Raisaite, CuMg[Te⁶⁺O₄(OH)₂] \cdot 6H₂O, a new mineral from Chukotka, Russia

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Abstract: Raisaite, $CuMg[Te^{6+}O_4(OH)_2] \cdot 6H_2O$, is a new mineral found at the Sentyabr'skoe deposit, Ilirney ore district, Western Chukotka, North-Eastern Region, Russia. It is associated with gypsum, malachite, azurite, cerussite, anglesite, brochantite, linarite, posnjakite, chlorargyrite, acanthite, gold, brucite, goethite, coronadite, paratellurite, and xocomecatlite in the oxidation zone of quartz veins with calcite, dolomite, ankerite, muscovite, pyrite, chalcopyrite, galena, sphalerite, hessite, petzite, altaite, primary acanthite and gold, etc. Raisaite occurs as prismatic crystals (up to 0.1×0.6 mm), as groups or crusts (up to 0.4×0.6 mm) and as dense roundish clusters (up to 0.2 mm in diameter) forming botryoidal aggregates (up to 1 mm across). Raisaite is transparent, light blue to bright sky blue, with a vitreous lustre. Its Mohs' hardness is ca. 2. Cleavage is imperfect, probably on (100), the fracture is uneven. $D_{\text{meas}} = 2.82(1), D_{\text{calc}} = 2.828$ g cm⁻³. Raisaite is optically biaxial (+), $\alpha = 1.626(3)$, $\beta = 1.642(5)$, $\gamma = 1.665(3)$ and $2V_{\text{meas}} = 80(10)^{\circ}$. The IR spectrum is reported. The chemical composition (average of 7 analyses, H₂O by difference) is: MgO 10.68, CuO 18.09, SO₃ 0.44, TeO₃ 41.19, H₂O_{calc} 29.60, total 100.00 wt%. The empirical formula calculated on the basis of 12 O apfu is: $Cu_{0.96}Mg_{1.11}Te_{0.99}S_{0.02}O_{4.20}(OH)_{1.80} \cdot 6.00H_2O$. Raisaite is monoclinic, C2/c, a = 9.9078(2), b = 10.1325(3), c = 9.8375(2) Å, $\beta = 91.839(2)$, V = 987.09(4) Å³ and Z = 4. The strongest reflections of the powder X-ray diffraction pattern [d, A(I)(hkl)] are: 7.088(100)(110), 5.815(35)(-111), 5.690(23)(111), 4.949(91)(200, 002), 4.507(50)(021), 3.533(17)(-202, 022), 3.358(17)(-221), 3.310(21)(221) and 2.694(29)(-132). The crystal structure (solved from singlecrystal X-ray diffraction data, R = 0.0186) is unique. It is based on heteropolyhedral zig-zag chains built by alternating edge-sharing $Te^{6+}O_4(OH)_2$ and $CuO_4(H_2O)_2$ octahedra. $Mg(H_2O)_6$ octahedra are connected with the chains from two sides *via* common O vertices. Adjacent chains are bound by H-bonding forming "layers" which are connected with each other by a system of H-bonds. The mineral is named in honour of the Russian mineralogist Raisa A. Vinogradova (born 1935), Moscow State University. Both the new mineral and its name have been approved by the IMA CNMNC (IMA2014-046).

Key-words: raisaite; new mineral; copper magnesium tellurate; crystal structure; oxidation zone of ore deposit; Sentyabr'skoe deposit; Ilirney ore district; Chukotka peninsula.

Introduction

Tellurium is one of the most deficient elements in nature: its abundance in the Earth's crust is about $1 \ \mu g \ kg^{-1}$. In spite of its rarity, more than 160 minerals with species-defining Te are known and some tellurides (sylvanite, petzite, calaverite, hessite) are ore-forming in large deposits actively mined at present for gold and silver. We believe that such diversity of Te minerals is mainly caused by the significant difference in effective ionic radii between tellurium and more abundant elements similar in their chemical properties, in particular sulfur and selenium, chalcogens belonging to the same group of the periodic table. This difference strongly hampers the incorporation of Te in compounds of S and Se and favours its separation, especially in oxygen-bearing minerals.

