МИНЕРАЛОГИЧЕСКАЯ КРИСТАЛЛОГРАФИЯ

$K_4Cu^{2+}Cu_2^+Cl_8 \cdot 2H_2O$: A NOVEL NON-CENTROSYMMETRIC MIXED-VALENT COPPER COMPOUND AND ITS RELATION TO MINERALS

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Reddish-brown crystals of $K_4Cu^{2+}Cu_2^+Cl_8 \cdot 2H_2O$ were prepared by chemical transport reactions. The crystal structure was solved using single-crystal diffraction data ($a = 9.0472(5)$, $b = 11.5591(4)$, $c = 9.1786(5)$ Å, $\beta = 118.692(7)°$, $V = 842.01(9)$ Å^3) and refined to $R_1 = 0.039$ for 4369 independent observed reflections. The crystal structure consists of the $\left[Cu^{2+}Cu_2^+Cl_8 \right]^{4-}$ anionic chains extended along the a axis and linked through the K$^+$ ions and H$_2$O molecules. There are three Cu sites in the title compound. The Cu1 and Cu3 sites are occupied by monovalent Cu$^+$ ions and coordinated tetrahedrally by four Cl atoms each with the Cu−Cl bond lengths in the range 2.309−2.441 Å. The (Cu1Cl$_4$) and (Cu3Cl$_4$) tetrahedra share Cl⋯Cl edge to form a (Cu$_2$Cl$_6$) dimer with relatively short Cu⋯Cu intermetallic distance of 2.585 Å. However, the theoretical analysis of the electron-density distribution shows the absence of bonding interaction between the adjacent Cu centers. The dimers are linked into 1D chains through the Cu$_2$ atoms in an octahedral coordination. According to its coordination geometry and bond-valence calculations, the Cu2 site is occupied by Cu^{2+} ions. The K1 and K2 sites are coordinated by seven Cl atoms each to form (KCl$_7$) capped trigonal prisms. In contrast, the K3 and K4 sites have a bicapped trigonal prismatic coordination by six Cl atoms and two H$_2$O groups. The $\left[Cu^{2+}Cu_2^+Cl_8 \right]^{4-}$ chains are linked via K−Cl and K−H$_2$O interactions as well as by H$_2$O⋯Cl hydrogen bonds. The non-centrosymmetricity of the overall structure is the result of the shift of the adjacent chains relative to each other in the direction parallel to the a axis. The title compound is chemically close to avdoninite, $K_2Cu_5Cl_8(OH)_4 \cdot 2H_2O$, mitscherlichite, $K_2CuCl_4 \cdot 2H_2O$, and romanorlovite, $K_{11}Cu_9Cl_{25}(OH)_4 \cdot 2H_2O$. However, it differs from them in its mixed-valence character. The title compound possesses neither unusually high or unusually low complexity and thus its formation as a secondary phase in fumaroles corresponds to the typical level of complexity observed in this geochemical environment.

Keywords: copper, mixed valence, non-centrosymmetric compounds, volcanic fumaroles, structural complexity

1. INTRODUCTION

In the recent years, there have been an explosive interest to structural chemistry and properties of copper oxysalt minerals and their synthetic analogues, mostly due to the whole range of new mineralogical discoveries and continuing exploration of natural copper-based − compounds in solid state physics and material sciences (Botana et al., 2018; Inosov, 2018; Volkova, Marinin, 2018; Winiarski et al., 2019; Dey, Botana, 2020, etc.). The Tolbachik eruptions in the Kamchatka Peninsula, Far East, Russia, provided an unprecedented paragenetic suite of unique and variable copper mineralization with many new copper mineral species that have no analogues in synthetic material chemistry (Pekov et al., 2018). The K−Cu−Cl−H$_2$O system is of particular interest. Kahlenberg (2004) reported the synthesis of a new compound, K$_2$Cu$_5$Cl$_8$(OH)$_4$ · 2H$_2$O, prepared as a by-product in a hydrothermal experiment. The compound showed a remarkable similarity to avdoninite, a technogenic phase found in oxidation zones of sulfide deposits in Ural (Bushmakin, Bazhenova, 1998). In 2006, N.V. Chukanov and co-authors established the status of avdoninite as a separate mineral species based on its findings in Tolbachik fumaroles (Chukanov et al., 2006), whereas Pekov et al. (2015) demonstrated that the mineral is indeed a natural analogue of synthetic phase K$_2$Cu$_5$Cl$_8$(OH)$_4$ · 2H$_2$O first reported by Kahlenberg (2004). Owing to its unique structural architecture, avdoninite attracted attention as an interesting magnetic material (Volkova, Marinin, 2018). There are two other minerals in the K−Cu−Cl−H$_2$O system: mitscherlichite, K$_2$CuCl$_4$ · 2H$_2$O (Zambonini, Carobbi, 1925; Chidambaram et al., 1970), and romanorlovite, K$_{11}$Cu$_9$Cl$_{25}$(OH)$_4$ · 2H$_2$O (Pekov et al., 2016), both having a fumarolic origin. Herein we report the synthesis and structural characterization of K$_4$Cu^{2+}Cu$_2^+$Cl$_8$ · 2H$_2$O, a new compound in the K−Cu−Cl−H$_2$O system, which remarkably contains Cu ions in two oxidation states, Cu$^+$ and Cu^{2+}. It is worthy to note that the only known mineral with well-defined Cu$^+$ and Cu^{2+} ions is allochalcoselite, Cu$^+$Cu$_5^{2+}$PbO$_2$(SeO$_3$)$_2$Cl$_5$, which was also discovered in Tolbachik fumaroles (Vergasova et al., 2005; Krivovichev et al., 2006).

