

# Dimers of oxocentred $[\text{OCu}_4]^{6+}$ tetrahedra in two novel copper selenite chlorides, $\text{K}[\text{Cu}_3\text{O}](\text{SeO}_3)_2\text{Cl}$ and $\text{Na}_2[\text{Cu}_7\text{O}_2](\text{SeO}_3)_4\text{Cl}_4$ , and related minerals and inorganic compounds

VADIM M. KOVRUGIN<sup>1,2</sup>, MARIE COLMONT<sup>2</sup>, OLIVIER MENTRÉ<sup>2</sup>, OLEG I. SIDRA<sup>1</sup> AND SERGEY V. KRIVOVICHEV<sup>1,\*</sup>

<sup>1</sup> Department of Crystallography, St Petersburg State University, Universitetskaya nab. 7/9, 199034 St Petersburg, Russia

<sup>2</sup> UCCS, ENSCL, Université Lille 1, CNRS, UMR 8181, 59652 Villeneuve d'Ascq, France

[Received 6 November 2014; Accepted 19 May 2015; Associate Editor: Mark Welch]

## ABSTRACT

Two novel copper selenite chlorides,  $\text{K}[\text{Cu}_3\text{O}](\text{SeO}_3)_2\text{Cl}$  (**I**) and  $\text{Na}_2[\text{Cu}_7\text{O}_2](\text{SeO}_3)_4\text{Cl}_4$  (**II**), have been synthesized by the CVT method. Their crystal structures have been solved by direct methods and refined by least-squares techniques. **I** is triclinic, space group  $P\bar{1}$ ,  $a = 7.6821(5)$ ,  $b = 8.1179(5)$ ,  $c = 8.7836(6)$  Å,  $\alpha = 113.193(3)$ ,  $\beta = 108.735(4)$ ,  $\gamma = 98.245(4)^\circ$ ,  $V = 453.32(5)$  Å<sup>3</sup>,  $R_1 = 0.0481$  for 1210 unique reflections with  $F \geq 4\sigma(F)$ ; **II** is triclinic, space group  $P\bar{1}$ ,  $a = 7.4362(6)$ ,  $b = 8.3361(7)$ ,  $c = 9.1343(11)$  Å,  $\alpha = 110.277(6)$ ,  $\beta = 106.212(6)$ ,  $\gamma = 105.158(4)^\circ$ ,  $V = 467.94(8)$  Å<sup>3</sup>,  $R_1 = 0.0265$  for 2498 unique reflections with  $F \geq 4\sigma(F)$ . The structures of **I** and **II** can be described in terms of dimers of copper oxocentred tetrahedra. In **I**, two  $(\text{OCu}_4)^{6+}$  tetrahedra share a common  $\text{Cu}\cdots\text{Cu}$  edge to form the  $[\text{O}_2\text{Cu}_6]^{8+}$  dimer, whereas the structure of **II** is based upon two  $(\text{OCu}_4)^{6+}$  tetrahedra linked together by one common Cu atom resulting in the formation of the  $[\text{O}_2\text{Cu}_7]^{10+}$  dimer. A comparison with related minerals and inorganic compounds is given.

**KEYWORDS:** crystal structure, oxocentred tetrahedra, lone electron pair, stereoactivity, euchlorine, fedotovite, prewittite, burnsite.

## Introduction

THE crystal chemistry of selenium-containing natural and synthetic oxocompounds of copper is of special interest owing to the specific structural features of both  $\text{Cu}^{2+}$  and  $\text{Se}^{4+}$  ions.  $\text{Cu}^{2+}$  may possess different and flexible coordination geometries (Burns and Hawthorne, 1995*a,b*; Rosner *et al.*, 2007; Melník *et al.*, 2011; Burrows *et al.*, 2012; Krivovichev *et al.*, 2012), while  $\text{Se}^{4+}$  cations form asymmetric  $(\text{SeO}_3)^{2-}$  groups due to the stereochemically active behaviour of the  $s^2$  lone electron pairs, resulting in structurally complex architectures and interesting physical properties (Mao *et al.*, 2008; Zhang *et al.*, 2010; Berdonosov *et al.*, 2013).

Most of the naturally occurring copper selenite chlorides have been reported from fumaroles of the Tolbachik volcano, Kamchatka Peninsula, Russia: ilinskite,  $\text{Na}[\text{Cu}_5\text{O}_2](\text{SeO}_3)_2\text{Cl}_3$  (Vergasova *et al.*, 1997; Krivovichev *et al.*, 2012), georgbokiite,  $\alpha\text{-}[\text{Cu}_5\text{O}_2](\text{SeO}_3)_2\text{Cl}_2$  (Krivovichev *et al.*, 1999*a*), chloromenite,  $[\text{Cu}_9\text{O}_2](\text{SeO}_3)_4\text{Cl}_6$  (Vergasova *et al.*, 1999), burnsite,  $\text{KCd}[\text{Cu}_7\text{O}_2](\text{SeO}_3)_2\text{Cl}_9$  (Burns *et al.*, 2002; Krivovichev *et al.*, 2002), allochalcoselite,  $\text{Cu}^+[\text{PbCu}_5^{2+}\text{O}_2](\text{SeO}_3)_2\text{Cl}_5$  (Krivovichev *et al.*, 2006), parageorgbokiite,  $\beta\text{-}[\text{Cu}_5\text{O}_2](\text{SeO}_3)_2\text{Cl}_2$  (Krivovichev *et al.*, 2007), prewittite,  $\text{KPb}_{0.5}\text{Cu}[\text{PbCu}_5\text{O}_2]\text{Zn}(\text{SeO}_3)_2\text{Cl}_{10}$  (Shuvalov *et al.*, 2013) and nicksobolevite,  $[\text{Cu}_7\text{O}_2](\text{SeO}_3)_2\text{Cl}_6$  (Vergasova *et al.*, 2014). The crystal structures of these mineral species contain so-called 'additional' or 'extra' oxygen atoms, which are coordinated solely by copper atoms to form oxocentred  $(\text{OCu}_4)^{6+}$  tetrahedra. A number of experimental and theoretical works on structural

\*E-mail: s.krivovichev@spbu.ru

DOI: 10.1180/minmag.2015.079.7.13

TABLE 1. Crystallographic data and refinement parameters for K[Cu<sub>3</sub>O](SeO<sub>3</sub>)<sub>2</sub>Cl (**I**) and Na<sub>2</sub>[Cu<sub>7</sub>O<sub>2</sub>](SeO<sub>3</sub>)<sub>4</sub>Cl<sub>4</sub> (**II**).