Natural oxygen compounds of tellurium are numerous (eighty species) but, unlike tellurides, they do not form substantial accumulations. The overwhelming majority of them occurs in the oxidation zone of ore deposits with primary telluride or sulfotelluride mineralization. There are mainly tellurites and tellurates, *i.e.*, salts of tellurious acid, $H_2Te^{4+}O_3$, and telluric acid, $H_6Te^{6+}O_6$, respectively. The mineralogy and crystal chemistry of oxygen compounds of S, Se and Te are especially different, much more so than those of their oxygen-free compounds; *e.g.*, sulfates are abundant in nature whereas sulfites are very rare. Selenium demonstrates opposite behaviour: selenites are common in the oxidation zone of selenide ores whereas natural selenates are extremely rare. Tellurite and tellurate minerals occur in the oxidation zone of ore deposits in comparable amounts, *i.e.*, tellurium easily adopts both tetra- and hexavalent forms in natural oxygen compounds. The Te⁶⁺ ion is significantly larger than Se⁶⁺ and S⁶⁺: their ionic radii in the tetrahedral coordination are 0.43, 0.28 and 0.12 Å, respectively (Shannon, 1976). Unlike Se⁶⁺ and S⁶⁺, forming tetrahedral (SeO₄)²⁻ and (SO₄)²⁻ anions, hexavalent tellurium forms in minerals octahedral (TeO₆)⁶⁻ or, rarely, [TeO₄(OH)₂]⁴⁻ anionic groups (Grice & Roberts, 1995; Mills *et al.*, 2014). These crystal-chemical features of tellurium favour the diversity of its supergene minerals due to the realization of structural types impossible for sulfur or selenium compounds.

In this paper we provide the mineralogical description and crystal-structure data of a new natural tellurate named raisaite (Cyrillic: Paucaut) in honour of the Russian mineralogist Dr. Raisa Aleksandrovna Vinogradova (born 1935), a specialist in ore mineralogy. She was also a teacher of mineralogy in the Moscow State University for many years.

Both the new mineral and its name have been approved by the IMA Commission on New Minerals, Nomenclature and Classification (IMA2014-046). The type specimen is deposited in the systematic collection of the Fersman Mineralogical Museum of the Russian Academy of Sciences, Moscow, with the catalogue number 94994.

Occurrence

Specimens containing raisaite were collected by authors (E.A.V. and A.V.A.) in 2013 at the Sentyabr'skoe silver and gold deposit belonging to the Ilirney ore district. It is situated 110 km ESE of the town of Bilibino at Western Chukotka, North-Eastern Region, Russia (67°41'N, 168°52'E).

The Sentyabr'skoe deposit is located within Lower Cretaceous volcanic rocks mainly represented by andesites, basaltic andesites, dacites, rhyolites and their tuffs belonging to the Tytyl'veem formation. They are intruded by Late Cretaceous quartz monzonites, granodiorites and granitic porphyries of the Ilirney magmatic complex. The deposit consists of numerous hydrothermal veins (from 5 to 30 cm thick) surrounded by aureoles of propylites and quartz–sericite and quartz–kaolinite rocks. Ores of the Sentyabr'skoe deposit were formed at 350–280°C and 250–380 bars, according to fluid-inclusion data (Nikolaev *et al.*, 2013).