The mixed-valence Cu$^+$/Cu^{2+} systems are of particular attention in metal-organic chemistry, due to their interesting electrical, magnetic, luminescent, and catalytic properties (Tanaka et al., 2013; Nakatani et al., 2015; Vinogradova et al., 2016). 1D and 2D polymeric complexes of Cu$^+$ and Cu^{2+} ions are of special interest due to the possibility of delocalized electron density and cuprophillic Cu−Cu interactions. The title compound is indeed based upon 1D copper chains consisting of alternating Cu$^+$ and Cu^{2+} ions that may well communicate with each other along the extension of the chain.

2. EXPERIMENTAL

Single crystals of title compound were obtained as a by-product in our experiments using chemical vapor transport reactions (Binnewies et al., 2013) in the course of our study of the KCl−CuO−V$_2$O$_5$ system. Copper oxide (0.0397 g), vanadium oxide (0.0910 g) and potassium chloride (0.0370 g) in a 1 : 1 : 1 molar ration were ground in an agate mortar with further annealing of the mixture at 250 °C for 16 h in air. The mixture was loaded into a fused silica ampule (ca. 16 cm), which was evacuated to 10^{-2} mbar before sealing. The ampule was placed horizontally into two-zone furnace and heated to 675 °C within 4 h. The temperature gradient between the source and deposition zones of the ampule was ~50 °C. After 2 days the ampule was cooled to 200 °C over a period of 64 h and then the furnace was switched off. Reddish brown single crystals of the title compound were found in the deposition zone covered by bluish transparent crystals of synthetic analogue of eriochalcite, CuCl$_2$ · 2H$_2$O, in association with crystals of α- and β-Cu$_2$V$_2$O$_7$ phases. The probable cause for the presence of H$_2$O molecules in the title compound is a hygroscopic nature of potassium chloride used as a reagent in the synthesis.

Diffraction data for K$_4$Cu^{2+}Cu$_2^+$Cl$_8$(H$_2$O)$_2$ were collected using a using a Rigaku XtaLAB Synergy S X-ray diffractometer operated with monochromated microfocus MoKα tube (λ = = 0.71073 Å) at 50 kV and 1.0 mA, and equipped with a CCD HyPix 6000 detector. The frame width was 1.0° in ω, and a 190 s count time for each frame. A *CrysAlisPro* software (Agilent, 2014) was used for integration and correction of diffraction data for polarization, background and Lorentz effects. A Gaussian absorption correction was performed using a *CrysAlisPro* software on the basis of multifaceted crystal model. The unit-cell parameters were refined using the least-squares techniques. The structure was solved by a dual-space algorithm and refined as an inversion twin using the *SHELX* programs (Sheldrick, 2015a, b) incorporated in the *OLEX*2 program package (Dolomanov et al., 2009). The H atoms of H$_2$O molecules were located from the inspection of difference Fourier maps and were included in the refinement with U$_{iso}$(H) set to 1.5 U$_{eq}$(O) and an O−H bond length restrain of 0.98 Å. The final model includes coordinates and anisotropic displacement parameters.