	<b>I</b>	<b>II</b>
<b>Crystal data</b>		
Crystal system	triclinic	triclinic
Space group	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$
Unit cell dimensions <i>a</i> , <i>b</i> , <i>c</i> (Å), $\alpha$ , $\beta$ , $\gamma$ (°)	7.6821(5), 8.1179(5), 8.7836(6), 113.193(3), 108.735(4), 98.245(4)	7.4362(6), 8.3361(7), 9.1343(11), 110.277(6), 106.212(6), 105.158(4)
Unit-cell volume (Å <sup>3</sup> )	453.32(5)	467.94(8)
<i>Z</i>	2	1
Calculated density (g cm <sup>-3</sup> )	3.920	4.160
Absorption coefficient (mm <sup>-1</sup> )	15.757	16.263
Crystal size (mm)	0.13 × 0.09 × 0.07	0.25 × 0.21 × 0.20
<b>Data collection</b>		
Temperature	293 K	293 K
Radiation, wavelength (Å)	MoK $\alpha$ , 0.71073	MoK $\alpha$ , 0.71073
<i>F</i> (000)	494	541
$\theta$ range (°)	2.95–27.46	2.60–30.52
<i>h</i> , <i>k</i> , <i>l</i> ranges	–8→9, –10→6, –11→10	–10→10, –11→11, –12→13
Total reflections collected	5607	11,190
Unique reflections ( <i>R</i> <sub>int</sub> )	1749 (0.0501)	2842 (0.0474)
Unique reflections <i>F</i> > 4 $\sigma$ ( <i>F</i> )	1210	2498
<b>Structure refinement</b>		
Refinement method	Full-matrix least-squares on <i>F</i> <sup>2</sup>	Full-matrix least-squares on <i>F</i> <sup>2</sup>
Weighting coefficients <i>a</i> , <i>b</i> *	0.0766, 0.0	0.0202, 0.0999
Extinction coefficient	0.0046(13)	0.0069(5)
Data/restraints/parameters	1749/0/128	2842/0/143
<i>R</i> <sub>1</sub> [ <i>F</i> > 4 $\sigma$ ( <i>F</i> )], <i>wR</i> <sub>2</sub> [ <i>F</i> > 4 $\sigma$ ( <i>F</i> )]	0.0481, 0.1170	0.0265, 0.0601
<i>R</i> <sub>1</sub> all, <i>wR</i> <sub>2</sub> all	0.0800, 0.1328	0.0322, 0.0621
Gof on <i>F</i> <sup>2</sup>	1.014	1.070
Largest diff. peak and hole	1.620, –1.617 e Å <sup>-3</sup>	0.851, –0.954 e Å <sup>-3</sup>

\* $R_{\text{int}} = \Sigma|F_o - F_o(\text{mean})|/\Sigma[F_o^2]$ . Gof =  $S = \{\Sigma[w(F_o^2 - F_c^2)^2]/(n-p)\}^{1/2}$  where *n* = no. of reflections, *p* = no. of refined parameters.  $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ .  $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$ .  $w^* = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$  where *P* is  $[2F_c^2 + \text{Max}(F_o^2, 0)]/3$ .

descriptions of anion-centred tetrahedra in inorganic compounds has been summarized by Krivovichev *et al.* (2013).

According to the original idea proposed by Filatov *et al.* (1992), polynuclear clusters based upon oxocentred copper tetrahedra can perform the role of transport agents of copper in high temperature environments in volcanic fumaroles. Further experimental work on preparation of mineral analogues by using chemical vapour transport reactions (CVT) provided additional (though indirect) evidence in favour of this hypothesis and demonstrated the suitability of the CVT method for the synthesis of copper oxoselenites with various structural architectures (Millet *et al.*, 2001; Krivovichev *et al.*, 2004; Becker *et al.*, 2007; Berdonosov *et al.*, 2009; Zhang *et al.*, 2010).

In this paper, we report on the syntheses and crystal structures of two novel copper oxoselenite chlorides, K[Cu<sub>3</sub>O](SeO<sub>3</sub>)<sub>2</sub>Cl (**I**) and Na<sub>2</sub>[Cu<sub>7</sub>O<sub>2</sub>](SeO<sub>3</sub>)<sub>4</sub>Cl<sub>4</sub> (**II**), obtained during exploration of synthetic copper selenite chloride systems close to ilinskite and prewittite. The structures of the new compounds are based upon topologically different types of dimers of (OCu<sub>4</sub>)<sup>6+</sup> tetrahedra, and herein we provide a short review of related minerals and inorganic compounds.

## Experimental

### Synthesis

Single crystals of K[Cu<sub>3</sub>O](SeO<sub>3</sub>)<sub>2</sub>Cl (**I**) and Na<sub>2</sub>[Cu<sub>7</sub>O<sub>2</sub>](SeO<sub>3</sub>)<sub>4</sub>Cl<sub>4</sub> (**II**), were prepared by the CVT method. Mixtures of CuO, CuCl<sub>2</sub>, SeO<sub>2</sub> and

TABLE 2. Coordinates and displacement parameters ( $\text{\AA}^2$ ) of atoms in the crystal structure of  $\text{K}[\text{Cu}_3\text{O}](\text{SeO}_3)_2\text{Cl}$ .

Atom	$x/a$	$y/b$	$z/c$	$U_{\text{iso}}$	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
Se1	1.23517(15)	1.17635(13)	0.64629(15)	0.0174(3)	0.0193(6)	0.0140(5)	0.0202(6)	0.0009(4)	0.0090(5)	0.0102(5)
Se2	0.71723(15)	0.69809(14)	0.67694(15)	0.0189(3)	0.0198(6)	0.0162(5)	0.0215(6)	0.0024(4)	0.0119(5)	0.0082(5)
Cu1	0.49212(18)	0.62544(17)	0.90290(18)	0.0192(4)	0.0216(8)	0.0128(6)	0.0247(8)	0.0014(5)	0.0122(7)	0.0096(6)
Cu2	1.46001(18)	0.93661(17)	0.80631(18)	0.0186(4)	0.0211(8)	0.0157(6)	0.0217(8)	0.0048(6)	0.0113(6)	0.0096(6)
Cu3	1.12983(18)	1.03779(18)	0.91313(19)	0.0204(4)	0.0179(8)	0.0221(7)	0.0228(8)	-0.0004(6)	0.0105(6)	0.0125(6)
K1	0.7620(4)	0.2614(4)	0.7322(4)	0.0354(7)	0.0420(18)	0.0280(14)	0.0405(17)	0.0170(13)	0.0221(15)	0.0139(13)
Cl1	0.1696(4)	0.6465(5)	0.8255(5)	0.0419(9)	0.0211(17)	0.0347(17)	0.060(2)	0.0014(13)	0.0139(16)	0.0175(17)
O1	0.5028(10)	0.7348(10)	0.6123(11)	0.0265(18)	0.020(4)	0.025(4)	0.026(4)	0.008(3)	0.005(4)	0.008(4)
O2	1.4202(11)	1.3595(10)	0.8331(11)	0.0266(18)	0.039(5)	0.020(4)	0.025(4)	0.005(4)	0.014(4)	0.015(4)
O3	1.0784(10)	1.1176(11)	0.7258(11)	0.0264(18)	0.018(4)	0.036(5)	0.027(5)	-0.001(4)	0.009(4)	0.020(4)
O4	1.3468(11)	1.0094(11)	0.6216(10)	0.0274(18)	0.038(5)	0.027(4)	0.021(4)	0.014(4)	0.012(4)	0.014(4)
O5	1.4020(10)	1.1104(9)	0.9949(10)	0.0176(16)	0.022(4)	0.010(3)	0.023(4)	0.003(3)	0.013(3)	0.008(3)
O6	0.8557(9)	0.9306(10)	0.8422(10)	0.0198(16)	0.008(4)	0.019(4)	0.025(4)	-0.005(3)	0.007(3)	0.008(3)
O7	0.7045(11)	0.5981(10)	0.8090(11)	0.0251(18)	0.036(5)	0.025(4)	0.037(5)	0.019(4)	0.028(4)	0.022(4)

