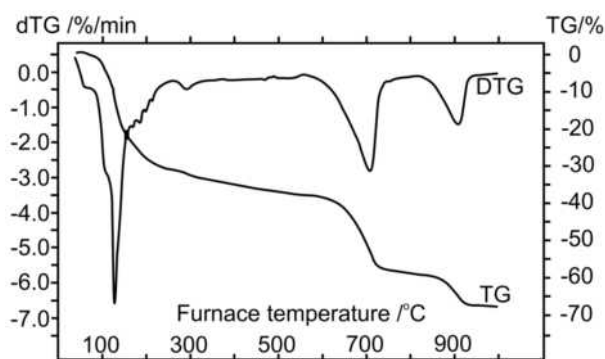


FIGURE 2. Thermogravimetric (TG) and differential thermogravimetric (DTG) curves of slavikite. LabSys TG-DTA/DSC, sample weight 45 mg, 10 °C/min, dynamic He atmosphere, 15 mL/min.

the non-H atoms are provided in Table 6, with the exception of O10A, O10B, O11, and O16 atoms, which were refined in the isotropic model only. Further details of the crystal structure investigations may be obtained from Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: (+49)7247-808-666; E-mail: crysdata@fiz-karlsruhe.de, http://www.fiz-karlsruhe.de/request_for_deposited_data.html) on quoting the appropriate CSD number: 419235. The CIF¹ file is on deposit.

The crystal structure of slavikite was previously described by Süssé (1975) as containing Na ions coordinated by water molecules. The Süssé (1975) structural model is not consistent with our conclusion that slavikite is a Na-free phase. The analysis of the neighborhood of the Na site in the structural model of Süssé (1975) raises serious doubts. The sites thought to be occupied by Na⁺ are located on the $\bar{3}$ axis of symmetry close to

the inversion center and the Na...Na distance is close to 3 Å. Süssé (1975) addressed this problem by setting the Na⁺ occupancy to 0.5. This model led to a very large equivalent thermal motion of the Na ion [$B = 22(3)$ Å² equivalent to $U = 0.279$ Å²], in comparison to the Mg ion [$B = 1.6(2)$ Å² equivalent to $U = 0.020$ Å²]. Such a huge discrepancy between the B parameters suggests an error in the structure refinement. One of the solutions

¹ Deposit item AM-10-006, CIF. Deposit items are available two ways: For a paper copy contact the Business Office of the Mineralogical Society of America (see inside front cover of recent issue) for price information. For an electronic copy, visit the MSA web site at <http://www.minsocam.org>, go to the *American Mineralogist* Contents, find the table of contents for the specific volume/issue wanted, and then click on the deposit link there.

TABLE 4. Crystallographic data and refinement parameters

Formula	Fe ₁₅ H ₂₂₃ Mg ₆ O ₂₀₃ S ₂₁
Formula weight	5129.65
Wavelength (Å)	0.71073
Crystal system	Trigonal
Space group	$R\bar{3}$
a (Å)	12.1347(6)
c (Å)	34.706(3)
V (Å ³)	4425.9(5)
Z	1
D_{calc} (g/cm ³)	1.915
T (K)	100(2)
Crystal size (μm)	80 × 80 × 20
μ (mm ⁻¹)	1.609
exptl absorpt correction	multi-scan
exptl absorpt correction, T_{min}	0.7943
exptl absorpt correction, T_{max}	0.9239
θ range (°)	1.76 to 29.99
Reflections collected	25516
Unique reflections	2867
Unique $I > 2\sigma(I)$	2149
R_{int}	0.0807
R_1 [$I > 2\sigma(I)$]	0.0356
wR_2 [all data]	0.0881
S	1.028
Largest diff. peak and hole (e Å ⁻³)	0.537 and -0.572

