Crystal chemistry of inorganic compounds based on chains of oxocentered tetrahedra
III. Crystal structure of georgbokiite, $Cu_5O_2(SeO_3)_2Cl_2$ [1]

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Abstract. The monoclinic crystal structure of georgbokiite, a new mineral with the chemical composition $Cu_5O_2(SeO_3)_2Cl_2$ ($a = 6.030(1)$ Å), $b = 13.744(3)$ Å, $c = 5.562(1)$ Å, $\beta = 95.75(1)°$, $V = 458.6(2)$ Å^3, $Z = 2$, $P2_1/c$) has been refined to an R index of 0.043 ($wR - 0.108$). The structure is similar to that previously determined for synthetic $Cu_5Se_2O_8Cl_2$. It is based on the unbranched *zweier* chains $\{uB, 1_{\infty}^1\}$ $[O_2Cu_5]$ running parallel to the **c** axis which are composed of $[OCu_4]$ oxocentered copper tetrahedra linked through corners and edges in turn. The pyramidal (SeO_3) groups are in "face-to-face" positions relative to the $[OCu_4]$ tetrahedra and together with the oxocentered chains form the more complex chains $\{[O_2Cu_5](SeO_3)_2\}$ lying side by side in the (010) plane. The chloride anions are located between the chains to link them into a three-dimensional framework. The main structural features of other inorganic compounds based on single chains of oxocentered condensed copper tetrahedra are discussed in comparison.

Introduction

The new exhalative mineral georgbokiite, ideally $Cu_5O_2(SeO_3)_2Cl_2$, has been described recently by Verga-sova, Semenova, Krivovichev, Filatov and Ananiev (1998) from fumaroles of the Tolbachik volcano, Kamchatka, Russia. It occurs as brown crystals with adamantine luster. The mineral was named georgbokiite in honour of Georgiy Borisovich Bokii, a well-known Russian crystallographer and crystal chemist.

In the course of investigations, it turned out that georgbokiite has a synthetic analogue, $Cu_5Se_2O_8Cl_2$, prepared by Galy, Bonnet and Andersson (1979) using chemical transport reactions. These authors determined the crystal structure of $Cu_5Se_2O_8Cl_2$ with $R = 0.055$ and described it in terms of copper coordination polyhedra. The structure analysis has revealed the presence of pyramidal (SeO_3)

groups and therefore the presence of additional oxygen atoms, which are not bonded with selenium. Consideration of this structure from the viewpoint of crystal chemistry of oxocentered polycations made it apparent that the additional oxygen atoms have tetrahedral coordination to copper atoms forming oxocentered $[OCu_4]$ tetrahedra (Krivo-vichev, Filatov, Semenova, 1997, 1998a). These tetrahedra with alternated corner and edge sharing form $[O_2Cu_5]$ chains parallel to the **c** axis.

The aim of this paper is to report the results of crystal structure refinement of georgbokiite on the natural sample and to discuss its structure in terms of condensed oxocentered copper tetrahedra. This is a final paper of the title

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

Crystal data	
Chemical formula	$Cu_5O_2(SeO_3)_2Cl_2$
Formula weight	674.52 g · mol^{-1}
Crystal system	Monoclinic
Space group; Z	$P2_1/c$; 2
Lattice constant at 293(2) K	$a = 6.030(1)$ Å
	$b = 13.744(3)$ Å
	$c = 5.562(1)$ Å
	$\beta = 95.75(1)°$
Unit cell volume	$458.6(2)$ Å^3
Density (calculated)	4.88 g · cm^{-3}
Data collection	
Radiation	MoK$_\alpha$ ($\lambda = 0.71069$ Å)
Diffractometer	Syntex $P2_1$
Scan mode	$\omega - 2\theta$
Independent reflections	1068
Observed reflections $[I > 2\sigma(I)]$	1052
Index ranges	$-10 \le h \le 8$
	$0 \le k \le 22$
	$0 \le l \le 9$
Range of 2θ	$3.0°-37.3°$
Linear absorption coefficient μ	19.944 mm^{-1}
Refinement	
Refinement on F	
$R(F)$	0.043
$wR(F^2)$	0.108
Goodness-of-fit S	1.095
Parameters refined	79
Weighting scheme	based on measured e.s.d.'s
$\delta\varrho_{min}$ and $\delta\varrho_{max}$	$-1.27 \le \delta\varrho \le 1.76$ e Å^{-3}

