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Revision of the symmetry and the crystal structure of čejkaite, $Na_4(UO_2)(CO_3)_3$†

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ABSTRACT

The crystal structure of čejkaite, $Na_4(UO_2)(CO_3)_3$, from the type locality, was determined for the first time by single-crystal X-ray diffraction. In contrast to the previously reported pseudohexagonal triclinic symmetry, the current data indicate čejkaite is monoclinic, triply twinned, and belongs to the space group *Cc*. Refined unit-cell parameters are a = 9.2919(8), b = 16.0991(11), c = 6.4436(3) Å, β = 91.404(5)°, and V = 963.62(12) Å^3. The monoclinic unit cell is also supported by the good fit to the powder diffraction data. The structure of čejkaite consists of uranyl tricarbonate clusters, forming sheets sub-parallel to (001) by sharing edges with (NaΦ) polyhedra. Sheets are interconnected through the uranyl O atoms and columns of (Na1Φ) polyhedra that share their trigonal faces. All Na atoms in the structure are in sixfold coordination . The structure refinement yielded R_{obs} = 0.0424 for 1687 observed reflections [$I_{obs} > 3\sigma(I)$] and 0.0538 for all 2016 unique reflections. Refinement and bond-valence analysis of the structure confirmed the previously proposed formula $Na_4(UO_2)(CO_3)_3$, Z = 4.

Keywords: Čejkaite, uranyl carbonate, symmetry, crystal structure, single-crystal, twinning, X-ray diffraction

INTRODUCTION

Čejkaite was described as a new mineral from Jáchymov, Western Bohemia, Czech Republic, by Ondruš et al. (2003) and named in honor of Jiří Čejka, for his contribution to science, especially to the knowledge of uranium minerals and their spectroscopy. Ondruš et al. (2003) used a Rietveld refinement to propose that it is triclinic, $P\bar{1}$ or $P1$, with the unit cell a = 9.291(2), b = 9.292(2), c = 12.895(2) Å, α = 90.73(2), β = 90.82(2), γ = 120.00(1)°, V = 963.7(4) Å^3, and formula $Na_4(UO_2)(CO_3)_3$, Z = 4. The lack of natural sample prompted Ondruš et al. (2003) to use Rietveld analysis of a synthetic powder sample. They also prepared trigonal $Na(UO_2)(CO_3)_3$ by a hydrothermal recrystallization and refined its crystal structure (Císařová et al. 2001). Based on the Rietveld refinement for the synthetic powder, Ondruš et al. (2003) described the structure of čejkaite as very similar to that of the trigonal analog (Císařová et al. 2001; Li et al. 2001), with refined triclinic unit-cell parameters only slightly deviating from hexagonal symmetry (see above). Catalano and Brown (2004) provided information on bond lengths in the uranium coordination polyhedron in čejkaite obtained by analysis of its EXAFS spectrum. Subsequently, Čejka et al. (2010) reported Raman spectra for čejkaite and its trigonal synthetic analog. Čejkaite, although rare in nature, has been found at several localities worldwide. In addition to the type locality, Jáchymov, it has been found in Rožná, Western Moravia, Czech Republic (Sejkora et al. 2008), in Mina Euréka, Pyrenees, Spain (Abella and Viñals 2009; Castillo et al. 2009), and is known from localities in Hungary and U.S.A. (see for details MinDat home page, www.mindat.org). Čejkaite was also found in sediments at the Hanford site where it results from uranium contamination (Deutsch et al. 2004; Krupka et al. 2006), and the trigonal analog occurs as the weathering product on the surface of the Chernobyl lava (Burakov et al. 1999).

Here we present the structure of čejkaite determined for the first time from single-crystal X-ray diffraction data that was collected for a twinned microcrystal, and re-determination of its symmetry.

