

# Crystal chemistry of inorganic compounds based on chains of oxocentered tetrahedra

## I. Crystal structure of chloromenite, $\text{Cu}_9\text{O}_2(\text{SeO}_3)_4\text{Cl}_6$

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**Abstract.** The crystal structure of chloromenite,  $\text{Cu}_9\text{O}_2(\text{SeO}_3)_4\text{Cl}_6$ ,  $a = 14.170(3)$  Å,  $b = 6.262(1)$  Å,  $c = 12.999(3)$  Å,  $\beta = 113.05(1)^\circ$ ,  $V = 1061.3(4)$  Å<sup>3</sup>,  $Z = 2$ , space group  $I2/m$ , has been solved by direct methods and refined to an  $R(F)$  index of 0.051 ( $wR(F^2) = 0.128$ ). The structure is based on unbranched *zweier* single chains  $[uB, 1^1_\infty][\text{O}_2\text{Cu}_6]$  of corner sharing  $[\text{OCu}_4]$  tetrahedra running parallel to the  $b$  axis. The geometry of structurally similar  $[uB, 1^1_\infty][\text{O}_2\text{M}_6]$  ( $M = \text{Cu}, \text{Zn}$ ) chains of oxocentered  $[\text{OM}_4]$  tetrahedra ( $M = \text{Cu}, \text{Zn}$ ) in inorganic compounds is discussed.

### Introduction

In crystal chemistry usually descriptions of cations as central atoms and anions as ligands are given. Many crystal structures may be analysed, however, on the basis of the coordination of anions. This is particularly suitable in the description of compounds with 'additional' oxygen atoms, i.e. atoms not included into the usual  $[\text{T}_n\text{O}_m]$  complexes where  $T = \text{Si}, \text{Ge}, \text{B}, \text{S}, \text{P}, \text{V}, \text{As}, \text{Se}, \text{etc.}$ , as well as into water molecules. In most cases, the 'additional' oxygen atoms have a tetrahedral coordination environment of metal atoms, therefore being centres in  $[\text{OM}_4]^{m-}$  cationic complexes. Relatively high bond strength in oxocentered tetrahedra allows to suggest their selection as independent structural subunits in compounds with 'additional' oxygen atoms.

Oxocentered  $[\text{OM}_4]$  tetrahedra are well known in metal-organic compounds as polynuclear metal complexes with  $\mu_4$ -bridging oxygen atoms. Their structures have been subjected to extensive investigation because of their interesting magnetic properties (see, e.g., Reim, Griesar, Haase, Krebs, 1995; Goldberg, Caneschi, Delfs, Sessoli, Lippard, 1995, and ref. therein) caused by the metal-metal interaction within  $[\text{OM}_4]$ -tetrahedra. Recently, Young, Charlton, Olmstead, Kauzlarich, Lee and Müller (1997) described some inorganic structures composed of infinite chains based on the 'empty'  $\text{Cu}_4$  tetrahedra, i.e. without central

oxygen atoms. Thus the role of  $M \cdots M$  interactions is favourable to the additional stabilisation of oxocentered tetrahedra, although they are considerably weaker than those in  $\text{Cu}_4$  clusters as may be concluded from the comparison of the Cu–Cu distances.

This paper is the first of a series of papers in which we would like to report the results on the crystal structures of inorganic compounds containing  $[\text{OCu}_4]$  oxocentered tetrahedra linked into variously shaped chains.

The first compound under investigation is chloromenite, a new mineral having the idealised formula  $\text{Cu}_9\text{O}_2(\text{SeO}_3)_4\text{Cl}_6$ , described recently by Vergasova, Krivovichev, Semenova, Filatov and Ananiev (1999) as ob-