Raisaite is a secondary, supergene mineral found in minor amounts in the oxidation zone comprising quartz veins with carbonates (calcite, dolomite and ankerite), muscovite, nacrite and chamosite and containing a rich ore mineralization represented by pyrite, chalcopyrite, galena, sphalerite, acanthite, gold, hessite, petzite, altaite, and coloradoite. The supergene minerals occur in cracks and small cavities within slightly oxidized near-surface parts of ore veins. These are gypsum, malachite, azurite, cerussite, anglesite, brochantite, linarite, posnjakite, secondary gold and acanthite, chlorargyrite, brucite, goethite, coronadite, paratellurite, xocomecatlite, raisaite and incompletely studied tellurites/tellurates of Cu, Mg, Mn, Zn, Fe and Pb.

Carbonates of the dolomite–ankerite series are an obvious source of Mg, chalcopyrite of Cu, and tellurides (abundant hessite, petzite and altaite) of Te for raisaite formation.

General appearance, physical properties and optical data

Raisaite occurs as prismatic crystals, usually well-shaped, with complex terminations (some crystals are doubly terminated) which form radial, bush-like or chaotic groups (Figs 1 and 2a) and crystal crusts. Separate crystals are typically up to 0.15 mm long and 0.03 mm thick, very rarely up to 0.6 mm long and 0.1 mm thick. Crystal crusts are up to 0.4×0.6 mm in size. Another morphological variety of the mineral forms dense, typically roundish to spherical clusters (Fig. 2b) up to 0.2 mm in diameter with a surface composed of tiny, well-shaped crystals (Fig. 1c); botryoidal aggregates (up to 1 mm across) consisting of such dense clusters were observed.

Raisaite overgrows dolomite, quartz, muscovite, chalcopyrite, hessite and petzite (Figs 1a,b, 2–4). In some cracks, colourless, aqua-transparent coarse-crystalline gypsum crusts cover aggregates of the new mineral (Fig. 3).

Raisaite is transparent, light blue to bright sky blue, with a white streak and vitreous lustre. It is brittle. Its Mohs' hardness is *ca.* 2. One direction of imperfect cleavage, probably on (100), was observed under the microscope. The fracture is uneven. The density measured by flotation in heavy liquids (bromoform + dimethylformamide) is 2.82(1) g cm⁻³. The density calculated based on the empirical formula is 2.828 g cm⁻³.

Raisaite is optically biaxial (+), $\alpha = 1.626(3)$, $\beta = 1.642(5)$, $\gamma = 1.665(3)$ (589 nm), $2V_{\text{meas}} = 80(10)^{\circ}$ and $2V_{\text{calc}} = 81^{\circ}$. Dispersion of the optical axes is weak, r < v. Pleochroism is weak: *Z* (bluish-greyish) > *Y* (pale bluish-greyish) > *X* (colourless). Elongation is positive. The extinction angle with *Z* (the crystal elongation direction) is 2(1)^{\circ}.

Infrared spectroscopy

The infrared (IR) absorption spectrum of raisaite was recorded for a powdered sample mixed with anhydrous KBr and pelletized. The pellet was analyzed using an ALPHA FTIR spectrometer (Bruker Optics) at a resolution of 4 cm⁻¹, with 16 sampling scans. The IR spectrum of a pure KBr disc was subtracted from the overall spectrum.



а



a





b



с

Fig. 1. Morphology of raisaite crystals and aggregates: (a) doubly terminated crystals on hessite; (b) bush-like crystal cluster on dolomite; (c) crystals composing the surface of a dense cluster. Scanning electron microscope (SEM) images (secondary electrons).

Fig. 2. Blue prismatic crystals and their groups (a) and dense crystal clusters (b) of raisaite on colourless to greyish quartz–dolomite aggregates and on dark lead-grey to iron-black nests of intimately intergrown hessite and petzite. Field of view: (a) 2.5 mm, (b) 2.8 mm. Photo: I.V. Pekov & A.V. Kasatkin.

The IR spectrum of raisaite (Fig. 5) is unique and can be used as a good diagnostic tool.