Table 2. Fractional atomic coordinates and atomic displacement parameters (Å^2) for georgbokiite, $Cu_5O_2(SeO_3)_2Cl_2$. $U_{eq} = (1/3) \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \mathbf{a}_j$.

Atom	x	y	z	U_{eq}	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Cu1	0.4304(2)	0.18954(8)	0.5552(2)	0.0177(2)	0.0200(6)	0.0171(5)	0.0167(4)	0.0016(4)	0.0054(3)	0.0020(4)
Cu2	$^1/_2$	0	0	0.0163(3)	0.0155(7)	0.0206(8)	0.0130(5)	0.0025(5)	0.0028(4)	0.0030(6)
Cu3	0.2593(2)	0.99640(8)	0.4868(2)	0.0160(2)	0.0126(5)	0.0191(5)	0.0164(4)	−0.0026(3)	0.0017(3)	0.0005(4)
Se	0.0620(1)	0.13521(6)	0.8999(1)	0.0149(2)	0.0134(4)	0.0174(4)	0.0143(3)	0.0003(3)	0.0024(2)	0.0009(3)
O1	0.5030(10)	0.0618(5)	0.6805(9)	0.0165(11)	0.015(3)	0.020(3)	0.015(2)	0.000(2)	0.003(2)	−0.002(2)
O2	0.2234(9)	0.0596(5)	0.0767(10)	0.0186(12)	0.012(3)	0.026(3)	0.018(2)	0.003(2)	0.002(2)	0.002(2)
O3	0.0270(10)	0.0728(5)	0.6330(9)	0.0173(11)	0.017(3)	0.017(3)	0.017(2)	−0.003(2)	0.001(2)	−0.002(2)
O4	0.2469(10)	0.2216(4)	0.8163(10)	0.0189(12)	0.021(3)	0.019(3)	0.016(2)	0.003(2)	0.004(2)	−0.003(3)
Cl	0.6712(4)	0.1750(2)	0.2657(3)	0.0209(4)	0.0208(11)	0.0239(10)	0.0187(8)	0.0025(7)	0.0053(7)	0.0027(8)

Table 3. Selected bond distances (Å) and angles (°) in georgbokiite, $Cu_5O_2(SeO_3)_2Cl_2$. Symbol i is used for designation of symmetrically equivalent atoms.