TABLE 3. Chemical composition of slavikite from Wieściszowice

	W-290A	W-345A	W-512A	W-531A	W-531B	W-531C	W-606A	W-721A	W-721B	W-805A	new formula
	wt%										
MgO	3.51	3.89	3.87	3.88	3.67	4.08	3.52	3.85	3.82	4.06	4.71
CaO	0.42	0.16	1.39	0.37	0.19	0.25	0.45	0.29	0.31	1.51	
MnO	0.02	0.02	0.03	0.03	0.03	0.03	0.02	0.03	0.03	0.03	
Fe ₂ O ₃	18.59	21.33	18.61	20.79	17.29	21.13	17.32	18.40	18.76	19.57	23.36
Al ₂ O ₃	1.13	0.53	1.05	0.61	1.80	0.75	1.07	1.32	1.15	0.92	
TiO ₂	0.02	0.02	0.00	0.04	0.02	0.04	0.00	0.03	0.03	0.00	
SO ₃	28.98	31.02	32.23	31.66	30.35	32.03	27.2	31.18	30.57	32.43	32.79
P ₂ O ₅	0.06	0.06	0.15	0.08	0.09	0.08	0.04	0.06	0.06	0.23	
H ₂ O	31.0	33.1	36.7	36.7	34.5	36.7	29.9	35.1	32.7	35.1	39.14
insol.*	15.95	8.94	8.75	9.37	14.35	6.63	20.68	10.35	11.87	5.40	
Total	99.68	99.07	102.78	103.53	102.29	101.72	100.20	100.61	99.30	99.25	100.00
	ppm										
Na	52	11	82	0	12	17	57	52	40	64	
K	61	42	67	34	41	40	88	75	68	64	
Cu	25	0	434	67	130	71	47	5	6	474	
Zn	47	29	32	62	81	67	36	37	40	24	
Co	41	32	36	54	47	57	18	68	63	37	
Ni	18	9	12	26	30	23	21	26	24	10	
Pb	9	7	0	11	4	8	5	2	9	11	
Cr	19	5	5	15	42	13	51	11	14	2	
V	10	6	6	7	10	5	8	15	13	4	
	apfu calculated on 21 St										
Mg	5.30	5.82	5.48	5.26	5.29	5.47	5.67	5.38	5.32	5.75	6.00
Fe	16.22	17.10	14.90	15.18	15.62	15.42	16.00	15.02	14.96	15.36	15.00
S	21.00	21.00	21.00	21.00	21.00	21.00	21.00	21.00	21.00	21.00	21.00
H ₂ O	102.0	99.4	112.7	110.4	109.8	108.9	104.9	107.9	107.7	106.5	111.50

* Quartz, sericite, pyrite, and goethite.

† After extracting of gypsum and pickeringite admixture calculated from the contents of CaO and Al₂O₃, respectively.

TABLE 5. Atomic coordinates, site occupation factors, and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 1000$) for slavikite

