

Crystal chemistry of inorganic compounds based on chains of oxocentered tetrahedra

II. Crystal structure of $\text{Cu}_4\text{O}_2[(\text{As},\text{V})\text{O}_4]\text{Cl}^1$

G. L. Starova, S. V. Krivovichev* and S. K. Filatov

St. Petersburg University, University Emb., 7/9, Department of Crystallography, 199034 St. Petersburg, Russia

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Abstract. The orthorhombic crystal structure of $\text{Cu}_4\text{O}_2[(\text{As},\text{V})\text{O}_4]\text{Cl}$, $a = 5.440(1) \text{ \AA}$, $b = 11.154(2) \text{ \AA}$, $c = 10.333(2) \text{ \AA}$, $V = 627.0(3) \text{ \AA}^3$, $Z = 4$, $Pbcm$, has been solved by direct methods and refined to an $R(F)$ index of 0.049 ($wR(F^2) = 0.048$). The structure is based on unbranched *vierer* chains $\{uB, 1^1_\infty\} [\text{O}_4\text{Cu}_8]$ running parallel to the c axis, which are composed of oxocentered tetrahedra $[\text{OCu}_4]$ linked *via* opposite edges. The chains are bent by the large chloride ions in zigzag fashion so that the periodicity of the chains is equal to four. $[(\text{As},\text{V})\text{O}_4]$ groups are located between the puckered chains of oxocentered tetrahedra and crosslink them into layers parallel to the (100) plane, which are held together by the $\text{Cu}-\text{O}_{\text{As/V}}$ bonds.

Introduction

A new natural compound from sublimates of the Tolbachik volcano, Kamchatka, Russia, ideally $\text{Cu}_4\text{O}_2[(\text{As},\text{V})\text{O}_4]\text{Cl}$, was recently described by Vergasova, Starova, Krivovichev, Filatov and Ananiev (1996). It occurs as small black crystals included in euchlorine, $\text{KNaCu}_3\text{O}(\text{SO}_4)_3$. Electron microprobe analyses have revealed a predominance of As over V with a compositional range from $\text{As}_{0.66}\text{V}_{0.36}$ to $\text{As}_{0.52}\text{V}_{0.47}$ and the presence of additional oxygen atoms commonly occurring in exhalative minerals. $\text{Cu}_4\text{O}_2[(\text{As},\text{V})\text{O}_4]\text{Cl}$ is proposed to be a new mineral and corresponding proposal is submitted to the Commission on New Minerals and Mineral Names of the International Mineralogical Association (IMA).

This paper contains the structure determination of $\text{Cu}_4\text{O}_2[(\text{As},\text{V})\text{O}_4]\text{Cl}$ and its description in terms of interconnected oxocentered tetrahedra $[\text{OCu}_4]$. Thus it represents the second paper of a series concerned with inorganic compounds based on chains of oxocentered tetrahedra,

where an article on chloromenite ($\text{Cu}_9\text{O}_2(\text{SeO}_3)_4\text{Cl}_6$) by Krivovichev, Filatov, Semenova and Rozhdestvenskaya (1998) is the first one.

Experimental

A single crystal of $\text{Cu}_4\text{O}_2[(\text{As},\text{V})\text{O}_4]\text{Cl}$ with dimensions $0.4 \times 0.2 \times 0.1 \text{ mm}^3$ was studied by Weissenberg techniques that revealed orthorhombic symmetry and the possible space groups $Pbcm$ and $Pbc2_1$. Details of the crystal data, X-ray data collection and structure refinement are given in Table 1. The structure was solved in the centro-

Table 1. Details of the crystal data, X-ray data collection and structure refinement.

Crystal data	
Chemical formula	$\text{Cu}_4\text{O}_2[(\text{As}_{0.54}\text{V}_{0.46})\text{O}_4]\text{Cl}$
Formula weight	449.5
Crystal system	Orthorhombic
Space group; Z	$Pbcm$; 4
Lattice constants at 293(2) K	$a = 5.440(1) \text{ \AA}$ $b = 11.154(2) \text{ \AA}$ $c = 10.333(2) \text{ \AA}$
Unit cell volume	$627.0(3) \text{ \AA}^3$
Density (calculated)	4.76 g cm^{-3}
Data collection	
Radiation	$\text{MoK}\alpha$ ($\lambda = 0.71069 \text{ \AA}$)
Diffractometer	Syntex P2 ₁
Scan mode	$\omega - 2\theta$
Independent reflections	910
Observed reflections [$I > 2\sigma(I)$]	910
Index ranges	$0 \leq h \leq 8$ $0 \leq k \leq 19$ $-18 \leq l \leq 17$
$2\theta_{\text{max}}$	79.8°
Linear absorption coefficient μ	18.292 mm^{-1}
Refinement	
Refinement on F	
$R(F)$	0.049
$wR(F^2)$	0.048
Goodness-of-fit S	3.280
Parameters refined	61
Weighting scheme	based on measured e.s.d.'s

* Correspondence author (e-mail: sergey@cryst.geol.pu.ru)

¹ Approved as a new mineral, coparsite, by the Commission on New Minerals and Mineral Names of the International Mineralogical Association (approval no. 96-064).