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

Crystal data	
Chemical formula	$\text{Cu}_9\text{O}_2(\text{SeO}_3)_4\text{Cl}_6$
Formula weight	1324.40 g·mol <sup>-1</sup>
Crystal system	Monoclinic
Space group, $Z$	$I2/m, 2$
Lattice constants at 293(2) K	$a = 14.170(3)$ Å $b = 6.262(1)$ Å $c = 12.999(3)$ Å $\beta = 113.05(1)^\circ$ $1061.3(4)$ Å <sup>3</sup>
Unit cell volume	
Density (calculated)	4.14 g·cm <sup>-3</sup>
Data collection	
Radiation	$\text{MoK}\alpha$ ( $\lambda = 0.71069$ Å)
Diffractometer	Syntex P2 <sub>1</sub>
Scan mode	$\omega - 2\theta$
Independent reflections	1566
Observed reflections ( $I > 2\sigma(I)$ )	1453
Index ranges	$-21 \leq h \leq 20$ $0 \leq k \leq 10$ $0 \leq l \leq 20$ $1.8^\circ - 25.0^\circ$
Range of $\theta$	
Linear absorption coefficient $\mu$	16.504 mm <sup>-1</sup>
Refinement	
Refinement on $F$	
$R(F)$	0.051
$wR(F^2)$	0.128
Goodness-of-fit $S$	1.065
Parameters refined	96
Weighting scheme	based on measured e.s.d.'s
$\Delta Q_{\text{min}}$ and $\Delta Q_{\text{max}}$	$-1.87 \leq \Delta Q \leq 2.26 \text{ e} \cdot \text{Å}^{-3}$

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**Table 2.** Fractional atomic coordinates and displacement parameters ( $\text{\AA}^2$ ) for chloromenite.  $U_{ij} = (\frac{1}{V}) \sum_i \sum_j U_{ij} a_i^* a_j^* a_i a_j$ 

Atom	<i>x</i>	<i>y</i>	<i>z</i>	$U_{01}$	$U_{11}$	$U_{22}$	$U_{33}$	$U_{23}$	$U_{13}$	$U_{12}$
Cu1	$\frac{1}{2}$	0	0	0.0192(4)	0.0167(9)	0.0261(10)	0.0152(8)	0	0.0066(7)	0
Cu2	0.3792(1)	0	0.1633(1)	0.0152(3)	0.0141(6)	0.0114(6)	0.0206(6)	0	0.0073(5)	0
Cu3	0.2835(1)	0	0.5526(1)	0.0214(3)	0.0230(7)	0.0140(6)	0.0258(7)	0	0.0108(6)	0
Cu4	0.1186(1)	0	0.0259(1)	0.0257(4)	0.0132(6)	0.0492(10)	0.0122(6)	0	0.0024(5)	0
Cu5	$\frac{1}{2}$	$-\frac{1}{4}$	$\frac{1}{4}$	0.0149(3)	0.0163(6)	0.0102(5)	0.0192(6)	0.0039(5)	0.0080(5)	0.0018(4)
Se1	0.2516(1)	0	0.88863(9)	0.0162(2)	0.0156(5)	0.0194(5)	0.0129(4)	0	0.0048(4)	0
Se2	0.03842(8)	0	0.23727(9)	0.0124(2)	0.0126(4)	0.0103(4)	0.0136(4)	0	0.0043(3)	0
O1	0.2381(5)	0	0.1601(6)	0.013(1)	0.014(3)	0.006(3)	0.015(3)	0	0.000(3)	0
O2	0.3761(4)	-0.2967(9)	0.2170(5)	0.021(1)	0.024(3)	0.016(3)	0.031(5)	0.015(2)	0.016(2)	3.005(2)
O3	0.3115(4)	-0.307(1)	0.5713(6)	0.036(1)	0.021(3)	0.014(3)	0.044(4)	0.006(3)	0.014(3)	0.000(2)
O4	0.3664(6)	0	0.0014(7)	0.025(2)	0.015(4)	0.046(6)	0.015(4)	0	0.308(3)	0
O5	0.0150(6)	0	0.0980(7)	0.022(2)	0.011(3)	0.035(5)	0.016(4)	0	0.001(3)	0
Cl1	0.3688(2)	0	0.4363(3)	0.0244(7)	0.0253(14)	0.0253(14)	0.0220(12)	0	0.0075(11)	0
Cl2	0.4460(2)	0	0.8068(2)	0.0266(6)	0.0382(12)	0.041(2)	0.0180(12)	0	0.0044(9)	0
Cl3	0.1484(3)	0	0.5968(4)	0.0431(9)	0.043(2)	0.042(2)	0.056(2)	0	0.032(2)	0

tained from the exhalations of Tolbachik volcano, Kamchatka, Russia. The mineral was named chloromenite according to its colour and chemical composition:  $\chi\lambda\omega\phi\phi\zeta$  – 'green' and  $\mu\pi\pi\phi\zeta$  – 'moon' that indicates the presence of chlorine and selenium, respectively. It occurs as brownish-green elongated transparent plates growing on the surface of crystals of melanothalite,  $\text{Cu}_2\text{OCl}_2$ . From electron microprobe analysis the empirical formula  $\text{Cu}_{2.71}\text{Zn}_{0.97}\text{Se}_{4.40}\text{O}_{13.80}\text{Cl}_{6.20}$ , having a ratio Cu:Zn close to 8:1, was derived.