KCl for **I** (NaCl for **II**) in a 4:1:2:3 molar ratio were loaded into a fused silica tube ( $\sim 15$  cm), which was evacuated to  $10^{-2}$  mbar before sealing. The tubes were placed horizontally into a two-zone tube furnace, and heated to  $500^\circ\text{C}$ . The temperature difference between the source and deposition zones of the tube was  $\sim 50^\circ\text{C}$ . After three days, the tubes were cooled to room temperature over 24 h. Tiny, green, blocky crystals of **I** and **II** were observed in the middle parts of the tubes.

### X-ray diffraction single-crystal analysis

Crystals selected for X-ray data collection were mounted on glass fibres, and studied using a Bruker X8 APEX II three-circle diffractometer equipped with a microfocus X-ray tube with  $\text{MoK}\alpha$  radiation at 50 kV and 40 mA. Unit-cell parameters (Table 1) were refined by least-squares techniques. Data were integrated and corrected for absorption using a multiscan model implemented in the Bruker programs *APEX* and *SADABS*.

The crystal structures of **I** and **II** were solved by direct methods in space group  $P\bar{1}$  and refined using least-squares techniques to  $R_1 = 0.048$  for **I** and 0.027 for **II**, calculated for 1210 and 2498 observed unique reflections for **I** and **II**, respectively, using *SHELXL* (Sheldrick, 2008). Atom coordinates and displacement parameters are given in Tables 2 and 3; selected interatomic distances are in Tables 4 and 5. Bond valence analyses for **I** and **II** are given in Tables 6 and 7. All empirical parameters required for the bond valence calculations were taken from Brese and O'Keeffe (1991). In both structures the values of bond-valence sums of Cl anions are rather low (0.53 vu for Cl1 in **I**; 0.69 and 0.70 vu for Cl1 and Cl2 in **II**, respectively), typical of copper oxoselenite chlorides (Krivovichev *et al.*, 2012). Additional structural information is provided in the Supporting Information (cif) which have been deposited with the Principal Editor of Mineralogical Magazine and are available from [www.minersoc.org/pages/e\\_journals/dep\\_mat\\_mm.html](http://www.minersoc.org/pages/e_journals/dep_mat_mm.html).

## Results

### Cation polyhedra and their arrangement

A review of the mixed-ligand  $\text{CuO}_m\text{Cl}_n$  atom environments of  $\text{Cu}^{2+}$  cations was given by Krivovichev *et al.* (2012). Coordination polyhedra of the  $\text{Cu}^{2+}$  cations observed in the crystal structures of **I** and **II** are similar to those that have

TABLE 3. Coordinates and displacement parameters ( $\text{\AA}^2$ ) of atoms in the crystal structure of  $\text{Na}_2[\text{Cu}_7\text{O}_2](\text{SeO}_3)_4\text{Cl}_4$ .

Atom	$x/a$	$y/b$	$z/c$	$U_{\text{eq}}$	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
Se1	0.80394(5)	0.70487(4)	0.03921(4)	0.00933(9)	0.01006(16)	0.00726(15)	0.00905(15)	0.00281(12)	0.00426(12)	0.00214(12)
Se2	0.19751(5)	0.58188(4)	0.38951(4)	0.01030(9)	0.01288(16)	0.00626(15)	0.00850(15)	0.00156(12)	0.00387(12)	0.00191(12)
Cu1	1/2	0	1/2	0.01074(12)	0.0159(3)	0.0073(3)	0.00774(2)	0.0024(2)	0.0058(2)	0.0024(2)
Cu2	0.44487(6)	0.16460(5)	0.22254(5)	0.01188(10)	0.0153(2)	0.00841(19)	0.01058(18)	0.00455(16)	0.00297(15)	0.00480(15)
Cu3	0.39381(6)	0.75727(5)	0.13594(5)	0.01176(10)	0.0152(2)	0.00709(18)	0.00861(18)	0.00344(15)	0.00260(15)	0.00141(15)
Cu4	0.82861(6)	0.05631(5)	0.35240(5)	0.01161(10)	0.00888(18)	0.00882(19)	0.01261(19)	0.00299(15)	0.00376(14)	0.00093(15)
Cl1	0.15293(12)	0.09108(12)	0.37902(10)	0.01866(18)	0.0110(4)	0.0195(4)	0.0193(4)	0.0053(3)	0.0051(3)	0.0036(3)
Cl2	0.23806(12)	-0.11216(11)	-0.03503(10)	0.01686(17)	0.0189(4)	0.0131(4)	0.0135(3)	0.0035(3)	0.0017(3)	0.0064(3)
Na1	0.7002(2)	0.59122(19)	0.31681(18)	0.0223(3)	0.0213(7)	0.0159(7)	0.0211(7)	-0.0011(6)	0.0008(6)	0.0117(6)
O1	0.5442(3)	0.0106(3)	0.3057(3)	0.0084(4)	0.0097(10)	0.0063(10)	0.0092(10)	0.0031(8)	0.0045(8)	0.0029(8)
O2	0.7574(4)	0.4941(3)	0.0353(3)	0.0170(5)	0.0261(13)	0.0071(10)	0.0092(10)	0.0067(10)	-0.0002(9)	0.0002(9)
O3	0.3796(4)	0.3415(3)	0.1450(3)	0.0166(5)	0.0238(13)	0.0119(11)	0.0120(11)	0.0077(10)	0.0038(9)	0.0055(9)
O4	0.0590(3)	0.6979(3)	0.4600(3)	0.0184(5)	0.0134(11)	0.0121(11)	0.0184(11)	0.0034(9)	0.0034(9)	-0.0013(10)
O5	0.6337(4)	0.3922(3)	0.4289(3)	0.0168(5)	0.0219(12)	0.0087(11)	0.0142(11)	0.0041(10)	0.0015(9)	0.0054(9)
O6	0.3492(4)	0.7335(3)	0.3429(3)	0.0182(5)	0.0319(14)	0.0086(11)	0.0106(10)	0.0013(10)	0.0118(10)	0.0031(9)
O7	0.7057(3)	0.7911(3)	0.1854(3)	0.0114(4)	0.0134(11)	0.0095(10)	0.0120(10)	0.0051(9)	0.0076(9)	0.0033(9)

TWO NEW COPPER SELENITE CHLORIDES

TABLE 4. Selected bond lengths (Å) in the crystal structure of K[Cu<sub>3</sub>O](SeO<sub>3</sub>)<sub>2</sub>Cl.\*

