Adolfpateraite, K(UO₂)(SO₄)(OH)(H₂O), a new uranyl sulphate mineral from Jáchymov, Czech Republic

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ABSTRACT

Adolfpateraite, monoclinic K(UO₂)(SO₄)(OH)(H₂O), is a new supergene mineral from the Svornost mine, Jáchymov ore district, Czech Republic. It forms sulfur yellow to greenish yellow crystalline aggregates, up to 2 mm in diameter. Crystals are transparent to translucent with a vitreous luster, without observable cleavage. The streak is pale yellow. The Mohs hardness is ~2. The mineral shows a green fluorescence in long-wave ultraviolet radiation. Adolf pateraite is pleochroic, with $\alpha =$ colorless and $\gamma =$ yellow (β could not been examined). It is biaxial, with $\alpha = 1.597(2)$, $\gamma = 1.659(2)$ (β could not been measured), birefringence 0.062. The empirical chemical formula (mean of 4 electron microprobe point analyses) was calculated based on 8 O apfu and is $K_{0.94}(UO_2)_{1.00}(SO_4)_{1.02}(OH)_{0.90}(H_2O)_{1.00}$ (water content calculated). The simplified formula is K(UO₂)(SO₄)(OH)(H₂O), requiring K₂O 10.70, UO₃ 64.97, SO₃ 18.19, H₂O 6.14, total 100.00 wt%. Adolfpateraite is monoclinic, space group $P2_1/c$, a = 8.0462(1), b = 7.9256(1), c = 11.3206(2) Å, β = 107.726(2)°, V = 687.65(2) Å³, Z = 4, and $D_{calc} = 4.24$ g/cm³. The five strongest reflections in the X-ray powder diffraction pattern are [d_{obs} in Å (I) (hkl)]: 7.658 (76) (100), 5.386 (100) (002), 5.218 (85) (102), 3.718 (46) (021), 3.700 (37) (202). The crystal structure has been refined from single-crystal X-ray diffraction data to $R_1 = 0.0166$ with GOF = 1.30, based on 1915 observed reflections $[I_{obs} > 3\sigma(I)]$. The crystal structure consists of chains of uranyl polyhedra extended along [010], with OH- located on the shared vertex between the bipyramids. The sulfate tetrahedra decorate the outer side of the chain with bridging bidentate linkages between the uranyl pentagonal bipyramids. H₂O groups are located on the edges of the chains on the non-linking vertex of each uranyl pentagonal bipyramid. K⁺ atoms are located between the chains providing additional linkage of these together with H-bonds. The fundamental vibrational modes of uranyl ion, sulfate tetrahedra, and H₂O groups were tentatively assigned in the infrared and Raman spectra. The new mineral is named to honor Adolf Patera (1819–1894), Czech chemist, mineralogist, and metallurgist.

Keywords: Adolfpateraite, uranyl sulfate, crystal structure, chemical composition, Jáchymov

INTRODUCTION

Adolfpateraite is a new mineral found in Jáchymov, Czech Republic, belonging to the group of uranyl sulfate minerals containing medium-sized and large cations. It is the second uranyl sulfate with potassium, but it is not member of the zippeite group of minerals (Plášil et al. 2011a). Adolfpateraite has been approved by the Commission of New Minerals, Nomenclature and Classification of the IMA (2011-042). The mineral is named in honor of Adolf Patera (born July 11, 1819, in Vienna; died June 26, 1894, in Teschen/Český Těšín), Czech chemist, mineralogist, and metallurgist, who invented the technology for processing uranium ores from Jáchymov for production of uranium colors (Vysoký 1866). These colors were and still are widely used for staining glass products. To honor Adolf Patera, the mineral pateraite was previously described and named by Haidinger (1856), and later re-examined by Laube (1864). Pateraite was considered to be a cobalt molybdate, CoMoO₄, however, reinvestigation of the cotype material, deposited in the collections of the National Museum in Prague, found pateraite to be a mixture of arsenolite, skutterudite, chalcopyrite, and tennantite (Veselovský et al. 1997). Therefore, pateraite was discredited as a mineral species, and according to the IMA rules, this name should not be used for the following 50 yr. However, we are convinced that there should be a mineral named after Adolf Patera and hence we proposed the name adolfpateraite. The type specimen is deposited in the collections of the Department of Mineralogy and Petrology of the National Museum in Prague, Václavské námestí 68, Praha 1 (Czech Republic), catalog number: P1P 3/2011.

MINERAL AND ITS PROPERTIES

Occurrence

Adolfpateraite was found in an old gallery on the Geschieber vein, at the fifth level of the Svornost (Einigkeit) shaft, Jáchy-

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mov (Sankt Joachimsthal) ore district, western Bohemia, Czech Republic (50°22'21.136"N, 12°54'46.150"E). The Jáchymov ore district is a classic representant of Ag-As-Bi-Co-Ni-U hydrothermal vein type deposit (Ondruš et al. 2003). More than 420 minerals have been described there, including an extremely rich association of supergene minerals. A brief overview of the history of mining, geology, and mineralogy of the locality was most recently published by Tvrdý and Plášil (2010). Gypsum, schoepite, čejkaite, and another new, not yet approved mineral—a hydrated potassium uranyl sulfate hydroxy-vanadate—have been observed in close association. Neither primary uranium minerals nor any sulfides have been observed in the samples. The mineral has formed from the dissolution of primary uraninite though is of recent supergene origin, forming in the environment of the old mining works.

