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SLAVKOVITE, $Cu_{13}(AsO_4)_6(AsO_3OH)_4 \cdot 23H_2O$, A NEW MINERAL SPECIES FROM HORNÍ SLAVKOV AND JÁCHYMOV, CZECH REPUBLIC: DESCRIPTION AND CRYSTAL-STRUCTURE DETERMINATION

JIŘÍ SEJKORA

Department of Mineralogy and Petrology, National Museum, Václavské náměstí 68, CZ–115 79 Praha 1, Czech Republic

JAKUB PLÁŠIL

Department of Mineralogy and Petrology, National Museum, Václavské náměstí 68, CZ–115 79 Praha 1, and Department of Geological Science, Faculty of Sciences, Masaryk University, Kotlářská 2, CZ–611 37 Brno, Czech Republic

PETR ONDRUŠ

Biskupský dvůr 2, CZ–110 00 Praha 1, Czech Republic

FRANTIŠEK VESELOVSKÝ

Czech Geological Survey, Geologická 6, CZ–152 00 Prague 5, Czech Republic

IVANA CÍSAŘOVÁ

Faculty of Science, Charles University, Hlavova 2030, CZ–128 40 Prague 2, Czech Republic

JAN HLOUŠEK

U Roháčových kasáren 24, CZ–100 00 Prague 10, Czech Republic

ABSTRACT

Slavkovite, $Cu_{13}(AsO_4)_6(AsO_3OH)_4 \cdot 23H_2O$, is a newly discovered supergene mineral from the Geschieber vein, Svornost mine at the Jáchymov (St. Joachimsthal) ore district, Czech Republic, commonly associated with lavendulan, geminite, lindackerite and ondrušite. It forms coatings of pale green rosettes up to 1 mm across or individual spherical aggregates up to 5 mm across. Individual acicular to lath-like crystals are up to 1 mm long and 0.05 mm thick, and are colorless with a greenish tint. Slavkovite is pale green, translucent (aggregates) to colorless with a greenish tint, transparent (crystals). It has a white streak and a vitreous luster, and does not fluoresce under both short- and long-wave ultraviolet light. The cleavage on {011} is perfect, and on {010}, it is good. The Mohs hardness is ~3.5–4; slavkovite is very brittle, with an irregular fracture. Its measured density, 3.05(1) g/cm^3, is identical to the calculated one. Slavkovite is biaxial positive; the indices of refraction are α' 1.591(2), β' 1.620(2), γ' 1.701(2), and the $2V$ (calc.) is approximately 64°. It is moderately pleochroic (X light gray to colorless, Y very light greenish gray, Z light green). Slavkovite is triclinic, space group $P\bar{1}$, a 6.408(3), b 14.491(5), c 16.505(8) Å, α 102.87(3), β 101.32(5), γ 97.13(3)°, V 1442(1) Å^3, Z = 1, $a:b:c$ = 0.4422:1:1.1390. The strongest eight lines in the X-ray powder-diffraction pattern [d in Å(I)(hkl)] are as follows: 15.70(3)(001), 11.98(100)($0\bar{1}1$), 6.992(3)($0\bar{2}1$, 020), 5.992(6)($0\bar{2}2$), 3.448(5)(040), 2.967(5)($0\bar{3}5$), 2.4069(4)($1\bar{5}4$), 2.4002(4)(115, $\bar{1}35$, $0\bar{4}6$, $0\bar{6}2$). The chemical analyses made with an electron microprobe yielded FeO 0.12, CuO 39.93, Al_2O_3 0.13, As_2O_5 44.71, H_2O 17.31, total 102.20 wt.%. The resulting empirical formula on the basis of 63(O, OH, H_2O) anions is $(Cu_{12.96}Al_{0.07}Fe_{0.04})_{\Sigma 13.07}(AsO_4)_{6.11}(AsO_3OH)_{3.93} \cdot 22.83H_2O$. The ideal end-member formula, $Cu_{13}(AsO_4)_6(AsO_3OH)_4 \cdot 23\ H_2O$, requires CuO 39.26, As_2O_5 43.36, H_2O 17.10, total 100.00 wt. %. The crystal structure of slavkovite has been solved by direct method and refined to a final R_{obs} of 4.37% on the basis of 6613 observed reflections collected on a single-crystal diffractometer with Mo$K\alpha$ X-radiation. The crystal structure is based upon sheets consisting of copper polyhedra linked by arsenate and hydrogen arsenate tetrahedra. The sheets are linked by bridging Cu6–Φ polyhedra. In

§ *E-mail address*: jiri_sejkora@nm.cz

the asymmetric unit of the slavkovite unit-cell, seven symmetrically independent Cu^{2+} atoms, five As^{5+} atoms and 34 O atoms were found. Two of the oxygen atoms belong to OH^- groups and fourteen to H_2O molecules. Slavkovite possesses a unique crystal structure that has not been found in any mineral or synthetic compound before. It was named after its first occurrence in the Krásno Sn–W ore district, near Horní Slavkov, Czech Republic. Selected data for slavkovite from this locality are also given.

Keywords: slavkovite, new mineral species, arsenate–acid arsenate, crystal structure, Jáchymov ore district, Krásno, Horní Slavkov ore district, Czech Republic.

Sommaire

La slavkovite, de formule idéale $Cu_{13}(AsO_4)_6(AsO_3OH)_4 \bullet 23H_2O$, est une espèce supergène nouvellement découverte dans la veine Geschieber de la mine Svornost du district minéralisé de Jáchymov (St. Joachimsthal), République Tchèque, où elle est associée à lavendulan, géminite, lindackerite et ondrušite. Elle se présente en revêtement de rosettes vert pâle atteignant 1 mm de diamètre ou en agrégats sphériques individuels atteignant un diamètre de 5 mm. Les monocristaux aciculaires ou en plaquettes atteignent une longueur de 1 mm et une épaisseur de 0.05 mm; ils sont incolores avec une teinte verdâtre. La slavkovite est vert pâle, translucide (agrégats) à incolores avec une teinte verdâtre (cristaux). Elle possède une rayure blanche, un éclat vitreux, et ne montre aucune fluorescence en lumière ultraviolette (ondes courtes ou longues). Le clivage {011} est parfait, et {010} est bon. La dureté de Mohs est ~3.5–4; la slavkovite est très cassante, avec une fracture irrégulière. Sa densité mesurée est 3.05(1) g/cm^3, ce qui est identique à sa densité calculée. Elle est biaxe positive, et ses indices de réfraction sont α' 1.591(2), β' 1.620(2), et γ' 1.701(2). L'angle 2*V* (calculé) est environ 64°. Elle est modérément pléochroïque (*X* gris pâle à incolore, *Y* gris verdâtre très pâle, *Z* vert pâle). La slavkovite est triclinique, groupe spatial $P\bar{1}$, *a* 6.408(3), *b* 14.491(5), *c* 16.505(8) Å, α 102.87(3), β 101.32(5), γ 97.13(3)°, *V* 1442(1) Å^3, Z = 1, *a*:*b*:*c* = 0.4422:1:1.1390. Les huit raies les plus intenses du spectre de diffraction X (méthode des poudres) [*d* en Å(I)(*hkl*)] sont: 15.70(3)(001), 11.98(100)(0$\bar{1}$1), 6.992(3)(0$\bar{2}$1, 020), 5.992(6)(0$\bar{2}$2), 3.448(5)(040), 2.967(5)(0$\bar{3}$5), 2.4069(4)(1$\bar{5}$4), 2.4002(4)(115, $\bar{1}$35, 0$\bar{4}$6, 0$\bar{6}$2). Les analyses chimiques, effectuées avec une microsonde électronique, ont donné FeO 0.12, CuO 39.93, Al_2O_3 0.13, As_2O_5 44.71, H_2O 17.31, pour un total de 102.20% (poids). La formule empirique qui en résulte est calculée sur une base de 63(O, OH, H_2O) anions: $(Cu_{12.96}Al_{0.07}Fe_{0.04})_{\Sigma 13.07}(AsO_4)_{6.11}(AsO_3OH)_{3.93} \bullet 22.83H_2O$. La formule idéale du pôle serait $Cu_{13}(AsO_4)_6(AsO_3OH)_4 \bullet 23\ H_2O$, et requiert CuO 39.26, As_2O_5 43.36, H_2O 17.10, pour un total de 100.00%. La structure cristalline a été résolue par méthodes directes et affinée jusqu'à un résidu final R_{obs} de 4.37% en utilisant 6613 réflexions observées, prélevées sur monocristal avec un diffractomètre et un rayonnement Mo*K*α. Cette structure contient des feuillets de polyèdres de coordinence de cuivre liés par des tétraèdres de type arsenate et arsenate acidifié. Les feuillets sont interconnectés grâce à des polyèdres Cu6–Φ. Dans la maille assymétrique, il y a sept atomes de Cu^{2+} symétriquement indépendants, cinq atomes As^{5+} et 34 atomes d'oxygène. Deux des atomes d'oxygène font partie des groupes OH^-, et quatorze font partie de groupes H_2O. La slavkovite semble posséder une structure unique non connue auparavant, soit dans un minéral ou un composé synthétique. Le nom rappelle l'endroit de sa découverte dans le district minéralisé en Sn–W de Krásno, près de Horní Slavkov, République Tchèque. Nous présentons aussi certaines données sur la slavkovite de cette dernière localité.