Bands in the range 3000–3600 cm⁻¹ correspond to O–H stretching vibrations of H₂O molecules and OH groups. Weak bands of acidic OH groups at 1865 and 2276 cm⁻¹ may be due to stretching vibrations of acid Te–O(3)–H(1) groups and/or additional Te–O–H groups formed as a result of proton transfer H(3)–O(5)–H(7) · · · O(2) \leftrightarrow H(3)–O(5) · · · H(7)–O(2) and (less probably) H(2)–O(4)–H(4) · · · O(1) \leftrightarrow H(2)–O(4) · · · H(4)–O(1). These equilibria (presumably shifted to the left) are supposed to be caused by strong hydrogen bonds O5–H7 · · · O2 and O(4)–H(4) · · · O(1) (see below). The bands at 1577, 1653 and 1670 (shoulder) cm⁻¹ correspond to non-degenerate H–O–H bending modes of three independent H₂O molecules present in the structure of raisaite.

Assignment of bands below 1150 cm^{-1} is ambiguous. The strongest characteristic IR bands of Te^{6+}O_6 octahedra



Fig. 3. Cluster of raisaite crystals (1) covered by a coarsely crystalline gypsum crust (2) on a matrix consisting of dolomite (3), chalcopyrite (4) and brucite (5). Chalcopyrite grains are surrounded by rims and are cross-cut by veinlets of fine-grained aggregates of unidentified tellurites/tellurates of Pb, Fe and Cu (6). Polished section. SEM back-scattered electron (BSE) image.



Fig. 5. The IR spectrum of raisaite.



Fig. 4. Clusters of raisaite crystals (1) on a matrix consisting of muscovite (2) with hessite ingrowths (3). Polished section. SEM (BSE) image.

are typically located below 630 cm⁻¹ (Pekov *et al.*, 2011). However, the presence of OH groups in the vertices of coordination polyhedra usually results in shifts of the bands towards higher frequency and in additional splitting (Chukanov, 2014). We assume that bands in the ranges 800–1120 and 450–800 cm⁻¹ correspond to Te–O–H bending and Te–O stretching vibrations, respectively, in Te⁶⁺O₄(OH)₂ octahedra. Bands at 371 and 400 cm⁻¹ can be assigned to lattice modes involving Cu–O and Mg–O stretching ones.

The absence of bands in the range from 1150 to 1500 $\rm cm^{-1}$ indicates the absence of groups with C–O, N–H, N–O and B–O bonds in the mineral.

Chemical composition

The chemical composition of raisaite was studied using a Jeol JSM-6480LV scanning electron microscope equipped with an INCA-Wave 500 wavelength-dispersive spectrometer (Laboratory of local methods of matter investigation, Faculty of Geology, Moscow State University), with an acceleration voltage of 20 kV, a beam current of 10 nA, and a 5 μ m beam diameter. The following standards were used: diopside (Mg), CuFeS₂ (Cu, S) and PbTe (Te). Contents of other elements with atomic numbers higher than oxygen are below detection limits. H₂O was not analysed because of paucity of material. The H₂O content calculated by total difference is in a good agreement with crystal-structure data (see below).

The chemical composition of raisaite (average of seven spot analyses, ranges are in parentheses) is: MgO 10.68 (10.41–10.97), CuO 18.09 (17.19–19.01), SO₃ 0.44 (0.05–1.26), TeO₃ 41.19 (39.96–42.16), H₂O_{calc} 29.60, total 100.00 wt%.

The empirical formula calculated on the basis of 12 O apfu is $Cu_{0.96}Mg_{1.11}Te_{0.99}S_{0.02}O_{4.20}(OH)_{1.80} \cdot 6.00H_2O$. The idealized formula is $CuMg[Te^{6+}O_4(OH)_2] \cdot 6H_2O$, which requires MgO 9.56, CuO 18.87, TeO₃ 41.65, H₂O 29.92, total 100.00 wt%.

The Gladstone-Dale compatibility index is: $1 - (K_p/K_c) = -0.018$ (superior) if D_{meas} is used and -0.016 (superior) if D_{calc} is used.