Table 2. Fractional atomic coordinates and displacement parameters (\AA^2) for $\text{Cu}_4\text{O}_2(\text{As}_{0.54}\text{V}_{0.46}\text{O}_4)\text{Cl}$. $U_{\text{eq}} = (1/3) \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \mathbf{a}_j$

Atom	<i>x</i>	<i>y</i>	<i>z</i>	s.o.f.	U_{eq}	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cu1	0.4691(4)	0.3503(2)	$3/4$		0.0058(5)	0.011(1)	0.0008(9)	0.0060(8)	-0.0019(9)	0	0
Cu2	0.3583(4)	0.4129(2)	$1/4$		0.0063(5)	0.011(1)	0.0020(9)	0.0062(8)	-0.0016(9)	0	0
Cu3	0.2704(2)	0.5500(1)	0.5410(1)		0.0072(3)	0.0082(6)	0.0068(6)	0.0066(5)	0.0023(6)	0.0005(5)	0.0002(6)
As	0.1803(4)	$1/4$	$1/2$	0.54(2)	0.0047(5)	0.006(1)	0.0021(9)	0.0057(8)	0	0	0.0006(8)
V	0.1803(4)	$1/4$	$1/2$	0.46(2)	0.0047(5)	0.006(1)	0.0021(9)	0.0057(8)	0	0	0.0006(8)
O1	0.449(1)	0.5304(7)	0.3797(6)		0.005(2)	0.008(4)	0.002(4)	0.005(3)	-0.001(3)	-0.002(3)	0.002(3)
O2	0.379(1)	0.2775(7)	0.3738(6)		0.008(2)	0.014(4)	0.005(4)	0.005(3)	0.004(3)	0.000(3)	0.003(3)
O3	0.987(1)	0.6276(7)	0.4653(6)		0.009(2)	0.011(4)	0.006(4)	0.010(3)	0.005(3)	-0.001(3)	0.004(3)
Cl	0.1159(8)	0.6018(5)	$3/4$		0.016(1)	0.010(2)	0.028(3)	0.012(2)	0.006(2)	0	0

symmetric space group *Pbcm* by direct methods and refined by full-matrix least-squares methods. The refinement of the (As,V) site occupation factor (s.o.f.) shows the best *R* value for the $\text{As}_{0.54}\text{V}_{0.46}$ composition which is in agreement with results of chemical analyses. Although V and As are in a ratio near to 1:1, no ordering was observed.

All calculations including Lorentz-polarization and absorption corrections were applied using the software package CSD (Acselrud, Grin, Zavalii, Pecharsky, Fundamensky, 1989). The fractional atomic coordinates and displacement parameters are given in Table 2, selected interatomic distances and angles in Table 3.

Table 3. Selected bond lengths and valence angles in $\text{Cu}_4\text{O}_2[(\text{As},\text{V})\text{O}_4]\text{Cl}$.

		[Å]		[°]	
Cu1–O1	2×	1.941(7)	O1–Cu1–O1	87.3(2)	
Cu1–O2	2×	1.977(7)	O1–Cu1–O2	2×	96.0(3)
			O1–Cu1–O2	2×	176.7(3)
			O2–Cu1–O2		80.7(3)
Cu2–O1	2×	1.938(7)	O1–Cu2–O2	2×	93.1(3)
Cu2–O2	2×	1.983(8)	O1–Cu2–O2	2×	161.2(3)
Cu2–Cl		2.585(5)	O1–Cu2–O1		87.5(3)
Cu2–Cl ⁱ		2.865(4)	O2–Cu2–O2		80.4(3)
			O1–Cu2–Cl	2×	107.2(2)
			O2–Cu2–Cl	2×	90.5(2)
			O1–Cu2–Cl ⁱ	2×	77.5(1)
			O2–Cu2–Cl ⁱ	2×	84.2(1)
			Cl–Cu2–Cl ⁱ		173.1(1)
Cu3–O1		1.940(7)	O1–Cu3–O1 ⁱ		85.3(3)
Cu3–O ⁱ		1.953(7)	O1–Cu3–O3		95.8(3)
Cu3–O3		1.934(8)	O1 ⁱ –Cu3–O3		178.6(3)
Cu3–O ⁱ		2.426(7)	O1–Cu3–O3 ⁱ		100.0(3)
Cu3–Cl		2.388(3)	O1 ⁱ –Cu3–O3 ⁱ		95.0(2)
			O3–Cu3–O3 ⁱ		83.9(2)
			O1–Cu3–Cl		168.4(3)
			O1 ⁱ –Cu3–Cl		90.4(2)
			O3–Cu3–Cl		88.7(3)
			O3 ⁱ –Cu3–Cl		91.0(1)
As/V–O2	2×	1.722(7)	O2–As/V–O2		102.1(4)
As/V–O3	2×	1.679(8)	O3–As/V–O3		114.4(4)
		<1.70>	O2–As/V–O3	2×	108.9(4)
			O2–As/V–O3	2×	110.9(4)
					<109.4>
O1–Cu1		1.941(7)	Cu1–O1–Cu2		92.6(3)
O1–Cu2		1.938(7)	Cu1–O1–Cu3		129.1(4)
O1–Cu3		1.940(7)	Cu1–O1–Cu3 ⁱ		115.1(4)
O1–Cu ⁱ		1.953(7)	Cu2–O1–Cu3		122.9(4)
Cu1–Cu2		2.803(3)	Cu2–O1–Cu3 ⁱ		100.3(3)
Cu1–Cu3		3.505(1)	Cu3–O1–Cu3 ⁱ		94.7(3)
Cu1–Cu ⁱ		3.285(1)			<109.1>
Cu2–Cu3		3.407(1)			
Cu2–Cu3 ⁱ		2.985(1)			
Cu3–Cu3 ⁱ		2.863(1)			
		<3.14>			