(Traduit par la Rédaction)

Mots-clés: slavkovite, nouvelle espèce minérale, groupes arsenate et arsenate acidifié, structure cristalline, district minéralisé de Jáchymov, Krásno, district minéralisé de Horní Slavkov, République Tchèque.

Introduction

Slavkovite is a new species of supergene copper arsenate mineral. It was discovered in 1990 at Huber, an abandoned quarry at Krásno near Horní Slavkov, in the Czech Republic, amongst a diverse assemblage of supergene copper minerals and named "UNK2" (Sejkora *et al.* 2006b). However, this occurrence did not provide material suitable for full definition of the new species. Later, well-formed crystals of slavkovite were found in the Jáchymov ore district in the Czech Republic; this occurrence was described as unnamed "Cu–AsO_4–H_2O (3)" by Ondruš *et al.* (1997b).

Slavkovite was named after its first occurrence in the well-known Sn–W ore district at Krásno, near Horní Slavkov, Czech Republic. The mineral data and name have been approved by the IMA Commission on New Minerals and Mineral Names (IMA 2004–38). The holotype specimen of slavkovite from Jáchymov has been deposited in the mineral collection of the National Museum, Prague, Czech Republic (catalogue number P1N 83.038).

Occurrence

Slavkovite was found in material from old workings at the Geschieber vein, Daniel level, at the Svornost mine, Jáchymov ore district (St. Joachimsthal), Krušné hory Mountains, approximately 20 km north of Karlovy Vary, northwestern Bohemia, Czech Republic. The Jáchymov ore district is a classic example of Ag + As + Co + Ni + Bi and of U vein-type hydrothermal mineralization. The ore veins cut a complex of medium-grade metasedimentary rocks of Cambrian to Ordovician age in the envelope of Variscan granite plutons. The majority of the ore minerals were deposited

during Variscan mineralization from mesothermal fluids (Ondruš *et al.* 2003a, 2003b). Primary and supergene mineralization in this district resulted in extraordinarily rich associations; up to now, more than 400 mineral species have been determined and described there (Ondruš *et al.* 1997a, 1997b, 2003c, 2003d). In Jáchymov, slavkovite was found in the association of lavendulan, geminite, lindackerite and ondrušite (IMA 2008–010); it formed by the weathering of primary tennantite and chalcopyrite.

Slavkovite has also been found in the abandoned Huber open pit at Krásno, near Horní Slavkov (Sn–W district; Slavkovský Les Mountains, western Bohemia, Czech Republic). At this open pit, the apical quartz and greisen part of a cupola of autometamorphosed Li-mica – topaz granite was mined for Sn and W ores during the years 1973–1976 and 1984–1987 (Beran & Sejkora 2006, Sejkora *et al.* 2006a). Here, slavkovite was found near a weathered vein carrying tennantite and cuprite in its center. It is associated with clay minerals and amorphous arsenates of Cu and Fe.

Physical Properties

Slavkovite from Jáchymov occurs as coatings formed by pale green rosettes up to 1 mm across (Fig. 1) or individual spherical aggregates up to 5 mm across (Fig. 2). Individual acicular to lath-like crystals (Fig. 3) up to 1 mm long and 0.05 mm thick are colorless with a greenish tint. Slavkovite is translucent (in aggregates) to transparent (in crystals), and has a white streak and a vitreous luster. It does not fluoresce under both short- and long-wave ultraviolet light. There are two cleavages, {011} perfect and {010} good. The Mohs hardness is about 3.5–4; slavkovite is very brittle with an irregular fracture. The density measured by flotation in methylene iodide is 3.05(1) g cm^{-3}; this value is identical with the calculated density, 3.05 g cm^{-3}, obtained from the empirical formula and the unit-cell parameters derived from single-crystal X-ray data.

Slavkovite from Krásno near Horní Slavkov forms light blue to blue-green crystalline coatings up to 2 cm is size, which are composed of imperfect very thin tabular crystals up to 50 μm in size (Fig. 4). It also occurs in a mixture with clay minerals as light blue aggregates cementing weathered gangue, or botryoidal aggregates in a weathered ore vein, material reminiscent of efflorescent chalcanthite.

Optical Properties

Slavkovite from Jáchymov has a moderate pleochroism: *X* grayish (light gray to colorless), *Y* very light greenish gray, and *Z* light green. Slavkovite is biaxial positive. The orientation of basic structural and optical directions and the optic axis plane are shown in Figure 5. The elongation on the (011) plane is negative, with an extinction angle 27°; on the (010) plane, it is positive with an extinction angle 17°. Its indices of refraction were measured in polarized Na light (589 nm) by the Becke line method; the indices of refraction of immersion liquids were measured by the minimum deviation method. The measured indices are: α' 1.591(2), β' 1.620(2), γ' 1.701(2); it was not possible to find the exact position of the individual optical orientations relative to the indices α, β and γ in this triclinic mineral with two cleavage planes. The calculated birefringence is ~0.110, and the 2*V* (calc.) is approximately 64°; owing to the inaccurately measured indices of refraction, both values are only approximate. The Gladstone–Dale index of compatibility could not be calculated owing to incomplete optical data (ideal mean N_{calc} = 1.596).

Chemical Composition

Samples of slavkovite from both occurrences were analyzed with a Cameca SX–100 electron microprobe (Laboratory of electron microscopy and microanalysis of Masaryk University and the Czech Geological Survey, Brno), operating in the wavelength-dispersion mode with an accelerating voltage of 15 kV, a specimen current of 5–10 nA, and a beam diameter of 5–10 μm. The following lines and standards were used: *K*α: andradite (Ca, Fe), sanidine (Al, Si, K), metallic Co (Co), fluorapatite (P), metallic Ni (Ni), ZnO (Zn), olivine (Mg), rhodonite (Mn), vanadinite (Cl, V), topaz (F); *L*α: InAs (As), dioptase (Cu); *L*β: metallic Sb (Sb) and *M*α: Pb (vanadinite). Peak counting times (CT) were 20 s for main elements and 60 s for minor elements; CT for each background was one half of peak time. The raw intensities were converted to concentrations automatically using the *PAP* (Pouchou & Pichoir 1985) matrix-correction software. The elements Na, K, Mg, Pb, Co, Ni, Mn, Sb, Si, V, S, Cl and F were sought but found to be below the detection limit (about 0.01–0.03 wt.%). The presence and quantity of (OH) and (H_2O) groups were established by crystal-structure refinement and confirmed by thermal analyses. Under the electron beam, slavkovite is unstable and partly dehydrates; experimental sums (81.76–88.82 wt.%) are usually higher than the theoretical anhydrous sum (82.90 wt.%) derived from the crystal structure and TG analyses.

