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Hloušekite, $(Ni,Co)Cu_4(AsO_4)_2(AsO_3OH)_2(H_2O)_9$, a new member of the lindackerite supergroup from Jáchymov, Czech Republic

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ABSTRACT

Hloušekite, $(Ni,Co)Cu_4(AsO_4)_2(AsO_3OH)_2(H_2O)_9$, is a new supergene arsenate mineral from the Geister vein (Rovnost mine), Jáchymov (St Joachimsthal), Western Bohemia, Czech Republic. It was found along with veselovskýite, pradetite, lavendulan, arsenolite, babánekite and gypsum on the surface of strongly altered ore fragments containing dominant tennantite and chalcopyrite. Hloušekite forms thin, lath-like crystals, locally elongated reaching up to 3 mm across. It is transparent, has a pale green colour with vitreous lustre, has a greyish-white streak and it is very brittle with an uneven fracture. It does not fluoresce under shortwave or longwave ultraviolet radiation. Cleavage on {010} is perfect; the Mohs hardness is 2–3. The calculated density is 3.295 g cm^{-3}. Hloušekite is optically biaxial with $\alpha' = 1.653(2)$ and $\gamma' = 1.73$. The estimated optical orientation is γ' *vs.* elongation (**c**) = 14(1)º. In larger grains it is weakly to moderately pleochroic (α = colourless, γ = pale green to green). Hloušekite is triclinic, space group $P\bar{1}$, $a = 6.4010(6)$, $b = 8.0041(6)$, $c = 10.3969(14)$ Å, $\alpha = 85.824(8)$, $\beta = 79.873(9)$, $\gamma = 84.655(7)$º and $V = 521.23(10)$ Å^3, with $Z = 1$, a:b:c = 0.800:1:1.299. The eight strongest lines in the powder X-ray diffraction (XRD) pattern [d in Å (I)(hkl)] are 10.211(100)(001), 7.974(9)(010), 3.984(6)(020), 3.656(5)(1$\bar{1}$2), 3.631(5)(0$\bar{2}$1), 3.241(5)(022), 3.145(5)(200) and 3.006(5)(210). Chemical analysis by electron microprobe yielded MgO 0.20, FeO 0.10, NiO 5.79, CoO 1.80, CuO 29.53, ZnO 0.66, Al_2O_3 0.14, P_2O_5 0.11, As_2O_5 45.01, H_2O 17.71 (calc.), for a total of 101.05 wt.%. The resulting empirical formula, calculated by stoichiometry ($9H_2O + 2OH$), obtained from the crystal structure, is $(Ni_{0.79}Co_{0.25})_{\Sigma 1.04}(Cu_{3.78}Zn_{0.08}Mg_{0.05}Al_{0.03}Fe_{0.01})_{\Sigma 3.95}(AsO_4)_{1.98}(PO_4)_{0.02}(AsO_3OH)_{2.00}(H_2O)_{9.00}$. The ideal endmember formula, $NiCu_4(AsO_4)_2(AsO_3OH)_2(H_2O)_{9.00}$, requires NiO 7.23, CuO 30.81, As_2O_5 44.51, H_2O 17.45, total 100.00 wt.%. The crystal structure of hloušekite was solved by charge flipping from single-crystal XRD data and refined to $R_1 = 0.0599$ for 1441 reflections with [$I_{obs} > 3\sigma(I)$]. Hloušekite is a new member of the lindackerite group (also including lindackerite, pradetite and veselovskýite) of the lindackerite supergroup. The ondrušite group of the lindackerite supergroup includes ondrušite, chudobaite, geigerite and klajite. The establishment of these two groups reflects the difference between the crystal structures of their members, mainly in the coordination environment of the *Me* cations.

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Keywords: hloušekite, new mineral, arsenate, lindackerite supergroup, lindackerite group, ondrušite group, crystal structure.

Introduction

The lindackerite supergroup, established here following the procedures of Mills *et al*. (2009), unifies triclinic hydrated arsenates with the generalized structural formula $MeM_4(AsO_4)_2(AsO_3OH)_2(H_2O)_{9-10}$, where *Me* and *M* sites are occupied by different divalent metal ions. To date, seven members of this supergroup have been reported. Five of them have the *M* position (consisting of two sites *M*1 and *M*2) occupied fully by Cu. These are lindackerite *sensu stricto* (Vogl, 1853; Sarp and Dominik, 1995; Hybler *et al*., 2003), pradetite (Sarp and Dominik, 1995; Burke *et al*., 2007), veselovskýite (Sejkora *et al*., 2010), ondrušite (Sejkora *et al*., 2011*b*) and klajite (Szakáll *et al*., 2011). The difference between them lies in the occupation and coordination of the *Me* site, which is dominated in the above-mentioned minerals by Cu, Co, Zn, Ca and Mn, respectively. Chudobaite (Strunz, 1960; Dorner and Weber, 1976) has both *Me* and *M* sites occupied by Mg and partially by Zn, while in geigerite (Graeser *et al*., 1989) both *Me* and *M* positions are occupied fully by Mn.

In this paper we report the description and characterization of the new mineral hloušekite, ideally $NiCu_4(AsO_4)_2(AsO_3OH)_2(H_2O)_9$, the Ni-Cu dominant member of the lindackerite supergroup, found in the Rovnost mine, Jáchymov, Czech Republic.