## Experimental

A single crystal of chloromenite with dimensions  $0.15 \times 0.20 \times 0.40 \text{ mm}^3$  was studied by Weissenberg techniques that indicates the monoclinic Laue symmetry  $2/m$  and the body-centered unit cell. The *I*-lattice was chosen according to the smaller  $\beta$  angle as compared with the *C*-lattice. Details of the crystal data, X-ray data collection and 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. The structure was solved in the space group  $I2/m$  by direct methods (AREN; Andrianov, 1987) and refined by full-matrix least-squares methods (SHELXL-93; Sheldrick, 1993). Attempts to localise the Zn position in the structure were not successful. The fractional atomic coordinates and thermal displacement parameters are given in Table 2, selected interatomic distances and angles in Table 3.

The measured strongest lines in the X-ray powder diffraction pattern ( $(h - d - hkl)$ :  $63 - 11.3 - 101$ ;  $21 - 7.49 - 101$ ;  $17 - 6.51 - 200$ ;  $83 - 5.56 - 011$ ;  $100 - 3.45 - 103$ ;  $39 - 3.24 - 204$ ;  $33 - 2.71 - 503$ ,  $312$ ;  $61 - 2.49 - 303$ ,  $402$ ) are in good agreement with those calculated on the basis of the crystal structure with regard to the perfect cleavage on (101).

## Discussion

As can be seen from Table 3, there are five copper positions in the chloromenite structure that correspond to five crystal chemically distinct coordination polyhedra: Cu(1) and Cu(5) – planar squares [2O + 2Cl] and [4O], Cu(2) and Cu(4) – trigonal bipyramids [4O + Cl] and [5O], respectively, Cu(3) – a flattened tetrahedron [2O + 2Cl]. In the [Cu(2)O<sub>4</sub>Cl] polyhedron there are four oxygen atoms at 1.98 Å–2.04 Å, whereas in the [Cu(4)O<sub>5</sub>] bipyramid the equatorial oxygen atoms are at 2.03 Å, 2.24 Å and the two apical ones at 1.90 Å and 1.95 Å.

It appears that the flattened tetrahedron with the chemical composition [CuO<sub>2</sub>Cl<sub>2</sub>] has been observed in inorganic compounds for the first time, although the structurally similar one [CuO<sub>2</sub>] formed by four oxygen atoms has often been reported, for instance, in  $\text{PbCu}_2\text{O}(\text{TeO}_4)$  (Wedel, Müller-Buschbaum, 1996).

Both selenite groups have trigonal pyramidal coordinations with usual mean Se–O bond lengths 1.70 Å.

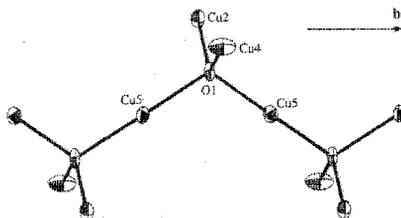
The 'additional' oxygen atom, O(1), is tetrahedrally coordinated by Cu(2), Cu(4) and two Cu(5) atoms with mean Cu–O bond length 1.93 Å (1.90 Å–1.98 Å). The mean bond length Cu–O for oxygen atoms of selenite groups, without regard for bonds longer than 2.20 Å, is 1.98 Å (1.90 Å–2.04 Å). The copper atoms Cu(1) and Cu(3) are not bonded to O(1) at all.