	x	y	z	sof	U_{eq}
Fe1	2/3	1/3	0.0286(1)	1	10(1)
Fe2	1/2	0	0	1	11(1)
S1	0.7219(1)	0.1145(1)	0.0625(1)	1	14(1)
O1	0.6831(2)	0.2123(2)	0.0665(1)	1	15(1)
O2	0.6637(2)	0.0409(2)	0.0263(1)	1	15(1)
O3	0.8595(2)	0.1748(2)	0.0591(1)	1	22(1)
O4	0.6744(2)	0.0279(2)	0.0951(1)	1	23(1)
O5	0.5543(2)	0.1823(2)	-0.0022(1)	1	13(1)
O6	0.4125(2)	-0.0130(2)	0.0511(1)	1	16(1)
Mg1	2/3	1/3	0.1769(1)	1	15(1)
O7	0.5198(2)	0.3169(2)	0.2101(1)	1	25(1)
O8	0.5529(2)	0.1845(2)	0.1406(1)	1	21(1)
S2	1/3	-1/3	1/6	1	15(1)
O9	0.3922(7)	-0.2032(6)	0.1809(2)	0.295(3)	26(2)
O10A	0.4546(11)	-0.2862(18)	0.1877(5)	0.116(2)	25(4)
O10B	0.4295(10)	-0.2604(10)	0.1968(3)	0.189(3)	24(3)
O11	1/3	-1/3	0.2084(5)	0.201(13)	24(6)
O12	0.6448(2)	-0.0142(2)	0.1735(1)	1	23(1)
O13	0.2272(2)	-0.2442(2)	0.0736(1)	1	20(1)
O14	1	1	0.0440(3)	1/3	27(2)
O15	0.7706(6)	0.8807(5)	0.0233(2)	0.363(4)	28(1)
O16	0.8540(30)	0.9260(30)	0.0100(8)	0.137(4)	84(8)*
H5	0.5330(40)	0.2080(30)	-0.0267(6)	1	49(11)
H6A	0.3880(30)	0.0510(20)	0.0580(11)	1	60(13)
H6B	0.3440(30)	-0.0952(16)	0.0607(11)	1	57(12)
H7A	0.4830(30)	0.2690(40)	0.2339(7)	1	78(15)
H7B	0.4540(30)	0.3300(50)	0.1978(11)	1	88(16)
H8A	0.4705(18)	0.1080(20)	0.1458(8)	1	38(10)
H8B	0.5740(30)	0.1790(30)	0.1136(5)	1	58(12)
H12A	0.6490(30)	0.0040(30)	0.1454(4)	1	47(11)
H12B	0.5650(20)	-0.0960(20)	0.1773(10)	1	73(14)
H13A	0.1400(17)	-0.2610(40)	0.0797(9)	1	59(12)
H13B	0.2590(30)	-0.2620(40)	0.0977(6)	1	50(11)

* Partially occupied position of disordered oxygen atom refined with isotropic temperature factor.

TABLE 6. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for atoms constituting of slavikite except O10A, O10B, and O16 disordered O atoms

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Fe1	8(1)	8(1)	15(1)	0	0	4(1)
Fe2	10(1)	8(1)	16(1)	0(1)	-1(1)	4(1)
S1	13(1)	9(1)	19(1)	-1(1)	-4(1)	6(1)
O1	18(1)	13(1)	18(1)	-1(1)	-3(1)	9(1)
O2	13(1)	14(1)	19(1)	-3(1)	-3(1)	8(1)
O3	11(1)	16(1)	36(1)	-2(1)	-6(1)	5(1)
O4	35(1)	15(1)	20(1)	2(1)	-3(1)	13(1)
O5	12(1)	9(1)	18(1)	0(1)	-2(1)	5(1)
O6	15(1)	12(1)	20(1)	1(1)	2(1)	6(1)
Mg1	14(1)	14(1)	18(1)	0	0	7(1)
O7	20(1)	33(1)	26(1)	12(1)	8(1)	16(1)
O8	20(1)	17(1)	20(1)	0(1)	1(1)	4(1)
S2	15(1)	15(1)	16(1)	0	0	7(1)
O9	30(4)	13(3)	29(4)	-8(3)	-4(3)	5(3)
O11	27(7)	27(7)	19(10)	0	0	13(4)
O12	21(1)	22(1)	25(1)	0(1)	-3(1)	11(1)
O13	14(1)	20(1)	22(1)	1(1)	2(1)	6(1)
O14	27(3)	27(3)	27(6)	0	0	14(2)
O15	23(3)	23(3)	34(3)	-4(2)	-5(2)	9(2)

of this problem could be a change in the occupancy of Na ion from 0.5 to a lower value (e.g., 0.25). This approach, however, violates the electrostatic neutrality condition of the unit cell of slavikite, introducing some excess negative charge. In addition, such a structure would still contain sodium, in contrast to the elemental analyses (cf. Tables 2 and 3). More evidence for the lack of Na ions in slavikite comes from the orientation of H_2O molecules of the $[\text{Mg}(\text{H}_2\text{O})_6]^{2+}$ cation, pointing to the supposed Na site. The distance $\text{Na}\cdots\text{H}$ would be unreasonably short, only 2.75 $\text{\AA}$, for two cations. It was possible to observe such tiny ef-