Table 1 gives the chemical composition of slavkovite from Jáchymov (mean of six determinations). Results of the chemical analyses correspond very well with the structural formula determined; only minor and variable contents of Fe (up to 0.08 *apfu*) and Al (up to 0.10 *apfu*) were observed. It is possible to express the empirical formula of slavkovite from Jáchymov based on 63 (O, OH, H_2O) anions [including four (OH) groups and 23 (H_2O) groups per formula unit (*pfu*)] as $(Cu_{12.96}Al_{0.07}Fe_{0.04})_{\Sigma 13.07}(AsO_4)_{6.11}(AsO_3OH)_{3.93}$•

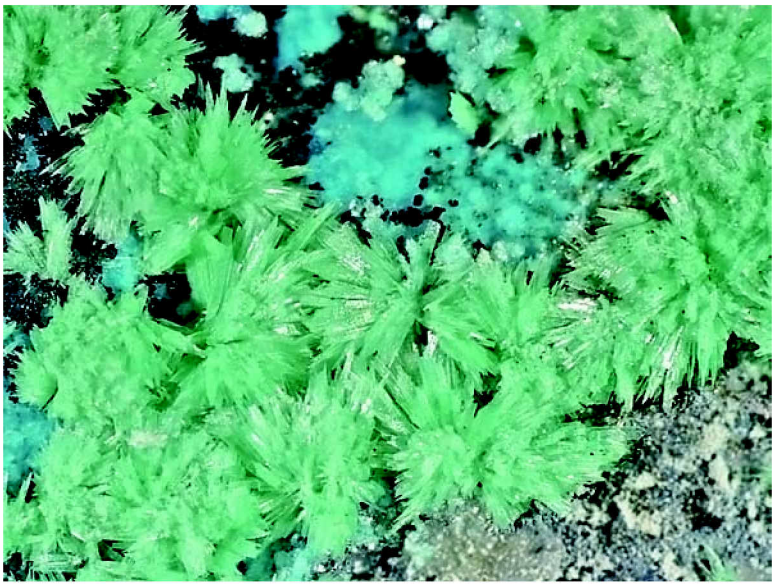

FIG. 1. Rosettes of slavkovite from Jáchymov (holotype sample) showing the individual lath-like crystals and their intensely vitreous luster. The field of view is 3.2 mm. Photo J. and E. Sejkora.

FIG. 2. Spherical group of lath-like crystals of slavkovite from Jáchymov (cotype sample). The field of view is 2.2 mm. Photo J. and E. Sejkora.

FIG. 3. SEM photograph of lath-like crystals of slavkovite, Jáchymov. The field of view is 100 μm.

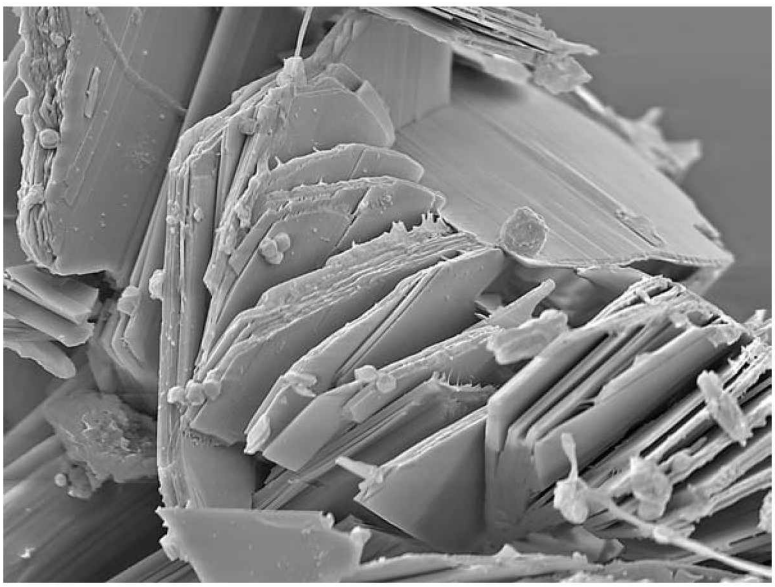

FIG. 4. SEM photograph of irregular tabular crystals of slavkovite from Krásno, near Horní Slavkov. The field of view 70 μm.

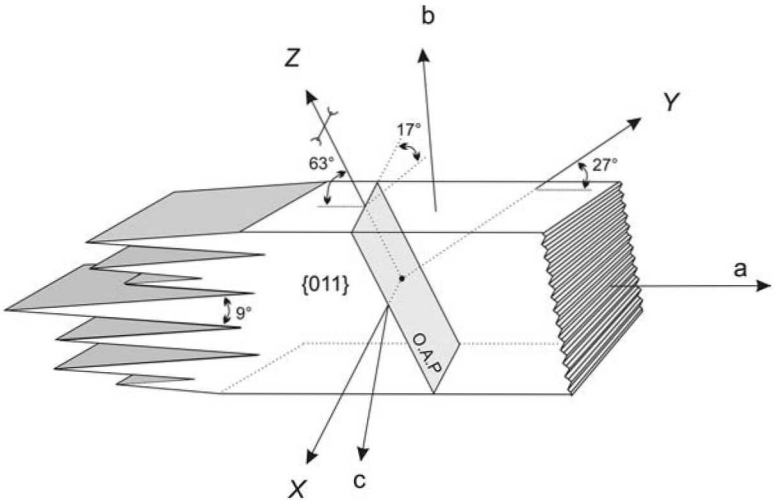

FIG. 5. Orientation of cleavage and basic structural and optical directions of slavkovite from Jáchymov (St. Joachimsthal), Czech Republic.

22.83H_2O. For the end-member formula of slavkovite, $Cu_{13}(AsO_4)_6(AsO_3OH)_4 \bullet 23H_2O$, the oxide contents should be CuO 39.26, As_2O_5 43.36, H_2O 17.10, total 100.00 wt.%.

In comparison with Jáchymov material, slavkovite from Krásno near Horní Slavkov shows a slightly greater variability in its chemical composition (Table 1), with minor and variable contents of Al (up to 0.25), Ca (up to 0.05), Zn (up to 0.04) and Fe (up to 0.04 *apfu*). In the tetrahedral anionic positions, minor amounts of P (0.03–0.05 *apfu*) were observed along with the prevailing As. The empirical formula of slavkovite from Krásno may be expressed (on the same basis) as $(Cu_{12.51}Al_{0.19}Zn_{0.04}Ca_{0.03}Fe_{0.01})_{\Sigma 12.78}(AsO_4)_{5.70}(PO_4)_{0.04}(AsO_3OH)_{4.27} \bullet 23H_2O$.

THERMOGRAVIMETRIC DATA

The thermogravimetric curve of slavkovite from Jáchymov (Fig. 6) was recorded with a TG 750 Stanton Redcroft thermobalance. The operating conditions were: sample weight 4.958 mg, heating rate 10°C/min, dynamic air atmosphere 10 mL/min, and temperature range 20–880°C. Slavkovite dehydrates in seven distinctive steps (Table 2). About eleven H_2O molecules are liberated first at 20–100°C, another twelve are released at five steps in the range 100–310°C, and about two additional ones [partly corresponding to (AsO_3OH) groups] are released in the range 310–530°C. The decrease in mass observed in the range 20–530°C, 17.31 wt.%, is equivalent to about 25 molecules of H_2O. The anhydrous phase formed is stable in the temperature range 530–880°C.

