

Crystal Structure of $\text{Cu(I)Cu(II)}_4\text{O}(\text{SeO}_3)\text{Cl}_5$, a New Heterovalent Copper Compound

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Oxygenous compounds of heterovalent copper are of considerable interest because of their extraordinary magnetic properties [1–3]. In this paper, we report on the synthesis and crystal structure of $\text{Cu(I)Cu(II)}_4\text{O}(\text{SeO}_3)\text{Cl}_5$, the first copper selenite containing both mono- and divalent copper cations. This compound is classified with copper selenite chlorides, which are interesting for both physics [3–6] and mineralogy [8–10]. In addition, $\text{Cu(I)Cu(II)}_4\text{O}(\text{SeO}_3)\text{Cl}_5$ contains so-called “extra” oxygen atoms and, thus, is one of the objects of the crystal chemistry of minerals and inorganic compounds with complexes of oxo-centered tetrahedra, which was developed in [11–13].

Crystals of $\text{Cu(I)Cu(II)}_4\text{O}(\text{SeO}_3)\text{Cl}_5$ were obtained by the chemical transport reaction method from 1 g of a

mixture of CuO , Al_2O_3 , SeO_2 , and CuCl_2 taken in a 3 : 1 : 2 : 3 ratio. The synthesis was carried out in a quartz ampoule under vacuum at a temperature gradient from 530(10) to 600(10)°C in the cold and hot portions of the ampoule, respectively. Analysis of the reaction products showed that Al_2O_3 remained unreacted. In the middle and cold portions of the ampoule, olive green tabular crystal of synthetic chloromenite $\text{Cu}_9\text{O}_2(\text{SeO}_3)_4\text{Cl}_6$ [8, 9] and brown needlelike crystals of CuCl_2 (synthetic tolba-chite) were deposited at the bottom; near the hot end of the ampoule, spherical aggregates of black nontransparent plates of $\text{Cu(I)Cu(II)}_4\text{O}(\text{SeO}_3)\text{Cl}_5$ were observed.

A single crystal, $0.08 \times 0.04 \times 0.007 \text{ mm}^3$, was used for X-ray diffraction analysis. Reflection intensities were collected on a Bruker SMART diffractometer

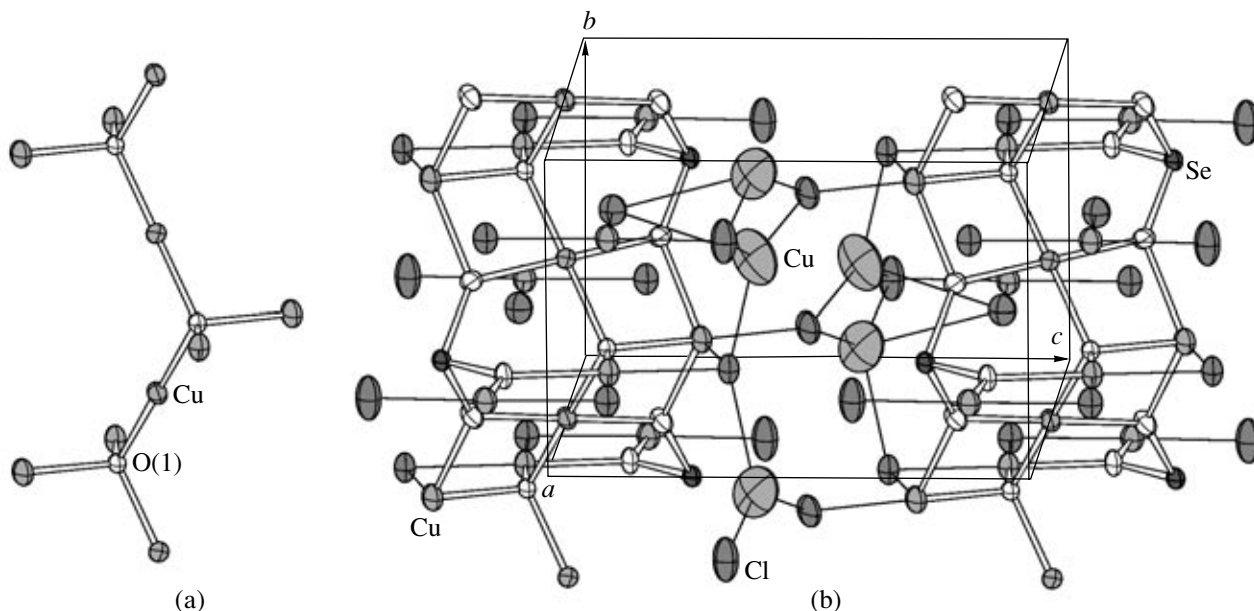


Fig. 1. (a) A chain of oxo-centered OCu_4 tetrahedra in the crystal structure of $\text{Cu(I)Cu(II)}_4\text{O}(\text{SeO}_3)\text{Cl}_5$ and (b) a general view of the structure. Thermal ellipsoids are drawn at 50% probability.