fects (contacts of H atoms) because of the improved quality of the hardware and low-temperature measurements, increasing the resolution of the experiment. Using this evidence, we propose that the structure of slavikite crystals contains no Na cations, and that its electroneutrality is maintained by the presence of disordered and protonated water molecules forming water clusters. Compared to the refinement of Süssé (1975), we replace the Na ion by a water molecule (O14) with occupancy $1/3$. Because of disorder, it was impossible to localize the H atoms in this group of water molecules. A total sum of water molecules in one cluster (coming from applying the $\bar{3}$ axis) is equal to $3\bar{3}$. This cluster contains half of H^+ moiety, which gives 3 H^+ cations in the formula of slavikite. The correct formula for slavikite should read $(\text{H}_3\text{O}^+)_3\text{Mg}_6\text{Fe}_{15}(\text{SO}_4)_{21}(\text{OH})_{18}\cdot 98\text{H}_2\text{O}$. This protonated water cluster is located at the inversion center on the $\bar{3}$ axis between two $[\text{Mg}(\text{H}_2\text{O})_6]^{2+}$ cations, also lying on this axis, but not at the inversion center (Fig. 3a). The list of O $\cdots$ O distances, that can be recognized as hydrogen bonds in this cluster is presented in Table 7. A possible hydrogen bond assignment in the cluster is presented in Figure 4. In this cluster, the positions of the O14 atoms form the top and bottom apices of an approximate cube. O16 atoms form the six equatorial vertices of the cube, and the six O15 atoms are H-bonded to O16. The O14 site cannot be occupied at the same time as the three nearest O16 sites (see Table 7). Distances to the other three O16 atoms confirm that they can be occupied simultaneously with O14. The maximum occupancies of the O14 and O16 sites are, therefore, achieved via three local configurations: tetrahedron of O14 and the three more distant O16, the inverse tetrahedron and hexagonal ring of six O16, with no O14 water moieties. This is why the true occupancy of O16 is lower (0.137), and the occupancy of O15 plus that of O16 sum up to 0.5.

In this model, the H atoms of the three water molecules of the

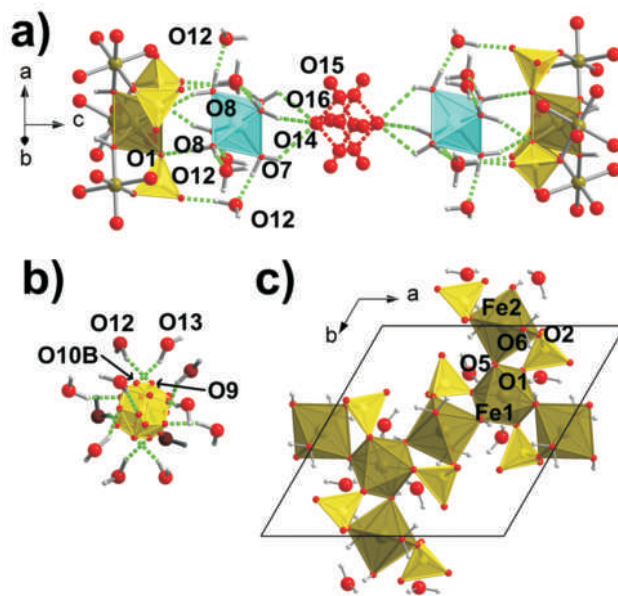
**FIGURE 3.** Protonated water cluster (a), disordered sulfate anion in water environment (b), two types of Fe-O octahedra (c), the reference coordinate system with the +c axis going up relative to the b-c plane.

TABLE 7. Distances (Å) between O atoms of water molecules in protonated cluster and O7

O14	O15	2.517(7)
O14	O16*	2.42(3)
O7	O14†	3.229(9)
O16	O15‡	2.39(3)
O16	O15§	2.43(3)

Notes: Symmetry transformations used to generate equivalent atoms:

* $2 - x, 2 - y, -z$;

† $5/3 - x, 4/3 - y, 1/3 - z$;

‡ $y, 1 - x + y, -z$;

§ $1 + x - y, x, -z$.