We consider the [O(1)Cu<sub>4</sub>] tetrahedra as independent structural subunits in the chloromenite structure. Oxocentered [O(1)Cu<sub>4</sub>] tetrahedra are linked *via* corners to unbranched *zweier* chains  $\{u\bar{b}, 1^1_{\infty}\}[\text{O}_2\text{Cu}_6]$  parallel to the *b* axis (Figs. 1, 2a). Selenite groups  $\text{Se}(2)\text{O}_3$  are in 'face-to-face' positions relative to the oxocentered tetrahedra (Figs. 2b, c). The chain  $\{O_2\text{Cu}_6\}$  together with  $\text{Se}(2)\text{O}_3$  groups (one group per one tetrahedron) form a complex chain  $\{[\text{O}_2\text{Cu}_6][\text{Se}(\text{O}_3)_2]\}$  decorated by the flattened tetrahedra  $[\text{Cu}(3)\text{O}_2\text{Cl}_2]$  and the second type of selenite groups. These entities are linked through  $\{[\text{Cu}(1)\text{O}_2\text{Cl}_2]\}$  'squares' (disphenoids) to layers parallel to (101) (Fig. 3).

Structurally similar chains  $\{u\bar{b}, 1^1_{\infty}\}[\text{O}_2\text{M}_6]$  of corner sharing oxocentered tetrahedra  $[\text{OM}_4]$  have been observed in inorganic compounds for  $\text{M} = \text{Cu}, \text{Zn}$ :  $\{u\bar{b}, 1^1_{\infty}\}$

Table 3. Selected bond lengths and valence angles in chloromennite.

	[Å]	[°]		[Å]	[°]
Cu1—O4	2×	1.906(9)	Cu5—O1	2×	1.922(4)
Cu1—Cl2	2×	2.322(3)	Cu5—O2	2×	2.016(6)
O4—Cu1—O4		180.0	O1—Cu5—O2		180.0
O4—Cu1—Cl2	2×	84.1(3)	O1—Cu5—O1	2×	97.9(3)
O4—Cu1—Cl2	2×	95.9(3)	O1—Cu5—O2	2×	82.1(3)
Cl2—Cu1—Cl2		180.0	O2—Cu5—O2		180.0
Cu2—O1		1.982(8)	Se1—O3	2×	1.700(6)
Cu2—O2	2×	1.991(6)	Se1—O4		1.711(8)
Cu2—O4		2.041(9)		(1.704)	90.3(4)
Cu2—Cl2		2.351(3)	O3—Se1—O3	2×	100.1(3)
O1—Cu2—O2	2×	81.2(2)	O3—Se1—O4		(96.8)
O2—Cu2—O2		137.9(4)	Se2—O2	2×	1.696(6)
O1—Cu2—O4		107.2(3)	Se2—O5		1.708(8)
O2—Cu2—O4	2×	110.9(2)		(1.70)	
O1—Cu2—Cl2		172.4(2)	O2—Se2—O2		97.3(4)
O2—Cu2—Cl2	2×		O2—Se2—O5	2×	100.8(3)
O4—Cu2—Cl2		80.4(2)		(99.6)	
Cu3—O5	2×	1.962(6)	O1—Cu2		1.982(8)
Cu3—Cl1		2.276(4)	O1—Cu4		1.896(7)
Cu3—Cl3		2.203(5)	O1—Cu5	2×	1.932(4)
O3—Cu3—O3		157.9(4)		(1.930)	
O3—Cu3—Cl1	2×	87.0(2)	Cu2—O1—Cu4		123.3(4)
O3—Cu3—Cl3	2×	97.0(2)	Cu2—O1—Cu5	2×	98.0(2)
Cl3—Cu3—Cl1		156.2(2)	Cu4—O1—Cu5	2×	113.2(2)
Cu4—O1		1.896(7)	Cu5—O1—Cu5		109.1(4)
Cu4—O3	2×	2.238(7)		(109.1)	
Cu4—O5		1.948(8)	Cu2—Cu4		3.414(1)
Cu4—O5 <sup>f</sup>		2.028(9)	Cu2—Cu5	2×	2.947(1)
O1—Cu4—O3	2×	94.9(3)	Cu4—Cu5	2×	3.187(1)
O1—Cu4—O5		171.8(4)	Cu5—Cu5 <sup>f</sup>		3.131(8)
O1—Cu4—O5 <sup>f</sup>		97.0(3)		(3.135)	
O3—Cu4—O3		65.2(3)			
O3—Cu4—O5	2×	92.0(3)			
O3—Cu4—O5 <sup>f</sup>	2×	145.2(2)			
O5—Cu4—O5 <sup>f</sup>		74.7(4)			

Fig. 1. Chloromennite: configuration of the chain  $\{uB, 1^{\infty}\}(\text{O}_2\text{Cu}_6)$  of corner sharing oxocentered tetrahedra  $\{\text{OCu}_3\}$ .