Discussion

There are three crystallographically independent copper positions in $\text{Cu}_4\text{O}_2[(\text{As},\text{V})\text{O}_4]\text{Cl}$ with different oxygen and chlorine coordinations: Cu(1) exhibits a square of [4O], Cu(2) is coordinated as tetragonal bipyramid by [4O + 2Cl], Cu3 – as tetragonal pyramid by [3O + Cl + O]. The $[(\text{As},\text{V})\text{O}_4]$ tetrahedra have the reasonably usual mean bond lengths (As,V)–O of 1.70 Å.

The additional O(1) oxygen atom is tetrahedrally surrounded by four copper atoms with mean Cu–O bond length equal to 1.94 Å, whereas that for oxygen atoms simultaneously bonded to (As,V) is 1.97 Å. In contrast to chloromenite ($\text{Cu}_9\text{O}_2(\text{SeO}_3)_4\text{Cl}_6$) described in a previous paper (Krivovichev et al., 1998), all copper atoms in $\text{Cu}_4\text{O}_2[(\text{As},\text{V})\text{O}_4]\text{Cl}$ are bonded to 'additional' oxygen atoms. We consider the $[\text{OCu}_4]$ oxocentered tetrahedra as independent structural subunits along with $[(\text{As},\text{V})\text{O}_4]$ tetrahedra and chloride ions. The oxocentered tetrahedra $[\text{OCu}_4]$ are linked *via* opposite edges to form unbranched *vierer* $\{uB, 1^1_\infty\}[\text{O}_4\text{Cu}_8]$ chains running parallel to the *c* axis (Fig. 1). Large chloride anions are attached to the chains and bend them by two Cu3–Cl bonds as it is shown in Fig. 2b. As a result, the chains are *vierer* and conformed in zigzag fashion in contrast to linear *zweier* chains (Fig. 2a). The similar conformation of single chains of anion-centered edge-sharing tetrahedra has been observed in a number of inorganic compounds, presumably in those based on $[\text{XA}_4]$ tetrahedra with X = O, N and A = rare earth element (for details see Krivovichev and Filatov (1998) and refs. therein). $[(\text{As},\text{V})\text{O}_4]$ groups are located between puckered oxocentered chains and link them into layers parallel to the (100) plane (Fig. 3). The resulting Cu–O_{As/V} bonds finally hold these layers together.

As can be seen from Table 3, linking of two tetrahedra through an edge diminishes the bond angles, which are opposite to the edge, in comparison with the ideal one (109.5°). In the title compound the edges Cu1–Cu2 and Cu3–Cu3ⁱ are shared so that the angles Cu1–O1–Cu2 and Cu3–O1–Cu3ⁱ are diminished and, as a result, the chain is stretched. One can observe that this is the general situation for units based on oxocentered tetrahedra (Krivovichev, Filatov, Semenova, 1998).