Physical and optical properties

Adolfpateraite is rare and forms hemispherical crystalline aggregates, up to 3 mm in size, mostly on quartz gangue and surrounding rocks with gypsum (Fig. 1). Sulfur yellow to greenish yellow crystals are transparent to translucent with a vitreous luster. The streak is pale yellow. Crystals are brittle, without obvious cleavage and have uneven fracture. Morphological observations are difficult due to the nature of adolfpateraite aggregates (Fig. 2). The Mohs hardness is ca. 2. The direct determination of density of adolfpateraite could not been done because of the small size of aggregates. A density of 4.24 g/cm3 was calculated based on the unit-cell dimensions from single-crystal X-ray data and electron microprobe results. Adolfpateraite exhibits green fluorescence in long-wave ultraviolet radiation. The mineral is pleochroic, with α = colorless and γ = yellow. It is biaxial, with α = 1.597(2), $\gamma = 1.659(2)$, birefringence 0.062. Optical orientation remains unknown since the mineral has no visible cleavage and no distinctive morphology. Hence, examination, and measurement of β was impossible as well as distinct assignment of the optical sign. Due to an incomplete optical data, a Gladstone-Dale compatibility index could not be calculated.

Chemical composition

The chemical composition of adolfpateraite was determined by a Cameca SX100 electron microprobe operating in the wavelength-dispersive mode with an acceleration voltage of 15 kV, specimen current of 4 nA, and 15 µm beam diameter. The following X-ray lines and standards were selected to minimize line overlaps: $K\alpha$ lines: S (SrSO₄), K (sanidine), $M\beta$ lines: U (rutherfordine). Other elements, as Na, Ca, or Mg were also sought, but they were found in concentrations below the detection limits of the analysis for these elements (~0.1 wt% with analytical conditions used). Peak counting times (CT) were 10–20 s and the counting time for background was 50% of the peak CT. The measured intensities were converted to element concentrations using the PAP program (Pouchou and Pichoir 1985).

Adolfpateraite is an uranyl sulfate mineral characterized by an U:S ratio of 1:1. The chemical composition of most crystals of adolfpateraite is quite homogeneous (Table 1). Its empirical formula (based on 8 O apfu) is $K_{0.94}(UO_2)_{1.00}(SO_4)_{1.02}(OH)_{0.90}$ (H₂O)_{1.00} (H₂O content calculated on the base of crystal structure results). The simplified formula is $K(UO_2)(SO_4)(OH)(H_2O)$



FIGURE 1. Crystal aggregates of adolfpateraite (greenish prismatic) associated with more yellow, hedgehog-like crystals aggregates composed of the needle crystals of the new unapproved phase (hydrated uranyl sulfate hydroxy-vanadate of potassium) and gypsum (colorless) on gangue. FOV is 2.5 mm (photo by P. Škácha). (Color online.)



FIGURE 2. Prismatic crystals of adolfpateraite. SE image.

TABLE 1. Results of electron microprobe analyses (in wt%) of adolfpateraite

tere	inte		
	Mean (n = 4)	Range	Std
K ₂ O	9.86	9.44-10.32	0.37
SO₃	18.17	17.73-18.43	0.32
UO₃	63.66	62.54-65.19	1.13
H ₂ O	5.80	5.65-5.96	0.14
Total	97.49		
	Calculated	on an 8 O basis	
К	0.940		
S ⁶⁺	1.020		
U ⁶⁺	1.000		
OH	0.900		
H-O	1 000		

and requires K_2O 10.70, UO_3 64.97, SO_3 18.19, H_2O 6.14, total 100.00 wt%.

An additional set of analyses has been collected on a sample different to the holotype specimen. It showed a slight zoning in BSE images (Fig. 3a) and the presence of an additional phase. Microprobe analyses did not reveal any trend in the differences of main constituents (for K, U, S) within the limits of the method.



FIGURE 3. (a) Internal zoning of adolfpateraite crystal aggregate in backscattered electrons (BSE image). (b) Additional phase, very light in BSE, most probably schoepite, overgrown by the crystal aggregate of adolfpateraite (BSE image).

However, BSE images suggest that zoning is due to crystal growth. Interesting is the presence of an additional phase locally distributed in the analyzed polished sample. It forms aggregates consisting of prismatic like crystals (Fig. 3b). However, precise WDS analysis of these aggregates was not possible, since they are inhomogeneous and intimately intergrown with adolfpateraite (omnipresent K and S content). However, the EDS analysis suggests that this phase is characterized by higher contents of U and possibly it could be an uranyl-oxide hydroxy-hydrate (e.g., schoepite).