The new mineral honours Dr Jan Hloušek (born 10 March, 1950 in Karlovy Vary, Western Bohemia, died 27 April 2014, Jáchymov, Western Bohemia), a prominent Czech mineralogist and famous collector of Jáchymov minerals. Thanks in part to his collecting and scientific efforts, Jáchymov has become one of the richest localities, in terms of the number of discovered and well-described mineral species (more than 420), and is considered accordingly as one of the classic mineral deposits in the World. Dr Hloušek discovered and co-authored descriptions of many new minerals from Jáchymov including adolfpateraite, agricolaite, babánekite, běhounekite, čejkaite, mathesiusite, metarauchite, pseudojohannite, slavkovite, štěpite, švenekite and vysokýite. It should be noted especially that one of the members of the lindackerite supergroup, ondrušite, was also collected and studied by him.

The new mineral and its name were approved by the IMA-CNMNC (IMA 2013-048). The type specimen is deposited in the collections of the Department of Mineralogy and Petrology of the National Museum in Prague, Cirkusová 1740, Praha 9, Czech Republic, catalogue number P1P 3/2013.

Occurrence

The Jáchymov ore district (Western Bohemia, Czech Republic) is a classic example of Ag-As-Bi-Co-Ni-U hydrothermal vein-type mineralization (Ondruš *et al*., 2003). The ore-bearing veins cut medium-grade metasedimentary rocks of Cambrian to Ordovician age that surround a Variscan granitic pluton. The majority of the primary ore minerals were deposited from mesothermal fluids during Variscian mineralization processes. During the last decade, mineralogical research on minerals from Jáchymov has been focused mainly on supergene minerals formed in the conditions prevailing in abandoned mine adits (e.g. Ondruš *et al*., 1997, 2013; Plášil *et al*., 2010, 2013*a*,*b*,*c*, 2014*a*,*b*; Sejkora *et al*., 2013) or in the oxide zone (e.g. Sejkora *et al*., 2011*a*,*b*, 2012).

Hloušekite was found by one of the authors (PŠ) in old workings located on the Geister vein on the 3rd Geister level in the Rovnost (formerly Werner) mine, Jáchymov (50º22′18.527″N, 12º53′32.635″E). It occurs as a constituent of the coatings on altered surfaces of the highly oxidized ore-bearing samples along with other supergene As-bearing minerals such as veselovskýite, pradetite, lavendulan, arsenolite and babánekite. Specimens are also covered by ubiquitous crystals of gypsum. Hloušekite was formed by weathering in strongly acidic conditions of primary sulfides (tennantite and chalcopyrite) and Ni-Co-arsenides disseminated in a quartz gangue.

Physical and optical properties

Hloušekite occurs as thin, lath-like crystals, locally elongated, which usually form complex intergrowths and radial aggregates (Fig. 1) up to 3 mm across. Crystals are pale green with a vitreous lustre. Hloušekite has a greyish-white

FIG. 1. A hloušekite crystal aggregate (pale green) growing on matrix along with babánekite (pink), gypsum (colourless) and remnants of primary sulfides, probably tennantite (metallic, black). Field of view is 3 mm across; photo by Pavel Škácha.

streak and is very brittle with an uneven fracture. The Mohs hardness is estimated at 2–3. The mineral has a perfect cleavage on {010}. A density of 3.295 g cm^{-3} was calculated using the empirical formula and unit-cell parameters obtained from single-crystal XRD data. Density measurements were not undertaken due to the paucity of the pure material. Hloušekite is non-fluorescent under shortwave or longwave ultraviolet radiation. It is optically biaxial, with $\alpha' = 1.653(2)$, $\gamma' = 1.73$. The estimated optical orientation is γ' *vs.* elongation (**c**) = 14(1)°. The exact position of individual optical orientations related to refractive indices, as well as further optical properties were not determined due to intimate intergrowths of the crystals, the perfect cleavage on {010} and the very small size of the crystal fragments. Larger grains of hloušekite show weak to moderate pleochroism (α = colourless, γ = pale green to green). Due to incomplete optical data a Gladstone–Dale compatibility index (Mandarino, 1981) could not be calculated. The n_{mean} value calculated from the Gladstone–Dale compatibility index is 1.651 (for ideal compatibility).

TABLE 1. Chemical composition of hloušekite.

	Mean (n = 12)	Range	SD
MgO	0.20	0.13–0.24	0.04
FeO	0.10	0.00–0.42	0.15
NiO	5.79	5.06–6.47	0.44
CoO	1.80	1.46–2.17	0.19
CuO	29.53	27.79–31.24	1.10
ZnO	0.66	0.36–1.01	0.19
Al_2O_3	0.14	0.05–0.27	0.07
P_2O_5	0.11	0.05–0.20	0.05
As_2O_5	45.01	40.72–48.84	2.28
H_2O	17.71*		
Total	101.05		
Calculated by stoichiometry ($9H_2O$ + 2OH) obtained from the crystal structure			
Mg	0.05		
Fe	0.01		
Ni	0.79		
Co	0.24		
Cu	3.78		
Zn	0.08		
Al	0.03		
P	0.02		
As	3.98		
OH	2.00		
H_2O	9.00		

* Based on the theoretical content of $9H_2O$ + 2OH.