The crystal data and experimental parameters of the X-ray diffraction experiment are given in Table 1, atom coordinates, and isotropic displacement parameters are provided in Table 2. Table 3 contains selected interatomic distances, whereas Table 4 provides information on the geometry of the hydrogen bonding system. Table 5 contains results of the bond-valence analysis (the bond-valence parameters for the Cu$^+$−Cl, Cu^{2+}−Cl, and K-φ bonds (φ = Cl, H$_2$O) were taken from Shields et al. (2000), Brese and O'Keeffe (1991), and Brown and Altermatt (1985), respectively.

In order to investigate electron-density distribution, the CRYSTAL14 software package was used to perform the solid-state DFT calculations (Dovesi et al., 2014). The Peintinger−Oliveira−Bredow split-valence triple-ζ (pob-TZVP) basis sets (Peintinger et al., 2013) were used for all atoms, along with the hybrid Becke-3−Lee−Yang−Parr (B3LYP) functional. The electron-density distribution function was calculated using experimentally observed geometries for each structure and analysed using the *TOPOND14* software (Gatti, Casassa, 2013) with respect to the properties of the bond critical points in electron density distributions and scalar fields of the electron-density Laplacian (Gatti et al., 1994).

3. RESULTS

The crystal structure of K$_4$Cu^{2+}Cu$_2^+$Cl$_8$ · 2H$_2$O is shown in Fig. 1. It consists of the [Cu^{2+}Cu$_2^+$Cl$_8$]$^{4-}$ anionic chains extended along the *a* axis and linked through the K$^+$ ions and H$_2$O molecules. The atomic structure of the chain is depicted in Fig. 2. There are three Cu sites in the title compound. The Cu1 and Cu3 sites are coordinated tetrahedrally by four Cl atoms each with the Cu−Cl bond lengths in the range 2.309−2.441 Å. The bond-valence calculations (Table 5) provide the bond-valence sums of 1.00 and 0.99 valence units (v. u.) for the Cu1 and Cu3 sites, respectively. The tetrahedral (Cu$^+$Cl$_4$) is quite typical for Cu$^+$ chloride compounds and was observed, for instance, in nantokite, CuCl (Pfitzner, Lutz, 1993), and synthetic CsCu$_2$Cl$_3$ (Meyer, 1984). The (Cu1Cl$_4$) and (Cu3Cl$_4$) tetrahedra share Cl···Cl edge to form a (Cu$_2$Cl$_6$) dimer with relatively short Cu···Cu intermetallic distance of 2.585 Å. The dimers are linked into 1D chains through the Cu2 atoms in an octahedral coordination (Fig. 2). The coordination is [4 + 2] distorted in accord with the Jahn-Teller effect (Jahn, Teller, 1937): there are four short (2.281−2.318 Å) and two long (3.118−3.125 Å) Cu2−Cl bonds. The bond-valence calculations indicate that the Cu2 site is occupied by Cu^{2+} ions.

There are four K sites in the crystal structure of K$_4$Cu^{2+}Cu$_2^+$Cl$_8$ · 2H$_2$O (Fig. 3). The K1 and K2 sites are coordinated by seven Cl atoms each to form (KCl$_7$) capped trigonal prisms. This type of coordination is one of the most common sevenfold coordination geometries in in-

Table 1. Crystal parameters, data collection and structure refinement parameters for $K_4Cu^{2+}Cu_2^+Cl_8 \cdot 2H_2O$

Таблица 1. Кристаллографические данные и экспериментальные параметры для $K_4Cu^{2+}Cu_2^+Cl_8 \cdot 2H_2O$

Crystal data	
Crystal system, space group	Monoclinic, $P2_1$
Temperature, K	296
a, b, c, Å	9.0472(5), 11.5591(4), 9.1786(5)
β, °	118.692(7)
V, Å^3	842.01(9)
Z	2
Radiation type	Mo$K\alpha$
μ, mm^{-1}	5.99
Crystal size, mm	$0.03 \times 0.02 \times 0.02$
Data collection	
Diffractometer	XtaLAB Synergy, Single source at home/near, HyPix 6000
Absorption correction	Gaussian
T_{min}, T_{max}	0.887, 0.922
No. of measured, independent and observed $[I > 2\sigma(I)]$ reflections	12 136, 5975, 4369
R_{int}	0.028
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.822
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.039, 0.071, 0.99
No. of reflections	5975
No. of parameters	168
No. of restraints	10
H-atom treatment	Only H-atom coordinates refined
$\Delta\rho_{max}, \Delta\rho_{min}$, e Å^{-3}	0.67, −0.88
Absolute structure	Refined as an inversion twin.
Absolute structure parameter	0.16(2)