	[Å]	[°]		[Å]	[°]
Cu1—O1	1.923(6)		Cu3—O1	1.952(6)	
Cu1—O4	1.962(6)		Cu3—O1^i	1.956(6)	
Cu1—O4^i	2.046(6)		Cu3—O3	1.989(6)	
Cu1—Cl	2.282(2)		Cu3—O3^i	2.024(6)	
Cu1—Cl^i	2.570(2)		Cu3—O2	2.430(5)	
Cu1—O3	2.982(9)		Cu3—Cl	2.739(2)	
O4—Cu1—O4^i		92.2(2)	O1—Cu3—O1^i		84.5(2)
O4—Cu1—O1		93.5(2)	O1—Cu3—O3		93.1(2)
O4^i—Cu1—O1		150.3(2)	O1^i—Cu3—O3		171.9(3)
O4—Cu1—Cl		171.0(2)	O1—Cu3—O3^i		165.5(2)
O4^i—Cu1—Cl		86.3(2)	O1^i—Cu3—O3^i		107.0(2)
O4^i—Cu1—Cl^i		96.2(2)	O3—Cu3—O3^i		76.7(2)
O4—Cu1—Cl^i		80.5(2)	O3—Cu3—O2		101.2(2)
O1—Cu1—Cl^i		113.5(2)	O1—Cu3—O2		110.2(2)
Cl—Cu1—Cl^i		90.8(2)	O3—Cu3—Cl		109.1(2)
			O1—Cu3—Cl		92.9(2)
Cu2—O1	2× 1.971(5)				
Cu2—O2	2× 1.944(6)		O1—Cu1	1.923(6)	
Cu—Cl	2× 2.954(1)		O1—Cu3	1.952(6)	
			O1—Cu3^i	1.956(6)	
O1—Cu2—O2	2×	84.2(2)	O1—Cu2	1.971(5)	
O1—Cu2—O2	2×	95.9(2)		<1.951>	
O1—Cu2—O1		180.0			
O1—Cu2—Cl		86.2(4)	Cu1—O1—Cu2		134.2(3)
O2—Cu2—O2		180.0	Cu1—O1—Cu3		95.1(3)
O2—Cu2—Cl		93.8(4)	Cu1—O1—Cu3^i		110.6(3)
Cl—Cu2—Cl		180.0	Cu2—O1—Cu3		103.0(3)
			Cu2—O1—Cu3^i		109.0(3)
Se—O2	1.674(6)		Cu3—O1—Cu3^i		95.5(2)
Se—O3	1.709(5)			<107.9>	
Se—O4	1.724(6)				
	<1.702>		Cu1—Cu2	3.587(1)	
O2—Se—O4		103.5(3)	Cu1—Cu3	2.860(2)	
O2—Se—O3		102.3(3)	Cu1—Cu3^i	3.190(2)	
O4—Se—O3		98.0(3)	Cu2—Cu3	3.069(1)	
		<101.3>	Cu2—Cu3^i	3.198(1)	
			Cu3—Cu3^i	2.894(2)	

series and in the last part we describe the main structural features of the inorganic copper compounds based on chains of oxocentered copper tetrahedra.

Experimental

The single crystal used for X-ray diffraction data is an isometric one with dimensions $0.15 \times 0.2 \times 0.2$ mm^3. It was first examined by Laue and oscillation methods using CuK_α-radiation. The details of the crystal data, X-ray data collection and the structure refinement are given in Table 1. Lorentz-polarization and absorption corrections were applied using the program systems AREN (Andrianov, 1987) and DIFABS (Walker, Stuart, 1983), respectively. Using the initial parameters of the structure given for $Cu_5Se_2O_8Cl_2$ by Galy et al. (1979), the structure was successfully refined by full-matrix least-squares techniques (SHELXL-93; Sheldrick, 1993). The fractional atomic coordinates and anisotropic thermal displacement parameters are given in Table 2, selected interatomic distances and angles are in Table 3.
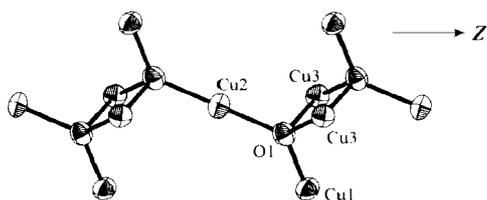
Fig. 1. Configuration of the oxocentered $\{uB, 1^1_\infty\}$ [O₂Cu₅] chain of condensed copper tetrahedra in georgbokiite, Cu₅O₂(SeO₃)₂Cl₂.
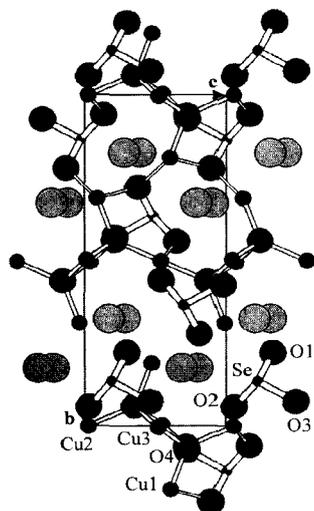
Fig. 2. Crystal structure of georgbokiite, Cu₅O₂(SeO₃)₂Cl₂ in projection onto the (100) plane.