EXPERIMENTAL METHODS

Occurrence

The čejkaite sample used in this study originates from the Rovnost mine (50°22′18.421″N, 12°53′32.83″E), Jáchymov, Western Bohemia, Czech Republic. The same specimen was studied previously in the course of the reinvestigation of grimselite by Plášil et al. (2012). The sample (~10 × 5 × 3.5 cm) of mostly quartz dolomitic vein is covered by Fe and Mn oxyhydroxides, which are X-ray amorphous. Rich aggregates composed of translucent light to grass green grimselite crystals (up to ~2 mm long) are partly covered by tiny prismatic (up to 0.4 mm long) čejkaite crystals. Čejkaite also forms rich crystalline aggregates of greenish color, covering areas of a few square centimeters (Fig. 1).

Single-crystal XRD

A crystal of čejkaite with dimensions 0.17 × 0.02 × 0.02 mm was selected for the single-crystal diffraction experiment. We used an Oxford Diffraction Gemini single-crystal diffractometer equipped with the Atlas CCD detector and graphite-monochromatized Mo$K\alpha$ radiation from a classical sealed X-ray tube,

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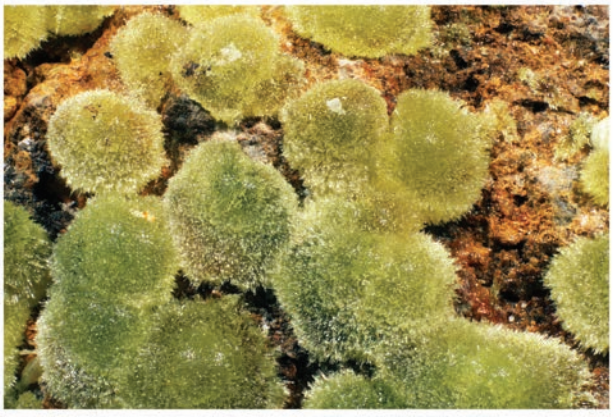

FIGURE 1. Aggregates of long prismatic čejkaite crystals on a limonite matrix. FOV 5 mm (photo P. Škácha). (Color online.)

collimated with fiber optics. The diffraction pattern revealed multiple twins, as best resolved along *c** (see Supplementary file[1]), and split reflections also along *b** (see Supplementary file). Three twin components are bounded by the operation of rotation, which can be described by two matrices given in Table 1. Čejkaite was found to be monoclinic, space group *Cc*, with unit-cell parameters $a = 9.2919(8)$ Å, $b = 16.0991(11)$ Å, $c = 6.4436(3)$ Å, $\beta = 91.404(5)°$, and $V = 963.62(12)$ Å^3, $Z = 4$. The unit cell was refined by a least-squares algorithm within the CrysAlis Pro Package (Agilent Technologies 2011) from 3248 reflections between 3.16 and 29.43° θ. A total of 14 213 reflections for all three twin-domains were collected.

Data reduction was performed for three twin domains described by the twin matrices. Data were corrected for background, Lorentz, and polarization effects, and an analytical correction for absorption was applied (Clark and Reid 1995) with corresponding $R_{int} = 0.0878$ for the strongest twin domain. There were 2016 unique and 1687 observed [$I_{obs} > 3\sigma(I)$] reflections for that twin domain.

The structure was solved by the charge-flipping algorithm of the Superflip program (Palatinus and Chapuis 2007) and subsequently refined using the JANA2006 software (Petříček et al. 2006). Details of the data collection and structure refinement are listed in Table 1. The solution provided a structure model, which refined to $R_{1obs} = 0.0425$, $R_{1all} = 0.0538$ and $wR_{2all} = 0.0526$ with a $GOF_{all} = 1.51$. The U and Na displacement parameters were refined anisotropically, with the remaining atoms treated with isotopic displacement parameters. All sites were fully occupied. Final atomic coordinates and displacement parameters are given in Table 2, selected bond distances in Table 3, and bond-valence analysis is listed in Table 4.