TABLE 2. Powder XRD data (d_{hkl} in Å) for hloušekite.*

I_{obs}	I_{calc}	d_{obs}	d_{calc}	h	k	l	I_{obs}	I_{calc}	d_{obs}	d_{calc}	h	k	l
100	100.00	10.211	10.194	0	0	1	1	2.19	2.2123	2.2123	0	2	4
9	11.56	7.974	7.967	0	1	0	<1	0.68	2.1627	2.1634	1	$\bar{3}$	2
1	0.83	6.290	6.282	1	0	0	1	0.92	2.0689	2.0689	3	1	0
3	4.06	6.089	6.090	0	$\bar{1}$	1	1	0.94	2.0607	2.0628	$\bar{2}$	$\bar{1}$	3
1	1.24	5.831	5.824	1	0	1	1	1.49	2.0444	2.0437	1	$\bar{2}$	4
4	5.47	5.139	5.135	1	1	0	1	1.06	2.0391	2.0389	0	0	5
1	1.80	5.088	5.097	0	0	2		1.43		2.0279	1	1	5
1	0.65	4.973	4.971	1	1	1	<1	0.98	2.0033	2.0024	2	$\bar{3}$	1
2	1.93	4.758	4.753	1	$\bar{1}$	0	1	1.79	1.9804	1.9789	0	4	1
2	3.26	4.476	4.473	1	$\bar{1}$	1	1	0.60	1.9565	1.9571	1	$\bar{3}$	3
2	1.28	4.425	4.425	0	1	2		0.61		1.9541	$\bar{3}$	$\bar{1}$	1
2	1.32	4.354	4.349	1	0	2	1	1.12	1.9501	1.9479	2	3	3
2	1.96	4.178	4.173	0	$\bar{1}$	2	1	1.22	1.9439	1.9436	1	4	0
2	0.91	4.170	4.160	$\bar{1}$	1	1	1	0.35	1.9145	1.9174	3	2	0
6	7.72	3.984	3.983	0	2	0	1	1.13	1.8984	1.8970	0	4	2
2	2.65	3.785	3.794	0	2	1	<1	0.18	1.8935	1.8921	1	2	5
5	3.59	3.656	3.652	1	$\bar{1}$	2	<1	0.31	1.8710	1.8694	$\bar{1}$	$\bar{4}$	1
5	8.99	3.631	3.632	0	$\bar{2}$	1	1	0.66	1.8662	1.8665	$\bar{2}$	2	3
1	1.25	3.494	3.492	1	2	0	1	1.43	1.8443	1.8442	$\bar{2}$	$\bar{3}$	2
4	5.63	3.397	3.398	0	0	3	<1	0.20	1.8105	1.8127	$\bar{1}$	1	5
1	1.97	3.324	3.323	$\bar{1}$	1	2	1	1.00	1.7887	1.8065	$\bar{3}$	$\bar{1}$	2
5	7.94	3.241	3.241	0	2	2		0.91		1.7871	$\bar{2}$	3	2
2	3.71	3.167	3.162	2	0	1	<1	0.46	1.7692	1.7687	0	4	3
5	7.15	3.145	3.141	2	0	0	1	0.81	1.7627	1.7634	2	2	5
1	0.85	3.110	3.111	1	1	3		1.22		1.7577	1	$\bar{2}$	5
2	5.98	3.062	3.062	0	2	2	<1	0.89	1.7423	1.7404	2	$\bar{3}$	3
4	5.50	3.053	3.056	0	$\bar{1}$	3	<1	0.94	1.7106	1.7101	1	1	6
5	1.14	3.006	3.005	2	1	0	1	1.04	1.6979	1.6956	3	$\bar{1}$	4
5	7.11	2.9181	2.9122	2	0	2	<1	0.46	1.6765	1.6740	3	$\bar{2}$	3
3	4.14	2.8979	2.8967	1	$\bar{1}$	3	<1	0.41	1.6625	1.6616	$\bar{2}$	2	4
3	6.64	2.8661	2.8637	$\bar{2}$	0	1	<1	1.51	1.6252	1.6238	1	$\bar{4}$	3
<1	0.96	2.7872	2.7889	1	$\bar{2}$	2	<1	0.21	1.6214	1.6207	0	4	4
4	7.73	2.6716	2.6714	0	2	3	<1	1.07	1.6078	1.6079	$\bar{1}$	$\bar{4}$	3
2	2.57	2.6576	2.6556	0	3	0	1	2.29	1.5972	1.5950	4	0	1
2	3.90	2.6483	2.6484	$\bar{1}$	1	3	<1	0.41	1.5918	1.5935	0	5	0
1	3.38	2.6206	2.6196	$\bar{1}$	$\bar{1}$	3	1	1.47	1.5578	1.5564	2	4	4
4	5.69	2.6102	2.6030	2	2	1	<1	1.14	1.5535	1.5541	$\bar{1}$	1	6
<1	0.85	2.5686	2.5677	2	2	0	<1	0.92	1.5302	1.5299	1	$\bar{2}$	6
2	3.54	2.5435	2.5395	2	0	3	<1	0.97	1.4847	1.4838	2	5	1
1	2.25	2.5344	2.5305	0	$\bar{3}$	1	1	0.94	1.4806	1.4797	0	5	3
1	0.34	2.5233	2.5238	1	3	1	<1	0.70	1.4516	1.4518	$\bar{3}$	$\bar{4}$	1
<1	1.07	2.5069	2.5068	0	$\bar{2}$	3	1	0.98	1.4207	1.4191	4	2	4
2	2.64	2.4859	2.4853	2	2	2	1	0.71	1.3793	1.3787	$\bar{3}$	$\bar{4}$	2
1	0.77	2.4724	2.4722	1	1	4	<1	0.61	1.3360	1.3357	3	3	6
1	0.95	2.4212	2.4198	0	3	2							
2	3.84	2.3787	2.3765	2	$\bar{2}$	0							
<1	0.66	2.2981	2.2954	0	$\bar{3}$	2							
1	2.20	2.2645	2.2626	$\bar{1}$	$\bar{2}$	3							

* 4–80º2θ (Cu*K*α radiation), step 0.0167º, 0.5 s per step; accumulation of 40 scans.

