

# The crystal structure of averievite, $\text{Cu}_5\text{O}_2(\text{VO}_4)_2 \cdot n\text{MX}$ : comparison with related compounds

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## Abstract

The crystal structure of averievite,  $\text{Cu}_5\text{O}_2(\text{VO}_4)_2 \cdot n\text{MX}$  has been determined. Trigonal system, space group  $P3$ ,  $a = 6.375(1)$ ,  $c = 8.399(1)$  Å,  $V = 295.6(1)$  Å<sup>3</sup>,  $Z = 1$ ,  $D_x = 4.01(1)$  g/cm<sup>3</sup>. The atomic arrangement is characterized by infinite nets parallel to (001) composed of  $[\text{OCu}_4]^{6+}$  tetrahedra linked via corners in hexagonal rings. The bases of neighbouring tetrahedra are in one plane and their non-shared corners are turned to the opposite sides. The  $[\text{VO}_4]^{3-}$  tetrahedra are attached to the bases of  $[\text{OCu}_4]$  tetrahedra. There are large ( $R > 3.2$  Å) channels in the structure where large molecular particles can enter. The comparison of the averievite structure with related compounds (in particular, copper oxovanadates) is given from the point of view of  $[\text{OT}_4]$  polyion crystal chemistry.

KEYWORDS: averievite, crystal structure.

## Introduction

AVERIEVITE was found as a product of post eruption volcanic activity of the Main Tolbachik Fracture Eruption (Kamchatka, 1975-76). It was discovered among new exhalation products of Second North Fracture cone. The mineral occurs as rare isolated grains associated with brush-like aggregates of piypite, alumokljuchevskite, langbeinite and pyroclastic materials (Vergasova *et al.*, 1996). The averievite crystals are the non-transparent black pseudohexagonal plates up to  $0.3 \times 0.3 \times 0.1$  mm<sup>3</sup>. The chemical composition has been studied by electron microprobe analysis (microsond 'Camebax'). The chemical studies were carried out using the following standards:  $\text{Fe}_2\text{O}_3$  (Fe), CuO (Cu), Ca-molybdate (Mo), synthetic Cl-apatite (Cl), orthoclase (K), synthetic pollucite (Cs), synthetic  $\text{V}_2\text{O}_5$  (V), Rb-lepidolite (Rb). The means (and ranges) from 17 analyses are: CuO 62.01 (63.41–60.06),  $\text{Fe}_2\text{O}_3$  0.62 (1.06–0.35),  $\text{K}_2\text{O}$  0.98 (1.27–0.65),  $\text{Cs}_2\text{O}$  3.35 (4.11–2.70),  $\text{Rb}_2\text{O}$  0.82 (1.13–0.55),  $\text{V}_2\text{O}_5$  23.84 (25.16–22.67),  $\text{MoO}_3$  1.51 (3.13–0.42), Cl 7.56 (7.93–7.26),  $\text{O}=\text{Cl}_2$  -1.70 [–(1.79–1.64)], sum 98.99 (100.54–97.82). Single crystal structure analysis enabled us to understand and explain the alignment of the elements obtained by the chemical study.

## Experimental

The structure analysis of a crystal of size  $0.3 \times 0.2 \times 0.1$  mm<sup>3</sup> was carried out using a Weissenberg camera and 4-circle diffractometer 'Syntex P21' and gave the following data: 318 unique reflections (Mo- $\text{K}\alpha$  radiation,  $\sin\theta/\lambda < 0.80$ ,  $I > 3\sigma I$ ), trigonal system, space group  $P3$ ,  $a = 6.375(1)$ ,  $c = 8.399(1)$  Å,  $V = 295.6(1)$  Å<sup>3</sup>,  $Z = 1$ ,  $D_x = 4.01(1)$  g/cm<sup>3</sup>. The structure was solved by direct methods and refined by full-matrix least-squares method with anisotropic thermal parameters to an R-factor of 0.052. The program complex 'CSD' was used (Akselrud *et al.*, 1989). The positions of oxygen and channel atoms were localized on difference Fourier maps. The final atomic positions are given in Table 1 (tables of the calculated and observed crystal structure factors and anisotropic atomic parameters are available from the author or editorial office).