X-ray crystallography and crystal-structure determination

Powder X-ray diffraction data of raisaite (Table 1) were collected with a Rigaku R-AXIS Rapid II single-crystal diffractometer equipped with a cylindrical image plate detector using Debye-Scherrer geometry (Co $K\alpha$ radiation, d = 127.4 mm). The monoclinic unit-cell parameters refined

Table 1. Powder X-ray diffraction data for raisaite.

Table	1.	Continue	d
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$\begin{array}{cccccccccccccccccccccccccccccccccccc$	Iobs	$d_{\rm obs}$	I_{calc}^*	$d_{\rm calc}^{**}$	h k l
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	100	7.088	100	7.082	110
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	35	5.815	34	5.810	-111
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	23	5.690	20 80-22	5.685 4.051 4.016	200,002
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	50	4.507	51	4.504	200, 002
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	17	3.533	6, 14	3.546, 3.528	-202,022
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	6	3.435	4	3.434	202
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	17	3.358	18	3.356	-221
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	21 4	3.310	24	3.307	221
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	15	3.140	18	3.139	310
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	4	3.052	2	3.049	-131
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	8	3.018	8	3.017	-311
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	15	2.951	16	2.949	113
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	8	2.907	12	2.905	-222
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	4	2.844	3	2.845	023
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	29	2.694	45	2.693	-132
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	4	2.458	3	2.458	004
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	6	2.434	8	2.433	-223
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	5	2.379	8	2.378	223
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	6	2.342	1 11	2.339	-331 114
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	4	2.253	1, 1	2.255, 2.252	240, 042
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	7	2.232	6, 8	2.233, 2.230	313, -204
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	3	2.207	2	2.205	-241
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	7	2.181	7,8	2.183, 2.174	-421,204
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	13	2.150	5, 23 10	2.156, 2.147	421, -332 -242
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	5	2.002	5 8	2.001	-422, 242
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	3	2.006	3, 0	2.005, 2.004	422, 043
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	1	1.965	1	1.965	-314
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	3	1.948	4, 3	1.949, 1.944	-151, 510
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	3	1.907	6	1.907	314
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	5	1.884	2 0	1.884	_243 _423
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	2	1.846	2, 9	1.845	-2+3, -423
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	4	1.834	7	1.833	025
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	4	1.817	8	1.816	423
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	3	1.774	6	1.773	-404
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	2	1.751	5	1.750	-441
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	2	1./3/	4, 3	1./36, 1./36	-225, 441
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	3	1.718	o 4	1.717	-351
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	3	1.692	2, 1, 7	1.695, 1.693, 1.689	-513, 153, 060
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	3	1.679	10	1.678	-442
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	1	1.667	2	1.664	061
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	3	1.654	6	1.654	442
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	1	1.644	3	1.644	315
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	1	1.629	75	1.028	-332
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	3	1.574	1, 2	1.575, 1.573	261, -443
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	5	1.556	2, 3, 4	1.559, 1.557, 1.553	026, -621, 045
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	4	1.544	3, 2, 2	1.549, 1.543, 1.542	-514, 443, 621
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	3	1.510	2	1.508	-622
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	3	1.502	1	1.502	514
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	5 2	1.497 1.487	1, 1	1.300, 1.495 1.482	-226, -425
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	2	1.474	1.1	1.474, 1.472	2.2.6. 2.45
3 1.454 1 1.453 425	2	1.466	3	1.464	-136
	3	1.454	1	1.453	425