Infrared and Raman spectroscopy

The infrared spectrum of adolfpateraite was recorded by the micro-diffuse-reflectance method (DRIFTS) on a Nicolet Magna 760 FTIR spectrometer (range 4000–600 cm⁻¹, resolution 4 cm⁻¹, 128 scans, Happ-Genzel apodization) equipped with a Spectra Tech InspectIR micro-FTIR accessory. A few crystals were mixed with KBr without using pressure, to avoid dehydration or solid-state reactions, and immediately measured. The same KBr was taken as a reference. The Raman spectrum of adolfpateraite was recorded on a Thermo Scientific DXR Raman Microscope interfaced to an Olympus microscope (objective 50×) in the 50-3150 cm⁻¹ spectral region with approximately 5 cm⁻¹ spectral resolution. The power of frequency-stabilized single mode diode laser (780 nm) impinging on the sample was ranging from 4 to 8 mW. The spectrometer was calibrated by software-controlled calibration procedure (within Omnic 8 software) using multiple neon emission lines (wavelength calibration), multiple polystyrene Raman bands (laser frequency calibration) and standardized white light sources (intensity calibration). Spectral manipulation such as background correction and band-component analysis was done with Omnic 8 software.

The infrared spectrum of the phase KUS1 (synthetic analog of adolfpateraite) has been published by Forbes et al. (2007). There are no Raman spectroscopic data available for the synthetic material.

The infrared and Raman spectra of adolfpateraite are displayed on Figures 4 and 5. In the following text only vibration modes of OH, H_2O , and UO_2^{2+} will be described more in detail. Wavenumbers of all vibrations observed are listed in Table 2 with tentative assignments.

Vibrations of OH and molecular H₂O

Infrared bands of weak and medium intensity at 3302 and 3187 cm⁻¹ with a shoulder at 3381 cm⁻¹ are assigned to the v O–H stretching vibrations of hydrogen-bonded water molecules. According to Libowitzky's correlation (Libowitzky 1999), H···O bond lengths vary around ~1.9 Å. A sharp band at 3546 cm⁻¹ (weak to medium) may be attributed to the v O–H stretching vibrations of hydrogen-bonded (OH) groups, with H···O bond lengths ranging from 2.0 to 2.2 Å. A weak infrared band at 1627 cm⁻¹ is assigned to the v₂ (δ) H₂O bending mode of H-O-H. A weak infrared band at 787 cm⁻¹ may be related to libration modes of an H₂O molecule. Similar features are obvious in the infrared spectrum of the synthetic analog of adolfpateraite (Forbes et al. 2007).



FIGURE 4. Infrared (DRIFTS) spectrum of adolfpateraite.



FIGURE 5. Raman spectrum of adolfpateraite.

 TABLE 2.
 Observed bands in infrared and Raman spectra of adolfpateraite

Infrared	Raman	Assignment
3546 (m-s)		O–H stretching of OH⁻
3381 (sh)		O–H stretching of H₂O
3302 (w)		O–H stretching of H₂O
3187 (m)		O–H stretching of H ₂ O
1627 (w-s)		H–O–H bending
1221 (sh)		δ U–OH bending
1179 (s)	1169 (w)	V ₃ (SO ₄) ²⁻
	1149 (w)	V ₃ (SO ₄) ²⁻
1119 (vs)	1116 (w)	V ₃ (SO ₄) ²⁻
	1063 (w)	V ₃ (SO ₄) ²⁻
1032 (s)	1029 (w)	v ₃ (SO ₄) ^{2–}
985 (m)	993 (s)	v ₁ (SO ₄) ²⁻
	935 (w)	δ U–OH bending
890 (m)	900 (w)	v ₃ (UO ₂) ²⁺
840 (w-m)	843 (vs)	v ₁ (UO ₂) ²⁺
787 (w)		H ₂ O libration
	638 (w)	V4 (SO4) ²⁻
	597 (w)	V ₄ (SO ₄) ^{2–}
	456 (m)	v ₂ (SO ₄) ²⁻
	442 (m)	v ₂ (SO ₄) ²⁻
	399 (w)	v U–O _{eq}
	350 (w)	v U–O _{eq} or K–O stretch
	320 (m)	v U–O _{eq}
	270 (m)	ν ₂ (δ) (UO ₂) ²⁺
	264 (m)	ν ₂ (δ) (UO ₂) ²⁺
	219 (m)	-
	198 (m)	-
	169 (w)	-
	130 (w)	-
	109 (w)	_

UO₂²⁺ vibrations

The infrared and Raman bands connected with U-O stretching vibrations are listed in Table 2. From observed wavenumbers of uranyl stretching modes, the U-O bond lengths were calculated based on empirical relation of Bartlett and Cooney (1989). The bond-lengths of ~1.79(1) Å were obtained. The value of ~1.8 Å is characteristic for compounds containing uranyl pentagonal bipyramidal coordination polyhedra (Burns et al. 1997; Burns 1999, 2005).

Raman bands of weak and medium intensity at 399, 350, and 320 cm^{-1} are connected with v U-O_{eq} stretching vibrations.

Vibration bands around 350 cm⁻¹ may be attributed also to K-O stretching modes (e.g., Volkovich et al. 1998; Plášil et al. 2010). The Raman bands at 270 and 264 cm⁻¹ may be assigned to the split doubly degenerate v_2 (δ) (UO₂)²⁺ bending vibrations.