## Discussion

From the chemical point of view averievite is a copper(II) oxovanadate(V). Its crystal structure contains the oxygen atoms which do not enter the  $[\text{VO}_4]$  groups and form tetrahedral  $[\text{OCu}_4]^{6+}$  complexes as central atoms. Therefore, it may be

TABLE I. Atomic parameters for averievite,  $\text{Cu}_5\text{O}_2(\text{VO}_4)_2\text{CuCl}_2$ 

Atom	x/a	y/b	z/c	U(is/eq)*100
Cu1	0	0	0	1.8(3)
Cu2	0.338(2)	0.161(2)	0.280(2)	0.96(11)
Cu3	2/3	1/3	0.5492(9)	2.3(4)
Cu4	1/3	2/3	0.01774	6.333
Cu5	1/3	2/3	0.53143	6.333
V1	2/3	1/3	-0.032(2)	0.8(4)
V2	1	0	0.584(2)	0.4(3)
O1	1	0	0.785(9)	3.2(24)
O2	2/3	1/3	0.339(8)	0.887
O3	0	0	0.244(6)	1.013
O4	2/3	1/3	-0.225(8)	0.9(17)
O5	0.379(8)	0.186(9)	0.031(4)	2.9(19)
Cl1	1/3	2/3	0.27140	6.333
Cl2	1/3	2/3	0.76793	6.333

$$U(\text{eq}) = 1/3[U_{11}a^2a^2 + \dots + 2U_{23}b^*c^*bc \cos\alpha]$$

## Occupations

Cl1	1.02(4) Cl
Cl2	0.97(5) Cl
Cu4	0.69(7) Cu
Cu5	0.32(8) Cu

described using a new crystal chemical approach based on the subdivision in the crystal structures of the polyions formed from oxocentred  $[\text{OT}_4]$  tetrahedra (Filatov *et al.*, 1992; Krivovichev *et al.*, 1995). The atomic arrangement in the averievite structure is characterized by infinite two-dimensional nets  $[\text{O}_2\text{Cu}_5]^{6+}$  parallel to (001). These nets are composed of oxocentred  $[\text{OCu}_4]^{6+}$  tetrahedra linked via corners in hexagonal rings (Figs. 1,2). The bases of neighbouring tetrahedra are in the (001) plane and their non-shared corners are turned to the opposite sides. The structural formula of nets, according to rules elaborated by Liebau (1985) (see also IUCr recommendations; Lima-de-Faria *et al.*, 1990), is  $\{\text{uB}, 1^2_\infty\}[\text{O}_2\text{Cu}_5]^{6+}$ . The  $[\text{VO}_4]$  tetrahedra are attached to the bases of oxocentred tetrahedra. The oxocentred  $[\text{O}_2\text{Cu}_5]^{6+}$  nets and  $[\text{VO}_4]$  tetrahedra may be represented as main structural units in the averievite structure. They form its framework so that there are large channels ( $R > 3.2 \text{ \AA}$ ) with a three-fold axis in the centre where large molecular particles can enter. After determination of atomic positions of nets and  $[\text{VO}_4]$  groups, the difference Fourier maps show four strong peaks in these channels which have no bonds with the main framework. Distances between the peaks were 1.99, 2.10, 2.13 and 2.18 Å. The comparison of the framework chemical formula with results obtained by electron microprobe

analysis showed that there was abundance of Cu atoms and some quantity of Cl, K, Rb and Cs, which do not substitute the framework elements according to crystal chemical reasons. It was logical to place

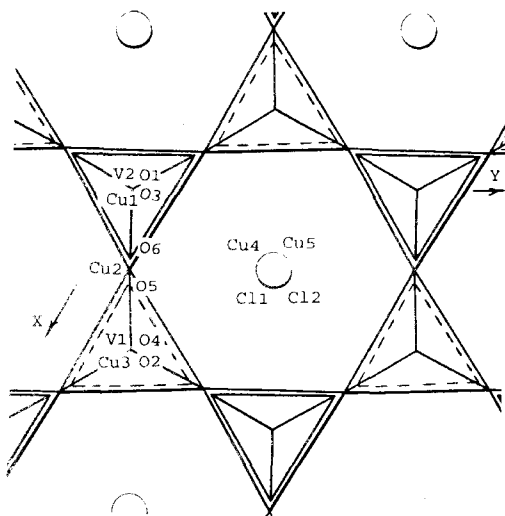


Fig. 1. Projection of the structure of averievite on (001) plane (representation in  $[\text{OT}_4]$  aspect).