Powder diffraction

To support the selected monoclinic unit cell and space group, powder diffraction data for čejkaite were acquired, since powder diffraction is not affected by twinning. Powder data were collected from a flat sample in Bragg-Brentano geometry using a PANalytical Empyrean powder diffractometer equipped with a Cu X-ray tube and PIXcel^{3D} solid-state detector. The powder pattern was measured from 6 to 80° 2θ with a step size 0.013° 2θ and a counting time 40 s per step (details of the measurement: Cu$K\alpha_{1,2}$, Ni β filter, incident 1/4° fixed divergence slit, 0.02 rad incident, and diffracted Soller slits). Prior to this measurement the diffractometer was calibrated against a LaB_6 standard with the same settings. Data were processed by the Jana2006 software (Petříček et al. 2006) utilizing Le Bail decomposition of the diffraction pattern (variables: background, shift, FWHM function, unit-cell parameters, asymmetry by divergence) (Fig. 2). Data were corrected for serial correlations after Bérar and Lelann (1991). The fit resulted in residuals $R_p = 0.0269$, $R_{wp} = 0.0383$ (with GOF = 1.66). Refined unit-cell parameters for the Le Bail fit are $a = 9.2944(4)$, $b = 16.0967(7)$, $c = 6.4356(3)$ Å, $\beta = 91.410(5)°$, with $V = 962.53(4)$ Å^3.

Since diffraction data for čejkaite with *hkl* indices based on previous descriptions are available, we provide here new diffraction data indexed according to the monoclinic unit cell (Table 5). Single-peak fitting procedure was done by Xfit software (Cheary and Coelho 1992, 1998a, 1998b; Cheary et al. 2004) utilizing a split PearsonVII shape function. Unit-cell parameters were refined by a non-linear least-squares algorithm in the Unitcell program (Holland and Redfern 1997), giving: $a = 9.294(1)$, $b = 16.105(4)$, $c = 6.442(1)$ Å, $\beta = 91.40(2)°$, with $V = 963.9(4)$ Å^3.

TABLE 1. Summary of data collection conditions and refinement parameters for čejkaite

Crystal data	
Structural formula	$Na_4(UO_2)(CO_3)_3$
Space group	*Cc*
a (Å)	9.2919(8)
b (Å)	16.0991(11)
c (Å)	6.4436(3)
β (°)	91.404(5)
V (Å^3)	963.62(12)
Z	4
Calculated density (g/cm^3)	3.74
μ (mm^{-1}), correction type	17.00, analytical
T_{min}/T_{max}	0.346/0.755
Crystal size (mm)	0.17 × 0.02 × 0.02
Radiation, wavelength (Å)	Mo*K*α, 0.71073
θ range for data collection (°)	3.16–29.43
h, *k*, *l* ranges	$-11 < h < 12$, $-20 < k < 22$, $-8 < l < 8$
Axis, frame width (°), time per frame (s)	ω, 0.9, 60
Total reflections collected	14123
Unique reflections	2016
Unique observed reflections [$I_{obs} > 3\sigma(I)$]	1687
Data completeness to θ_{max} (%), R_{int}	99.80, 0.0878
Refinement method	Full-matrix least-squares on *F*
No. parameters, constraints, restraints	103, 3, 2
Weighting details	σ, $w = 1/[\sigma^2(I) + 0.004I^2]$
R_1, wR_2 for [$I_{obs} > 3\sigma(I)$]	0.0424, 0.0507
R_1, wR_2 for all data	0.0537, 0.0528
Goodness-of-fit (S) on F_{obs}/on F_{all}	1.51/1.43
Largest diff. peak and hole (e/Å^3)	4.28, –2.14
Twin fractions	0.40(5)/0.32(4)/0.28(4)
Twin matrices $Tw_{1,2}$; $Tw_{1,3}$	$\begin{pmatrix} -0.5 & -0.5 & 0 \\ 1.5 & -0.5 & 0 \\ 0 & 0 & 1 \end{pmatrix}$; $\begin{pmatrix} 0.5 & 0.5 & 0 \\ 1.5 & -0.5 & 0 \\ 0 & 0 & -1 \end{pmatrix}$