TABLE 1. CHEMICAL COMPOSITION OF SLAVKOVITE

	Jáchymov		Krásno (Horní Slavkov)		Ideal
	mean	range (6 points)	mean	range (3 points)	
CaO wt.%	0.00	0.00 - 0.00	0.07	0.06 - 0.12	
FeO	0.12	0.00 - 0.21	0.04	0.00 - 0.11	
CuO	39.93	37.48 - 43.09	39.99	38.94 - 41.69	39.26
ZnO	0.00	0.00 - 0.00	0.12	0.09 - 0.13	
Al_2O_3	0.13	0.07 - 0.19	0.38	0.30 - 0.51	
As_2O_5	44.71	43.77 - 45.60	46.03	45.52 - 46.53	43.63
P_2O_5	0.00	0.00 - 0.00	0.10	0.08 - 0.13	
subtotal	84.88	81.76 - 88.60	86.74	85.57 - 88.82	82.90
H_2O^*	17.31		18.20		17.10
total	102.20		104.93		100.00
Ca^{2+} *apfu*	0.000		0.031		
Fe^{2+}	0.043		0.014		
Cu^{2+}	12.957		12.508		13.000
Zn^{2+}	0.000		0.037		
Al^{3+}	0.066		0.185		
Σ	13.066		12.775		13.000
As^{5+}	10.042		9.966		10.000
P^{5+}	0.000		0.035		
Σ	10.042		10.001		10.000
OH	3.928		4.265		4.000
H_2O	22.83		23.00		23.00

Atom proportions are calculated on the basis (O,OH,H_2O) = 63 atoms per formula unit (*apfu*); H_2O^*: contents of H_2O were derived from thermal analysis (Jáchymov) or calculated from ideal formula and charge-balance considerations (Krásno, near Horní Slavkov); Ideal: the theoretical chemical composition is calculated from the ideal formula, $Cu_{13}(AsO_4)_6(AsO_3OH)_4 \bullet 23H_2O$.

Infrared Absorption Spectroscopy

The powder infrared absorption spectrum of slavkovite from Jáchymov (dispersed in a KBr disk) was recorded with the Nicolet FTIR 740 spectrophotometer in the range 4000–400 cm^{-1} (Fig. 7). The following tentative assignment is based on the data published by Keller (1971), Vansant *et al.* (1973), Farmer *et al.* (1974), Myneni *et al.* (1998) and Đorđević & Karanović (2008). In the crystal structure of slavkovite, $(AsO_4)^{3-}$, $(AsO_3OH)^{2-}$ groups and H_2O molecules are present.

The intense band at 3434 cm^{-1} with a shoulder at 3265 cm^{-1} was assigned to the ν OH stretching vibrations of hydrogen-bonded H_2O molecules ($R_{O-H...O}$ 2.83 and 2.74 Å, respectively, Libowitzky 1999), and those bands in the range 1550–1750 with a maximum at 1635 cm^{-1}, to the δ H–O–H bending vibrations of H_2O molecules. The presence of shoulders in these regions of the spectrum indicates the existence of more structurally non-equivalent H_2O molecules in slavkovite, which is in agreement with the results of the crystal-structure study. The $(AsO_4)^{3-}$ and $(AsO_3OH)^{2-}$ tetrahedra in the crystal structure of slavkovite are distorted, and their point symmetries are lowered. Therefore, all vibrations may become active in the infrared spectrum, and degenerate vibrations may split. The stretching vibrations ν (O–H) in strongly hydrogen-bonded (AsO_3OH) groups can be related to indistinct shoulders in the range of 3000–2500 cm^{-1}. The δ (As–OH) in-plane bending vibrations were observed in the range of 1550–1000 cm^{-1} with maxima at 1461, 1158, 1113, 1065 and 1020 cm^{-1}. Some coincidences with overtones and combination bands in this region are possible. The shoulders at 896, 863 and the band at 798 cm^{-1} were assigned to the split triply degenerate antisymmetric stretching vibration ν_3 $(AsO_4)^{3-}$, with possible coincidence with the ν_1 $(AsO_4)^{3-}$ symmetric stretching. The shoulder at 832 cm^{-1} is attributed to the ν_3 $(AsO_3OH)^{2-}$ antisymmetric stretching vibration. The shoulders at 745 and 715 cm^{-1}

TABLE 2. THERMAL ANALYSIS OF SLAVKOVITE FROM JÁCHYMOV

Range [°C]	wt.% H_2O	mol.% H_2O	assignment
20 – 100	7.60	11.11	dehydration
100 – 160	1.33	1.94	dehydration
160 – 190	1.44	2.11	dehydration
190 – 210	1.98	2.89	dehydration
210 – 270	2.71	3.96	dehydration
270 – 310	0.71	1.04	dehydration
310 – 530	1.54	2.25	dehydroxylation
530 – 880	0.00		
20 – 880	17.31	25.30	

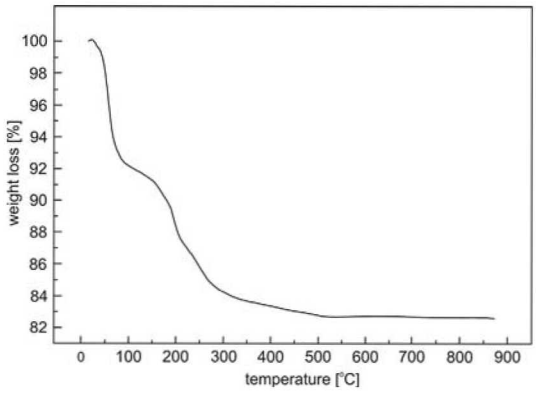

FIG. 6. Thermogravimetric curve of slavkovite from Jáchymov.

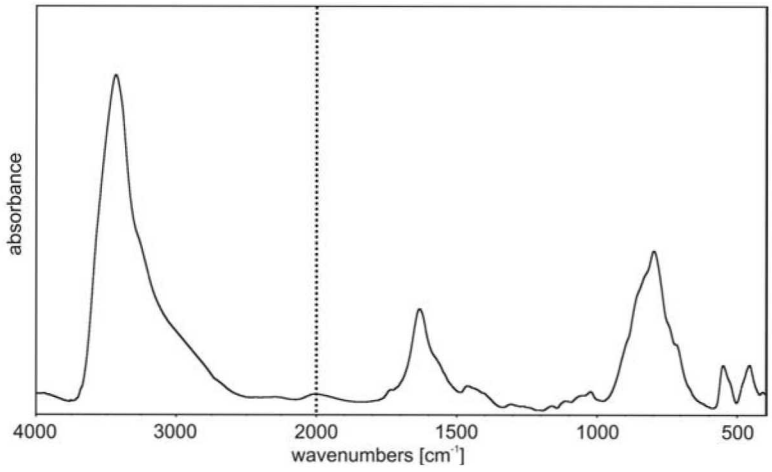

FIG. 7. Infrared absorption spectrum of slavkovite from Jáchymov (split at 2000 cm^{-1}).