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Table 1. Atomic coordinates and displacement parameters (\AA^2) in the crystal structure of $\text{Cu(I)Cu(II)}_4\text{O}(\text{SeO}_3)\text{Cl}_5$

Atom	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}	BVS*
Se	0.24288(13)	1/4	0.31815(14)	0.0166(4)	4.02
Cu(1)	0.27863(18)	-1/4	0.49740(19)	0.0263(5)	2.04
Cu(2)	0.10980(17)	-1/4	0.77315(18)	0.0223(4)	1.91
Cu(3)	-0.12606(17)	-1/4	0.01184(17)	0.0223(4)	1.90
Cu(4)	0	0	1/2	0.0194(4)	2.08
Cu(5)**	0.5859(4)	-0.1188(7)	0.2094(4)	0.083(1)	1.02
Cl(1)	0.1253(4)	-1/4	0.0102(4)	0.0276(8)	0.92
Cl(2)	0.3556(3)	-1/4	0.7419(4)	0.0262(8)	0.99
Cl(3)	0.4917(4)	-1/4	0.3983(5)	0.044(1)	0.97
Cl(4)	-0.1187(4)	-1/4	0.2486(4)	0.0286(8)	0.56
Cl(5)	-0.3686(4)	-1/4	0.9947(4)	0.042(1)	0.86
O(1)	0.0900(9)	-1/4	0.5747(9)	0.017(2)	2.21
O(2)	0.1045(9)	1/4	0.1934(9)	0.022(2)	2.15
O(3)	0.1886(6)	0.039(1)	0.4159(7)	0.023(2)	2.14

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Se	0.0134(7)	0.0166(7)	0.0203(8)	0	0.0059(5)	0
Cu(1)	0.0177(9)	0.0262(10)	0.036(1)	0	0.0109(8)	0
Cu(2)	0.0158(9)	0.0288(10)	0.023(1)	0	0.0031(7)	0
Cu(3)	0.0195(9)	0.0268(10)	0.021(1)	0	0.0045(7)	0
Cu(4)	0.0149(8)	0.0158(9)	0.028(1)	0.0038(8)	0.0053(7)	0.0017(7)
Cu(5)**	0.082(3)	0.111(3)	0.060(2)	-0.020(2)	0.0418(19)	-0.020(2)
Cl(1)	0.022(2)	0.036(2)	0.025(2)	0	0.0015(15)	0
Cl(2)	0.016(2)	0.033(2)	0.030(2)	0	0.0029(14)	0
Cl(3)	0.025(2)	0.036(2)	0.072(3)	0	0.0280(19)	0
Cl(4)	0.028(2)	0.035(2)	0.023(2)	0	0.0035(15)	0
Cl(5)	0.024(2)	0.077(3)	0.026(2)	0	0.0048(16)	0
O(1)	0.012(5)	0.013(5)	0.026(5)	0	0.005(4)	0
O(2)	0.012(5)	0.025(5)	0.029(6)	0	0.007(4)	0
O(3)	0.020(4)	0.019(4)	0.031(4)	0.009(3)	0.011(3)	0.004(3)

* BVS is the bond valence sum for corresponding positions calculated using parameters from [14, 15].

** The position occupancy is 50%.

with a plane 1K CCD detector. The unit cell parameters were determined from the least-squares fit of 865 strong reflections. Crystals are monoclinic: $a = 9.203(3) \text{ \AA}$, $b = 6.232(2) \text{ \AA}$, $c = 9.557(3) \text{ \AA}$, $\beta = 91.970(8)^\circ$, $V = 547.8(3) \text{ \AA}^3$. Space group $P2_1/m$ was defined by systematic absences and reflection distribution statistics. The array of structure factors was obtained with the SAINT program after corresponding corrections had been applied. The structure was solved by direct methods and refined to $R_1 = 0.052$ ($wR_2 = 0.102$) for 793 reflections with $|F_{hkl}| \geq 4\sigma|F_{hkl}|$. The final model included the coordinates and isotropic thermal parameters for all atoms (Table 1). The interatomic distances are summarized in Table 2. Bond valence sums

for cations and anions calculated using parameters from [14, 15] are given in Table 1.