Table 2. Fractional atomic coordinates and isotropic displacement parameters (Å^2) for K$_4$Cu^{2+}Cu$_2^+$Cl$_8\cdot$ 2H$_2$O

Таблица 2. Координаты и изотропные параметры смещения атомов (Å^2) для кристаллической структуры K$_4$Cu^{2+}Cu$_2^+$Cl$_8\cdot$ 2H$_2$O

Atom	x	y	z
Cu1	0.74117(8)	0.49791(9)	0.77334(9)
Cu2	0.37857(8)	0.50456(7)	0.74706(8)
Cu3	−0.00166(8)	0.50831(8)	0.72279(8)
K1	0.07086(17)	0.80483(11)	0.63697(17)
K2	0.17752(18)	0.19545(11)	0.86180(17)
K3	0.32459(16)	0.67572(12)	0.15181(18)
K4	0.42644(17)	0.33561(11)	0.34474(18)
Cl1	0.74272(16)	0.43600(12)	1.01326(15)
Cl2	0.47748(14)	0.56320(11)	0.56863(14)
Cl3	0.43029(18)	0.68574(12)	0.85923(18)
Cl4	0.32874(18)	0.32184(12)	0.63716(18)
Cl5	0.27224(14)	0.45195(10)	0.92242(14)
Cl6	0.00847(15)	0.56290(11)	0.48192(15)
Cl7	−0.17460(18)	0.33933(12)	0.65841(19)
Cl8	−0.07767(18)	0.66796(13)	0.84151(19)
O1	0.5959(4)	0.5097(5)	0.2709(5)
H1A	0.614(7)	0.466(6)	0.193(6)
H1B	0.708(3)	0.532(6)	0.349(6)
O2	0.1534(4)	0.4946(5)	0.2217(5)
H2A	0.139(6)	0.500(6)	0.319(4)
H2B	0.045(4)	0.472(6)	0.139(5)

Table 3. Selected interatomic distances (Å) for $K_4Cu^{2+}Cu_2^+Cl_8 \cdot 2H_2O$

Таблица 3. Избранные межатомные расстояния (Å) для $K_4Cu^{2+}Cu_2^+Cl_8 \cdot 2H_2O$

Cu1—Cl1	2.3091(15)	K2—Cl1^{v}	3.168(2)
Cu1—Cl2	2.3425(13)	K2—Cl3^{v}	3.230(2)
Cu1—Cl7^{i}	2.4136(17)	K2—Cl4	3.312(2)
Cu1—Cl8^{i}	2.4407(18)	K2—Cl5	3.0622(19)
⟨Cu1—Cl⟩	2.377	K2—Cl6^{vi}	3.1677(19)
		K2—Cl7	3.269(2)
Cu2—Cl2	2.3129(14)	K2—Cl8	3.270(2)
Cu2—Cl3	2.2809(18)	⟨K2—Cl⟩	3.211
Cu2—Cl4	2.2901(17)		
Cu2—Cl5	2.3179(14)	K3—Cl1^{vii}	3.291(2)
Cu2—Cl1	3.118(2)	K3—Cl2	3.6277(19)
Cu2—Cl6	3.125(2)	K3—Cl3^{viii}	3.257(2)
⟨Cu2—Cl⟩	2.574	K3—Cl4^{vii}	3.257(2)
		K3—Cl5^{viii}	3.2234(19)
Cu3—Cl5	2.3586(13)	K3—Cl7^{iv}	3.2745(18)
Cu3—Cl6	2.3429(14)	K3—Cl8^{viii}	3.378(2)
Cu3—Cl7	2.3926(17)	K3—O1	2.885(5)
Cu3—Cl8	2.4053(17)	K3—O2	2.854(5)
⟨Cu2—Cl⟩	2.375		
		K4—Cl2^{ix}	3.262(2)
K1—Cl1^{iii}	3.2017(19)	K4—Cl2	3.2321(19)
K1—Cl3	3.203(2)	K4—Cl3^{ix}	3.2429(19)
K1—Cl4^{iv}	3.272(2)	K4—Cl4	3.208(2)
K1—Cl6^{iv}	3.1389(19)	K4—Cl5^{viii}	3.6862(18)
K1—Cl6	3.0647(19)	K4—Cl7^{i}	3.368(2)
K1—Cl7^{iv}	3.291(2)	K4—Cl8^{vi}	3.3845(19)
K1—Cl8	3.202(2)	K4—O1	2.804(6)
<K1—Cl>	3.196	K4—O2	2.842(5)