TABLE 3. X-RAY POWDER-DIFFRACTION PATTERN OF SLAVKOVITE FROM JÁCHYMOV

I	d_{meas}	d_{calc}	h	k	l	I	d_{meas}	d_{calc}	h	k	l	I	d_{meas}	d_{calc}	h	k	l
3.4	15.70	15.65	0	0	1	2.1	3.322	3.324	1	$\bar{3}$	3	1.2	2.720	2.722	2	$\bar{2}$	2
100.0	11.98	12.02	0	$\bar{1}$	1	2.6	3.291	3.307	0	$\bar{4}$	3			2.716	$\bar{2}$	$\bar{1}$	4
1.4	9.260	9.290	0	1	1			3.287	1	$\bar{4}$	0			2.716	$\bar{2}$	$\bar{2}$	3
3.3	6.992	7.054	0	$\bar{2}$	1			3.271	1	1	3	1.5	2.697	2.694	$\bar{2}$	3	2
		6.953	0	2	0	1.2	3.236	3.235	0	$\bar{1}$	5	1.3	2.691	2.691	0	$\bar{1}$	6
2.7	6.171	6.182	0	1	2	0.9	3.170	3.177	$\bar{2}$	0	1	1.1	2.676	2.676	1	$\bar{4}$	4
6.0	5.992	6.012	0	$\bar{2}$	2	2.0	3.137	3.138	2	$\bar{1}$	0	1.0	2.617	2.617	1	5	1
2.5	5.814	5.829	0	2	1			3.135	$\bar{2}$	0	2	1.5	2.609	2.609	0	0	6
0.8	5.170	5.165	$\bar{1}$	$\bar{1}$	2	1.5	3.081	3.093	2	0	0	1.5	2.599	2.599	2	$\bar{3}$	2
0.6	5.089	5.086	$\bar{1}$	1	2			3.091	0	2	4	0.9	2.583	2.583	$\bar{2}$	$\bar{2}$	4
0.5	4.847	4.844	$\bar{1}$	2	1	1.7	3.005	3.009	$\bar{2}$	$\bar{1}$	2	1.4	2.570	2.570	1	$\bar{3}$	5
2.3	4.624	4.645	0	2	2			3.006	0	$\bar{4}$	4			2.570	0	$\bar{3}$	6
		4.636	0	3	0	2.8	2.976	2.977	2	$\bar{1}$	1	0.5	2.513	2.515	1	2	4
		4.633	1	1	1	4.5	2.967	2.968	0	$\bar{3}$	5			2.510	$\bar{2}$	0	5
1.5	4.530	4.543	1	$\bar{1}$	2	2.2	2.945	2.947	$\bar{1}$	$\bar{4}$	1	0.7	2.504	2.504	$\bar{1}$	1	6
1.5	4.527	4.540	$\bar{1}$	0	3			2.943	$\bar{2}$	2	2	0.5	2.4332	2.4330	0	5	2
		4.524	0	$\bar{3}$	2			2.941	1	$\bar{4}$	3	3.5	2.4069	2.4061	1	$\bar{5}$	4
		4.522	0	1	3	2.8	2.923	2.926	1	$\bar{3}$	4	3.9	2.4002	2.4043	1	1	5
0.3	4.268	4.274	$\bar{1}$	2	2	3.2	2.913	2.913	2	$\bar{2}$	1			2.4004	$\bar{1}$	3	5
1.1	4.013	4.007	1	$\bar{3}$	1			2.911	$\bar{1}$	4	2			2.3998	0	$\bar{4}$	6
0.5	3.878	3.871	$\bar{1}$	3	1	3.0	2.900	2.900	0	1	5			2.3941	0	$\bar{6}$	2
0.9	3.853	3.854	0	$\bar{2}$	4			2.900	$\bar{2}$	$\bar{1}$	3	0.7	2.3216	2.3214	$\bar{1}$	$\bar{1}$	7
1.6	3.723	3.721	$\bar{1}$	$\bar{1}$	4	2.9	2.895	2.892	$\bar{1}$	$\bar{4}$	3	0.8	2.3176	2.3178	0	6	0
		3.719	1	$\bar{3}$	2	1.5	2.869	2.867	0	$\bar{5}$	1	0.9	2.2570	2.2568	1	5	1
1.4	3.631	3.634	1	$\bar{2}$	3	1.4	2.835	2.831	1	3	2	0.9	2.2513	2.2510	1	3	4
2.6	3.560	3.607	0	3	2	1.2	2.827	2.826	1	4	0	0.4	2.1640	2.1641	$\bar{2}$	5	2
		3.593	0	$\bar{4}$	1	1.0	2.781	2.780	$\bar{2}$	$\bar{2}$	2	0.9	2.1435	2.1410	0	$\bar{6}$	5
		3.588	$\bar{1}$	$\bar{3}$	2	1.3	2.763	2.763	0	$\bar{5}$	3	0.4	2.0992	2.0992	$\bar{1}$	$\bar{6}$	4
1.7	3.545	3.540	0	1	4	1.9	2.741	2.759	$\bar{2}$	$\bar{2}$	1	1.4	2.0254	2.0257	1	$\bar{6}$	5
		3.527	0	$\bar{4}$	2			2.733	2	1	1			2.0239	1	$\bar{7}$	2
4.5	3.448	3.477	0	4	0							1.4	2.0091	2.0099	0	$\bar{5}$	7

(I > 0.1%, d_{meas} > 2.000).

TABLE 4. UNIT-CELL PARAMETERS OF SLAVKOVITE FROM JÁCHYMOV AND KRÁSNO NEAR HORNÍ SLAVKOV

	Jáchymov powder data this paper	Jáchymov single-crystal data this paper	Krásno, near Horní Slavkov powder data Sejkora *et al.* (2006b)
a [Å]	6.408(3)	6.4240(1)	6.407(7)
b	14.491(5)	14.3700(3)	14.402(7)
c	16.505(8)	16.5590(3)	16.60(2)
α [°]	102.87(3)	102.882(1)	102.89(6)
β	101.32(5)	101.036(1)	100.5(1)
γ	97.13(3)	98.022(1)	98.23(8)
V [Å^3]	1442.(1)	1435.81(1)	1441

are assigned to the ν As–OH stretching vibrations, and the band at 549 and the shoulder at 523 cm^{-1}, to the δ As–OH bending vibrations. The shoulders at 479 and 470 cm^{-1} and the band at 456 cm^{-1} are connected with the ν_4 $(AsO_4)^{3-}$ and ν_4 $(AsO_3OH)^{2}$ bending vibrations.

A digital copy of the infrared spectrum is available from the Depository of Unpublished Data on the MAC website [document Slavkovite CM48_1157].

X-Ray Powder Diffraction

A hand-picked sample of slavkovite from Jáchymov was used to collect the X-ray powder-diffraction pattern using a Philips X'Pert powder diffractometer at 40 kV, 40 mA, with graphite-monochromated Cu*K*α X-radiation (λ = 1.54178 Å). To minimize the background, the ground sample was placed on a flat low-background silicon wafer. The powder pattern was collected in the range from 3 to 110°2θ with a step size of 0.02°2θ and counting time of 40 s per step. The powder-diffraction pattern obtained (Table 3) is close to data calculated from the crystal-structure information and those of slavkovite from Krásno, near Horní Slavkov (Sejkora *et al.* 2006b). The unit-cell parameters of slavkovite from Jáchymov (triclinic, space group $P\bar{1}$; Table 4) were refined from the powder data with the Rietveld method (FullProf software: Rodriguez-Carvajal 1990).

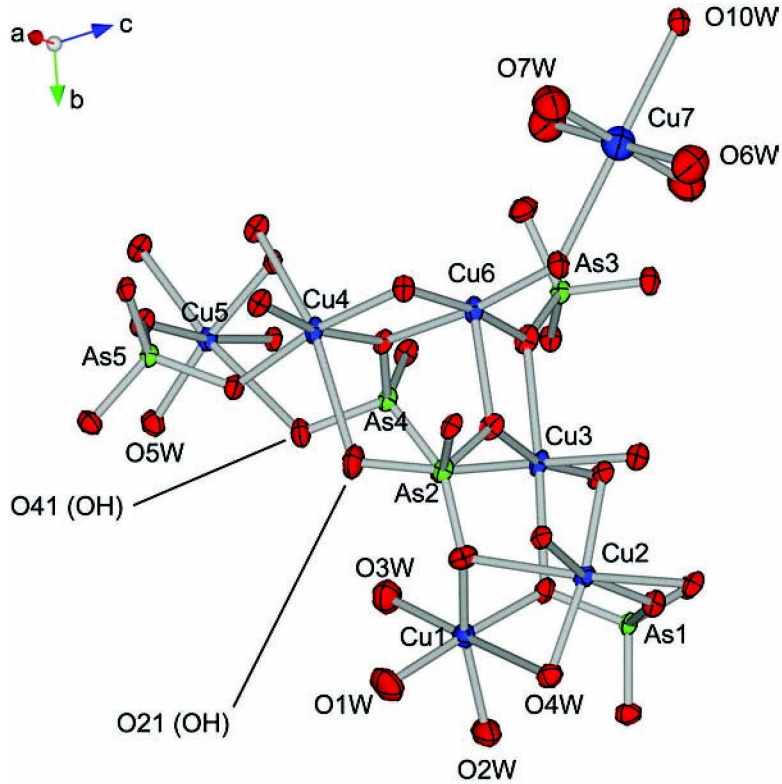

FIG. 8. The content of the asymmetric unit of the slavkovite unit-cell. Atomic types and numbers are labeled. Thermal ellipsoid represents 50% probability of an atom's location. The molecules of H_2O in the interlayer were omitted for clarity.