Chemical composition

The chemical composition of hloušekite (Table 1) was determined using a Cameca SX100 electron microprobe (wavelength dispersive spectroscopy mode, 15 kV, 10 nA and 5 μm beam diameter) from 12 point analyses. The following X-ray lines and standards were selected: $L\alpha$ line: As (lammerite); $K\alpha$ lines: P (fluorapatite), Al (sanidine), Zn (gahnite), Cu (lammerite), Co (metallic Co), Ni (synthetic Ni_2SiO_4), Fe (almandine), Mg (synthetic Mg_2SiO_4). Peak counting times were 10–20 s and the counting time for background was 50% of the peak. Measured intensities were processed for matrix effects using the '*PAP*' correction routine (Pouchou and Pichoir, 1985).

The empirical formula of hloušekite, based on the electron microprobe results, calculated by stoichiometry ($9H_2O$ + 2OH), obtained from the crystal structure, is $(Ni_{0.79}Co_{0.25})_{\Sigma 1.04}(Cu_{3.78}Zn_{0.08}Mg_{0.05}Al_{0.03}Fe_{0.01})_{\Sigma 3.95}(AsO_4)_{1.98}(PO_4)_{0.02}(AsO_3OH)_{2.00}(H_2O)_{9.00}$. The simplified formula, $NiCu_4(AsO_4)_2(AsO_3OH)_2(H_2O)_9$, requires NiO 7.23, CuO 30.81, As_2O_5 44.51, H_2O 17.45, total 100.00 wt.%.

Powder X-ray diffraction

Powder XRD data for hloušekite were collected on a PANanalytical Empyrean diffractometer with a Cu X-ray tube (operating at 45 kV, 40 mA) and a PIXcel detector and primary Göbel mirror, providing a focused beam for Debye–Scherrer geometry ($CuK\alpha_{1,2}$). Data are given in Table 2. The unit cell was refined using *Checkcell* software (LMPG suite of programs;

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

Structural formula	$(Ni_{0.75}Co_{0.25})_{\Sigma 1.00}Cu_4(AsO_4)_2(AsO_3OH)_2(H_2O)_9$
a, *b*, *c* (Å)	6.4010(6), 8.0041(6), 10.3969(14)
α, β, γ (°)	85.824(8), 79.873(9), 84.655(7)
V (Å^3)	521.23(10)
Space group	$P\bar{1}$
Z	1
$D_{calc.}$ (g cm^{-3}) for the above formula	3.225
Temperature	301 K
Wavelength	Mo$K\alpha$, 0.71073 Å
Crystal dimensions (mm)	0.30 × 0.14 × 0.06
Collection mode, frame width, count time	ω scans, 0.75°, 85 s
Limiting θ angles	3.15–26.37°
Limiting Miller indices	$-7 \leqslant h \leqslant 7$, $-9 \leqslant k \leqslant 9$, $-12 \leqslant l \leqslant 12$
No. of reflections measured	5597
No. of unique reflections	2031
No. of observed reflections (criterion)	1441 [$I_{obs} > 3\sigma(I)$]
Completeness, R_{int}	0.9986, 0.053
Absorption correction (mm^{-1}), T_{min}/T_{max}	Analytical (11.36), 0.248/0.657
F_{000}	476
Refinement by *Jana2006* on F^2	
Parameters refined, restraints, constraints	139, 0, 6
R_1, wR_2 (obs)	0.0599, 0.1146
R_1, wR_2 (all)	0.0849, 0.1215
Gof obs/all	2.07/1.82
$\Delta\rho_{min}$, $\Delta\rho_{max}$ (e Å^{-3})	−1.56, 2.31
Weighting scheme, weights	σ, $w = 1/(\sigma^2(F) + 0.0004F^2)$
Domain fractions 1, 2	0.96(2), 0.04(2)
Domain matrix	$\begin{pmatrix} 1 & 0.01 & 0.07 \\ 0 & 1 & -0.07 \\ -0.02 & 0.03 & 1 \end{pmatrix}$

TABLE 4. Atom coordinates and displacement parameters (U_{iso}/U_{eq}, in Å^2) for hloušekite.