CRYSTAL STRUCTURE OF ADOLFPATERAITE

Experimental methods

A $0.24 \times 0.23 \times 0.07$ mm short-prismatic crystal of adolfpateraite was selected for the single-crystal X-ray diffraction experiment using an Oxford diffraction Gemini single-crystal diffractometer with Atlas CCD detector, using monochromatized MoKa radiation, $\lambda = 0.71073$ Å, with a fiber-optics Mo-Enhance collimator. The unit cell was refined from 9520 diffractions by the least-squares method with the CrysAlis software (Agilent Technologies 2010) giving a monoclinic cell with a = 8.0462(1), b = 7.9256(1), c = 11.3206(2) Å, $\beta = 107.726(2)^\circ$, and V = 687.65(2) Å³. Data were corrected for background, Lorentz, and polarization effects, an analytical correction for absorption was applied (Clark and Reid 1995), leading to the R_{int} of the merged data equal to 3.4%. The summary of the data collection, crystallographic data and refinement is listed in Table 3.

The crystal structure of adolfpateraite (Table 4) was solved by the chargeflipping method from the single-crystal X-ray diffraction data using the Superflip program (Palatinus and Chapuis 2007) and subsequently refined by the software Jana2006 (Petříček et al. 2006). The space group $P2_1/c$ was suggested by the Superflip program, confirmed by systematic extinctions and verified by the subsequent refinement. The positions of heavy atoms and almost all oxygen atoms were found during initial structure solution. Subsquently, the positions of hydrogen atoms were located in the difference Fourier maps and were refined with the soft restraint that O-H bonds be 0.96(6) Å and their U_{iso} be equal to $1.2 U_{eq}$ and $1.4 U_{eq}$ of the parent atom, respectively. Higher U_{eq} was set in case of less-strongly bonded H2O group. All atoms except hydrogen atoms were refined anisotropically (Table 4). The final cycle of the refinement converged to $R_1 =$ 0.0165, w $R_1 = 0.0431$, and a GOF = 1.31. The atomic positions and displacement parameters are listed in Table 4. For structure-graphics the program Diamond v.3.1 (Brandenburg and Putz 2005) was used. Some geometrical characteristics were calculated using program Vesta (Momma and Izumi 2008). Crystal structure data were standardized utilizing the algorithm of the Structure Tidy program (Gelato and Parthé 1987) included in Vesta software (Momma and Izumi 2008).

TABLE 3. Summary of data collection conditions and refinement parameters for adolfpateraite

Structural formula	K[(UO ₂)(SO ₄) ₂ (OH)(H ₂ O)]						
Unit-cell parameters (based on 9520 refl	ections)						
a (Å)	8.0462(1)						
b (Å)	7.9256(1)						
<i>c</i> (Å)	11.3206(2)						
β (°)	107.726(2)						
V (Å ³)	687.65(2)						
Z	4						
Space group	P21/c						
Temperature	293 K						
Anode, wavelength	MoKa, 0.7107 Å						
Crystal dimensions	0.237 x 0.225 x 0.066 mm						
Collection mode	ω scans to fill an Ewald sphere						
Limiting θ angles	3.18–30.43°						
Limiting Miller indices	-11 < h < 11, -11 < k < 11, -16 < l < 16						
No. of reflections	12427						
No. of unique reflections	2099						
No. of observed reflections (criterion)	1915 [<i>l</i> >3σ(<i>l</i>)]						
R _{int}	0.0340						
Absorption correction (mm ⁻¹), method	25.52, analytical						
T_{\min}/T_{\max}	0.027/0.305						
F ₀₀₀	776						
Refinement by J	ana2006 on <i>F</i> ²						
Parameters refined, restraints	109, 3						
<i>R</i> ₁ , <i>wR</i> ₁	0.0166, 0.0431						
R_2, WR_2	0.0199, 0.0446						
GOF (obs)	1.30						
$\Delta \rho_{min}, \Delta \rho_{max} (e/Å^3)$	-0.74, 0.90						
Weighting scheme, weights	$\sigma, w = 1/[\sigma^2(l) + 0.0004l^2]$						