Discussion

The description of the crystal structure on the base of cation-centered polyhedra ([Cu(1)O₃Cl₂]⁶⁻, [Cu(2)O₄Cl₂]⁸⁻ and [Cu(3)O₅Cl₂]⁹⁻) was previously given by Galy et al. (1979). Therefore we shall consider here only its oxocentered aspect. The additional oxygen atom is O(1), tetrahedrally coordinated by four copper atoms with a mean O—Cu bond length equal to 1.95 Å, whereas that for oxygen atoms bonded with selenium is 1.98 Å. Oxocentered [OCu₄] tetrahedra are linked through Cu(3)—Cu(3ⁱ) edges and Cu(2) corners into unbranched *zweier* single chains, $\{uB, 1^1_\infty\}$ [O₂Cu₅], running parallel to the **c** axis (Fig. 1). The (SeO₃) groups are in "face-to-face" positions relative to the [OCu₄] tetrahedra as it was described by Krivovichev, Filatov, Semenova and Rozhdestvenskaya (1998b). It should be noted that these relationships are possible due to the linkage of tetrahedra via corners in contrast to edge-sharing chains for which the "face-to-face" positions are

unfavourable. The oxocentered chains together with (SeO₃) groups form the complex chains {[O₂Cu₅](SeO₃)₂} lying side by side in the (010) plane. The chlorine atoms are located between the chains and link them into a three-dimensional framework (Fig. 2).

It should be mentioned that the analogous chains of cation-centered tetrahedra with alternating linkage through corners and through edges have been observed in the structure of Rb₄In₂S₅ which contains $\{uB, 1^1_\infty\}$ [In₂S₅]⁴⁻ chains of [InS₄]⁵⁻ tetrahedra (Deiseroth, 1980).

Table 4 gives a comparison of $\{uB, 1^1_\infty\}$ [O₂Cu₅] homometallic chains of oxocentered metal tetrahedra found in other inorganic copper(II) compounds. In addition to the parameters defined in our previous works of the series, the O—M$_{b.c.}$, O—M$_{b.e.}$ and O—M$_t$ bond lengths are given for bridging corner (M$_{b.c.}$), corner belonging to the bridging edge (M$_{b.e.}$), and terminal corner (M$_t$) respectively. It is evident that, in general, the structural geometry of chains under consideration is the same. However, in georgbokiite and its synthetic analogue, Cu₅Se₂O₈Cl₂, the O—M$_{b.c.}$ bond length is greater than the O—M$_t$ one, unlike to the corner-sharing oxocentered copper tetrahedra in the chains recently described by Krivovichev et al. (1998b) for Cu₉O₂(SeO₃)₄Cl₆ (chloromenite).

Concluding remarks

1. The low charge of the oxide anion (-2) together with its large ionic radius give rise to a linkage of oxocentered tetrahedra not only *via* corners, but also *via* edges. The face-sharing between oxocentered metal tetrahedra is rather exceptional (however, is observed, e.g. between [OHgBa₃] tetrahedra in BaHgO₂ (Soll, Müller-Buschbaum, 1990)), but it is more usual, for instance, in F⁻ centered tetrahedra (Krivovichev, Filatov, Zaitsev, 1998c). The low charge of oxide anions gives rise to weaker bond strength in these oxocentered polycations than that in polyanions formed with cations of higher valence (e.g., in silicates). Thus oxocentered metal tetrahedra may be considered as strongest structural subunits subsequent to cation-centered polyhedra with high-charged central atoms.