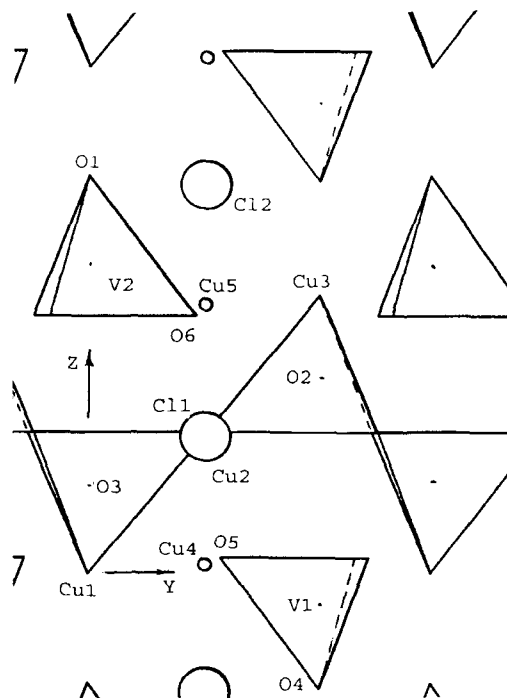


FIG. 2. Projection of the structure of averievite on (100) plane (representation in  $[OT_4]$  aspect).

these atoms in the structure channels as  $CuCl$ ,  $CuCl_2$  or  $(K,Rb,Cs)Cl$ . The anion-cation distance for  $CuCl$  is 2.05 Å, for  $CuCl_2$  — 2.3 Å and for  $KCl$ ,  $RbCl$ ,  $CsCl$  — 2.6, 2.7 and 2.9 Å, respectively (Wells, 1986). Refinement of the channel position occupation shows that one  $Cu(II)$  atom (in sum) occupies two positions and two chlorine atoms occupy two other ones (Table 1). Therefore, the 'molecules' of  $CuCl_2$

are located in structure channels of the studied crystal so that its chemical formula is  $Cu_5O_2(VO_4)_2 \cdot CuCl_2$ . The wide and exotic range of alkali elements in the chemical analyses of averievite can be explained by the location of these atoms in the structure channels. In general, the chemical formula of averievite is  $Cu_5O_2(VO_4)_2 \cdot nMX$ , where  $MX$  are particles depending on the environment of mineral formation.

The similar nets of oxocentred tetrahedra may be subdivided in the structure of the synthetic compound  $Pb_2Cu_3O_2(NO_3)_2(SeO_3)_2$  (Effenberger, 1986). According to the  $[OT_4]$  crystal chemical approach we describe this structure as composed of oxocentred  $[O_2Cu_3Pb_2]^{6+}$  nets,  $(SeO_3)^{2-}$  and  $(NO_3)^-$  groups. The nets consist of  $[OCu_3Pb]^{6+}$  tetrahedra so that  $Cu$  atoms are shared corners and  $Pb$  atoms are non-shared ones. The oxygen bases of  $(SeO_3)^{2-}$  pyramids are attached to oxocentred tetrahedra in the same way as  $[VO_4]$  groups in the averievite structure.  $(NO_3)^-$  groups occur in channels of the structure as  $MX$  particles in averievite. Topologically equivalent oxocentred  $[O_2Cu_5]^{6+}$  nets are found in the structure of the natural compound  $NaCu_5O_2(SeO_3)_2Cl_3$  which was also discovered as an exhalation product of the Tolbachik volcano (Shuvalov *et al.*, 1995). But in this compound the orientation of non-shared corners of oxocentred tetrahedra is different from averievite nets.

The left part of the averievite formula is identical to stoiberite,  $Cu_5O_2(VO_4)_2$ , a mineral from exhalation products of the Izalco volcano (Salvador) (Birnie and Hughes, 1979). But X-ray data and the crystal structure of this mineral are different from averievite (Table 2) (Shannon and Calvo, 1973). In stoiberite the 'free' oxygen atoms are also contained and they are also coordinated by four copper atoms. Using  $[OT_4]$  crystal chemistry, we can consider its structure as composed of oxocentred polyion and  $[VO_4]$  groups. But in stoiberite the oxocentred structural unit is a 1-dimensional one (Fig. 3d). It consists of two pyroxene-like chains linked by edge linkage.