K1–O7	2.685(7)	Cu2–O1 <sup>iv</sup>	2.003(8)
K1–O4 <sup>v</sup>	2.759(8)		
K1–O3 <sup>vi</sup>	2.850(8)	Cu3–O5	1.893(7)
K1–O1 <sup>vii</sup>	3.072(8)	Cu3–O3	1.944(7)
K1–O2 <sup>ii</sup>	3.138(8)	Cu3–O6	1.945(7)
K1–O4 <sup>ii</sup>	3.142(8)	Cu3–O6 <sup>i</sup>	2.025(7)
K1–O6 <sup>vi</sup>	3.288(7)	Cu3–O7 <sup>i</sup>	2.749(8)
K1–Cl1 <sup>viii</sup>	3.495(5)	Cu3–Cl1	3.046(8)
K1–Cl1 <sup>iv</sup>	3.712(4)		
		Se1–O3	1.675(7)
Cu1–O5 <sup>i</sup>	1.892(6)	Se1–O4	1.685(8)
Cu1–O2 <sup>ii</sup>	1.934(7)	Se1–O2	1.702(8)
Cu1–O7	2.053(7)	<Se1–O>	1.687
Cu1–O2 <sup>i</sup>	2.144(8)		
Cu1–Cl1	2.400(3)	Se2–O1	1.673(7)
		Se2–O7	1.675(7)
Cu2–O4	1.932(7)	Se2–O6	1.754(7)
Cu2–O5	1.936(7)	<Se2–O>	1.701
Cu2–O5 <sup>iii</sup>	1.942(7)		

\*Symmetry codes: (i)  $-x+2, -y+2, -z+2$ ; (ii)  $x-1, y-1, z$ ; (iii)  $-x+3, -y+2, -z+2$ ; (iv)  $x+1, y, z$ ; (v)  $-x+2, -y+1, -z+1$ ; (vi)  $x, y-1, z$ ; (vii)  $-x+1, -y+1, -z+1$ ; (viii)  $-x+1, -y+1, -z+2$ .

TABLE 5. Selected bond lengths (Å) in the crystal structure of Na<sub>2</sub>[Cu<sub>7</sub>O<sub>2</sub>](SeO<sub>3</sub>)<sub>4</sub>Cl<sub>4</sub>.\*

Na1–O5	2.253(3)	Cu3–O1 <sup>v</sup>	1.909(2)
Na1–O3	2.352(3)	Cu3–O6	2.073(2)
Na1–O7	2.365(3)	Cu3–O7	2.156(2)
Na1–O4 <sup>vi</sup>	2.371(3)	Cu3–Cl2 <sup>v</sup>	2.4067(9)
Na1–O2	2.607(3)		
Na1–Cl1 <sup>ii</sup>	2.7603(16)	Cu4–O4 <sup>ii</sup>	1.925(2)
Na1–O6	3.169(3)	Cu4–O1	1.940(2)
		Cu4–O7 <sup>iv</sup>	1.969(2)
Cu1–O1	1.919(2)	Cu4–Cl1 <sup>vi</sup>	2.2842(9)
Cu1–O1 <sup>iii</sup>	1.919(2)		
Cu1–O6 <sup>ii</sup>	1.960(2)	Se1–O2	1.685(2)
Cu1–O6 <sup>iv</sup>	1.960(2)	Se1–O3 <sup>i</sup>	1.683(2)
		Se1–O7	1.729(2)
Cu2–O1	1.905(2)	<Se1–O>	1.699
Cu2–O5	1.943(2)		
Cu2–O3	1.954(2)	Se2–O5 <sup>ii</sup>	1.679(2)
Cu2–Cl2	2.3633(9)	Se2–O4	1.694(2)
		Se2–O6	1.717(2)
Cu3–O2 <sup>i</sup>	1.902(2)	<Se2–O>	1.697

\*Symmetry codes: (i)  $-x+1, -y+1, -z$ ; (ii)  $-x+1, -y+1, -z+1$ ; (iii)  $-x+1, -y, -z+1$ ; (iv)  $x, y-1, z$ ; (v)  $x, y+1, z$ ; (vi)  $x+1, y, z$ .

TABLE 6. Bond valence analysis (in valence units, vu) for the crystal structure of K[Cu<sub>3</sub>O](SeO<sub>3</sub>)<sub>2</sub>Cl.

	O1	O2	O3	O4	O5	O6	O7	Cl1	Σ
K1	0.08	0.07	0.14	0.18, 0.07			0.22	0.08, 0.05	0.89
Cu1		0.50, 0.28			0.56		0.36	0.34	2.04
Cu2	0.42			0.50	0.50, 0.49				1.91
Cu3			0.49		0.56	0.49, 0.39	0.06	0.06	2.05
Se1		1.34	1.44	1.41					4.19
Se2	1.45					1.17	1.44		4.06
Σ	1.95	2.19	2.07	2.16	2.11	2.05	2.08	0.53	

TABLE 7. Bond valence analysis (in valence units, vu) for the crystal structure of Na<sub>2</sub>[Cu<sub>7</sub>O<sub>2</sub>](SeO<sub>3</sub>)<sub>4</sub>Cl<sub>4</sub>.

	O1	O2	O3	O4	O5	O6	O7	Cl1	Cl2	Σ
Na1		0.11	0.23	0.22	0.30		0.22	0.23		1.31
Cu1	0.52 <sup>2x→</sup>					0.47 <sup>2x→</sup>				1.98
Cu2	0.54		0.48		0.49				0.37	1.88
Cu3	0.54	0.55				0.34	0.28		0.33	2.04
Cu4	0.49			0.51			0.46	0.46		1.92
Se1		1.41	1.41				1.25			4.07
Se2				1.37	1.43	1.29				4.09
Σ	2.09	2.07	2.12	2.10	2.22	2.10	2.21	0.69	0.70	