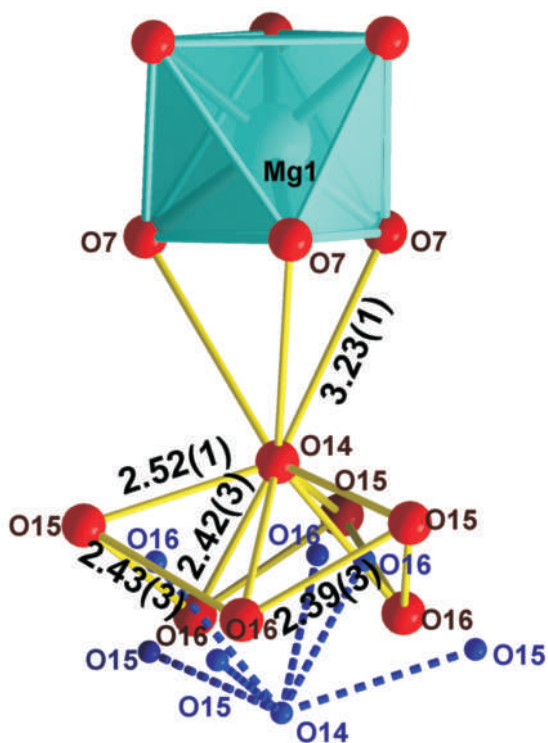


FIGURE 4. A possible assignment of the O···O contacts in the disordered protonated water cluster. The yellow and dashed blue lines represent possible hydrogen bonds in the cluster. The superposition of the yellow and blue states gives the disordered moiety.

Mg-hexaaqua complex ions point to the O14 water moiety. The relatively large O14···H7A distance [2.74(4) Å] indicates some weak attractive interactions keeping together the water cluster and neighboring Mg complex ions. Although the above H···O distance is slightly longer than a formal limiting value assumed for a hydrogen bond, it still can be treated as very weak interaction because of the electrostatic nature of hydrogen bonding. This effect can be responsible for crystal disintegration in a strong X-ray beam. Apparently, different water molecules are bound with different strengths, which is well illustrated on Figure 5, showing complex DTA curves. In such a complex situation, the IR studies appeared to be inconclusive. Our corrected structure of slavikite can shed light on dehydration studies of this mineral (for example, August 1991).

The new model of the structure of slavikite presented in this work is based on chemical analysis and a careful examination of the X-ray structure (see Fig. 6). Our model differs from the previous one (Süsse 1975) by the lack of Na, which we replace

by protonated water clusters. The refinement of our structure in the model proposed by Süsse leads us to unreasonably large temperature factors of the Na cation, although the measurements were accomplished at low temperature (100 K), which reduces the amount of thermal motion of atoms. We have no access to the original Süsse slavikite sample, but we obtained the same unit-cell parameters, indicating the same mineral. Most important is the fact that we did not detect any Na⁺ by our chemical analysis and additionally, there is no literature evidence of a possible isomorphic series of slavikite with Na⁺ or H₃O⁺. Instead of Na⁺, we regard the “H⁺” cation as a counterion in this mineral. Due to disorder of O atoms potentially carrying the proton, we propose the proton localization in an indirect way, especially that the occupancy of this moiety should be 0.5 in the asymmetric part of the unit cell. In slavikite, electroneutrality could be also maintained by the presence of hydrogen sulfate ions. This can be associated with the S-O bond with attached H⁺ ion elongated in comparison to the S-O one. In the S2 sulfate, such analysis is difficult due to disorder. This SO₄²⁻ anion is disordered in such a way that the O atoms occupy 20 positions (2 for O11, and 6 each for O9, O10A, and O10B). The SO₄²⁻ tetrahedron thus adopts five different orientations. However, this anion is surrounded by 12 ordered water molecules with their H atoms pointing to the sulfate moiety. In consequence, none of the neighboring water molecules can act as a donor of a potential proton attached to the sulfate anion. However, in the ordered S1 sulfate oxyanion coordinating also the Fe ions, there are slight discrepancies in the S-O bond lengths (see Table 8). This effect is associated with the coordination of Fe by O1 and O2 atoms, while O3 and O4 remain the terminal ones. Such an effect can also be observed in other minerals, for example, in rhomboclase [(H₃O)Fe(SO₄)₂(H₂O)₃] (see for example Majzlan et al. 2006) or hydronium jarosite