TABLE 2. Comparison of some parameters for averievite and stoiberite

Parameter	Averievite	Stoiberite
Chemical formula	$Cu_5O_2(VO_4)_2 \cdot nMX$	$Cu_5O_2(VO_4)_2$
Space group	$P3$	$P2/n$
$a$ , Å	6.375(1)	15.654(15)
$b$ , Å	—	6.054(4)
$c$ , Å	8.399(1)	8.385(11)
$\beta$ , °	—	102.29(12)
$Z$	1	4
$D$ , g/cm <sup>3</sup>	4.01	4.96
Type of oxocentred polyions in structure	$\{uB, 1_{\infty}^2\}[O_2Cu_5]^{6+}$ sheets parallel to (001)	$\{uB, 2_{\infty}^1\}[O_2Cu_5]^{6+}$ chains parallel to [010]

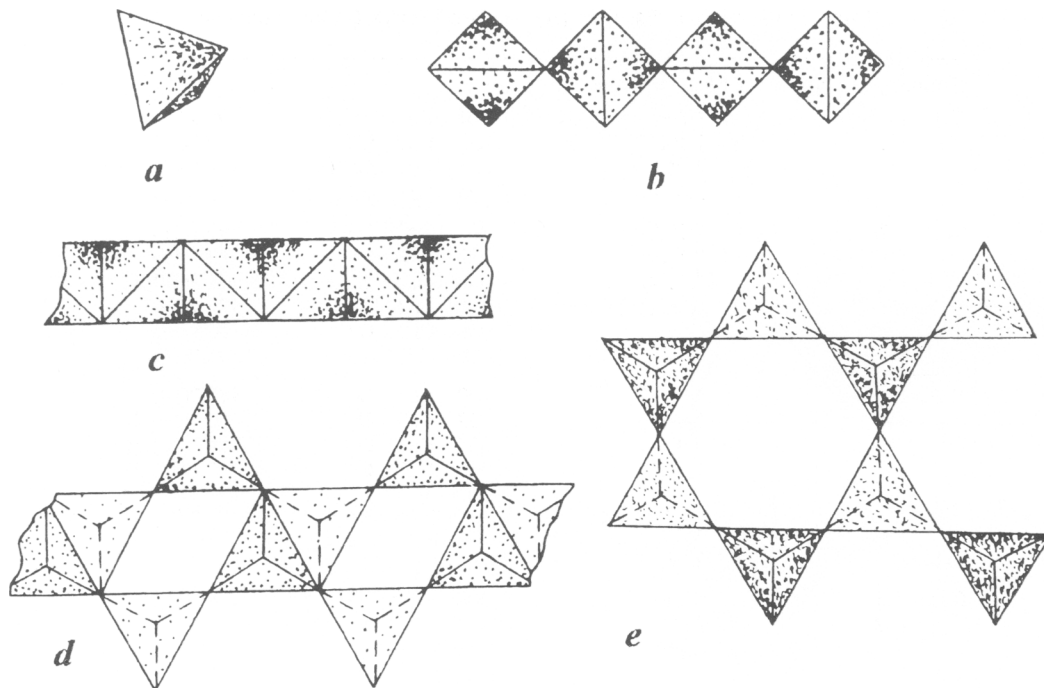


FIG. 3. Types of oxocentred tetrahedral  $[OT_4]$  polyions in the structures of copper oxovanadates (see text).

According to the principles of Liebau (1985), this fragment may be described as unbranched zweier double chain  $\{uB, 2^1_\infty\}[O_2Cu_5]^{6+}$ . Other known copper oxovanadates are fingerite  $Cu_{11}O_2(VO_4)_6$  (Hughes and Hadidiacos, 1985; Finger, 1985), the natural compound  $Cu_4O_2(VO_4)Cl$  (Starova *et al.*, 1995) and the synthetic compound  $Cu_3O(V_2O_7)(H_2O)$  (or  $Cu_3V_2O_8(H_2O)$ ) (Leblanc and Ferey, 1990). Their structures also contained 'free' oxygen atoms coordinated by four copper atoms. The analysis of their structures shows that there are 5 different types of oxocentred polyions in copper oxovanadates (Fig. 3): single tetrahedron  $[OCu_4]^{6+}$  in fingerite (Fig. 3a); single pyroxene-like chains in  $Cu_3O(V_2O_7)(H_2O)$  (Fig. 3b); single edge-sharing chains in natural  $Cu_4O_2(VO_4)Cl$  (Fig. 3c); double pyroxene-like chains in stoiberite (Fig. 3d); and  $[O_2Cu_5]^{6+}$  sheets in averievite (Fig. 3e). We do not consider other oxovanadates which have no copper (e.g. kombatite,  $Pb_{14}O_9(VO_4)_2Cl_4$ ) but in their structures the oxocentred polyions may be also subdivided (Krivovichev *et al.*, 1995).