	x/a	y/b	z/c	U_{iso}/U_{eq}	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
As1	0.42207(17)	0.38306(12)	0.36377(12)	0.0167(4)	0.0101(6)	0.0083(5)	0.0332(8)	−0.0020(4)	−0.0064(5)	−0.0026(5)
As2	0.07807(17)	1.01392(12)	0.66670(12)	0.0141(4)	0.0073(5)	0.0089(5)	0.0272(8)	−0.0043(4)	−0.0040(5)	−0.0018(5)
Cu1	0.1077(2)	0.63571(15)	0.55777(15)	0.0204(5)	0.0082(7)	0.0122(7)	0.0436(11)	−0.0033(5)	−0.0080(6)	−0.0087(6)
Cu2	−0.39958(19)	1.07595(15)	0.59897(14)	0.0166(5)	0.0072(7)	0.0141(7)	0.0299(10)	−0.0051(5)	−0.0047(6)	−0.0028(6)
Ni[#]	0	1	1	0.0209(7)	0.0140(11)	0.0202(11)	0.0299(15)	−0.0070(9)	−0.0045(10)	−0.0012(9)
Co[#]	0	1	1	0.0209(7)	0.0140(11)	0.0202(11)	0.0299(15)	−0.0070(9)	−0.0045(10)	−0.0012(9)
O1	0.1028(11)	1.0817(8)	0.8100(7)	0.016(3)	0.011(4)	0.014(4)	0.023(5)	−0.005(3)	−0.005(3)	0.002(3)
O2	0.5121(13)	0.5193(9)	0.2452(9)	0.031(3)	0.030(5)	0.013(4)	0.049(6)	−0.013(4)	−0.005(4)	0.005(4)
O3	0.0200(11)	0.8106(8)	0.6857(8)	0.019(3)	0.020(4)	0.009(4)	0.028(5)	−0.008(3)	−0.002(4)	−0.005(3)
O4W	−0.4981(11)	1.1610(8)	0.7730(7)	0.018(3)	0.012(4)	0.019(4)	0.025(5)	−0.010(3)	−0.003(3)	0.000(3)
O5	0.1788(11)	0.4381(8)	0.4483(7)	0.0185(17)*						
O6H	0.3854(12)	0.2044(8)	0.2876(8)	0.022(3)	0.020(4)	0.012(4)	0.037(6)	−0.003(3)	−0.009(4)	−0.010(3)
O7	−0.1128(11)	1.1340(8)	0.6028(7)	0.0157(16)*						
O8	0.3123(11)	1.0374(8)	0.5658(7)	0.0133(16)*						
O9	0.5896(11)	0.3268(8)	0.4672(8)	0.018(3)	0.009(4)	0.007(3)	0.040(6)	0.001(3)	−0.008(3)	−0.010(3)
O10W[$]	0.9555(19)	0.5388(12)	0.2006(13)	0.074(5)	0.067(8)	0.038(6)	0.126(12)	0.008(6)	−0.040(7)	−0.019(6)
O11W[$]	0.121(3)	0.7519(19)	0.9613(16)	0.030(4)*						
O12W[$]	0.551(3)	0.623(2)	0.983(2)	0.053(5)*						
O13W[$]	−0.280(3)	0.9400(19)	0.9468(17)	0.030(4)*						
O14W[$]	0.309(3)	0.872(2)	1.0016(18)	0.038(5)*						
O15W[$]	−0.102(3)	0.771(2)	0.9596(17)	0.036(4)*						

[#] During final cycles, occupancies were set to Ni = 0.75, Co = 0.25; [$]occupancies set to 0.5; * atom was refined with isotropic displacement parameters.

TABLE 5. Selected interatomic distances (in Å) in hloušekite.*

Cu1–O3	1.976(7)	Cu2–O4W	1.958(8)	O1–O3	2.743(11)	O4–O14W^{vii}	2.81(2)
Cu1–O5	1.988(7)	Cu2–O6H^{i}	2.460(7)	O1–O4W^{viii}	2.645(10)	O5–O5^{i}	2.500(9)
Cu1–O5^{i}	1.991(8)	Cu2–O7	1.943(7)	O1–O7	2.744(11)	O5–O6H	2.693(10)
Cu1–O7^{ii}	2.394(7)	Cu2–O8^{v}	1.990(7)	O1–O8	2.686(10)	O5–O9	2.732(10)
Cu1–O9^{iii}	1.958(7)	Cu2–O8^{ii}	1.966(7)	O1–O11W	2.977(17)	O5–O9^{iii}	2.780(11)
Cu1–O10W^{iii}	2.768(11)	Cu2–O9^{vi}	2.349(7)	O1–O11W^{vii}	2.896(17)	O6H–O9	2.742(12)
<*Cu1–Φ*>	2.18	<*Cu2–Φ*>	2.11	O1–O13W	2.894(17)	O6H–O13W^{i}	2.98(2)
				O1–O13W^{vii}	2.94(2)	O7–O8	2.726(9)
	Ni/Co–O1	2.049(7)		O1–O14W	2.924(19)	O7–O8^{ii}	2.837(11)
	Ni/Co–O1^{vii}	2.049(7)		O1–O15W^{vii}	2.75(2)	O7–O9^{vi}	2.842(10)
	Ni/Co–O11W	2.103(15)		O2–H–O4W^{ii}	2.546(10)	O8–O8^{x}	2.588(9)
	Ni/Co–O11W^{vii}	2.103(15)		O2–H–O5	2.812(10)	O8–O9^{iii}	2.956(9)
	Ni/Co–O13W	2.074(17)		O2–H–O6H	2.702(10)	O9–O9^{iii}	2.979(9)
	Ni/Co–O13W^{vii}	2.074(17)		O2–H–O9	2.774(11)	O11W–O12W	2.89(3)
	Ni/Co–O14W	2.142(17)		O2–H–O10W	2.811(14)	O11W–O13W	2.87(2)
	Ni/Co–O14W^{vii}	2.142(17)		O2–H–O12W^{ix}	2.77(2)	O11W–O14W	1.73(3)
	Ni/Co–O15W	2.099(17)		O2–H–O12W^{iii}	2.81(2)	O11W–O15W	1.42(2)
	Ni/Co–O15W^{vii}	2.099(17)		O3–O6H^{i}	2.574(10)	O12W–O12W^{xi}	2.12(3)
	<*Ni/Co–Φ*>	2.09		O3–O7	2.773(9)	O12W–O13W^{viii}	2.83(2)
				O3–O7^{ii}	2.963(11)	O12W–O14W	2.41(2)
As1–O2	1.647(8)	As2–O1	1.660(8)	O3–O8	2.799(9)	O12W–O15W^{viii}	2.58(3)
As1–O5	1.684(7)	As2–O3	1.693(7)	O3–O9^{iii}	2.886(9)	O13W–O13W^{xii}	2.94(2)
As1–O6H	1.737(8)	As2–O7	1.683(7)	O3–O10W^{iii}	2.967(12)	O13W–O14W^{v}	2.69(2)
As1–O9	1.660(8)	As2–O8	1.689(7)	O3–O15W	2.820(19)	O13W–O14W^{vii}	1.62(2)
<*As1–Φ*>	1.68	<*As2–Φ*>	1.68	O4–O7	2.772(9)	O13W–O15W	1.70(2)
				O4–O8^{v}	2.923(11)	O14W–O15W	2.94(3)
				O4–O13W	2.882(18)		