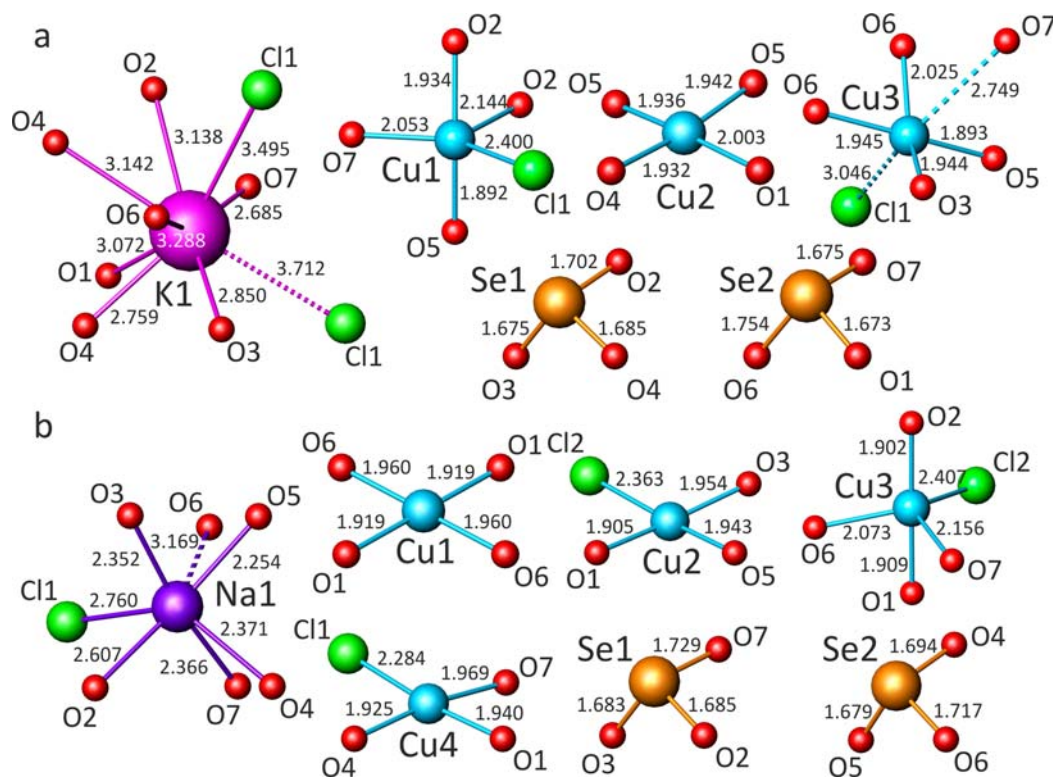


FIG. 1. Coordination of cations in the crystal structures of  $K[Cu_3O](SeO_3)_2Cl$  (a) and  $Na_2[Cu_7O_2](SeO_3)_4Cl_4$  (b). Legend:  $K^+$  = pink;  $Cu^{2+}$  = cyan;  $Se^{4+}$  = orange;  $O^{2-}$  = red;  $Cl^-$  = green.

been described in other natural and synthetic copper compounds.

The structure of **I** contains three symmetrically independent Cu sites (Fig. 1a). The Cu1 site is surrounded by four O and one Cl atoms to form an unusual, distorted  $[CuO_4Cl]^{7-}$  trigonal bipyramid with the O7, O2 and Cl1 atoms forming a triangular equatorial plane. This type of coordination geometry,  $[(2O+Cl)+2O]$ , has previously been reported for the structure of  $\beta-Cu_3(SeO_3)_2Cl_2$  (Becker *et al.*, 2007). The Cu1–O bond lengths vary from 1.892 to 2.144 Å; the Cu1–Cl1 bond length is equal to 2.400 Å. Cu2 has a typical square planar  $[CuO_4]^{6-}$  coordination, which has been observed, e.g. in the structure of francisite,  $[Cu_3BiO_2](SeO_3)_2Cl$  (Pring *et al.*, 1990). Four oxygen atoms are located at distances ranging between 1.932 and 2.003 Å from the Cu2 atom. The Cu3 coordination polyhedron can be described as a distorted  $[(4O)+(O+Cl)]$  octahedron, and is similar to that observed in the crystal structures of georgbokiite,  $\alpha-[Cu_5O_2](SeO_3)_2Cl_2$  (Krivovichev *et al.*, 1999a),

kamchatkite,  $K[Cu_3O](SO_4)_2Cl$  (Varaksina *et al.*, 1990) and nabokoite,  $K_2Cu_7(TeO_4)(SO_4)_5Cl$  (Pertlik and Zemann, 1988). The average  $\langle Cu3-O_{eq} \rangle$  bond length in the equatorial plane of the octahedron is 1.952 Å. Apical O7 and Cl1 atoms are located at 2.749 and 3.046 Å from Cu3, respectively. Various Cu coordination polyhedra are combined into layers parallel to (001) (Fig. 2a). The structure of **I** contains two symmetrically independent  $Se^{4+}$  cations that form  $(SeO_3)^{2-}$  triangular pyramids with Se located at its apical corner and a stereoactive lone pair acting as a complementary ligand. The average  $\langle Se-O \rangle$  distance is 1.687 Å and 1.701 Å for the Se1 and Se2 sites, respectively. The  $K^+$  cation is coordinated by seven  $O^{2-}$  and two  $Cl^-$  anions in a distorted arrangement (Fig. 1a).

In the crystal structure of **II**, there are four symmetrically independent Cu sites (Fig. 1b). The Cu1 site forms a  $[CuO_4]^{6-}$  square with an average  $\langle Cu1-O \rangle$  bond length of 1.940 Å, similar to the Cu2 site in the structure of **I**. Cu2 and Cu4 sites are

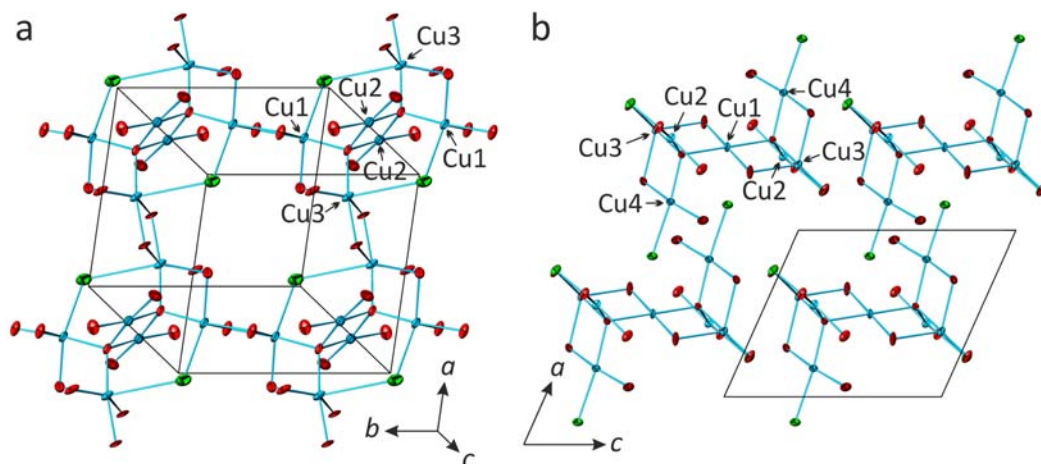


FIG. 2. Mode of linkage of the Cu coordination polyhedra in the crystal structures of  $K[Cu_3O](SeO_3)_2Cl$  (a) and  $Na_2[Cu_7O_2](SeO_3)_4Cl_4$  (b). Legend:  $Cu^{2+}$  = cyan;  $O^{2-}$  = red;  $Cl^-$  = green. Displacement ellipsoids are drawn at the 50% probability level.