	TABLE 4. Atomic	positions and dis	placement	parameters ((U _{eg} , U _{ani} in Å	²) for the cr	ystal structure of	of adolfpateraite
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Atom	х	У	Z	$U_{\rm eq}$	U_{11}	U ₂₂	U ₃₃	U ₁₂	U ₁₃	U ₂₃
U	0.57544(2)	0.39873(2)	0.29873(1)	0.01234(5)	0.01067(7)	0.01020(8)	0.01605(7)	-0.00011(4)	0.00391(5)	-0.00059(4)
S	0.2038(1)	0.2656(1)	0.03944(8)	0.0137(2)	0.0136(4)	0.0122(4)	0.0141(4)	0.0009(3)	0.0024(3)	0.0006(3)
K	0.0606(1)	0.5351(1)	0.29766(8)	0.0210(3)	0.0175(4)	0.0202(4)	0.0248(4)	0.0014(3)	0.0057(3)	0.0021(3)
01	0.2158(3)	0.0791(3)	0.0607(3)	0.0193(8)	0.0185(13)	0.0127(13)	0.0226(13)	-0.0001(10)	0.0001(10)	0.0014(10)
02	0.4336(3)	0.1436(3)	0.3097(2)	0.016(1)	0.0165(12)	0.0133(12)	0.0186(12)	-0.0007(10)	0.0071(10)	-0.0020(10)
03	0.1482(3)	0.2038(4)	0.4062(2)	0.0210(8)	0.0225(13)	0.0228(15)	0.0152(12)	-0.0007(11)	0.0017(10)	-0.0031(11)
04	0.7482(3)	0.3253(4)	0.2440(3)	0.0195(8)	0.0185(12)	0.0175(14)	0.0246(13)	0.0017(10)	0.0095(10)	-0.0051(11)
O5	0.4108(3)	0.4851(4)	0.3545(3)	0.0195(9)	0.0164(12)	0.0184(14)	0.0257(14)	0.0008(11)	0.0093(10)	-0.0020(11)
06	0.3786(3)	0.3421(4)	0.0946(3)	0.022(1)	0.0212(13)	0.0200(15)	0.0195(13)	-0.0091(11)	-0.0001(10)	0.0007(11)
07	0.0797(4)	0.3332(4)	0.0974(3)	0.0256(9)	0.0239(14)	0.0283(17)	0.0264(14)	0.0050(12)	0.0102(11)	-0.0034(12)
08	0.2654(4)	0.7336(4)	0.0135(3)	0.0289(8)	0.0211(14)	0.0329(19)	0.0280(15)	0.0038(13)	0.0004(12)	-0.0125(13)
H2a	0.359(5)	0.137(6)	0.335(4)	0.022*						
H8a	0.159(6)	0.695(7)	0.002(5)	0.0347†						
H8b	0.325(7)	0.645(6)	0.008(5)	0.0347†						
Note: The	anisotropic dis	splacement fact	or exponent tak	es the form: -2	$\pi^{2}[h^{2} a^{*2}U^{11} +$	+ 2hka*b*U12].				

* Refined as U_{iso} and set as 1.2 U_{eq} of the parent O2 atom.

+ Refined as U_{iso} and set as 1.4 U_{eq} of the parent O2 atom.

Description of the crystal structure

The crystal structure of the new mineral adolfpateraite is identical to its synthetic analog described by Forbes et al. (2007), labeled as KUS1 with the nominal composition $K(UO_2)$ $(SO_4)(OH)(H_2O)$. The only slight difference lies in the proposed hydrogen-bonding network (see Discussion).

All atoms occupy 4e sites in the crystal structure of adolfpateraite. There is one unique U atom strongly bonded to two O atoms at 1.782(3) and 1.769(3) Å (Table 5) forming an uranyl ion $(UO_2)^{2+}$ (Fig. 6a). Uranium is further coordinated by five ligands, including O, one OH- (symmetrically unique) and one H₂O (symmetrically unique), arranged at the equatorial vertices of pentagonal bipyramids that are capped by the O atoms belonging to the uranyl ion (Fig. 6a). The bond lengths of the equatorial ligands vary between 2.285(3) and 2.493(3) Å (Table 5). There is one unique S atom in the crystal structure of adolfpateraite, tetrahedrally coordinated by four O atoms within the range of 1.453(4) and 1.497(3) Å. There is one unique K atom, localized in an interlayer (Fig. 7), coordinated by 7 O atoms with bond lengths in range between 2.722(3) and 2.997(3) Å. Bond-valence analysis for the crystal structure of adolfpateraite is listed in Table 6. The obtained bond-valence sums are in agreement with the expected values for U⁶⁺, K⁺, and S⁶⁺.

Structural connectivity

Each uranyl pentagonal bipyramid in the crystal structure of adolfpateraite shares two equatorial vertices with two adjacent bipyramids, resulting in a chain of uranyl polyhedra extending along [010] (Fig. 6). An OH⁻ group is located at each shared vertex (Fig. 6b). The hydrogen bonds in the OH⁻ group (O2) extend to the oxygen acceptor, with hydrogen-acceptor length of 2.09(5) Å and an A···H-D angle 160(4)° (Table 6, Fig. 8a). The sulfate tetrahedra adjoin the outer side of the chain with bridging bidentate linkages between the uranyl pentagonal bipyramids. The sulfate tetrahedra are oriented alternatively at either side of the chain, with the vertex of the sulfate tetrahedra heading up on one side and down on the other (Fig. 7). At the edges of the chain of uranyl polyhedra an H₂O group is located on the non-linking vertex of each uranyl pentagonal bipyramid. The additional hydrogen bonds from O8 (H8a and H8b) extend to O acceptors of the sulfate tetrahedra (O6 and O7) (Fig. 8a). The bond lengths are 2.56(4) and 1.90(5) Å