* Symmetry codes: (i) $-x, -y+1, -z+1$; (ii) $-x, -y+2, -z+1$; (iii) $-x+1, -y+1, -z+1$; (iv) $-x-1, -y+2, -z+1$; (v) $x-1, y, z$; (vi) $x-1, y+1, z$; (vii) $-x, -y+2, -z+2$; (viii) $x+1, y, z$; (ix) $x, y, z-1$; (x) $-x+1, -y+2, -z+1$; (xi) $-x+1, -y+1, -z+2$; (xii) $-x-1, -y+2, -z+2$.

Laugier and Bochu, 2003). The experimental powder pattern was indexed in accordance with the calculated values of intensities obtained from the crystal-structure refinement, based on the *Powder Cell* program (Kraus and Nolze, 1996).

Single-crystal X-ray diffraction

A short prismatic to tabular crystal of hloušekite, with dimensions 0.30 mm × 0.14 mm × 0.06 mm, was selected for the diffraction experiment on an Oxford Diffraction Gemini single-crystal, four-circle diffractometer. Graphite-monochromatized Mo*K*α radiation (λ = 0.71073 Å) from a conventional sealed X-ray tube, collimated with a fibre optics Mo-Enhance collimator was detected with an Atlas CCD detector. According to the diffraction data, hloušekite is triclinic, $P\bar{1}$, with a = 6.4010(6), b = 8.0041(6), c = 10.3969(14) Å, α = 85.824(8), β = 79.873(9), γ = 84.655(7)º and V = 521.23(10) Å^3, with Z = 1. From the 5597 collected reflections, 2031 were unique and 1441 were classified as observed using the criterion $I_{obs} > 3\sigma(I)$. Data were corrected for background, Lorentz and polarization effects. A combined absorption correction [multi-scan and analytical after Clark and Reid (1995)] was applied to the data (*CrysAlis RED*; Agilent Technologies, 2012), leading to R_{int} = 0.0530. Details of data collection and refinement are given in Table 3. The structure of hloušekite was solved independently to confirm the earlier structure models given by Hybler *et al.* (2003) for lindackerite. The charge-flipping algorithm (Oszlányi and Sütő, 2004, 2008; Palatinus, 2013), implemented in the *Superflip* program (Palatinus and Chapuis, 2007), was used for the structure solution. The structure was refined subsequently using full-matrix least-squares on F^2 with the *Jana2006* program (Petříček *et al.*, 2006, 2014). The structure solution obtained from *Superflip* confirmed the chosen space group $P\bar{1}$. Bond-valence analysis was performed following the procedure of Brown (1981, 2002). A twinning matrix was introduced into the refinement by *Jana2006* to detect fully overlapped, partially separated and fully separated reflections. The matrix, as well as the ratio, of particular twin domains is given in Table 3. All atoms were found by the structure solution except the O atoms of the disordered H_2O groups coordinated to the M^{2+} bridging octahedron, which were localized from difference-Fourier maps. Hydrogen atoms were not located. All atoms, except for these, which belong to the disordered H_2O groups, were refined with anisotropic displacement parameters. Refinement including 139 parameters converged to R_1 = 0.0599 for 1441 unique observed reflections (Table 3). Final atom coordinates and displacement parameters are given in Table 4. Selected interatomic distances are listed in Table 5. The bond-valence analysis is given in Table 6.

Crystal structure of hloušekite

The structure of hloušekite is shown in Fig. 2. Coordination polyhedra with refined bond lengths

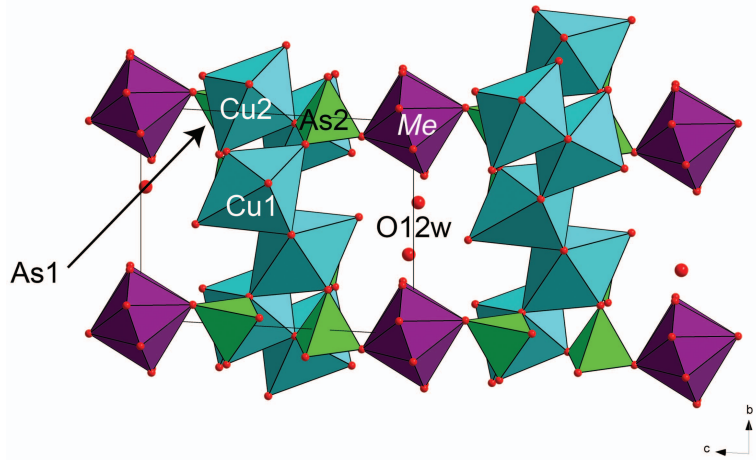

FIG. 2. The hloušekite crystal structure viewed along [100]. Adjacent sheets of $Cu^{2+}\Phi_6$ polyhedra (blue) and AsO_4/AsO_3OH tetrahedra (green) are linked *via Me* (Ni/CoΦ_{10}) polyhedra (violet) in the interlayer, along with the H_2O group (O12w) not bonded directly to any cation.