2. The linear condensation of [OA₄] tetrahedra results in the formation of single chains with different types of linkage: through corners, e.g. $\{uB, 1^1_\infty\}$ [O₂Cu₆]⁸⁺ chains in chloromenite (Krivovichev et al., 1998b), through edges, e.g. $\{uB, 1^1_\infty\}$ [O₂Cu₄]⁴⁺ chains in Cu₄O₂[(As, V)O₄]Cl (Starova, Krivovichev, Filatov, 1998), and through corners and edges in turn, e.g. $\{uB, 1^1_\infty\}$ [O₂Cu₅]⁶⁺ chains in georgbokiite (this work). These three types of chains are

Table 4. Structural geometry of $\{uB, 1^1_\infty\}$ [O₂Cu₅] chains of oxocentered tetrahedra in different copper compounds.

Compound [ref.]	Symmetry	l$_{chain}$, Å	O—M$_{b.c.}$, Å	O—M$_{b.e.}$, Å	O—M$_t$, Å	M$_{b.e.}$—O—M$_{b.e.}$, °	<M—O—M>, °
Cu₅O₂(PO₄)₂ [1]	$\bar{1}$	5.304	1.908	1.936	1.943	95.1	109.0
Cu₅Se₂O₈Cl₂ [2]	$\bar{1}$	5.572	1.981	1.952	1.928	95.9	108.0
Cu₅O₂(SeO₃)₂Cl₂ georgbokiite [3]	$\bar{1}$	5.562	1.971	1.954	1.923	95.5	107.9

Refs.: [1] Brunel-Laugt, Guitel, 1977; [2] Galy, Bonnet, Andersson, 1979; [3] this work.

described by distinct values of linkedness of polyion, ML (Krivovichev, Filatov, Semenova, 1997). The first has ML = 1, the second ML = 2, and the third ML = 1, 2. All these chains are built from one kind of crystallographically equivalent tetrahedra and therefore from tetrahedra of identical topological and configurational type. The simplicity of the chain construction results in the great abundance of these three types of chains in inorganic compounds. The linking of the chains produces an exceptional variety of multiple chains, layers and frameworks (Krivovichev, Filatov, Semenova, 1998a).

3. The following empirical rules of structural geometry of oxocentered chains may be recognized, as obtained from observations and immediately follow from the principles claimed in (1):

(a) In chains of corner-sharing oxocentered metal tetrahedra the mean bond length $O-M_{b.c.}$ is smaller than the $O-M_{t.c.}$ one. As a rule, this is observed very often in oxocentered complexes, but not always.

(b) Linking of two tetrahedra through an edge diminishes the bond angles, which are opposite to the shared edge. The average $M-O-M$ angles for all M atoms under consideration are close to the ideal value of $109.5°$. Diminition of one or several $M-O-M$ bond angles due to sharing of their opposite edges, is compensated by an increase of the bond angles opposite to non-shared edges.

4. The shape of single oxocentered chains depends on the characteristics of the structural subunits in their environment.

(a) As it follows from the structures with tetrahedral (sulfates, chromates, etc.) and pyramidal (selenites) oxoanions, these groups are positioned on the bases of oxocentered tetrahedra according to the "face-to-face" relationship which do not generate a chain conformation. The "face-to-face" position is made possible due to the approximate commensurability between the Cu—Cu edges of oxocentered tetrahedra and the O—O edges of $[TO_n]$ groups (n = 3, 4) (Krivovichev, Starova, Filatov, 1999).

(b) In certain situations, the single chains of edge-sharing oxocentered metal tetrahedra can be conformed in the presence of large halide anions such as observed in $Cu_4O_2[(As, V)O_4]Cl$. In this compound chloride ions give rise to rotation of the oxocentered copper tetrahedra in the chain by way of two Cu—Cl bonds each.

The consideration of these conclusions in detail exhibits the "inverted" character of the crystal chemistry of polycations based on oxocentered metal tetrahedra in comparison to that of silicates or other compounds based on

strongly polymerized cation-centered polyhedra of anions. One was inclined to expect this fact considering the negative charge for the central ion and the positive one for the ligands.

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