TABLE 5.	Interatomic distances (in angstroms) and selected geometri-
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Cai par	ameters for the ci	ystal structure of a	uonpateraite
U-04	1.783(3)	S-01"	1.497(3)
U-05	1.769(3)	S-O3	1.456(3)
U-01	2.402(2)	S-06	1.484(3)
U-02	2.286(2)	S-07	1.453(4)
U–O2 ⁱ	2.344(2)	<s-0></s-0>	1.473
U-06	2.413(2)	Δ	0.012
U-08	2.494(3)	σ^2	2.005
$$	176.2(1)	ECoN	3.978
<u-o<sub>Ur></u-o<sub>	1.776		
<u-o<sub>eq></u-o<sub>	2.384		
K–O1 ^{vi}	2.997(3)	K-07	2.817(3)
K–O3 ^{vii}	2.753(3)	<k-o></k-o>	2.855
K–O3 ^{∞iii}	2.893(3)	V _K	28.558 ų
K–O4 ⁱ	2.885(3)	Δ	0.027
K–O4 ^v	2.919(3)	ECoN	6.700
K-05	2.722(3)		
01–02 ⁱ	2.875(4)	04-08	2.873(4)
01–03 ⁱ	2.395(4)	04–08 ⁱⁱⁱ	2.920(4)
01–04	2.936(4)	05–05 ^{vi}	3.177(4)
01–05	2.958(4)	05-06	3.088(4)
01–05 ^{vi}	3.225(4)	05–06 ⁱ	3.259(4)
01–06 ⁱ	2.430(4)	05–08	3.260(4)
01–07 ⁱ	2.389(4)	05–08 ^{vi}	3.296(5)
01–08	2.842(4)	06–07	2.416(4)
02–03 ^{viii}	2.867(4)	06–08 ⁱ	3.286(4)
02–04	3.191(4)	07–08 ^{iv}	2.728(4)
02–04 ⁱⁱ	2.887(4)	05–05 ^{×vi}	2.677(15)
02–05	2.777(4)	05–05 ⁱ	2.708(12)
02–05"	2.831(4)	O5–O6a	3.324(11)
02–06	2.818(4)	06a–06b	0.85(6)
02–06 ⁱⁱ	2.860(4)	O6a–O6b ^{xvi}	3.17(6)
02–08	2.727(4)	06a–07b ^{xvii}	2.80(7)
03–05 ⁱⁱⁱ	3.246(4)	O6a–O7b ^{xi}	3.16(9)
03–06	2.389(3)	O6b–O6b ^{xvi}	2.46(6)
03–07	2.407(5)	07a–07b	0.92(8)
04–05"	3.048(4)	07b–07b ^{×ii}	3.00(12)
04-06	2.943(3)		

Note: Symmetry codes: (i) -x+2, y-1/2, -z+1/2; (ii) -x+2, y+1/2, -z+1/2; (iii) x, -y+3/2, z+1/2; (iv) x+1, -y+3/2, z+1/2; (v) x+1, y, z; (vi) -x+2, -y+1, -z; (vii) -x+3, -y+1, -z+1; (viii) x, -y+3/2, z-1/2; (ix) -x+3, y-1/2, -z+1/2; (x) -x+2, -y+2, -z. Δ, Bond-length distortion after Brown and Shannon (1973); σ², bond-angle distortion after Robinson et al. (1971); ECoN, an effective coordination number after Hoppe (1979); V_{κ} , polyhedral volume (in Å³).

with A···H-D angles 152(5) and 140(4)°, respectively (Table 6). Hydrogen bonds crosslink chains. Uranyl sulfate chains are therefore linked through K atoms in the interlayer and via hydrogen bonds (Figs. 7 and 8a).



FIGURE 6. (a) Coordination environment of U atom in adolfpateraite crystal structure. The UO_2 group is surrounded by five ligands arranged in the equatorial apices of pentagonal bypiramid, capped by O4 and O5 atoms. (b) Uranyl sulfate chain in adolfpateraite. Uranyl pentagonal bipyramids are blue, sulfate tetrahedra are yellow, oxygen and hydrogen atoms are red and gray, respectively. (Color online.)



FIGURE 7. The crystal structure of adolfpateraite with displayed hydrogen-bonds. Uranyl pentagonal bipyramids are blue, sulfate tetrahedra are yellow, potassium atoms in interlayer are purple, hydrogen atoms are gray, and O atoms are red. Hydrogen bonds are sketched by light blue dashed lines. (Color online.)

Powder X-ray diffraction data

The X-ray powder diffraction data of adolfpateraite was collected using a Bruker D8 Advance diffractometer equipped with a LynxEye 1D solid-state detector (sensitive solid angle 3.2°), operating at 40 kV and 40 mA, using CuK α radiation (Ni-filtered). A small amount of adolfpateraite crystals was placed onto a low-background silicon holder, crushed under a small amount of acetone and scanned in Bragg-Brentano geometry. A step size of 0.01° in the range of 4–80 °20 with the variable counting time utility (total counting time was 12 h) was used; the sample was rotated. For profile fitting of each diffraction maximum DIFFRAC TOPAS software version 4.2 (BrukerAXS) was utilized. The pseudo-Voigt profile shape function corrected for asymmetry (full-axial model) was used. The experimental