TABLE 6. Bond-valence analysis for hloušekite.

	Cu1	Cu2	As1	As2	Ni*	Co*	ΣBV	Assignment
O1				1.34	$0.73^{\times 0.75\rightarrow}$	$0.76^{\times 0.25\rightarrow}$	2.07	O
O2			1.38				1.38	O#
O3	0.45			1.22			1.67	O#
O4W		0.47					0.47	H_2O
O5	0.86		1.25				2.11	O
O6H		0.12	1.08				1.20	OH
O7	0.14	0.49		1.25			1.88	O
O8		0.89		1.23			2.12	O
O9	0.47	0.16	1.34				1.97	O
O10W*	0.05						0.05	H_2O
O11W*					$0.31^{\times 0.75\rightarrow}$	$0.33^{\times 0.25\rightarrow}$	0.32	H_2O
O12W							0.00	H_2O
O13W*					$0.34^{\times 0.75\rightarrow}$	$0.36^{\times 0.25\rightarrow}$	0.28	H_2O
O14W*					$0.28^{\times 0.75\rightarrow}$	$0.30^{\times 0.25\rightarrow}$	0.29	H_2O
O15W*					$0.33^{\times 0.75\rightarrow}$	$0.33^{\times 0.25\rightarrow}$	0.26	H_2O
ΣBV	1.97	2.13	5.05	5.04	1.98	2.08		

All values are in valence units (vu). * Site occupancies taken into account in calculations. # These terminal O atoms of the As tetrahedra are acceptors of the H bond. Bond-valence parameters for Cu^{2+}–O, Co^{2+}–O and As^{5+}–O were taken from Brown and Altermatt (1985), for Ni^{2+}–O from I.D. Brown (pers. comm. 2013).

are shown in Fig. 3. Hloušekite is isostructural with lindackerite. The final model obtained is similar to that provided for lindackerite by Hybler *et al.* (2003). In terms of similarity calculated by *COMPSTRU* (Tasci *et al.*, 2012), the degree of lattice distortion (Capillas *et al.*, 2007) S = 0.0038. The arithmetic mean of the distances of paired (symmetrically equal) atoms in compared structures (Orobengoa *et al.*, 2009) d_{av} = 0.0576 Å; the measure of similarity (Bergerhoff *et al.*, 1999) Δ = 0.016. As the structure of lindackerite is known it is not repeated here. Based on final structure

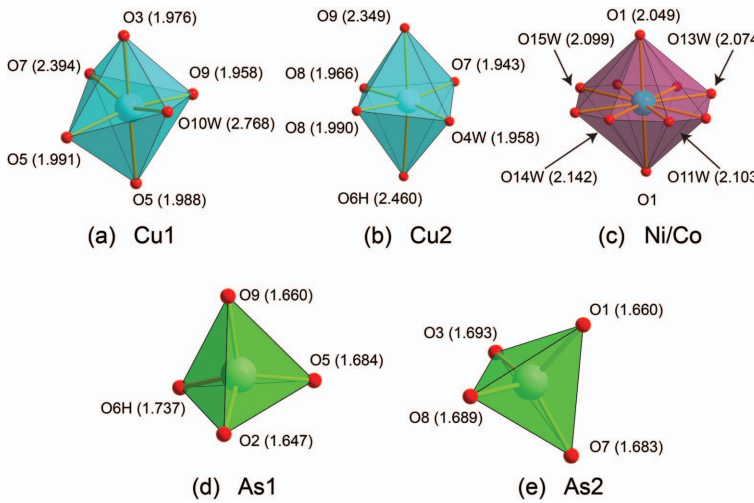

FIG. 3. Coordination polyhedra in the structure of hloušekite; (*a*) Cu(1); (*b*) Cu(2); (*c*) Ni/Co, (*d*) As1, (*e*) As2. Red circles: ligands including O^{2-} anions, OH^- group (O6H) or (H_2O) groups (W). Interatomic distances are shown in parentheses (in Å).

TABLE 7. Overview of the lindackerite supergroup mineral members.