X-ray diffraction analysis of the $\text{Cu(I)Cu(II)}_4\text{O}(\text{SeO}_3)\text{Cl}_5$ structure showed that it belongs to a new structural type of inorganic compound. The structure has four positions of Cu(II) atoms coordinated by oxygen and chlorine atoms. The Cu(I) is bound to a distorted trigonal-bipyramidal array of three oxygen atoms and two chlorine atoms. The apical positions are occupied by Cl and O atoms, while the equatorial plane is formed by two O atoms and one Cl atom. The coordination polyhedron $\text{Cu(2)O}_2\text{Cl}_2$ is a flat square centered by the Cu(2) atom. The Cl atoms are *cis* to each other. The Cu(3) atom also has a square coordination, but the square is composed of three Cl atoms

Table 2. Interatomic distances (Å) in the crystal structure of $\text{Cu(I)Cu(II)}_4\text{O}(\text{SeO}_3)\text{Cl}_5$

Se(1)–O(3)	1.697(6) 2×	Cu(3)–O(2)	1.979(9)
Se(1)–O(2)	1.714(9)	Cu(3)–Cl(5)	2.233(4)
		Cu(3)–Cl(4)	2.261(4)
Cu(1)–O(1)	1.910(8)	Cu(3)–Cl(1)	2.314(4)
Cu(1)–O(3)	2.120(6) 2×		
Cu(1)–Cl(3)	2.206(4)	Cu(4)–O(1)	1.893(5) 2×
Cu(1)–Cl(2)	2.419(4)	Cu(4)–O(3)	1.953(6) 2×
Cu(2)–O(1)	1.899(9)	Cu(5)–Cl(3)	2.188(5)
Cu(2)–O(2)	2.008(8)	Cu(5)–Cl(5)	2.261(5)
Cu(2)–Cl(1)	2.265(4)	Cu(5)–Cl(2)	2.402(5)
Cu(2)–Cl(2)	2.292(4)	Cu(5)–Cl(4)	2.860(5)

and one O atom. The Cu(4) atom has a square-planar coordination composed of four O atoms. The Cu(5) position is the only site occupied by monovalent copper cations. This position has a 50% occupancy and is coordinated by four chlorine atoms (the coordination polyhedron can be approximated by a trigonal pyramid or a severely distorted tetrahedron Cu(I)Cl_4). Noteworthy is an increased isotropic thermal factor of the Cu(5) position, which is, most likely, due to the interlayer location of Cu^+ cations (see below) and the low occupancy of this position.

The $\text{Cu(I)Cu(II)}_4\text{O}(\text{SeO}_3)\text{Cl}_5$ structure contains one symmetry-unique Se(IV) position, which is coordinated with three oxygen atoms. The SeO_3 group thus formed is a trigonal pyramid with the Se(IV) cation at the apex. Such a coordination is typical of selenites and is caused by the stereochemical activity of the lone pair of electrons at the Se(IV) cation.

The $\text{Cu(I)Cu(II)}_4\text{O}(\text{SeO}_3)\text{Cl}_5$ structure is best described in terms of the crystal chemistry of inorganic compounds with complexes of oxo-centered tetrahedra [11–13]. The structure has two types of O atoms: the atoms incorporated in SeO_3 groups (the O(2) and O(3) atoms) and so-called extra O atoms (the O(1) position). The O(1) atom has a tetrahedral coordination composed of four copper atoms, thus being the center of the OCu_4 tetrahedron. The OCu_4 tetrahedra share vertices to form two-unit chains $[\text{O}_2\text{Cu}_6]$ extended along the *b* axis (Fig. 1a). Similar chains were previously found in the structures of chloromenite [9] and some compounds with oxo-centered tetrahedra [13]. The chains contain the Cu(1) or Cu(4) and Cu(2) atoms, whereas the Cu(3) atom is not bonded to extra oxygen atoms and links the chains in layers parallel to the (100) plane. The SeO_3

groups share faces with OCu_4 tetrahedra [13]. The SeO_3 groups link the copper–oxygen chains in layers parallel to the (100) plane, Cu^+ cations and Cl^- anions being located between these layers (Fig. 1b).

The compound $\text{Cu(I)Cu(II)}_4\text{O}(\text{SeO}_3)\text{Cl}_5$ is the first known heterovalent Cu(I/II) selenite. The fact that this compound was synthesized by the chemical transport reaction method implies the possibility of formation of similar Cu(I/II) oxide systems in fumarole deposits at volcanoes.

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