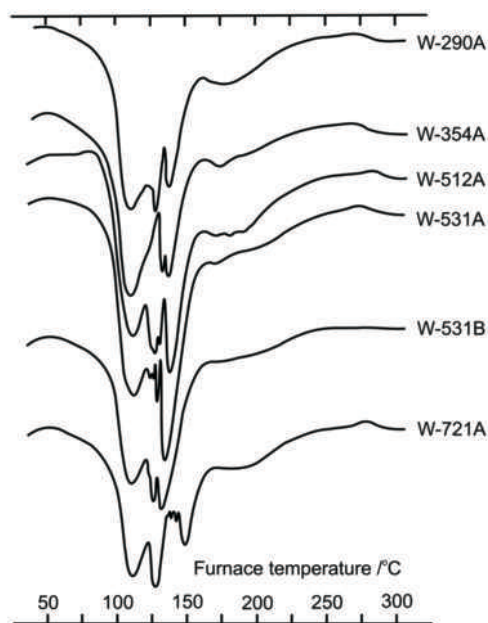


FIGURE 5. Dehydration of selected slavikite samples shown by DTA curves. LabSys TG-DTA/DSC, samples weight 40 mg, 10 °C/min, dynamic He atmosphere, 15 mL/min.

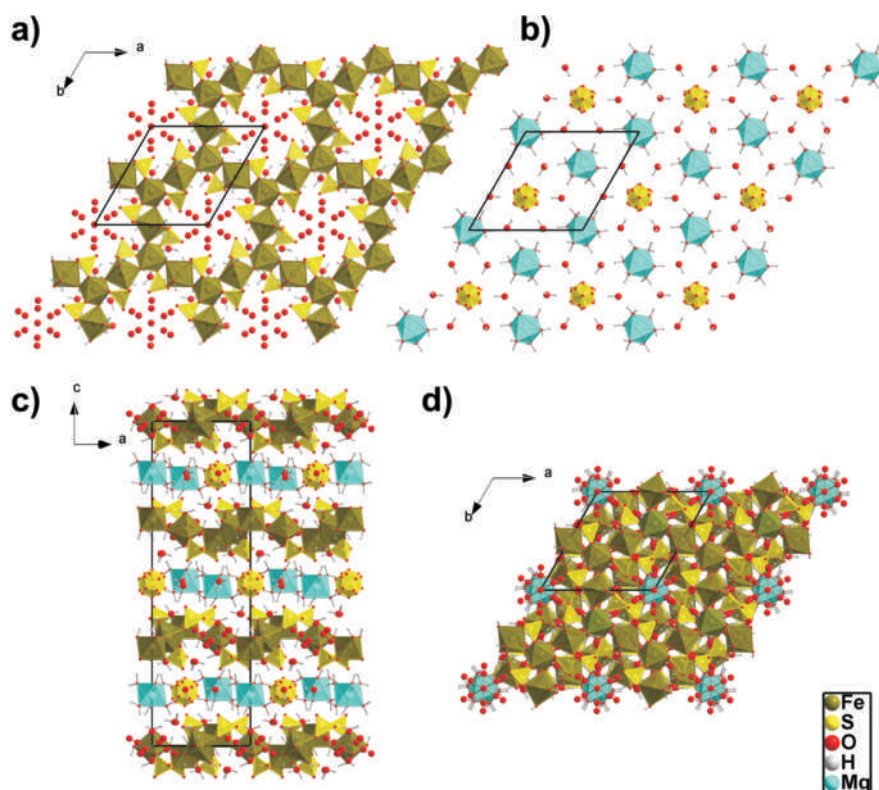


FIGURE 6. Honeycomb-like structure of the Fe-hydroxy-sulfate layer (a), Mg-aqua cations, disordered SO₄²⁻ anions, and water moieties forming layer (b), the unit cell of slavikite view along the Y axis (c) and Z axis (d).