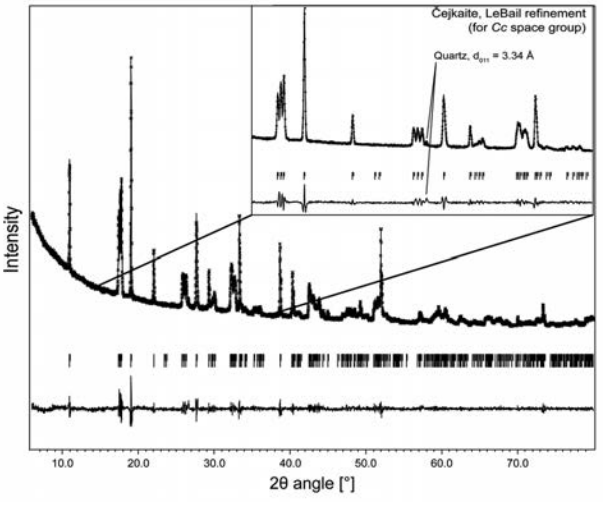

FIGURE 2. Le Bail decomposition of the diffraction data of čejkaite, performed for the monoclinic space group *Cc*. All observed diffraction peaks are described by the model except one, which belongs to an admixture of quartz (indicated on the difference profile).

[1] Deposit item AM-13-032, Supplementary files and 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 2. Atomic coordinates, site occupancies, and atomic displacement parameters (in Å^2) for čejkaite

Atom	x	y	z	U_{eq}	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
U	0.43392(8)	0.33354(4)	0.32192(7)	0.01095(16)	0.0090(3)	0.0080(3)	0.0159(3)	−0.0001(4)	0.0020(2)	−0.0014(4)
Na1	0.437(3)	−0.0026(12)	0.073(3)	0.025(2)	0.026(4)	0.024(4)	0.025(2)	0.001(3)	0.005(2)	−0.003(3)
Na2	0.6545(10)	0.3473(5)	−0.1412(12)	0.022(2)	0.020(5)	0.012(4)	0.034(4)	0.002(3)	0.000(3)	−0.003(3)
Na3	0.3456(10)	0.2161(5)	−0.1967(14)	0.029(3)	0.012(4)	0.019(5)	0.056(4)	0.010(4)	0.002(4)	0.005(4)
Na4	0.3039(10)	0.4363(5)	0.7959(13)	0.026(3)	0.006(4)	0.019(4)	0.052(5)	−0.003(3)	0.003(3)	−0.002(3)
C1	0.634(2)	0.130(2)	−0.161(3)	0.019(4)						
C2	1.023(3)	0.337(1)	−0.160(3)	0.017(4)						
C3	0.643(2)	0.535(2)	−0.205(3)	0.023(4)						
O1	0.236(2)	0.573(1)	0.872(2)	0.026(3)						
O2	0.896(2)	0.311(1)	−0.137(2)	0.030(3)						
O3	0.508(2)	0.1081(10)	−0.153(2)	0.024(3)						
O4	1.064(2)	0.4098(9)	−0.160(2)	0.026(3)						
O5	0.178(2)	0.1163(9)	−0.240(2)	0.018(3)						
O6	0.682(2)	0.2049(9)	−0.165(2)	0.019(3)						
O7	0.507(2)	0.5217(8)	0.823(2)	0.013(2)						
O8	0.733(2)	0.4806(9)	−0.211(2)	0.020(3)*						
O9	0.116(2)	0.2748(10)	−0.193(2)	0.020(3)*						
O10	0.455(2)	0.334(1)	0.607(2)	0.010(2)*						
O11	0.438(2)	0.332(1)	0.030(2)	0.010(2)*						

Notes: U_{eq} is defined as a third of the trace of the orthogonalized U_{ij} tensor; the anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11} + ... + 2hka^*b^*U_{12}]$. * Atoms were constrained to have same U_{eq}.