coordinated by three O ( $\langle Cu2-O \rangle = 1.934 \text{ \AA}$ ,  $\langle Cu4-O \rangle = 1.945 \text{ \AA}$ ) and one Cl atom ( $Cu2-Cl2 = 2.363 \text{ \AA}$ ,  $Cu4-Cl1 = 2.284 \text{ \AA}$ ) to form  $[CuO_3Cl]^{5-}$  square planes. The same  $[(3O+Cl)]$  coordination has been observed previously in the crystal structure of ilinskite,  $Na[Cu_5O_2](SeO_3)_2Cl_3$  (Vergasova *et al.*, 1997; Krivovichev *et al.*, 2012). The Cu3 site has a triangular bipyramidal  $[(2O+Cl)+2O]$  coordination with Cu3–O bond lengths of 1.902–2.156  $\text{\AA}$ , and a Cu3–Cl2 distance of 2.407  $\text{\AA}$ . The copper polyhedra form the arrangement shown in Fig. 2b. Two symmetrically independent Se sites form  $(SeO_3)^{2-}$  trigonal pyramids with average  $\langle Se-O \rangle$  bond lengths of

1.699 and 1.697  $\text{\AA}$  for Se1 and Se2, respectively. One symmetrically unique  $Na^+$  cation is surrounded by six  $O^{2-}$  and one  $Cl^-$  anion. The Na1–O6 contact corresponds to a weak interaction and its distance is rather long (3.169  $\text{\AA}$ ), but it helps to form an approximately triangular prismatic oxygen environment for  $Na^+$ .

#### Dimers of $[OCu_4]^{6+}$ tetrahedra and their linkage

By analogy with many copper minerals of fumarolic origin (see, e.g. Krivovichev *et al.* (2013); Pekov *et al.* (2013a, b)), analysis of the

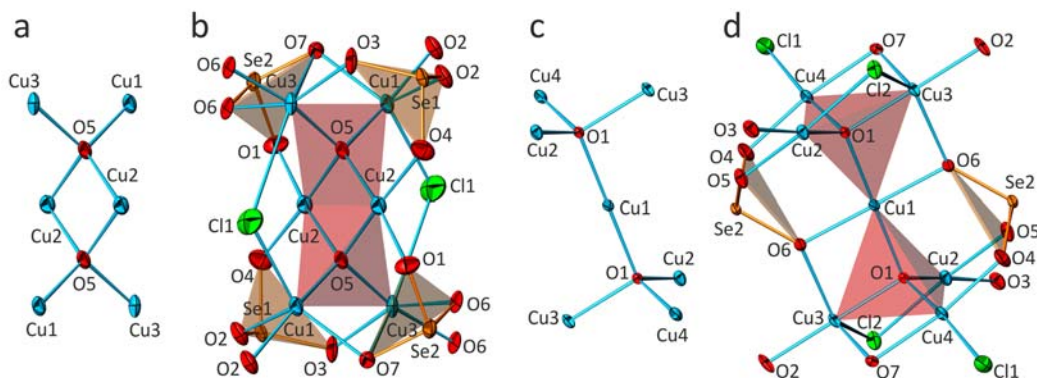


FIG. 3. Structural units based upon oxocentred  $(OCu_4)^{6+}$  tetrahedra and their environment in the crystal structures of  $Na_2[Cu_7O_2](SeO_3)_4Cl_4$  (a, b) and  $K[Cu_3O](SeO_3)_2Cl$  (c, d). Legend as in Fig. 2. Displacement ellipsoids are drawn at the 50% probability level.

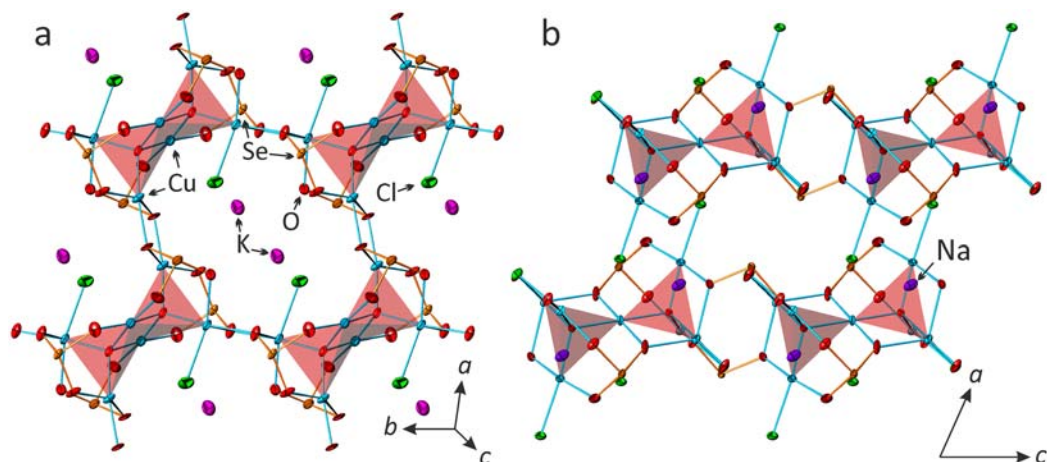


FIG. 4. The crystal structures of **I** (a) and **II** (b) in projections featuring the presence of dimers of  $(\text{OCu}_4)^{6+}$  tetrahedra. Legend:  $\text{K}^+$  = pink;  $\text{Cu}^{2+}$  = cyan;  $\text{Se}^{4+}$  = orange;  $\text{O}^{2-}$  = red;  $\text{Cl}^-$  = green; the  $[\text{OCu}_4]^{6+}$  tetrahedra are highlighted by red.  $\text{K}-\text{O}$ ,  $\text{K}-\text{Cl}$  and  $\text{Cu}-\text{Cl}$  bonds are omitted for clarity. Displacement ellipsoids are drawn at the 50% probability level.

crystal structures of **I** and **II** in terms of oxocentred tetrahedra seems appropriate to describe the structural organization and to reveal relations between different structures with similar chemical compositions.

In the crystal structure of **I**, two  $[\text{OCu}_4]^{6+}$  tetrahedra share a common  $\text{Cu}\cdots\text{Cu}$  edge to form the  $[\text{O}_2\text{Cu}_6]^{8+}$  dimer shown in Fig. 3a. The selenite groups and Cl atoms surround these dimers to form  $\{[\text{O}_2\text{Cu}_6](\text{SeO}_3)_4\text{Cl}_2\}^{2-}$  units shown in Fig. 3b, which are further interconnected into layers parallel to (001) (Fig. 4a). The interlayer space is occupied by  $\text{K}^+$  cations.  $(\text{SeO}_3)^{2-}$  triangular pyramids are attached to the  $[\text{O}_2\text{Cu}_6]^{8+}$  cluster in such a way that four selenite triangular  $\text{O}-\text{O}-\text{O}$  bases are parallel to the four triangular  $\text{Cu}-\text{Cu}-\text{Cu}$  faces of the oxocentred tetrahedra. This mode of interaction between oxocentred tetrahedra and cation-centred groups is known as a ‘face-to-face’ mode and has been reported previously by Krivovichev and Filatov (1999) and Krivovichev *et al.* (1999b). It is of interest that the same linkage between copper oxocentred dimers and selenite triangular pyramids has been observed in a monoclinic polymorph of  $\text{Cu}[\text{Cu}_3\text{O}](\text{SeO}_3)_3$  (Effenberger and Pertlik, 1986). It is noteworthy that, despite similarity in their chemical formulae, kamchatkite,  $\text{K}[\text{Cu}_3\text{O}](\text{SO}_4)_2\text{Cl}$  (Varaksina *et al.*, 1990), is not isotypical with **I**,  $\text{K}[\text{Cu}_3\text{O}](\text{SeO}_3)_2\text{Cl}$ . In contrast to the latter, the former is based upon chains of corner-sharing  $(\text{OCu}_4)^{6+}$  tetrahedra.