$\times(\text{O}_2\text{Cu}_6)$  in kamchatkite  $\text{KCu}_3\text{OCl}(\text{SO}_4)$  (Varakina, Fundamensky, Filatov, Vergasova, 1990),  $\text{Cu}_3\text{O}(\text{MoO}_4)_2$  (Kihlberg, Norrestam, Olivecrona, 1971; Kihlberg, Norrestam, 1972; Steiner, Reichelt, 1997),  $\text{Cu}_3\text{O}(\text{V}_2\text{O}_7)(\text{H}_2\text{O})$  (Leblanc, Ferry, 1990),  $\text{Na}_2\text{Cu}(\text{I})\text{Cu}(\text{II})_3\text{O}(\text{PO}_4)_2\text{Cl}$  (Etheredge, Hwu, 1996);  $\{uB, 1^{\infty}\}(\text{O}_2\text{Zn}_6)$  in  $\text{Zn}_3\text{O}(\text{SO}_4)_2$  (Bald, Gruhn, 1981) and  $\text{Zn}_3\text{O}(\text{MoO}_4)_2$  (Söhnel, Reichelt, Oppermann, Mattausch, Simon, 1996). The geometric parameters of these chains are given in Table 4 as follows:

- (i) symmetry of a chain;
- (ii) chain identity period  $I_{\text{chain}}$ ;
- (iii) mean bond lengths (O—M) for bridging  $\{M_{b.c.}$  (b.c. = bridging corner) and terminal  $\{M_{t.c.}$  (t.c. = terminal corner) cations (Fig. 2a);
- (iv) mean valence angle  $\langle M_{b.c.}-O-M_{b.c.} \rangle$ ;
- (v) mean valence angle  $\langle M-O-M \rangle$ ;
- (vi) mean distance  $\langle M_{b.c.}-M_{b.c.} \rangle$ ;
- (vii) mean distance  $\langle M-M \rangle$  in the oxocentered tetrahedra chain.

A comprehensive treatment of the data given in Table 4 shows the following basic features of the chains:

- (1) Symmetry of the chain is no less than 2, and the bridging metal atoms lie on the screw axis. As a result, the chains under consideration are *zweier* single chains, all tetrahedra in the chain are crystallographically equivalent and, therefore, the equation:

$$I_{\text{chain}} = 2 \langle M_{b.c.}-M_{b.c.} \rangle$$

is fulfilled. Following in general Liebau and Pallas (1981), we define the stretching factor of a chain of corner sharing tetrahedra,  $\zeta_{\text{c}}$ , as

$$\zeta_{\text{c}} = I_{\text{chain}} \left[ \sum_{i=1}^P \langle M_{b.c.}-M_{b.c.} \rangle \right]^{-1}$$

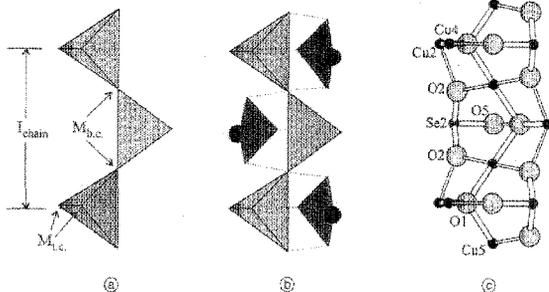


Fig. 2. Chloromenite: chain of oxocentered tetrahedra in polyhedral representation (a), relationships between  $(OCu_4)$  tetrahedra and  $(SeO_3)$  groups in polyhedral (b), and 'ball-and-stick' (c) representations.

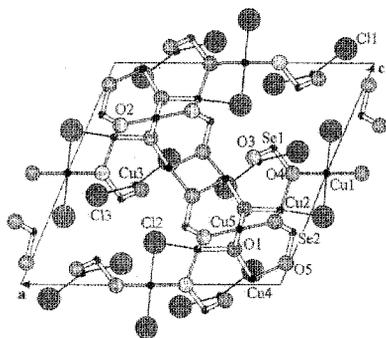


Fig. 3. Chloromenite: projection of the structure onto the (010) plane.