TABLE 3. Selected interatomic distances and polyhedral geometry for čejkaite

U1-O1^{i}	2.402(17)	C1-O1^{vii}	1.34(3)	C3-O5^{ix}	1.37(3)
U1-O2^{ii}	2.377(17)	C1-O3	1.22(3)	C3-O7^{viii}	1.30(3)
U1-O5^{iv}	2.447(15)	C1-O6	1.29(3)	C3-O8	1.21(3)
U1-O6^{ii}	2.421(15)	<C1-O>	1.28	<C3-O>	1.29
U1-O7^{i}	2.426(13)				
U1-O9^{iv}	2.434(15)	C2-O2	1.27(3)		
U1-O10	1.841(11)	C2-O4	1.23(2)		
U1-O11	1.885(11)	C2-O9^{ix}	1.35(3)		
<U-O_{Ur}>	1.86	<C2-O>	1.28		
<U-O_{Eq}>	2.42				
Na1-O3	2.40(3)	Na2-O2	2.31(2)		
Na1-O3^{v}	2.52(2)	Na2-O5^{iv}	2.656(15)		
Na1-O4^{ii}	2.55(3)	Na2-O6	2.313(17)		
Na1-O4^{vi}	2.39(3)	Na2-O8	2.313(17)		
Na1-O8^{ii}	2.41(3)	Na2-O10^{viii}	2.443(18)		
Na1-O8^{vi}	2.62(3)	Na2-O11	2.33(2)		
<Na1-O>	2.48	<Na2-O>	2.39		
Na3-O2^{iv}	2.918(17)	Na4-O1	2.340(19)		
Na3-O3	2.314(18)	Na4-O1^{iii}	2.794(16)		
Na3-O5	2.251(17)	Na4-O4^{xii}	2.292(19)		
Na3-O9	2.333(18)	Na4-O7	2.335(16)		
Na3-O10^{viii}	2.506(19)	Na4-O10	2.507(19)		
Na3-O11	2.501(19)	Na4-O11^{xiii}	2.561(19)		
<Na3-O>	2.47	<Na4-O>	2.47		

Notes: Symmetry codes: (i) x, −y+1, z−1/2; (ii) x−1/2, −y+1/2, z+1/2; (iii) x, −y+1, z+1/2; (iv) x+1/2, −y+1/2, z+1/2; (v) x, −y, z+1/2; (vi) x−1/2, y−1/2, z; (vii) x−1/2, y+1/2, z+1; (viii) x, y, z−1; (ix) x+1, y, z; (x) x+1/2, −y+1/2, z−1/2; (xi) x+1/2, y+1/2, z; (xii) x+1, y, z−1; (xiii) x, y, z+1; (xiv) x−1/2, y−1/2, z−1; (xv) x−1/2, −y+1/2, z−1/2.

TABLE 4. Bond-valence analysis for čejkaite

	U	Na1	Na2	Na3	Na4	C1	C2	C3	∑BV
O1	0.51				0.30	1.14			1.95
O2	0.53		0.25	0.05			1.38		2.21
O3		0.34		0.25		1.58			2.17
O4		0.34			0.27		1.54		2.15
O5	0.47		0.10	0.30				1.06	1.93
O6	0.49		0.25			1.31			2.05
O7	0.49				0.24			1.28	2.01
O8		0.30	0.25					1.63	2.18
O9	0.48			0.24			1.11		1.83
O10	1.50		0.18	0.15	0.15				1.98
O11	1.38		0.24	0.15	0.13				1.89
∑BV	5.84	0.98	1.27	1.14	1.09	4.03	4.03	3.97	

Notes: Values are expressed in valence units (v.u.). Na-O, bond strengths from Brown and Altermatt (1985); C-O bond strengths from Brese and O'Keeffe (1991); U^{6+}-O bond strengths (r_0 = 2.051, b = 0.519) from Burns et al. (1997).