The coordination polyhedra of Cu atoms in averievite are characterized by strong Jahn-Teller distortions. There are two types of Cu coordination: fivefold (a perfect trigonal bipyramid) for Cu1 and

Cu3, and fourfold (a distorted square) for Cu2 (Table 3). The trigonal bipyramids are usual for copper vanadates, but more often distorted octahedra occur (Finger, 1985; Leblanc and Ferey, 1990; Shannon and Calvo, 1973). A square occurs only infrequently in copper vanadates. The Cu polyhedra are connected with each other so that the square has common edges with both trigonal bipyramids forming a copper-oxygen complex (Fig. 4). The vanadium tetrahedra are slightly distorted and have typical distances and angles. The coordination of 'free' oxygen atoms O2 and O3 is tetrahedral with mean angles Cu-O-Cu  $109.3^\circ$  and  $108.36^\circ$  for O2 and O3, respectively. The bond distances O-Cu for 'free' oxygen (mean 1.895 Å) are shorter than O-Cu distances for oxygen from  $(VO_4)^{2-}$  groups (2.015 Å) approximately on 6% (0.12 Å).

#### Acknowledgements

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TABLE 3. Interatomic distances (Å) and bond angles (°) for averievite

Geometry of copper coordination polyhedra			
Cu1— O1	1.806	O1 - O5	96.99 3x
O5	2.108 3x	O5 - Cu1 - O3	180.00
O3	2.048	O5 - Cu1 - O5'	118.54 3x
	2.036	O5 - Cu1 - O3	83.01 3x
Cu2— O2	1.88(2)	O2 - Cu2 - O5	99.1(19)
O5	2.11(4)	O2 - Cu2 - O6	80.4(17)
O6	1.93(4)	O2 - Cu2 - O3	173.3(17)
O3	1.892(15)	O5 - Cu2 - O6	179.1(19)
	1.953	O5 - Cu2 - O3	86.8(17)
		O6 - Cu2 - O3	93.7(15)
Cu3— O2	1.76(7)	O2 - Cu3 - O4	180.0(18)
O4	1.89(7)	O2 - Cu3 - O6	80.3(16) 3x
O6	2.03(4) 3x	O4 - Cu3 - O6	99.7(16) 3x
	1.948	O6 - Cu3 - O6'	117.2(15) 3x
Cu4— Cl1	2.184	Cl1 - Cu4 - Cl2	180.00
Cl2	1.986		
	2.085		
Cu5— Cl1	2.130	Cl1 - Cu5 - Cl2	180.00
Cl2	2.098		
	2.114		
Geometry of [VO <sub>4</sub> ] groups			
V1— O4	1.63(7)	O4 - V1 - O5	108.2(23) 3x
O5	1.67(4) 3x	O5 - V1 - O5'	110.7(24) 3x
	1.66		109.5
V2— O1	1.69(8)	O1 - V2 - O6	110.7(20) 3x
O6	1.79(4) 3x	O6 - V2 - O6'	108.3(17) 3x
	1.765		109.5
Geometry of oxocentred [OCu <sub>4</sub> ] <sup>6+</sup> tetrahedra			
O2— Cu2	1.88(2) 3x	Cu2 - O2 - Cu3	105.3(20) 3x
Cu3	1.76(7)	Cu2 - O2 - Cu2'	113.3(20) 3x
	1.85		109.3
O3— Cu1	2.048	Cu1 - O5 - Cu2	99.32 3x
Cu2	1.892(15) 3x	Cu2 - O5 - Cu2'	117.4(17) 3x
	1.931		108.36

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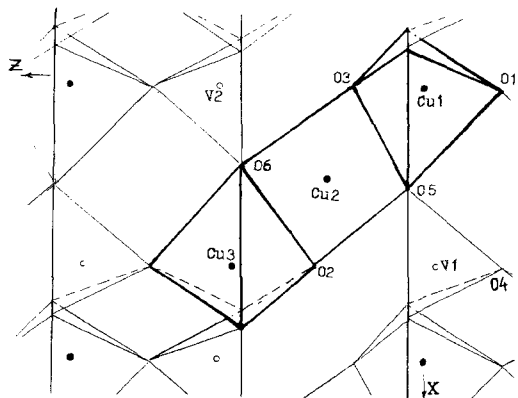


FIG. 4. Projection of the structure of averievite on (010) plane (representation in traditional aspect).

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