CRYSTAL-STRUCTURE SOLUTION AND REFINEMENT

A green, bar-shaped single crystal of slavkovite from Jáchymov, with dimensions of 0.25 × 0.23 × 0.027 mm, was selected for the single-crystal X-ray diffraction experiment. The diffraction data for the crystal-structure solution and refinement were collected on an Enraf Nonius Kappa CCD single-crystal diffractometer. The data were collected using monochromatic Mo$K\alpha$ radiation (λ = 0.71073 Å) adopting Ψ and ω scans to fill the Ewald sphere (99.9% completeness). Unit-cell dimensions (Table 4) were refined on the basis of 33,394 diffraction maxima using the least-squares method. The data were corrected for Lorentz and polarization factor and background effects with the software COLLECT and DENZO. A total number of 44,253 diffraction maxima was collected; the merging of equivalent maxima gave 7721 unique and 6613 reflections that were classified as observed [$I > 2\sigma(I)$]. The crystallographic data and data pertinent to the measurement are listed in Table 5. The crystal structure of slavkovite was solved by direct methods with SIR92 software (Altomare *et al.* 1994) and refined by full-matrix least-square algorithm based on F^2 (SHELXL97, Sheldrick 2008). Scattering factors were those employed in the SHELX programs. The crystal structure of slavkovite was solved and refined in the triclinic space-group $P\overline{1}$. Correction for absorption by the PLATON software (Spek 2008) was implemented. All non-hydrogen atoms were found; attempts to locate hydrogen atoms from the final difference-Fourier maps failed. The refinement converged with the final R_{obs} = 4.37%. Crystal-structure visualization and additional calculations were done using the VESTA (Momma & Izumi 2008) and DIAMOND software (Crystal Impact). A list of structure factors (the .hkl file) and the crystallographic information file are available from the Depository of Unpublished Data on the MAC website [document Slavkovite CM48_1157].

Crystal Structure

Cation coordination

There are seven independent Cu^{2+} atoms in the asymmetric unit of the slavkovite unit-cell (Table 6, Fig. 8). The Cu^{2+} cations are octahedrally coordinated by anions O^{2-}, OH^- and H_2O. The Cu^{2+}-based octahedra exhibit strong distortion characteristic of Cu^{2+} compounds owing to the Jahn–Teller effect (Jahn & Teller 1937, Burns & Hawthorne 1995, Hawthorne & Schindler 2000, Krivovichev *et al.* 2006). The extent of the distortions depend on the atomic site. With respect to the crystal-structure study, there are two types of distortions of Cu^{2+} coordination polyhedra, (4 + 1) and (4 + 2). The first mentioned belongs to the Cu6 coordination polyhedron. One Cu6–Φ bond is significantly longer [Cu6–Φ O^{2-} (O24) 2.28 Å] than the others [Cu6–Φ O^{2-}, H_2O (O44, O34, O32, O10W) 1.96 Å] (Table 7), typical of square-pyramidal coordination (Burns & Hawthorne 1995). The coordination of the remaining copper atoms is represented approximately by four shorter (1.93–2.05 Å) and two longer bonds (2.26–2.97 Å; Table 7); this can be described as varying between distorted octahedral and square-pyramidal (Burns & Hawthorne 1995).

Slavkovite contains three symmetrically independent As^{5+} sites (As1, As3, As5), tetrahedrally coordinated by four O atoms, and two As^{5+} sites (As2, As4) coordinated by three O atoms and one OH^- group (O21, O41) (Table 8). The AsO_3OH^- polyhedra exhibit considerable distortion, characterized by a tetrahedral angle variance (after Robinson *et al.* 1971), σ^2 = 10.18 (As2), and σ^2 = 17.10 (As4) in the case of the AsO_3OH^- polyhedra, as opposed to the AsO_4^{3-} polyhedra, σ^2 = 2.61 (As1), σ^2 = 5.21 (As3), and σ^2 = 2.51 (As5). These values represent lowering of tetrahedral (T_d) to trigonal-pyramidal (C_{3v}) symmetry.

TABLE 5. SLAVKOVITE: SELECTED CRYSTALLOGRAPHIC DATA AND CRYSTAL-STRUCTURE REFINEMENT PARAMETERS

Formula		$Cu_{13}(AsO_4)_6(AsO_3OH)_4$•23 H_2O	
Space group	$P\bar{1}$	Unit-cell parameters	
		a [Å]	6.4240(1)
Z	1	*b*	14.3700(3)
D_{calc} [g•cm^{-3}]	3.05	*c*	16.5590(3)
F_{000}	1261	α [°]	102.882(1)
μ [mm^{-1}]	multiscan, 10.56	β	101.036(1)
T_{min}, T_{max}	0.626, 0.908	γ	98.022(1)
Temperature [K]	293(2)	*V* [Å^3]	1435.81(5)
Scan type		φ and ω scans to fill the Ewald sphere	
θ range for data collection [°]		2.59-29.12	
Limiting Miller indices		$-8 < h < 8$, $-19 < k < 19$, $-22 < l < 22$	
Reflections collected		42052	
Unique reflections		7724	
Observed reflections ($I > 2\sigma(I)$)		6613	
Refinement method		full-least square on F^2	
R_{all}		0.0533	
R_{obs}		0.0437	
wR_{obs}		0.1173	
S_{obs}		1.043	
Parameters refined		402	
Weighting scheme		$1 / [\sigma^2(F_o) + (0.03\|F_o\|/2)^2]$	
$(\Delta/\sigma)_{mean}$		0	
Extinction parameter		0.0020(3)	
$\Delta\rho_{max}$ [e•Å^{-3}]		4.249	
$\Delta\rho_{min}$ [e•Å^{-3}]		−3.547	
Extinction correction		0.0020(3)	

Crystal-Structure Description, Bond-Valence Analysis, Hydrogen Bonding and Structural Formula of Slavkovite

The sheets of $Cu^{2+}\Phi_x$ polyhedra linked by AsO_4 and AsO_3OH groups are located approximately along $(0\bar{2}2)$ planes. These sheets are linked by the "bridging" copper atom Cu6, resulting in an interlayer distance of ~ 6 Å. Its doubled value, ~12 Å, is related to the perfect cleavage, causing the preferred orientation effects in the powder pattern (Table 3), corresponding to $d_{0\bar{1}1}$. The sheets embody an unique structural arrangement built up on a particular edge- and corner-sharing of the Cu^{2+}–Φ distorted octahedra and their linkage through As^{5+} polyhedra (Fig. 9). The other six non-bonding O atoms were found in the interlayer of slavkovite. Slavkovite possesses a unique structure, without relationship to that of any known mineral or inorganic compound.

Bond-valence analysis (Table 8) of the slavkovite crystal structure was performed using bond-valence parameters of Brown & Altermatt (1985). The oxygen atoms found by difference-Fourier maps in the interlayer space belong to hydrogen-bonded H_2O molecules.