Symmetry code(s): (i) $x + 1$, y, z; (ii) $x − 1$, y, z; (iii) $−x + 1$, $y + 1/2$, $−z + 2$; (iv) $−x$, $y + 1/2$, $−z + 1$; (v) $−x + 1$, $y − 1/2$, $−z + 2$; (vi) $−x$, $y − 1/2$, $−z + 1$; (vii) $−x + 1$, $y + 1/2$, $−z + 1$; (viii) x, y, $z − 1$; (ix) $−x + 1$, $y − 1/2$, $−z + 1$; (x) x, y, $z + 1$; (xi) $−x$, $y + 1/2$, $−z + 2$.

Table 4. Geometrical parameters of hydrogen bonding system for $K_4Cu^{2+}Cu_2^+Cl_8 \cdot 2H_2O^*$

Таблица 4. Геометрические параметры системы водородных связей для $K_4Cu^{2+}Cu_2^+Cl_8 \cdot 2H_2O^{**}$

D—H	D—H [Å]	H⋯A [Å]	D—H⋯A [°]	D⋯A [Å]	A
O1—H1A	0.96	2.42	156	3.325	Cl1
O1—H1B	0.95	2.41	162	3.335	Cl6
O2—H2A	0.96	2.42	156	3.325	Cl6
O2—H2B	0.94	2.44	157	3.331	Cl1

* **D** = donor; **A** = acceptor ** **D** = donor; **A** = acceptor

Table 5. Bond-valence analysis for K$_4$Cu^{2+}Cu$_2^+$Cl$_8 \cdot$ 2H$_2$O
Таблица 5. Анализ распределения валентностей связей для K$_4$Cu^{2+}Cu$_2^+$Cl$_8 \cdot$ 2H$_2$O

	Cu1	Cu2	Cu3	K1	K2	K3	K4	H1A	H1B	H2A	H2B	Σ
Cl1	0.30	0.05		0.16	0.17	0.12		0.2			0.2	1.20
Cl2	0.27	0.43				0.05	0.13 + 0.15					1.03
Cl3		0.47		0.16	0.15	0.14	0.14					1.05
Cl4		0.46		0.13	0.12	0.14	0.16					1.00
Cl5		0.24	0.26		0.23	0.15	0.04					1.10
Cl6		0.06	0.27	0.19 + 0.23	0.17				0.2	0.2		1.31
Cl7	0.22		0.24	0.12	0.13	0.13	0.10					0.94
Cl8	0.21		0.23	0.16		0.10	0.10					0.79
O1						0.13	0.16	0.8	0.8			1.89
O2						0.14	0.15			0.8	0.8	1.89
Σ	1.00	1.87	0.99	1.14	0.97	1.10	1.13	1	1	1	1	

Table 6. Chemical and structural complexity parameters of minerals and synthetic phases in the K−Cu−Cl−H$_2$O system
Таблица 6. Параметры химической и структурной сложности минералов и синтетических фаз в системе K−Cu−Cl−H$_2$O

Mineral name	Chemical formula	$^{chem}I_G$	$^{str}I_G$	$^{chem}I_{G,total}$	$^{str}I_{G,total}$
Avdoninite	K$_2$Cu$_5$Cl$_8$(OH)$_4 \cdot$ 2H$_2$O	2.211	3.892	57.484	225.763
Romanorlovite	K$_{11}$Cu$^{2+}{}_9$Cl$_{25}$(OH)$_4 \cdot$ 2H$_2$O	2.117	3.755	124.889	364.192
Mitscherlichite	K$_2$CuCl$_4 \cdot$ 2H$_2$O	2.162	2.470	28.106	64.211
−	K$_4$Cu^{2+}Cu$^+{}_2$Cl$_8 \cdot$ 2H$_2$O	2.017	4.392	36.304	184.477

organic chemistry (Hoffmann et al., 1977). In contrast, the K3 and K4 sites have a bicapped trigonal prismatic coordination by six Cl atoms and two H$_2$O groups. The latter are arranged at the corners of a vertical edge of the (KCl$_4$(H$_2$O)$_2$) trigonal prism with two tetragonal faces capped by Cl atoms (Fig. 3). This type of an eightfold coordination is again quite common for inorganic and metal-organic compounds (Burdett et al., 1978).