TABLE 5. Powder diffraction data for čejkaite

I_{rel}	d_{obs}	d_{calc}	*h k l*	I_{rel}	d_{obs}	d_{calc}	*h k l*
42	8.058	8.052	020	7	2.0631	2.0632	113
		8.047	110			2.0618	062
31	5.084	5.081	$\bar{1}11$	3	2.0394	2.0397	332
41	5.029	5.029	021	3	2.0132	2.0131	080
47	4.971	4.977	111			2.0117	440
100	4.647	4.648	130	5	1.9088	1.9109	$\bar{2}23$
		4.646	200			1.9087	441
22	4.025	4.026	040	4	1.8952	1.8957	$\bar{2}62$
		4.023	220			1.8942	043
13	3.450	3.446	$\bar{2}21$	4	1.8780	1.8774	223
13	3.415	3.414	041	4	1.8724	1.8735	262
13	3.380	3.380	221			1.8470	280
35	3.220	3.220	002	8	1.8469	1.8466	370
		3.043	150			1.8459	510
16	3.042	3.042	240	2	1.8299	1.8300	172
		3.041	$\bar{3}10$	2	1.8176	1.8195	$\bar{3}52$
2	3.009	3.012	$\bar{1}12$	4	1.7873	1.7861	$\bar{5}11$
4	2.9908	2.9897	022	7	1.7819	1.7824	$\bar{3}71$
7	2.9687	2.9678	112	5	1.7776	1.7740	$\bar{3}13$
15	2.7781	2.7761	$\bar{3}11$	9	1.7703	1.7708	281
20	2.7714	2.7685	$\bar{2}41$	4	1.7689	1.7683	$\bar{3}71$
19	2.7616	2.7603	$\bar{1}51$			1.7675	$\bar{2}43$
12	2.7419	2.7429	151	4	1.7619	1.7631	511
13	2.7326	2.7338	241	39	1.7565	1.7571	190
43	2.6839	2.6841	060			1.7562	460
22	2.6792	2.6823	$\bar{3}30$			1.7559	530
3	2.6656	2.6623	$\bar{1}32$	3	1.7483	1.7475	153
2	2.6314	2.6317	132	3	1.7401	1.7408	243
1	2.6163	2.6165	$\bar{2}02$	3	1.7342	1.7342	313
2	2.5441	2.5406	$\bar{2}22$	1	1.7078	1.7070	082
3	2.5155	2.5147	042	1	1.6912	1.6901	442
3	2.4873	2.4883	222	4	1.6106	1.6099	004
30	2.3241	2.3238	260			1.6105	0 10 0
		2.3228	400	4	1.5627	1.5657	$\bar{4}23$
		2.2331	170	4	1.5552	1.5570	$\bar{5}32$
19	2.2327	2.2322	350	7	1.5493	1.5492	390
		2.2316	420			1.5485	600
2	2.2172	2.2208	$\bar{1}52$	6	1.5289	1.5299	462
2	2.2018	2.2028	152			1.5292	$\bar{4}23$
2	2.1909	2.1938	$\bar{2}42$	3	1.4865	1.4881	$\bar{6}21$
14	2.1224	2.1244	$\bar{4}21$			1.4861	$\bar{4}81$
		2.1212	$\bar{3}51$			1.4462	1 11 0
11	2.1136	2.1140	$\bar{1}71$	2	1.4458	1.4454	570
9	2.1059	2.1060	171			1.4452	640
9	2.0978	2.0977	$\bar{3}51$	3	1.4172	1.4173	$\bar{6}41$
5	2.0819	2.0851	$\bar{1}13$			1.4168	$\bar{5}13$
		2.0830	$\bar{3}32$	3	1.3819	1.3806	$\bar{5}71$
5	2.0754	2.0741	023				