An extensive network of hydrogen bonds is developed in the structure. Molecules of H_2O coordinate copper atoms to form $Cu^{2+}\Phi_x$ polyhedra, and molecular H_2O non-bonded to any cation is located in the interlayer. The O···O distances obtained from the crystal-structure refinement match those of regular range for hydrogen bonds in solids (Libowitzky 1999, Lutz 2003), even if a few distances reveal a very short O···O lengths, as for example in case of O13 and O14 (split site, 0.67 Å).

On the basis of results of the structure and bond-valence analysis, the idealized structural formula of slavkovite is $Cu_{13}(AsO_4)_6(AsO_3OH)_4$•23 H_2O, Z = 1.

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TABLE 6. COORDINATES AND DISPLACEMENT PARAMETERS OF ATOMS IN SLAVKOVITE

Atom	x/a	y/b	z/c	U_{iso}	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cu1	0.41461(12)	0.42842(6)	0.20614(5)	0.0228	0.0253(4)	0.0253(4)	0.0230(4)	0.0094(3)	0.0106(3)	0.0097(3)
Cu2	0.12578(10)	0.42043(5)	0.01258(4)	0.0158	0.0111(3)	0.0171(3)	0.0201(3)	0.0042(2)	0.0056(2)	0.0039(2)
Cu3	0.69605(10)	0.65150(5)	0.15208(4)	0.0161	0.0100(3)	0.0211(3)	0.0154(3)	0.0044(2)	0.0030(2)	0.0001(2)
Cu4	0.29739(10)	0.86071(5)	0.33729(4)	0.0160	0.0104(3)	0.0240(3)	0.0135(3)	0.0056(2)	0.0032(2)	0.0030(2)
Cu5	1.11363(10)	1.03619(5)	0.43914(4)	0.0153	0.0103(3)	0.0209(3)	0.0162(3)	0.0054(2)	0.0041(2)	0.0052(3)
Cu6	0.49273(10)	0.84667(5)	0.18181(4)	0.0164	0.0106(3)	0.0248(3)	0.0144(3)	0.0055(2)	0.0035(2)	0.0047(3)
Cu7	0.5	1	0	0.0408	0.0373(7)	0.0468(8)	0.0385(7)	0.0128(6)	0.0054(6)	0.0113(6)
As1	0.62686(8)	0.40379(4)	0.04914(3)	0.0137	0.0101(2)	0.0164(3)	0.0147(2)	0.00329(19)	0.00408(18)	0.00283(19)
As2	0.20616(8)	0.62084(4)	0.18253(3)	0.0150	0.0099(2)	0.0187(3)	0.0155(3)	0.00386(19)	0.00270(19)	0.0019(2)
As3	0.99458(8)	0.89560(4)	0.16282(3)	0.0150	0.0109(2)	0.0204(3)	0.0145(3)	0.0060(2)	0.00289(19)	0.0042(2)
As4	0.78782(8)	0.80345(4)	0.33903(3)	0.0142	0.0094(2)	0.0180(3)	0.0141(2)	0.00388(19)	0.00243(18)	0.00158(19)
As5	0.63285(8)	1.09735(4)	0.45695(3)	0.0133	0.0093(2)	0.0176(3)	0.0131(2)	0.00416(19)	0.00277(18)	0.00289(19)
O11	0.8317(6)	0.4510(3)	0.0106(2)	0.0152	0.0099(16)	0.0174(18)	0.0196(18)	0.0038(14)	0.0062(14)	0.0044(14)
O12	0.6708(7)	0.2956(3)	0.0638(3)	0.0215	0.020(2)	0.020(2)	0.027(2)	0.0068(16)	0.0076(16)	0.0076(16)
O13	0.6115(6)	0.4773(3)	0.1413(3)	0.0194	0.0180(19)	0.021(2)	0.0184(19)	0.0028(15)	0.0078(15)	0.0009(15)
O14	0.3898(6)	0.3904(3)	-0.0220(2)	0.0180	0.0123(17)	0.023(2)	0.0165(18)	0.0037(15)	0.0019(14)	0.0017(15)
O21	0.2302(8)	0.6700(4)	0.2904(3)	0.0306	0.035(3)	0.039(3)	0.015(2)	0.009(2)	0.0051(18)	0.0007(18)
O22	-0.0202(6)	0.6456(3)	0.1312(2)	0.0168	0.0107(17)	0.0210(19)	0.0173(18)	0.0068(14)	0.0023(14)	0.0005(15)
O23	0.2011(7)	0.5019(3)	0.1653(3)	0.0225	0.021(2)	0.0176(19)	0.027(2)	0.0047(16)	0.0030(17)	0.0035(16)
O24	0.4155(6)	0.6821(3)	0.1577(3)	0.0183	0.0086(16)	0.0182(19)	0.025(2)	0.0002(14)	0.0046(14)	0.0001(15)
O31	1.0095(7)	0.8755(3)	0.0602(2)	0.0208	0.0190(19)	0.031(2)	0.0143(18)	0.0115(17)	0.0037(15)	0.0056(16)
O32	1.2245(6)	0.8691(3)	0.2166(2)	0.0168	0.0098(16)	0.026(2)	0.0140(17)	0.0053(15)	0.0009(13)	0.0041(15)
O33	0.9920(8)	1.0142(3)	0.1991(3)	0.0272	0.031(2)	0.023(2)	0.027(2)	0.0123(18)	0.0031(18)	0.0038(17)
O34	0.7750(6)	0.8225(3)	0.1697(3)	0.0204	0.0095(17)	0.026(2)	0.024(2)	0.0035(15)	0.0047(15)	0.0024(16)
O41	0.7596(7)	0.7923(3)	0.4382(3)	0.0229	0.023(2)	0.036(2)	0.0143(18)	0.0125(18)	0.0071(16)	0.0090(17)
O42	0.7921(7)	0.6917(3)	0.2817(3)	0.0203	0.021(2)	0.0199(19)	0.0193(19)	0.0051(16)	0.0067(16)	0.0013(15)
O43	1.0141(6)	0.8822(3)	0.3510(2)	0.0180	0.0103(17)	0.0206(19)	0.0186(18)	0.0016(14)	0.0017(14)	-0.0016(15)
O44	0.5744(6)	0.8523(3)	0.3037(2)	0.0153	0.0102(16)	0.0209(19)	0.0146(17)	0.0061(14)	0.0026(13)	0.0026(14)
O51	0.6942(7)	1.1659(3)	0.3924(3)	0.0217	0.021(2)	0.026(2)	0.023(2)	0.0065(16)	0.0090(16)	0.0118(17)
O52	0.6227(6)	1.1698(3)	0.5516(2)	0.0184	0.0184(19)	0.023(2)	0.0143(18)	0.0082(16)	0.0044(15)	0.0028(15)
O53	0.8264(6)	1.0278(3)	0.4680(2)	0.0151	0.0114(16)	0.0215(19)	0.0149(17)	0.0071(14)	0.0054(13)	0.0053(14)
O54	0.3919(6)	1.0236(3)	0.4115(2)	0.0178	0.0075(16)	0.0210(19)	0.0199(19)	0.0006(14)	0.0011(14)	-0.0018(15)
O1W	0.2142(9)	0.3729(4)	0.2666(4)	0.0436	0.043(3)	0.051(3)	0.054(3)	0.014(3)	0.029(3)	0.030(3)
O2W	0.5648(9)	0.3157(4)	0.2133(3)	0.0381	0.048(3)	0.041(3)	0.041(3)	0.024(2)	0.023(2)	0.022(2)
O3W	0.6186(9)	0.5332(4)	0.3272(3)	0.0384	0.045(3)	0.038(3)	0.029(3)	0.003(2)	0.009(2)	0.005(2)
O4W	0.0873(7)	0.3037(3)	0.0547(3)	0.0219	0.020(2)	0.021(2)	0.025(2)	0.0047(16)	0.0064(16)	0.0053(17)
O5W	1.0471(7)	1.1133(3)	0.3579(3)	0.0230	0.023(2)	0.029(2)	0.023(2)	0.0104(17)	0.0096(17)	0.0116(17)
O6W	0.6738(10)	1.0762(5)	0.1108(4)	0.0505	0.051(4)	0.053(4)	0.041(3)	0.017(3)	-0.003(3)	0.006(3)
O7W	0.2486(10)	1.0460(5)	0.0336(4)	0.0511	0.051(4)	0.063(4)	0.051(4)	0.027(3)	0.016(3)	0.025(3)
O8W	0.3739(12)	0.2818(6)	0.3877(5)	0.0635	0.061(4)	0.071(5)	0.071(5)	0.019(4)	0.016(4)	0.039(4)
O9W	0.4334(12)	0.1265(6)	0.2293(4)	0.0616	0.066(4)	0.073(5)	0.048(4)	0.007(4)	0.018(3)	0.020(3)
O10W	0.4077(7)	0.8592(3)	0.0649(3)	0.0209	0.0192(19)	0.027(2)	0.0179(19)	0.0057(16)	0.0063(15)	0.0059(16)
O11W*	0.999(2)	0.4655(11)	0.3746(9)	0.0541	0.041(6)	0.078(9)	0.055(7)	0.034(6)	0.019(6)	0.020(7)
O12W*	0.977(2)	0.3433(9)	0.4825(9)	0.0543	0.055(8)	0.033(6)	0.062(8)	-0.011(5)	-0.002(6)	0.011(6)
O13W*	0.408(3)	0.5941(16)	0.4533(14)	0.034(3)						
O14W*	0.459(3)	0.5629(16)	0.4698(14)	0.034(3)						