The [Cu^{2+}Cu$_2^+$Cl$_8$]$^{4-}$ chains are linked via K−Cl and K−H$_2$O interactions as well as by H$_2$O⋯Cl hydrogen bonds. Each H$_2$O group is coordinated by two K$^+$ ions and donates two hydrogen bonds to two adjacent Cl$^-$ ions. As a result, the H$_2$O groups, K$^+$ and Cl$^-$ ions form chains running parallel to the *a* axis (Fig. 4).

4. DISCUSSION

The crystal structure of K$_4$Cu^{2+}Cu$_2^+$Cl$_8 \cdot$ 2H$_2$O was solved and refined in the non-centrosymmetric space group *P*2$_1$. It is remarkable that each [Cu^{2+}Cu$_2^+$Cl$_8$]$^{4-}$ chain is itself centrosymmetric with inversion centers located in each Cu3 site and in the midpoints of the Cl⋯Cl edges shared between the (Cu1Cl$_4$) and (Cu3Cl$_4$) tetrahedra. The non-centrosymmetricity of the overall structure is the result of the shift of the adjacent chains relative to each other in the direction parallel to the *a* axis.
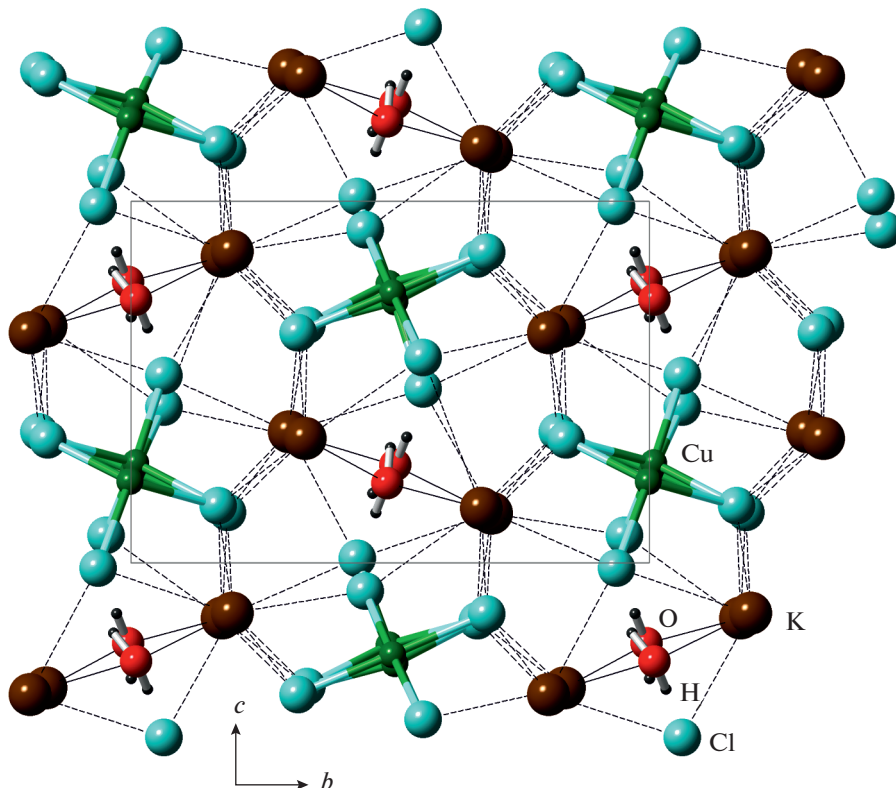
Fig. 1. The crystal structure of $K_4Cu^{2+}Cu_2^+Cl_8 \cdot 2H_2O$ in projection along the *a* axis.

Рис. 1. Кристаллическая структура $K_4Cu^{2+}Cu_2^+Cl_8 \cdot 2H_2O$ в проекции вдоль оси *a*.