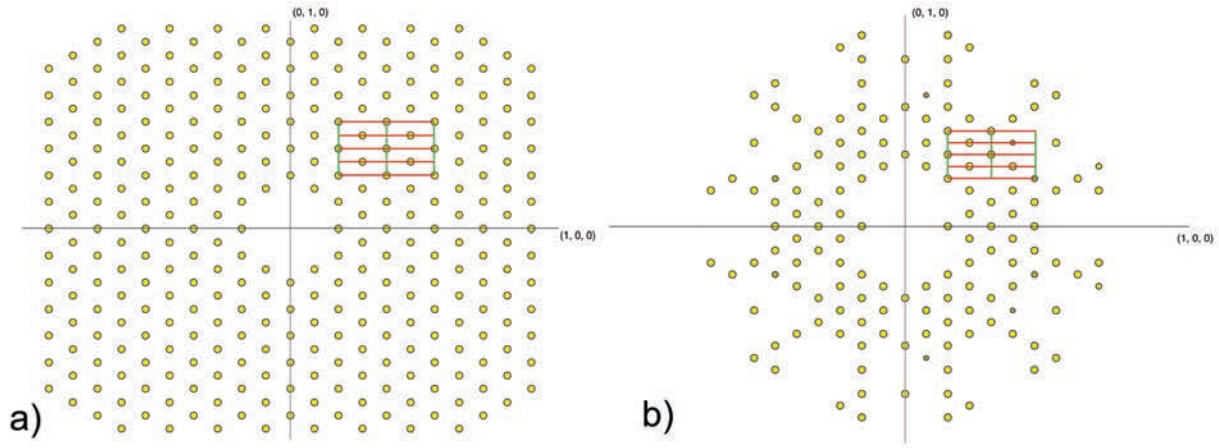

Figure 3. Reciprocal space reconstruction of the *hk*0 layer based on I_{calc}, (**a**) where only U atoms are included in the calculation, showing apparent pseudohexagonal symmetry, (**b**) where only the "light" atoms (all except uranium) are included in the calculation, showing the violation of pseudohexagonal symmetry. The reciprocal unit-cell is displayed with a* red and b* green. (Color online.)

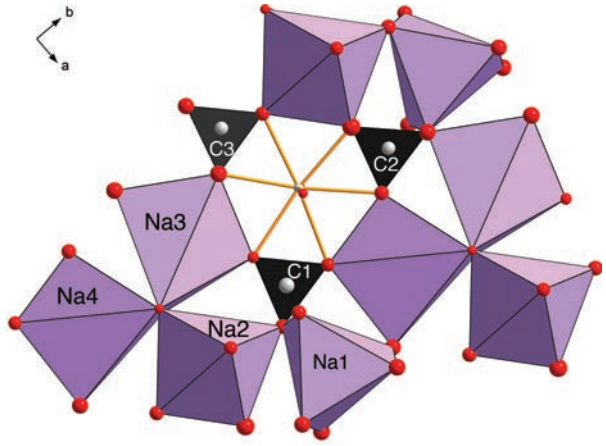

Figure 4. Cluster of polyhedra around the U atom in the structure of čejkaite, coordinated by eight O atoms to form a hexagonal uranyl bipyramid that shares three edges with C1, C2, and C3 carbonate groups and the remaining three edges with Na2 and Na3 polyhedra. Na1 polyhedra share their trigonal faces (parallel to the plane of the sketch) and form columns extending in the [001] direction. (Color online.)