(Majzlan et al. 2004). Moreover, a careful analysis of the bond lengths in ordinary Fe³⁺ sulfates also shows that the distances from S to bridging O atoms are slightly longer than the ones to the terminal atoms (see data for roemerite; Fanfani et al. 1970). The only possibility for the presence of charge balancing protons is the group of disordered water molecules located on the $\bar{3}$ axis close to the inversion center between the [Mg(H₂O)₆]²⁺ complex octahedra.

This structure contains also another disordered moiety—an isolated sulfate (S2) anion located at the inversion center of the $\bar{3}$ axis. The independent part of the sulfate has O9, O10A, O10B, and O11 O atoms with a sum of occupancies equal to $\frac{3}{4}$. This anion is linked by hydrogen bonds to O12 and O13 ordered water molecules with refined positions of H atoms. So by applying the $\bar{3}$ inversion axis one can easily generate a disordered sulfate anion surrounded by 12 ordered water molecules, thus forming a sphere-like water environment around the sulfate (Fig. 3b).

The O12 O atoms are additionally linked with [Mg(H₂O)₆]²⁺ ions through O7 and O8 O atoms and with O4 O atoms from the ordered SO₄²⁻ anion, while the O13 atoms interact with the O5 and O6 hydroxyl groups of the infinite layers of Fe-hydroxy-sulfate. A list of all hydrogen bonds is presented in Table 9.

TABLE 8. Selected distances (Å) in the structure of slavikite

Fe1-O1 (SO ₄ ²⁻)	2.0546(17)	Mg1-O7 (H ₂ O)	2.046(2)
Fe1-O5 (OH ⁺)	1.9638(17)	Mg1-O8 (H ₂ O)	2.064(2)
Fe2-O2 (SO ₄ ²⁻)	2.0095(17)	S1-O1	1.4866(17)
Fe2-O5 (OH ⁺)	1.9688(16)	S1-O2	1.4976(18)
Fe2-O6 (H ₂ O)	2.0327(18)	S1-O3	1.4537(18)
		S1-O4	1.4520(19)

The layers containing Fe are perpendicular to the Z axis. The infinite layers are built from two types of Fe octahedra with O and OH (Fe1) and O, OH, and H₂O (Fe2) as ligands (Fig. 3c).

The Fe1 ion is located at the $\bar{3}$ axis and surrounded by three

TABLE 9. Hydrogen bonds for slavikite

D-H...A	D-H (Å)	H...A (Å)	D...A (Å)	DHA (°)
O5-H5...O13*	0.988(10)	1.850(12)	2.829(3)	170(3)
O6-H6A...O3†	0.992(10)	1.705(15)	2.671(2)	163(4)
O6-H6B...O13	0.986(10)	1.705(10)	2.688(3)	174(3)
O7-H7A...O3‡	0.982(10)	1.97(2)	2.887(3)	154(3)
O7-H7B...O12†	0.989(10)	1.759(10)	2.747(3)	177(3)
O8-H8A...O12‡	0.985(10)	1.742(10)	2.723(3)	174(3)
O8-H8B...O1	0.986(10)	2.010(14)	2.950(3)	158(3)
O8-H8B...O1†	0.986(10)	2.58(4)	3.122(3)	114(3)
O12-H12A...O4	0.994(10)	1.772(11)	2.759(3)	171(3)
O12-H12B...O9	0.989(10)	1.84(2)	2.773(7)	156(4)
O12-H12B...O9‡	0.989(10)	1.96(3)	2.794(7)	140(3)
O12-H12B...O10B	0.989(10)	1.965(16)	2.933(11)	165(3)
O12-H12B...O10A	0.989(10)	2.04(3)	2.974(18)	157(4)
O12-H12B...O10A‡	0.989(10)	2.04(3)	2.842(19)	137(3)
O12-H12B...O10B‡	0.989(10)	2.65(3)	3.426(14)	136(2)
O13-H13A...O4‡	0.994(10)	1.845(18)	2.791(3)	158(3)
O13-H13B...O10B‡	0.989(10)	1.720(19)	2.667(11)	159(3)
O13-H13B...O11	0.989(10)	1.80(2)	2.720(11)	153(3)
O13-H13B...O9‡	0.989(10)	1.91(2)	2.820(7)	152(3)
O13-H13B...O10A	0.989(10)	2.08(3)	2.953(17)	146(3)
O13-H13B...O10B	0.989(10)	2.12(3)	2.983(11)	145(3)
O13-H13B...O10A‡	0.989(10)	2.30(3)	3.22(2)	153(3)