The crystal structure of **II** is based upon the  $[\text{O}_2\text{Cu}_7]^{10+}$  dimeric units shown in Fig. 3c, formed

by two  $(\text{OCu}_4)^{6+}$  tetrahedra sharing a common Cu atom. The dimers are linked by  $(\text{SeO}_3)^{2-}$  groups to produce layers parallel to (100) with the interlayer space filled by  $\text{Na}^+$  cations,  $\text{Cl}^-$  anions and lone electron pairs of  $\text{Se}^{4+}$  cations (Fig. 4b).  $[\text{O}_2\text{Cu}_7]^{10+}$  dimers are coordinated by selenite groups and Cl atoms to form the  $\{[\text{O}_2\text{Cu}_7](\text{SeO}_3)_4\text{Cl}_4\}^{2-}$  unit shown in Fig. 3d. Note that in the crystal structure of **II** the selenite anions play different structural roles. Whereas the  $(\text{Se}_2\text{O}_3)$  triangular pyramids are in ‘face-to-face’ orientations relative to the  $(\text{O}1\text{Cu}_4)$  tetrahedra, the  $(\text{Se}1\text{O}_3)$  groups are located in between the copper oxoselenite clusters and provide their linkage into the metal-oxide layers through the formation of  $\text{Se}-\text{O}-\text{Cu}$  links.

## Discussion

The novel compounds **I** and **II** reported herein are new members of the structural family of minerals and synthetic compounds that are based upon dimers composed of  $(\text{OCu}_4)^{6+}$  groups (Krivovichev *et al.*, 2013; Table 8). Figure 5 provides an overview of the observed coordination environments of the dimers of oxocentred tetrahedra in the crystal structures of related copper minerals and synthetic compounds.

Structures based upon dimers of edge-sharing oxocentred tetrahedra have been observed previously in two polymorphs of  $\text{Cu}[\text{Cu}_3\text{O}](\text{SeO}_3)_3$  (Effenberger and Pertlik, 1986). Here the  $[\text{O}_2\text{Cu}_6]^{8+}$



TABLE 8. Crystallographic data for minerals and inorganic compounds based upon dimers composed of  $(OCu_4)^{6+}$  tetrahedra.

O:Cu	Chemical formula	Mineral name	Space group	$a$ (Å); $\alpha$ (°)	$b$ (Å); $\beta$ (°)	$c$ (Å); $\gamma$ (°)	$V$ (Å <sup>3</sup> )	Ref.*
2:6	$NaK[Cu_3O](SO_4)_3$	euchlorine	$C2/c$	18.41; 90	9.43; 113.7	14.21; 90	2259	1
	$K_2[Cu_3O](SO_4)_3$	fedotovite	$C2/c$	19.037; 90	9.479; 111.0	14.231; 90	2397	2
	$KPb_{0.5}Cu[PbCu_5O_2]Zn(SeO_3)_2Cl_{10}$	prewittite	$Pnmm$	9.132; 90	19.415; 90	13.213; 90	2343	3
	$Cu[Cu_3O](SeO_3)_3$ <b>I</b>		$P2_1/a$	15.990; 90	13.518; 90.5	17.745; 90	3836	4
	$Cu[Cu_3O](SeO_3)_3$ <b>II</b>		$P\bar{1}$	7.992; 77.3	8.141; 66.6	8.391; 81.4	484	4
2:7	$K[Cu_3O](SeO_3)_2Cl$		$P\bar{1}$	7.682; 113.2	8.118; 108.7	8.784; 98.2	453	6
	$KCd[Cu_7O_2](SeO_3)_2Cl_9$	burnsite	$P6_3/mmc$	8.781; 90	8.781; 90	15.521; 90	1036	5
	$Na_2[Cu_7O_2](SeO_3)_4Cl_4$		$P\bar{1}$	7.436; 110.3	8.336; 106.2	9.134; 105.2	468	6

\* 1: Scordari and Stasi (1990); 2: Starova *et al.* (1991); 3: Shuvalov *et al.* (2013); 4: Effenberger and Pertlik (1986); 5: Burns *et al.* (2002); Krivovichev *et al.* (2002); 6: this work.

dimers are surrounded by selenite groups and Cu atoms not bonded to 'additional' O atoms. Coordination environments of the dimers in the two polymorphs are different. In the monoclinic structure, four selenite anions attach to four faces of the  $(OCu_4)^{6+}$  tetrahedra in a 'face-to-face' orientation (Fig. 5a), very similar to the arrangement observed in **I**. In the crystal structure of the triclinic phase, in addition to the four 'face-to-face'-attached selenite groups, each dimer is surrounded by two other selenite groups (Fig. 5b). Euchlorine,  $NaK[Cu_3O](SO_4)_3$  (Scordari and Stasi, 1990) and fedotovite,  $K_2[Cu_3O](SO_4)_3$  (Starova *et al.*, 1991), were the first minerals described as being based on  $[O_2Cu_6]^{8+}$  dimers. In the structures of these minerals, four sulfate tetrahedra are 'face-to-face'-attached to the dimers, whereas two other sulfate tetrahedra provide their linkage in two dimensions (Fig. 5d). Very similar copper oxo-sulfate clusters have been observed recently in the structures of novel Cu metal-organic polymers  $(NMe_2H_2)_4[Cu_6O_2](SO_4)_6(DMF)_4$  (Fig. 5e) and  $(NMe_2H_2)_4[Cu_6O_2](SO_4)_6(DMF)_2$  (Fig. 5f) (Burrows *et al.*, 2012). In the structure of prewittite,  $KPb_{0.5}Cu[PbCu_5O_2]Zn(SeO_3)_2Cl_{10}$  (Shuvalov *et al.*, 2013), two adjacent heterometallic oxocentred  $(OCu_3Pb)^{6+}$  tetrahedra share a common  $Cu \cdots Pb$  edge to form the  $[O_2Cu_5Pb]^{8+}$  dimer (Fig. 5c). Two selenite groups are in 'face-to-face' positions relative to the oxocentred tetrahedra.