* The site occupancies for O11W and O12W are 0.5, for O13W and O14W are 0.25, respectively.

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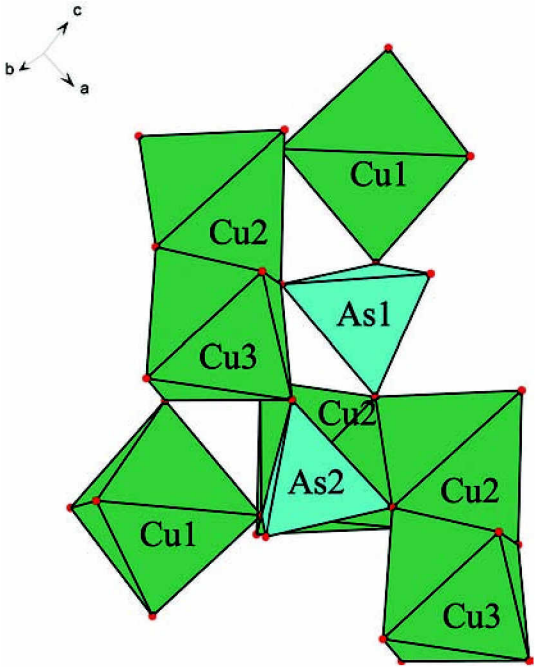

FIG. 9. Detail on the bonding of the Cu^{2+} octahedra and As^{5+} tetrahedra.

TABLE 7. SELECTED INTERATOMIC DISTANCES IN THE STRUCTURE OF SLAVKOVITE

As1 – O11	1.692(3)	Cu3 – O14	2.045(4)
As1 – O12	1.679(4)	Cu3 – O13	2.445(4)
As1 – O13	1.680(4)	Cu3 – O22	1.929(4)
As1 – O14	1.695(3)	Cu3 – O24	1.928(4)
<As1 – O>	1.69	Cu3 – O34	2.378(4)
		Cu3 – O42	2.040(5)
As2 – O21	1.736(5)	<Cu3 – Φ>	2.13
As2 – O22	1.664(3)		
As2 – O23	1.663(4)	Cu4 – O21	2.625(5)
As2 – O24	1.672(3)	Cu4 – O32	1.998(3)
<As2 – O>	1.68	Cu4 – O43	1.935(4)
		Cu4 – O44	1.975(4)
As3 – O31	1.683(3)	Cu4 – O52	1.975(3)
As3 – O32	1.710(3)	Cu4 – O54	2.322(4)
As3 – O33	1.680(4)	<Cu4 – Φ>	2.14
As3 – O34	1.676(4)		
<As3 – O>	1.69	Cu5 – O41	2.727(4)
		Cu5 – O43	2.290(3)
As4 – O41	1.726(4)	Cu5 – O53	1.965(3)
As4 – O42	1.680(3)	Cu5 – O53	1.987(4)
As4 – O43	1.662(3)	Cu5 – O54	1.950(4)
As4 – O44	1.691(3)	Cu5 – O5W	1.949(3)
<As4 – O>	1.69	<Cu5 – Φ>	2.15
As5 – O51	1.671(3)	Cu6 – O24	2.275(4)
As5 – O52	1.696(3)	Cu6 – O32	1.964(4)
As5 – O53	1.709(3)	Cu6 – O34	1.932(4)
As5 – O54	1.681(3)	Cu6 – O44	1.966(3)
<As5 – O>	1.69	Cu6 – O10W	1.964(4)
		<Cu6 – Φ>	2.02
Cu1 – O13	1.963(3)		
Cu1 – O23	1.955(3)	Cu7 – O6W	1.947(5)
Cu1 – O1W	1.964(4)	Cu7 – O6W	1.947(5)
Cu1 – O2W	2.012(5)	Cu7 – O7W	1.958(5)
Cu1 – O3W	2.258(4)	Cu7 – O7W	1.958(5)
Cu1 – O4W	2.974(3)	Cu7 – O10W	2.545(3)
<Cu1 – Φ>	2.19	Cu7 – O10W	2.545(3)
		<Cu7 – Φ>	2.15
Cu2 – O11	1.994(4)		
Cu2 – O11	1.962(4)		
Cu2 – O14	1.964(3)		
Cu2 – O22	2.286(3)		
Cu2 – O23	2.460(5)		
Cu2 – O4W	1.958(4)		
<Cu2 – Φ>	2.10		

Note: Φ = O, OH, H_2O. Interatomic distances are expressed in Å.

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TABLE 8. BOND-VALENCE ANALYSIS OF THE STRUCTURE OF SLAVKOVITE

	As1	As2	As3	As4	As5	Cu1	Cu2	Cu3	Cu4	Cu5	Cu6	Cu7	ΣBV
O11	1.225						0.892						2.12
O12	1.269												1.27
O13	1.265					0.464		0.126					1.86
O14	1.215						0.463	0.372					2.05
OH21		1.087							0.078				1.17
O22		1.321					0.194	0.509					2.02
O23		1.325				0.474	0.121						1.92
O24		1.293						0.510			0.200		2.00
O31			1.255										1.26
O32			1.167						0.422		0.463		2.05
O33			1.265										1.27
O34			1.279	0.052				0.151			0.505		1.99
OH41				1.117						0.059			1.18
O42				1.265				0.377					1.64
O43				1.328					0.501	0.192			2.02
O44				1.228					0.449		0.460		2.14
O51					1.296								1.30
O52					1.212				0.449				1.66
O53					1.170					0.897			2.07
O54					1.262				0.176	0.481			1.92
O1W						0.463							0.46
O2W						0.407							0.41
O3W						0.209							0.21
O4W							0.470						0.47
O5W										0.482			0.48
O6W												0.485(×2)	0.49
O7W												0.470(×2)	0.47
O8W											0.463	0.096(×2)	0.56
O9W													0.00
O10W													0.00
O11W													0.00
O12W													0.00
O13W													0.00
O14W													0.00
ΣBV	4.97	5.03	4.97	4.99	4.94	2.02	2.14	2.05	2.08	2.11	2.09	2.10	

Bond valences are expressed in valence units (*vu*).

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