Crystal structure of čejkaite

We present here the structure of čejkaite in the non-centrosymmetric monoclinic space group *Cc*. The output from the Superflip program (Palatinus and Chapuis 2007) indicated *C*2/*c* symmetry from the distribution of electron density (F_o). The program Superflip may encounter some problems when used for structure solution from data affected by twinning. Furthermore, the refinement indicated that the symmetry operators for *C*2/*c* are applicable only for the heavy atoms. Space group *Cc* provided an acceptable refinement for the light atoms and generated reasonable positions of the CO_3 groups. Pseudo-hexagonal symmetry of the *hk*0 reciprocal lattice of čejkaite, reported from SAED by Ondruš et al. (2003), was also encountered in the current data and we concluded that this pseudo-symmetry is due to the positions of U atoms in the structure only. The contribution of the U atom in the structure is displayed in Figure 3a, giving a pseudohexagonal pattern where viewed along c*. The light atoms are inconsistent with the pseudo-hexagonality as shown by the difference in the intensities of reflections Figure 3b. The choice of the unit cell by Ondruš et al. (2003) apparently overlooked centering of the cell, which not unexpected for powder data. However, the triclinic symmetry of čejkaite reported by Ondruš et al. (2003), as derived from the Rietveld refinement (see the unit-cell parameters), may have been questioned had higher symmetry been sought [a comparison of the current unit cell choice and the unit cell of Ondruš et al. (2003) is provided also on Deposit Figure 1[1]]. The monoclinic space group was confirmed by powder diffraction, showing very good match between calculated and observed diffractions. The diffraction peaks observed are consistent with the proposed monoclinic unit cell (Fig. 2).

According to the single-crystal diffraction data, there is 1 symmetrically unique U atom, 3 non-equivalent C atoms, 4 Na atoms, and 11 O atoms in the asymmetric unit of the čejkaite structure. The uranium atom is strongly bonded to two O atoms forming a nearly linear uranyl ion $(UO_2)^{2+}$, with <O10-U-O11> angle 172.4(3)°. The bond lengths obtained from the refinement (Table 3) are higher than the value given by Burns et al. (1997), 1.80 Å, as the most common for [8]-coordinated U atom. However, we are convinced that obtained value arises from the quality of data, affected by some unresolved twinning features. The uranyl ion is further coordinated by six O atoms, arranged in the equatorial apices of hegaxonal bipyramids. The three edges of the bipyramid are shared with planar CO_3^{2-} groups, forming the basic structural motif, a characteristic uranyl tricarbonate cluster, $[(UO_2)(CO_3)_3]^{4-}$ (Fig. 4). This cluster has been found in chemically related, however not isotypic, minerals such as agricolaite, $K_4[(UO_2)(CO_3)_3]$, *C*2/*c* (Skála et al. 2011) and grimselite, $K_3Na[(UO_2)(CO_3)_3]$, $P\bar{6}2/c$ (Li and Burns 2001; Plášil et al. 2012). Uranyl tricarbonate clusters are oriented with their equatorial planes perpendicular to [001]. All Na^+ cations in the čejkaite structure are [6]-coordinated by O atoms. The coor-

dination polyhedron around Na1 atoms is a strongly distorted ($Na1\Phi_6$) octahedron, sharing its trigonal faces with two other ($Na1\Phi_6$) octahedra, and thus forming irregular columns along [001]. Polyhedra (Na2Φ), (Na3Φ), and (Na4Φ) share common edges, forming a triplet, with composition Na_3O_{16} (Fig. 4). These triplets are also linked with (Na1Φ) polyhedra by sharing apices, and due to this linkage a complex uranyl-carbonate-(NaΦ) sheet extends sub-parallel to (001) in čejkaite. These sheets are then interconnected through the O_{Ur} atoms, in common edge of the triplets, and by irregular columns of (Na1Φ) polyhedra. Structure refinement and bond-valence analysis (Table 4) confirmed the formula proposed for čejkaite by Ondruš et al. (2003), $Na_4(UO_2)(CO_3)_3$, $Z = 4$.

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