Another interesting aspect of the crystal structure is the arrangement of Cu ions along the extension of the chains. As it was noted above, the Cu1···Cu3 distance across the shared Cl···Cl edge is remarkably short (2.585 Å). The Cl–Cu1–Cl and Cl–Cu3–Cl3 valence angles are 114.2 and 116.2°, respectively. This is in drastic contrast with usual values of angles opposite to the shared edges in tetrahedral dimers: as a rule, they are shortened with respect to the "ideal" tetrahedral value of 109.5° (see, e.g., Krivovichev et al., 1998). The possible explanation for the existence of such a short $Cu^+ \cdots Cu^+$ contact in the observed coordination geometry would the presence of attractive interaction between the adjacent Cu^+ centers, i.e. a cuprophillic interaction (Jansen, 1987; Carvajal et al., 2004). However, the analysis of the electron-density distribution shows that the midpoint Cu1···Cu3 distance (the point with the coordinates $x = -0.1248$, $y = -0.4793$, $z = -0.2419$) is a $(3, +1)$ critical point, which is a ring critical point that indicates the absence of bonding interactions between the adjacent Cu centers.

In terms of chemistry, the title compound is close to avdoninite, $K_2Cu_5Cl_8(OH)_4 \cdot 2H_2O$, mitscherlichite, $K_2CuCl_4 \cdot 2H_2O$, and romanorlovite, $K_{11}Cu_9Cl_{25}(OH)_4 \cdot 2H_2O$. However, it differs from them in its mixed-valence character. However, since mixed-valent copper compounds can exist in volcanic fumaroles, and $K_4Cu^{2+}Cu_2^+Cl_8 \cdot 2H_2O$ was prepared by means of chemical transport reactions, its formation under natural conditions is likely. The analysis of
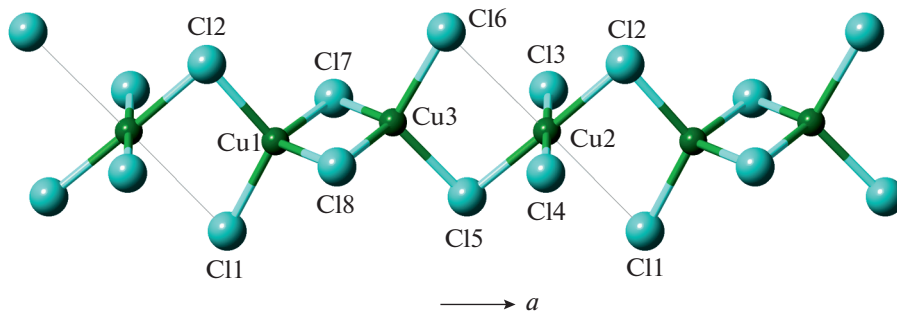
Fig. 2. The copper chloride [Cu$^+_2$Cu^{2+}Cl$_8$] chain in the crystal structure of K$_4$Cu^{2+}Cu$^+_2$Cl$_8 \cdot$ 2H$_2$O.

Рис. 2. Медь-хлоридная цепочка [Cu$^+_2$Cu^{2+}Cl$_8$] в кристаллической структуре K$_4$Cu^{2+}Cu$^+_2$Cl$_8 \cdot$ 2H$_2$O.
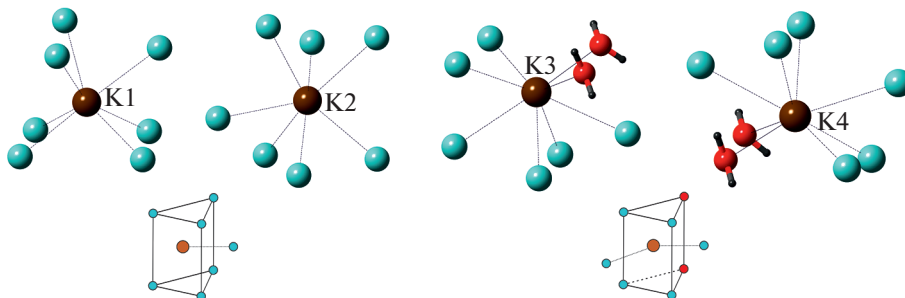

Fig. 3. The coordination of K$^+$ ions in the crystal structure of K$_4$Cu^{2+}Cu$_2^+$Cl$_8 \cdot$ 2H$_2$O.

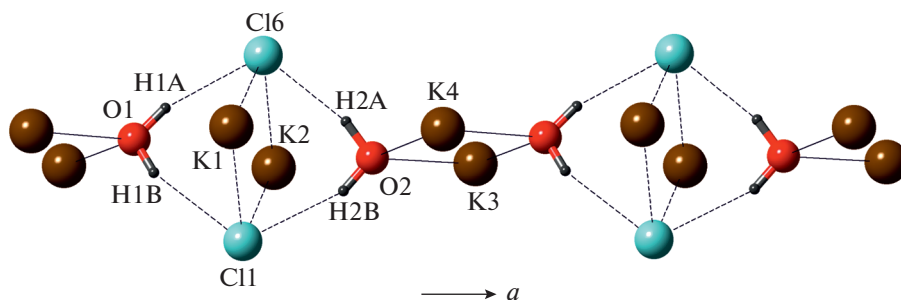**Рис. 3**. Координация ионов K$^+$ в кристаллической структуре K$_4$Cu^{2+}Cu$_2^+$Cl$_8 \cdot$ 2H$_2$O.