TABLE 6. Bond-valence analysis for crystal structure of adolfpateraite

	U	К	S	∑BVn	H2a	H8a	H8b	ΣBV	
01	0.50	0.10	1.41	2.07				2.01	
02	1.18			1.18	0.77			1.95	OH
03		0.31	1.57	1.88	0.20			2.08	
04	1.67	0.25		1.92				1.92	
05	1.72	0.20		1.92				1.92	
06	0.49		1.46	1.95			0.12	2.07	
07		0.25	1.59	1.83		0.24		1.98	
08	0.42			0.42		0.72	0.71	1.85	H_2O
	5.97	1.02	6.03		0.97	0.96	0.83		

Notes: Values are expressed in valence units (v.u.). ΣBV^n , bond-valence sums do not take into account hydrogen bonds, ΣBV , bond-valence sums do take into account hydrogen bonds. U^{6+} –O bond strengths ($r_0 = 2.045$, b = 0.51) from Burns et al. (1997); K–O, S^{6+} –O bond strengths from Brown and Altermatt (1985), H–O bond strengths from Brown (2002).

powder pattern was indexed in accordance with calculated values for intensities obtained from the crystal structure refinement. The unit-cell parameters were refined from 88 reflections (Table 7) by the least-square algorithm of the software Celref (LMGP Suite of Programs). The following results were obtained: (space group $P2_1/c$) a = 8.049(1), b = 7.929(1), c = 11.316(1) Å, $\beta =$ $107.71(2)^\circ$, and V = 688.0(1) Å³.

DISCUSSION

Differences in hydrogen-bonding in adolfpateraite and its synthetic analogue

As mentioned above, there are slight differences in the hydrogen bonding scheme for synthetic KUS1 as reported by Forbes et al. (2007) and for our structure determination of natural adolfpateraite. The analysis of hydrogen-bond geometry in both structures was carried out using the Platon software (Speck 2003, 2009).

Calculations of hydrogen-bond geometries for both structures are listed in Table 8. Comparison of both hydrogen-bonding schemes is displayed on Figures 8a and 8b. Hydrogen bonds mainly differ in bonding angles, which seem to be more realistic (less acute angles) in this adolfpateraite study.



FIGURE 8. Hydrogen-bonding in the structure of adolfpateraite (**a**) and its synthetic analog KUS1 (**b**). Coloring of the polyhedra is same as in previous figures, hydrogen bonds are represented by dashed azure blue lines. Note the position of H3 in the structure of KUS1 and the direction of the pertinent hydrogen bond. (Color online.)

	Jac	.nymc)V								
$d_{\rm obs}$	$d_{\rm calc}$	I_{obs}	h k			$d_{\rm obs}$	$d_{\rm calc}$	I_{obs}	h	k	1
7.658	7.667	76	1 0	0)	1.9304	1.9301	1	1	3	4
6.381	6.387	9	0 1	1		1.9184	1.9191	3	1	4	0
5.386	5.390	100	0 0	2	2	1.9138	1.9132	4	2	2	5
5.218	5.219	85	10	2	2	1.9058	1.9066	1	2	3	2
4.521	4.523	7	11	1		1.8994	1.8994	1	4	1	3
3.886	3.888	3	1 0	2	2	1.8873	1.8869	1	0	3	4
3.832	3.834	5	20	C)	1.8731	1.8736	1	1	1	5
3.718	3.721	46	0 2	1		1.8603	1.8603	7	0	4	2
3.700	3.701	37	2 0	2	2	1.8529	1.8530	3	1	4	2
3.583	3.584	4	2 1	1		1.8504	1.8503	2	4	0	4
3.520	3.521	3	1 2	C)	1.8373	1.8372	3	3	3	0
3.489	3.495	27	1 2	1		1.8302	1.8301	1	1	1	6
3.451	3.451	4	21	C)	1.8093	1.8094	1	2	1	6
3.351	3.353	3	2 1	2	2	1.7880	1.7883	<1	3	1	3
3.272	3.273	5	0 1	3	3	1.7636	1.7638	1	3	2	5
3.218	3.217	2	12	1		1.7602	1.7607	1	2	4	0
3.193	3.193	9	02	2	2	1.7514	1.7511	1	4	1	1
3.154	3.157	2	12	2	2	1.7476	1.7479	2	1	3	4
3.052	3.053	7	21	1		1.7399	1.7397	<1	3	0	6
2.822	2.822	4	22	1		1.6770	1.6763	1	2	4	3
2.755	2.753	4	20	2	2	1.6659	1.6657	<1	3	2	3
2.747	2.748	17	1 1	3	3	1.6413	1.6418	1	1	0	6
2.711	2.712	5	12	3	3	1.6375	1.6380	2	2	1	5
2.694	2.695	5	0 0	4	ŀ	1.6335	1.6333	1	3	3	2
2.661	2.662	3	02	3	3	1.5769	1.5760	6	2	1	7
2.610	2.610	5	20	4	ŀ	1.5736	1.5738	2	4	2	5
2.601	2.601	3	21	2	2	1.5724	1.5724	3	4	3	3
2.551	2.552	4	0 1	4	Ļ	1.5421	1.5422	1	2	2	5
2.536	2.536	2	3 1	1		1.5330	1.5324	1	1	3	6
2.461	2.462	2	22	3	3	1.5157	1.5158	1	4	3	4
2.355	2.356	2	31	3	3	1.5117	1.5117	1	0	1	7
2.329	2.330	1	1 0	4	ŀ	1.4860	1.4858	2	0	3	6
2.235	2.236	5	11	4	ŀ	1.4091	1.4091	<1	4	1	7
2.223	2.222	4	30	4	ŀ	1.3948	1.3946	1	1	3	6
2.205	2.206	4	21	3	3	1.3745	1.3746	1	5	3	2
2.185	2.186	3	13	2	2	1.3679	1.3681	<1	5	2	1
2.179	2.180	2	22	4	ŀ	1.3577	1.3580	2	3	2	5
2.140	2.140	1	3 1	4	ŀ	1.3473	1.3467	1	4	2	7
2.095	2.095	4	32	3	3	1.3438	1.3437	1	1	2	7
2.080	2.080	4	0 1	5	5	1.3211	1.3208	1	6	1	3
2.009	2.010	2	31	2	2	1.2779	1.2774	1	0	5	5
1.9824	1.9821	1	04	C)	1.2676	1.2674	1	6	1	5
1.9642	1.9622	1	13	3	3	1.2457	1.2459	1	2	3	8
1.9347	1.9345	1	4 1	1		1.2380	1.2384	1	1	3	8
Note: Th	he e.s.d.	values	on obs	erv	/ed ma	kima (°2θ) ba	ased on si	ngle-	orofil	e fi	itting