Analogous chains of edge-sharing oxocentered $[\text{OA}_4]$ tetrahedra were considered as main structural units in $\text{Yb}_2\text{O}(\text{SiO}_4)_2$ (Smolin, 1969, 1971, 1997), lanarkite, $\text{Pb}_2\text{O}(\text{SO}_4)$ (Sahl, 1970), piypite (caratiite = discredited name), $\text{K}_2\text{Cu}_2\text{O}(\text{SO}_4)_2 \cdot \text{MeCl}$ (Me is possibly alkali metal) (Effenberger, Zemmann, 1984), klyuchevskite, $\text{K}_3\text{Cu}_3(\text{Fe},\text{Al})\text{O}_2(\text{SO}_4)_4$ (Gorskaya, Filatov, Rozhdestvenskaya, Vergasova, 1992), $\text{Na}(\text{Pr}_4\text{O}_2)\text{Cl}_9$ and $\text{K}(\text{Pr}_4\text{O}_2)\text{Cl}_9$ (Mattfeld, Meyer, 1994) and some other compounds (Krivovichev, Filatov, Semenova, 1998). Similar chains were described in compounds based on nitrogen-centered (Schleid, 1996 and refs. therein; Lulei, Corbett, 1996; Mattausch, Simon, 1996a, b) and mixed oxygen- and ni-

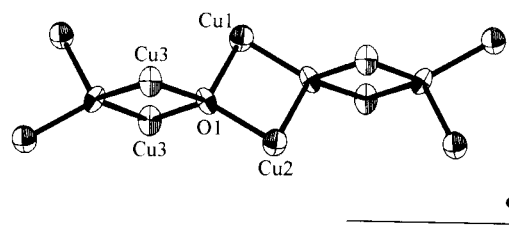


Fig. 1. Configuration of the $\{uB, 1^1_\infty\}[\text{O}_4\text{Cu}_8]$ chain of oxocentered tetrahedra $[\text{OCu}_4]$ in $\text{Cu}_4\text{O}_2[(\text{As},\text{V})\text{O}_4]\text{Cl}$.

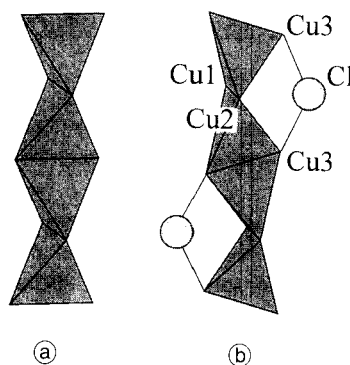


Fig. 2. Mechanisms of conformation of single chains of edge-sharing anion-centered tetrahedra: (a) *zweier* chain in e.g. $[\text{Nd}_2\text{N}]\text{Cl}_3$ (Uhrlandt, Meyer, 1995); (b) *vierer* chain due to adaptation to chloride anions in $[\text{Cu}_4\text{O}_2][(\text{As},\text{V})\text{O}_4]\text{Cl}$.

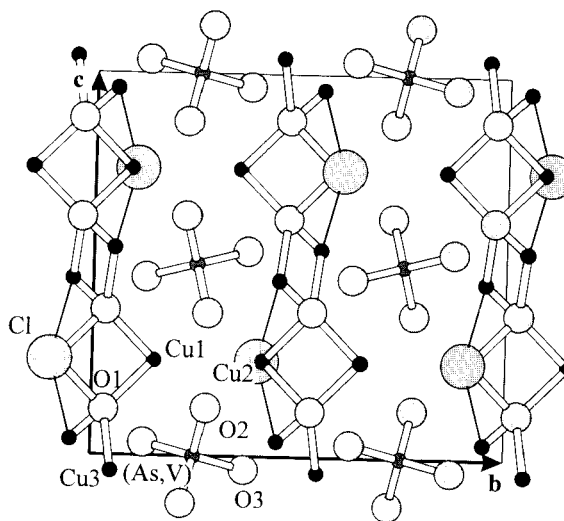


Fig. 3. Crystal structure of $\text{Cu}_4\text{O}_2[(\text{As},\text{V})\text{O}_4]\text{Cl}$ in projection onto the (100) plane.

trogen-centered tetrahedra (Lulei, Steinwand, Corbett, 1995; Beck, Simon, 1997; Lulei, 1998). A detailed analysis of single chains of anion-centered edge-sharing tetrahedra in compounds with halide ions was also given recently (Krivovichev, Filatov, 1998).

This is the second paper of a series devoted to structures based on chains of oxocentered tetrahedra. In the first one (Krivovichev, et al., 1998) we described a chain with linkage of oxocentered tetrahedra *via* corners ($\text{Cu}_9\text{O}_2(\text{SeO}_3)_4\text{Cl}_6$), here we presented one with linkage *via* edges. In a following paper (Krivovichev, Shuvalov, Semenova, Filatov, 1998) we shall describe a chain with both edge and corner linkage ($\text{Cu}_5\text{O}_2(\text{SeO}_3)_2\text{Cl}_2$).

² For a proper understanding of structure data on $\text{Yb}_2\text{O}(\text{SiO}_4)_2$ given in (Smolin, 1969, 1971) and in Inorganic Structure Database (ICSD, collection code 4446) the *x* and *y* coordinates for the space group *B2/b* should be replaced with each other.

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