In accord with this definition, all chains listed in Table 4 have  $f_c$  values invariably equal to 1 in contrast to silicates in which the stretching factor (but with slightly different definition) for topologically similar corner-sharing chains may range from 1.000 for shattuckite  $Cu_5[Si_2O_6]_2(OH)_2$  to 0.234

for  $Na_{24}Y_6[Si_{12}O_{72}]$  (Liebau, Pallas, 1981; Liebau, 1985).

- (2) With the exception of kamchatkite, the mean bond lengths ( $O-M_{b,c}$ ) are shorter than their corresponding ( $O-M_{c,c}$ ). Quite different situation holds for the silicate anions in which  $Si-O_{b,c}$  bond lengths are usually longer than  $Si-O_c$  ones (Liebau, 1985).
- (3) The linking of tetrahedra via corners leads to an increase in  $M_{b,c}-O-M_{b,c}$  valence angles relative to the ideal value  $109.5^\circ$  for the tetrahedral angle.

It is obvious that the structural geometry of chains of corner sharing oxocentered tetrahedra is different from that observed for analogous silicate anions.

The following argument may be used for a qualitative explanation of these facts. Owing to the low absolute charge of the oxide anion  $O^{2-}$ , the repulsive forces between the centres of corner sharing oxocentered  $\{O(Cu^{2+})_4\}$  tetrahedra are considerably weaker than those between the centres of corner sharing  $\{SiO_4\}$  tetrahedra. For similar reasons, the bonds between the central atom and atoms at the corners in  $\{OM_4\}$  tetrahedra are weaker than those in  $\{SiO_4\}$  tetrahedra. The bridging metal atom,  $M_{b,c}$ , is firmly bound by two 'additional' oxygen atoms, whereas the terminal ones,  $M_{c,c}$ , are only bound to a sin-

Table 4. Structural geometry of *zwiter* single chains ( $aB, 1^1_{\infty}$ ) $[O_2M_c]_n$  of corner sharing  $\{OM_4\}$  tetrahedra ( $M = Cu, Zn$ ) in inorganic compounds.

Compound [ref.]	Symn.	$l_{chain}$ [Å]	$(O-M_{b,c})$ [Å]	$(O-M_{c,c})$ [Å]	$(M_{b,c}-O-M_{b,c})$ [°]	$(M-O-M)$ [°]	$(M_{b,c}-M_{c,c})$ [Å]	$(M-M)$ [Å]
$KCu_3OCl(SO_4)$	$2_1$	7.001	<b>1.92</b>	<b>1.92</b>	<b>131.6</b>	<b>109.4</b>	3.500	3.120
kamchatkite [1]			[1.86-1.98]	[1.92]		[99.6-131.6]		
$Cu_3O(MoO_4)_2$	$2_1$	6.862	<b>1.861</b>	<b>1.934</b>	<b>134.4</b>	<b>109.3</b>	3.431	3.077
[2]			[1.861]	[1.927-1.941]		[102.1-134.4]		
$Cu_3O(V_2O_7)(H_2O)$	$2_1/m$	6.658	<b>1.881</b>	<b>1.923</b>	<b>124.5</b>	<b>108.9</b>	3.329	3.087
[3]			[1.881]	[1.916-1.929]		[102.0-124.5]		
$Na_2Cu(II)Cu(III)_2O(PO_4)_2Cl$	$2_1/mmm$	6.372	<b>1.853</b>	<b>1.912</b>	<b>118.6</b>	<b>109.5</b>	3.186	3.072
[4]			[1.853]	[1.912]		[107.0-118.6]		
$Cu_3O_1(SeO_3)_2Cl_6$	$2_1/m$	6.262	<b>1.922</b>	<b>1.939</b>	<b>109.1</b>	<b>109.1</b>	3.135	3.142
chloromenite			[1.922]	[1.896-1.982]		[98.0-123.3]		
$Zn_3O(SO_4)_2$	$2_1/m$	6.690	<b>1.91</b>	<b>1.97</b>	<b>121.8</b>	<b>109.6</b>	3.345	3.163
[5]			[1.91]	[1.96-1.97]		[104.5-121.8]		
$Zn_3O(MoO_4)_2$	$2_1$	7.132	<b>1.943</b>	<b>1.955</b>	<b>133.2</b>	<b>109.5</b>	3.566	3.168
[6]			[1.943]	[1.953-1.957]		[102.4-133.2]		