is ~0.01°.

TABLE 7.	X-ray powder	diffraction	pattern	ot	adolfpateraite	from
	láchymov					

TABLE 8.	Comparison of proposed calculated hydrogen-bond
	geometries for crystal structures of adolfpateraite and its
	synthetic analogue (KUS1)

391	inite the unfullo	gue (ROST)		
D-H-A	D–H (Å)	H…A (Å)	D–A (Å)	D–H…A angle (°)
		Adolfpatera	ite	
02-H2aO3	0.81(4)	2.09(4)	2.867(4)	160(5)
08-H8a…07	0.88(5)	1.92(5)	2.728(5)	153(5)
08H8b06	0.89(4)	2.56(4)	3.285(4)	140(4)
		KUS1		
02-H3-O6	0.95(9)	2.48(8)	2.868(5)	105(6)
08-H1-07	0.96(8)	2.23(8)	2.732(6)	112(6)
08-H2-O4	0.95(8)	2.48(9)	2.919(5)	108(6)
Noto The Jaholin	a of the stom	s is the same i	n hoth structu	

Note: The labeling of the atoms is the same in both structures.

Relations to the other uranyl sulfates and conditions of origin

Adolfpateraite represents the first uranyl sulfate occurring in nature with the structure based upon chain units and containing medium- or large-sized cations. There are numerous synthetic compounds and minerals based upon structural units of infinite chains of uranyl polyhedra (e.g., Burns 2005). However as stated by Forbes et al. (2007), the linkage found in synthetic KUS1 is unique within uranyl sulfate compounds. Direct sharing of uranyl polyhedral units is quite rare within a group of compounds based on infinite chains (Forbes et al. 2007). One of the few examples that could be cited is the mineral uranopilite, $[(UO_2)_6(SO_4)$ $O_2(OH)_6(H_2O)_6]$, which contains infinite chains with direct linkages between uranyl polyhedra (Burns 2001).

The only other hydrated uranyl sulfate occurring in nature that contains K^+ is the mineral zippeite with a crystal structure based upon edge-sharing uranyl pentagonal bipyramids forming chains, which are two polyhedra wide (Burns et al. 2003; Plášil et al. 2011a, 2011b). These are linked by vertices of sulfate tetrahedra producing sheets. These sheets are of zippeite uranyl-anion topology (Burns 1999, 2005) with the characteristic U:S ratio of 2:1.

There is a second compound synthesized by Forbes et al. (2007) with a chemical composition very similar to that of adolfpateraite, labeled KUS2, with nominal chemical composition K[(UO₂)(SO₄)(OH)] (orthorhombic, Pbca). In contrast to KUS1 and adolfpateraite, the KUS2 structure has a sheet topology. It contains uranyl pentagonal bipyramids linked into infinite chains by the sharing of a single vertex between neighboring uranyl polyhedra. KUS2, may not be called "dehydrated adolfpateraite" because it has a completely different structure. The pH of the solution was adjusted to 2.03 during the synthesis, while in the case of synthetic adolfpateraite, pH was set to 4.04-4.45 (Forbes et al. 2007). KUS2 is characterized by a lower value of charge-deficiency per anion, reflecting the lower pH of the parental solution as demostrated by Hawthorne et al. (2006). Consequently, the structure topology is driven by the pH of the solution, since the ratio of cations to anions is the same for both compounds. In this case, the amount of (H₂O) in the structure [which is related to the pH or the charge deficiency per anion (CDA)] controls the degree of polymerization of both structures, more polymerized KUS2 (sheets) or H₂O-containing KUS1 (chains) (see e.g., Hawthorne 2011). The pH conditions, under which adolfpateraite formed are reflected by the presence of čejkaite and also of another uranyl-oxide hydroxy-hydrate phase, probably schoepite. These phases are easily soluble under low pH and occur from weakly acid to alkaline conditions (pH up to 8).

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