$I_{\rm obs}$	$d_{\rm obs}$	$I_{\rm calc}^{*}$	d_{calc}^{**}	h k l
3	1.434	3, 3	1.433, 1.432	-623, 170
2	1.400	1, 1, 2	1.402, 1.401, 1.399	-155,710,623
3	1.394	1, 2, 2, 3	1.395, 1.393, 1.392,	460, 155, 064,
			1.391	-604
3	1.377	7	1.376	046
2	1.363	1, 3	1.364, 1.361	641, -336
2	1.354	3	1.354	027
3	1.349	2, 3	1.350, 1.346	604, -264
3	1.336	3, 2	1.335, 1.334	-246, 264
2	1.324	2, 3	1.326, 1.322	370, 642
2	1.318	3, 2	1.317, 1.316	246, -227
2	1.304	2	1.303	-713
2	1.297	1, 2	1.297, 1.296	-317, 227
2	1.289	1, 1	1.289, 1.287	553, 355

*For the calculated pattern, only reflections with intensities ≥ 1 are given. **For unit-cell parameters calculated from single-crystal data.

Table 2. Crystal data, data collection information and structure refinement details for raisaite.

Formula	$(Cu_{0.95}Mg_{0.05})Mg(Te_{0.97}S_{0.03})$ $O_4(OH)_2 \cdot 6H_2O$
Formula weight	417.11
Temperature, K	293(2)
Radiation and wavelength, Å	ΜοΚα; 0.71073
Crystal system, space group, Z	Monoclinic, C2/c, 4
Unit-cell dimensions, Å/°	a = 9.9078(2) b = 10.1325(3)
	$\beta = 91.839(2) c =$
	9.8375(2)
$V, Å^3$	987.09(4)
Absorption coefficient μ , mm ⁻¹	5.055
F ₀₀₀	805
Crystal size, mm	$0.05 \times 0.06 \times 0.19$
Diffractometer	Xcalibur S CCD
Absorption correction	Analytical
θ range for data collection, °	2.88-30.51
Index ranges	$-14 \le h \le 14, -14 \le k \le 14, \\ -14 \le l \le 14$
Reflections collected	10194
Independent reflections	$1504 \ (R_{\rm int} = 0.0449)$
Independent reflections with $I > 2\sigma(I)$	1411
Structure solution	direct methods
Refinement method	full-matrix least-squares on F^2
Number of refined parameters	104
Final <i>R</i> indices $[I > 2\sigma(I)]$	R1 = 0.0186, w $R2 = 0.0358$
<i>R</i> indices (all data)	R1 = 0.0217, wR2 = 0.0366
GoF	1.110
Largest diff. peak and hole, $e/Å^3$	0.387 and -0.512

from the powder data are: a = 9.914(2), b = 10.134(3), c = 9.841(3) Å, $\beta = 91.88(2)^{\circ}$ and V = 988.2(4) Å³.

Single-crystal X-ray studies of raisaite were carried out using an Xcalibur S diffractometer equipped with a CCD detector. A full sphere of three-dimensional data was collected. Data reduction was performed using CrysAlisPro Version 1.171.35.21 (Agilent,

463

(Continued)

Site	x	у	z	$U_{ m eq}$	s.o.f.	Q
Те	0	0.151803(18)	1/4	0.00815(6)	$Te_{0.973(5)}S_{0.026(14)}$	4
Cu	0	0	0	0.01097(12)	$Cu_{0.946(8)}Mg_{0.055(17)}$	4
Mg	0	0.34201(10)	3/4	0.0136(2)	1	4
O(1)	0.89460(13)	0.14169(14)	0.08515(13)	0.0132(3)	1	8
O(2)	0.88943(13)	0.02261(14)	0.33531(14)	0.0132(3)	1	8
O(3)	0.11172(14)	0.29143(16)	0.17529(15)	0.0175(3)	1	8
O(4)	0.87932(16)	0.35354(17)	0.92077(16)	0.0178(3)	1	8
O(5)	0.87113(16)	0.47976(16)	0.65831(16)	0.0176(4)	1	8
O(6)	0.11466(16)	0.18866(17)	0.83394(17)	0.0193(4)	1	8
H(1)	0.111(3)	0.359(3)	0.235(3)	0.037(8)*	1	8
H(2)	0.796(3)	0.361(3)	0.911(3)	0.040(9)*	1	8
H(3)	0.891(3)	0.510(3)	0.5878(16)	0.034(9)*	1	8
H(4)	0.884(3)	0.291(4)	0.977(3)	0.067(12)*	1	8
H(5)	0.116(3)	0.122(3)	0.772(3)	0.050(10)*	1	8
H(6)	0.201(3)	0.212(4)	0.845(3)	0.057(10)*	1	8
H(7)	0.776(3)	0.474(3)	0.662(3)	0.047(9)*	1	8