Note: Symmetry transformations used to generate equivalent atoms:

* $x - y, x, -z$;

† $1 - x + y, 1 - x, z$;

‡ $-\frac{1}{3} + x - y, -\frac{2}{3} + x, \frac{1}{3} - z$;

§ $\frac{2}{3} + y, \frac{1}{3} - x + y, \frac{1}{3} - z$;

|| $\frac{2}{3} - x, -\frac{2}{3} - y, \frac{1}{3} - z$;

$5 - y, -1 + x - y, z$.

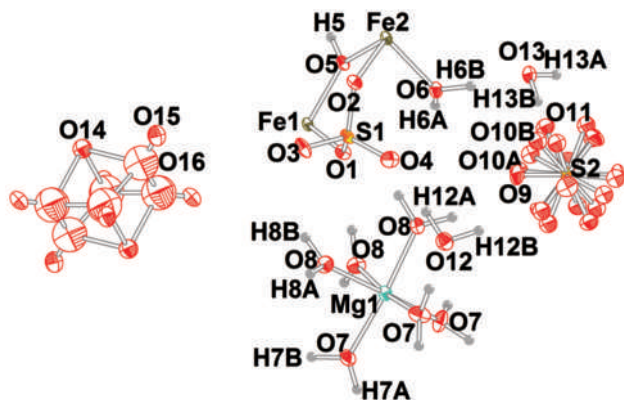


FIGURE 7. Thermal ellipsoids at the 50% probability level.

O1 atoms of the ordered sulfate (S1) and three hydroxyl O5 groups. The Fe2 ion is located at the inversion center. Two ligands (O2 atoms) come from the sulfate (S1): two from the O5 atoms and two from the O6 water molecules. The hydroxyl group is a bridging one, linking the Fe1 and Fe2 central ions of the complex moieties into six member rings all forming a honeycomb-like structure (Fig. 6a).

The free space in the rings is filled with disordered, protonated water clusters. The unit cell contains three Fe-hydroxy-sulfate layers, each translated relative to another by $\sqrt{3}/3 \times a$ in the [120] direction. Because of this shift, the structure of slavikite does not contain channels along the [001] direction. Between such layers isolated $[\text{Mg}(\text{H}_2\text{O})_6]^{2+}$ cations, disordered SO_4^{2-} anions, and water molecules are present (Fig. 6b). Complete [010] and [001] views of the slavikite structure are shown on Figures 6c and 6d. Finally, the thermal ellipsoids of atoms are presented in Figure 7. In Table 8, we compile selected bond lengths in Fe1-O, Fe2-O, and Mg1-O octahedra and also for ordered sulfate S1 tetrahedra.

In conclusion, we would like to stress that the results of chemical analyses and careful single-crystal X-ray diffraction structure determinations of slavikite from Wieściszowice, SW Poland, have led us to state that, instead of Na cations in this mineral, disordered protonated water clusters balance the excess of negative charge in the structure. We propose a new formula for slavikite: $(\text{H}_3\text{O}^+)_3\text{Mg}_6\text{Fe}_{15}(\text{SO}_4)_{21}(\text{OH})_{18} \cdot 98\text{H}_2\text{O}$.

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