Fig. 4. The chain of H$_2$O molecules, Cl$^-$ anions and K$^+$ cations in the crystal structure of K$_4$Cu^{2+}Cu$_2^+$Cl$_8 \cdot$ 2H$_2$O.

Рис. 4. Цепочка из молекул H$_2$O и ионов Cl$^-$ и K$^+$ в кристаллической структуре K$_4$Cu^{2+}Cu$_2^+$Cl$_8 \cdot$ 2H$_2$O.

the structural and chemical complexity parameters (Krivovichev, 2013; Krivovichev S.V., Krivovichev V.G., 2020) listed in Table 6 shows that $K_4Cu^{2+}Cu_2^+Cl_8 \cdot 2H_2O$ possesses neither unusually high nor unusually low complexity and thus its possible formation as a secondary phase in fumaroles does correspond to the typical level of complexity observed in this geochemical environment.

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$K_4Cu^{2+}Cu^+_2Cl_8 \cdot 2H_2O$: НОВОЕ НЕЦЕНТРОСИММЕТРИЧНОЕ СМЕШАННО-ВАЛЕНТНОЕ СОЕДИНЕНИЕ МЕДИ И ЕГО СРАВНЕНИЕ С МИНЕРАЛАМИ

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Красновато-коричневые кристаллы нового соединения $K_4Cu^{2+}Cu^+_2Cl_8 \cdot 2H_2O$ были получены методом химических транспортных реакций. Кристаллическая структура ($a = 9.0472(5)$, $b = 11.5591(4)$, $c = 9.1786(5)$ Å, β = 118.692(7)°, $V = 842.01(9)$ Å^3) решена с использованием монокристальной дифракции и уточнена до $R_1 = 0.039$ для 4369 независимых рефлексов. Кристаллическая структура соединения содержит

анионные цепочки $[Cu^{2+}Cu_2^+Cl_8]^{4-}$, вытянутые вдоль оси *a* и связанные посредством ионов K^+ и молекул H_2O. В структуре имеется три позиции меди. Позиции Cu1 и Cu3 заселены одновалентными катионами Cu^+ и координированы четырьмя атомами Cl с длинами связей Cu−Cl в диапазоне 2.309−2.441 Å. Тетраэдры $(Cu1Cl_4)$ и $(Cu3Cl_4)$ связаны общим ребром Cl···Cl с образованием димера (Cu_2Cl_6) с весьма коротким расстоянием Cu···Cu, равным 2.585 Å. Теоретический анализ распределения электронной плотности показывает отсутствие связывающего взаимодействия между соседними Cu-центрами. Димеры связываются в одномерные цепочки через атомы Cu2, находящиеся в октаэдрической координации. Исходя из координационной геометрии и расчетов валентностей связей, позиция Cu2 заселена ионами Cu^{2+}. Позиции K1 и K2 координированы семью атомами Cl с образованием тригональной призмы (KCl_7) с одним колпачком. В отличие от этого, позиции K3 и K4 имеют восьмерную тригонально-призматическую координацию с двумя колпачками, состоящую из шести атомов Cl и двух молекул H_2O. Цепочки $[Cu^{2+}Cu_2^+Cl_8]^{4-}$ связаны через взаимодействия K−Cl и K−H_2O, а также водородные связи H_2O···Cl. Нецентросимметричный характер структуры создается за счет смещения соседних цепочек друг относительно друга в направлении оси *a*. Соединение химически близко к вулканическим минералам авдониниту $K_2Cu_5Cl_8(OH)_4 \cdot 2H_2O$, митчерлихиту $K_2CuCl_4 \cdot 2H_2O$ и романорловиту $K_{11}Cu_9Cl_{25}(OH)_4 \cdot 2H_2O$, но отличается от них смешанновалентным характером. Структура изученного соединения имеет среднюю сложность, характерную для вторичных фаз на фумарольных полях, что определяет потенциальную возможность его образования на фумаролах.