Table 3. Atom fractional coordinates and thermal displacement parameters (U_{eq} , in Å²), site occupancy factors (s.o.f.) and site multiplicities (Q) for raisaite.

 $*U_{iso}$.

Table 4. Selected interatomic distances (\AA) in the structure of raisaite.

Te - O(1) - O(2) - O(3) < Te - O> Cu - O(2) - O(1) - O(6) Mg - O(5) - O(6) - O(6)	$\begin{array}{c} 1.9032(13) \times 2\\ 1.9175(14) \times 2\\ 1.9543(15) \times 2\\ 1.925\\ 1.9400(13) \times 2\\ 1.9773(14) \times 2\\ 2.7807(17) \times 2\\ 2.0781(17) \times 2\\ 2.0801(17) \times 2\\ 2.0963(15) \times 2\\ 2.095\end{array}$
<mg-o></mg-o>	2.085
e	

2012). The data were corrected for Lorentz factor and polarization effects. Analytical numeric absorption correction using a multifaceted crystal model based on expressions derived by Clark & Reid (1995) was applied. The crystal structure of the new mineral was solved by direct methods and refined using the SHELX-97 software package (Sheldrick, 2008) to R = 0.0186 for 1411 unique reflections with $I > 2\sigma(I)$. Hydrogen atoms were found in a difference Fourier map and freely refined, except for H(3): its position was constrained to an O(5)–H(3) distance of 0.80(1) Å. The crystal data and the experimental details are presented in Table 2, atom coordinates, thermal displacement parameters and site occupancies in Table 3,

Table 5.	Hydrogen-bond	geometry ((Å,°) iı	1 the	structure of	f raisaite.
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$D-H\cdot\cdot\cdot A$	$D-\mathrm{H}$	$\mathrm{H}\cdot\cdot\cdot A$	$D \cdot \cdot \cdot A$	$< (D - H \cdot \cdot \cdot A)$
$\overline{O(3) - H(1) \cdot \cdot \cdot O(5)}$	0.90(3)	1.95(3)	2.840(2)	170(3)
$O(4) - H(2) \cdot \cdot \cdot O(1)$	0.83(3)	1.89(3)	2.713(2)	170(3)
$O(4) - H(4) \cdot \cdot \cdot O(1)$	0.84(4)	1.85(4)	2.689(2)	174(4)
$O(5) - H(3) \cdot \cdot \cdot O(4)$	0.789(10)	2.145(15)	2.887(2)	157(3)
$O(5) - H(7) \cdot \cdot \cdot O(2)$	0.95(3)	1.64(3)	2.584(2)	175(3)
$O(6) - H(5) \cdot \cdot \cdot O(2)$	0.91(3)	1.81(3)	2.711(2)	173(3)
$O(6) - H(6) \cdot \cdot \cdot O(3)$	0.89(3)	1.88(3)	2.723(2)	159(3)

Table 6. Bond-valence calculations for raisaite*.