Refs.: [1] Varakina, Fundamenskiy, Filatov, Vergasova, 1990; [2] Steiner, Reichel, 1997; [3] Leblanc, Ferey, 1990; [4] Etheredge, Hwa, 1996; [5] Bald, Gruehn, 1981; [6] Söhl, Reichel, Oppermann, Mattausch, Simon, 1996.

gle. In addition, the  $M_{b,c}$  metal atom has six  $M \cdots M$  metal-metal contacts, whereas the  $M_{a,c}$  atom has only three. Therefore, the  $M_{b,c}$  atoms are secured to the chain more firmly than the  $M_{a,c}$  ones and may more easily be retracted from the central oxygen atoms. Shortening of the  $\text{O}-\text{Cu}_{b,c}$  distances leads to the shortening of distances and hence causes the  $\text{Cu}_{b,c}-\text{Cu}_{b,c}$  repulsion. These repulsive forces are compensated by an increase of the  $\text{Cu}_{b,c}-\text{O}-\text{Cu}_{b,c}$  valence angles and  $\text{Cu}_{b,c}-\text{Cu}_{b,c}$  distances (Table 4).

However, it should be noted that this scheme does not work completely if there are some factors limiting an increase in the  $\text{Cu}_{b,c}-\text{O}-\text{Cu}_{b,c}$  angle. Chloromenite is an example of how the chain may shrink due to the additional bonds external to its sub-structure. In chloromenite translationally equivalent chain tetrahedra are bonded by the  $[\text{SeO}_3]$  groups as it is shown in Fig. 2c. This prevents the stretching of the chain and, in this case, the proposed scheme works in the reverse order: an approach of bridging copper atoms is compensated not by an increase of  $\text{Cu}_{b,c}-\text{O}-\text{Cu}_{b,c}$  angle but by an increase of  $\text{O}-\text{Cu}_{b,c}$  distances as a result of which the difference between  $\text{O}-\text{Cu}_{a,c}$  and  $\text{O}-\text{Cu}_{b,c}$  distances is reduced.

Another interesting aspect of the data given in Table 4 is that the chains are not bent and always have the periodicity  $P = 2$ . In most of the listed structures this may be explained by the regular relationships between oxocentered tetrahedra in corner-sharing chains and strong cation-centered complex anions,  $[\text{TO}_4]$  ( $n = 3, 4$ ;  $T = \text{Se, S, Mo}$ ). These relationships, we called them 'face-to-face', imply that the  $M-M-M$  triangular face of oxocentered  $[\text{OM}_4]$  groups and the  $\text{O}-\text{O}-\text{O}$  one of  $[\text{TO}_4]$  group are parallel to each other and their orientations are identical (Fig. 2b). This was first illustrated by Starova, Krivovichev, Fundamensky and Filatov (1997) for averievite,  $\text{Cu}_3\text{O}_2(\text{VO}_4)_2 \cdot \text{MCl}$  ( $M = \text{K, Rb, Cs}$ ), in which  $[\text{VO}_4]$  groups are tripodally positioned at the bases of  $[\text{OCu}_4]$  tetrahedra.

In this paper we considered the crystal structure of chloromenite,  $\text{Cu}_9\text{O}_2(\text{SeO}_3)_4\text{Cl}_6$ , based on chains of corner sharing oxocentered  $[\text{OCu}_4]$  tetrahedra. In the following ones on  $\text{Cu}_6\text{O}_2[(\text{As, V})\text{O}_4]\text{Cl}$  (Starova, Krivovichev, Filatov, 1998) and  $\text{Cu}_3\text{O}_2(\text{SeO}_3)_2\text{Cl}_2$  (gaorbokite; Krivovichev, Shuvalov, Semenova, Filatov, 1999) we shall report on structures in which oxocentered tetrahedra  $[\text{OCu}_4]$  share edges.

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