Lindackerite group

	Hloušekite Jáchymov This work	Lindackerite Jáchymov Sarp and Dominik (1995)	Lindackerite Jáchymov Hybler *et al.* (2003)	Pradetite Cap Garonne Sarp and Dominik (1995); Burke *et al.* (2007)	Veselovskýite Jáchymov Sejkora *et al.* (2010)
*M**	Cu	Cu	Cu	Cu	Cu
*Me** (ideal)	Ni	Cu	Cu	Co	Zn
*Me** (meas.)	$Ni_{0.79}Co_{0.25}$	$Cu_{0.78}Co_{0.18}Ni_{0.07}$	$Cu_{0.79}-Cu_{0.95}$	$Co_{0.46}Cu_{0.18}$	$Zn_{0.43}Cu_{0.24}Co_{0.13}$
*n**	9	10	9	10	9
Crystal system	triclinic	triclinic	triclinic	triclinic	triclinic
Space group	$P\bar{1}$	$P\bar{1}$ or $P1$	$P\bar{1}$	$P\bar{1}$ or $P1$	$P\bar{1}$
a	6.4010(6)	6.453(2)	6.415–6.440	6.434(5)	6.4022(4)
b	8.0041(6)	8.035(2)	8.048–8.065	8.059(5)	8.0118(4)
c	10.397(1)	10.368(4)	10.332–10.411	10.399(8)	10.3665(4)
α	85.824(8)	86.17(3)	85.41–85.44	85.70(6)	85.491(3)
β	79.873(9)	79.60(3)	79.38–79.50	79.41(7)	79.377(4)
γ	84.655(7)	84.83(3)	84.65–84.71	84.87(7)	84.704(5)
V	521.2(1)	525.9(2)	521.2–528.1	526.9(7)	519.34(4)
Z	1	1	1	1	1
Selected lines in X-ray powder pattern	10.211/100 7.974/9 3.984/6 3.656/5 3.397/4 3.241/5	10.2/100 8.02/70 4.001/40 3.668/60 3.399/25 3.264/30		10.2/100 8.01/60 4.001/50 3.667/60 3.404/35 3.258/30	10.185/100 7.974/15 3.987/16 3.637/15 3.395/24 3.238/16

Ondrušite group

	Ondrušite	Geigerite	Chudobaite	Klajite	Klajite
	Jáchymov Sejkora *et al.* (2011*b*)	Fallota Graeser *et al.* (1989)	Tsumeb Strunz (1960); Dorner and Weber (1976)	Recsk Szakáll *et al.* (2011)	Jáchymov Plášil *et al.* (2014)
*M**	Cu	Mn	Mg	Cu	Cu
*Me** (ideal)	Ca	Mn	Zn?	Mn	Mn
*Me** (meas.)	$Ca_{0.92}Co_{0.01}Pb_{0.01}$	Mn	Zn?	$Mn_{0.82}Cu_{0.10}$ $Ca_{0.08}$	$Mn_{0.46}Ca_{0.22}$ $Cu_{0.07}Mg_{0.02}$
*n**	10	10	10	9	10
Crystal system	triclinic	triclinic	triclinic	triclinic	triclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a	6.432(1)	6.770(1)	6.616	6.441(3)	6.4298(8)
b	7.986(1)	7.944(1)	7.797	7.983(4)	7.9716(8)
c	10.827(1)	10.691(1)	10.485	10.562(3)	10.707(2)
α	85.75(1)	81.85(1)	82.12	85.28(4)	85.737(12)
β	81.25(1)	80.97(1)	80.53	80.63(5)	80.994(13)
γ	85.04(1)	84.20(1)	84.23	84.80(4)	84.928(10)
V	546.6(1)	560.3(1)	526.8	532.4(3)	538.85(14)
Z	1	1	1	1	1
Selected lines in X-ray powder pattern	10.671/100 7.934/7 3.970/10 3.648/11 3.438/3 3.286/10	10.45/100 7.85/13 3.92/9 3.837/9 3.507/21 3.340/20	10.163/100 7.694/30 4.058/40 3.746/50 3.440/80 3.273/80	10.39/100 7.95/22 3.956/27 3.786/12 3.479/17 3.264/16	

* *M*, *Me*, *n* for the formula: $MeM_4(AsO_4)_2(AsO_3OH)_2 \cdot nH_2O$ (*M** = *M*1 and *M*2 position; *Me** = *M*3 position in the crystal structure).

refinement and the bond-valence analysis (Table 6), the structural formula of hloušekite is $(Ni_{0.64}Co_{0.36})_{\Sigma 1.00}Cu_4(AsO_4)_2(AsO_3OH)_2(H_2O)_9$.

The lindackerite supergroup of minerals: nomenclature issues

The present description of hloušekite increases the number of minerals in the lindackerite supergroup to eight. Sejkora *et al.* (2011*b*) proposed "two subgroups (or two series) inside the lindackerite group", but based on the general nomenclature rules given by Mills *et al.* (2009), the "lindackerite group" of Sejkora *et al.* (2011*b*) is renamed here as the lindackerite supergroup and the "subgroups" of Sejkora *et al.* (2011*b*) as groups. Following this, we establish here the lindackerite supergroup as unifying two groups, the lindackerite group and the ondrušite group. The difference between the two groups reflects differences in the crystal structures of their members. The lindackerite group includes lindackerite, pradetite, veselovskýite and hloušekite. The ondrušite group includes ondrušite, chudobaite, geigerite and klajite. The structure of the Mn-Cu-dominant member klajite has been studied recently using material originating from Jáchymov (Plášil *et al.*, 2014*a*) and the study proved its structural equality with ondrušite (Sejkora *et al.*, 2011*b*). Thus we include it here in the ondrušite group of the lindackerite supergroup. A general comparison of all members of the lindackerite supergroup is given in Table 7, based on available data from the literature and the current study. Note that chudobaite, being interpreted by Graeser *et al.* (1989) as the Mg-Zn analogue of geigerite (and geigerite as the Mn analogue of chudobaite), is much more similar in unit-cell metrics to the members of the first group. Unit-cell volumes of members of the lindackerite group range around ~520 $Å^3$, while ondrušite group members have larger unit cells, ~540 to 560 $Å^3$. Therefore, we suggest that the re-investigation of the chudobaite structure would be an important task and might lead to changes in the proposed nomenclature of the lindackerite supergroup.

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