	Te	Cu	Mg	\sum	H-bonding	Σ
O(1)	1.03 ^{x2↓}	$0.45^{x2\downarrow}_{-2\downarrow}$		1.48	+0.22(O(4)) + 0.23(O(4))	1.93
O(2)	$1.00^{\text{ x2}}$	$0.49^{x_{2\downarrow}}$		1.49	+0.30(O(5)) + 0.22(O(6))	2.01
O(3) = OH	0.94 ^{x2↓}			0.94	-0.17(O(5)) + 0.21(O(6))	0.98
$O(4) = H_2O$			0.34 ^{x2↓}	0.34	-0.22(O(1)) - 0.23(O(1)) + 0.16(O(5))	0.05
$O(5) = H_2O$			$0.35^{x2\downarrow}$	0.35	+0.17(O(3)) - 0.16(O(4)) - 0.30(O(2))	0.06
$O(6) = H_2O$		0.05 ^{x2↓}	0.35 ^{x2↓}	0.40	-0.22(O(2)) - 0.21(O(3))	-0.03
Σ	5.94	1.98	2.08			

*Bond-valence parameters are taken from Brese & O'Keeffe (1991) for Cu–O and Mg–O, from Mills & Christy (2013) for Te–O and from Ferraris & Ivaldi (1988) for hydrogen bonding.



Fig. 6. A "layer" formed by heteropolyhedral chains in the crystal structure of raisaite (a) and the structure projected along the c axis (b). Small black circles are hydrogen atoms. The unit cell is outlined.

selected interatomic distances in Table 4, H-bond geometry in Table 5 and bond-valence calculations in Table 6.

Crystal structure: description and discussion

The crystal structure of raisaite (Fig. 6) is unique. It is based on heteropolyhedral zig-zag chains running along the *c* axis and built by alternating edge-sharing, almost regular Te⁶⁺-centred TeO₄(OH)₂ octahedra and Cu²⁺centred CuO₄(H₂O)₂ octahedra significantly distorted due to the Jahn-Teller effect (four short Cu–O distances in the range 1.940–1.977 Å and two elongated Cu–O bonds of 2.781 Å; Table 4). Regular Mg(H₂O)₆ octahedra are connected to the chains from two sides *via* common O(6) vertices. Adjacent chains are bound by hydrogen bonding forming "layers" coplanar to the *bc* plane (Fig. 6a). The "layers" are connected with each other by a system of hydrogen bonds (Table 5). This is a reason to assume (100) as the cleavage plane.

The hexavalent state of tellurium is undoubtedly confirmed by the octahedral coordination of Te, typical for tellurates but not for tellurites, with Te–O distances varying from 1.903 to 1.954 Å (Table 4), and by the bondvalence calculations (Table 6). This is also in a good agreement with the IR spectrum (see above).

Among minerals the octahedral anion $[TeO_4(OH)_2]^{4-}$ was reported in frankhawthorneite, Cu₂[Te⁶⁺O₄(OH)₂] (Grice & Roberts, 1995), and mojaveite, $Cu_6[Te^{6+}O_4(OH)_2](OH)_7Cl$ (Mills et al., 2014). In the structure of housleyite, Pb₆CuTe₄O₁₈(OH)₂, one of two crystallographically nonequivalent Te^{6+} sites centres a $TeO_5(OH)$ octahedron (Kampf et al., 2010). Among synthetic copper tellurates the chains formed by edge-sharing CuO4 squares and $TeO_4(OH)_2$ octahedra were reported in K_2 {Cu[TeO₄ $(OH)_2$] \cdot H₂O (Effenberger & Tillmanns, 1993) and groups formed by Cu³⁺O₄ square connected via common edges with two $TeO_4(OH)_2$ octahedra were described in Na₅{Cu[TeO₄(OH)₂]₂} · 16H₂O (Levason *et al.*, 1988; Al Ansari et al., 2007).

After leisingite, $(Cu,Mg)_2(Mg,Fe)Te^{6+}O_6 \cdot 6H_2O$ (Roberts *et al.*, 1996; Margison *et al.*, 1997), raisaite is the second mineral with species-defining Cu, Mg and Te. These two natural tellurates have different stoichiometry and are quite different in terms of crystal structure but in both minerals Cu^{2+} is slightly substituted by Mg. For raisaite it is confirmed by both electron-probe data and the refined scattering value (e_{ref}) for the Cu site (Table 3).

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