The  $[O_2Cu_7]^{10+}$  dimer formed by two corner-sharing  $(OCu_4)^{6+}$  tetrahedra has been described in the structure of burnsite,  $KCd[Cu_7O_2](SeO_3)_2Cl_9$  (Burns *et al.*, 2002; Krivovichev *et al.*, 2002), and compound **II** described here is a second example. In contrast to the crystal structure of **II**, where the selenite groups are attached to the lateral faces of the oxocentred tetrahedra (Fig. 5g), in the structure of burnsite, selenite groups are in a 'face-to-face' orientation relative to the opposite Cu-Cu-Cu faces of the dimer so that they are parallel to each other (Fig. 5h). The resulting copper oxoselenite complexes are linked via Cu-O bonds into a 3D framework that contains large channels filled by  $(KCl_6)^{5-}$  triangular prisms and  $(CdCl_6)^{4-}$  octahedra. The interesting case of a  $[O_4Cu_{13}]^{18+}$  tetramer formed by successive linkage of two  $[O_2Cu_7]^{10+}$  dimers has recently been reported for nick-sobolevite,  $Cu[Cu_{13}O_4](SeO_3)_4Cl_{12}$  (Vergasova *et al.*, 2014). The tetramers are interconnected by selenite groups and additional copper cations into ladder-like layers.

The observed complex clusters consisting of oxocentred tetrahedral units surrounded by selenite

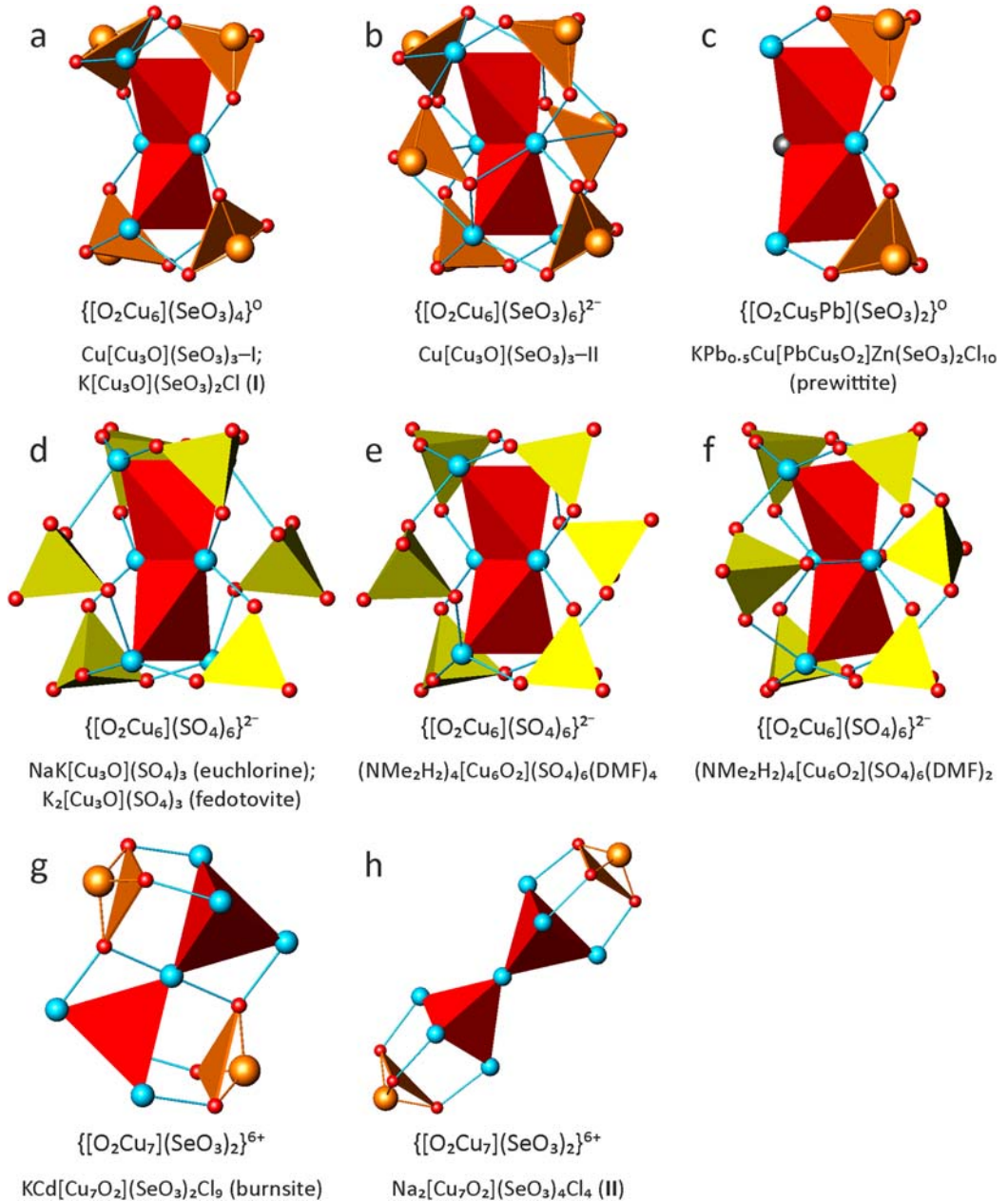


FIG. 5. Coordination environment of the dimers composed of  $[OCu_4]^{16+}$  tetrahedra in the crystal structures of different minerals and synthetic compounds. See text for details.

groups form metal-oxide backbones of many copper oxoselenite chlorides. Whereas Cu coordination is diverse and changes from structure to structure, the oxocentred units appear to be

relatively robust. Their existence and frequent occurrence in different structures provides indirect evidence for the importance of such units as pre-nucleation building blocks existing in gaseous

media as occurs in volcanic fumaroles or evacuated silica ampoules used in the CVT method. The two new compounds,  $\text{K}[\text{Cu}_3\text{O}](\text{SeO}_3)_2\text{Cl}$  and  $\text{Na}_2[\text{Cu}_7\text{O}_2](\text{SeO}_3)_4\text{Cl}_4$ , are very similar in their chemistry and structures to the natural copper oxoselenite chlorides and one may thus predict their possible formation in fumarolic environments under appropriate physical and chemical conditions. It is worth noting that recently a number of interesting new Te-bearing mineral species have been described in the literature (e.g. Kampf *et al.* (2010); Christy and Mills, 2013). As for  $\text{Se}^{4+}$ ,  $\text{Te}^{4+}$  cations possess lone electron pairs and are able to form triangular pyramidal  $\text{TeO}_3$  groups structurally analogous to selenite anions observed in the title compounds and in the structures of many Tolbachik minerals. However, no direct structural correspondence between tellurites and selenites can be observed, due to the possibility of  $\text{Te}^{4+}$  adopting different coordination numbers and the ability of  $\text{Te}^{4+}\text{O}_n$  units to polymerize to form extended polyanions.

## Acknowledgements

The authors thank Ian Grey and an anonymous reviewer for useful comments on the manuscript. VMK, OIS and SVK have been supported in this work by the Russian Science Foundation (grant 14-17-00071). This work was supported for MC and OM under the framework of the Multi-InMaDe project supported by the ANR (grant ANR 2011-JS-08 00301). The Fonds Européen de Développement Régional (FEDER), CNRS, Région Nord Pas-de-Calais, and Ministère de l'Éducation Nationale de l'Enseignement Supérieur et de la Recherche are acknowledged for funding the X-ray diffractometers.

## References

- Becker, R., Berger, H. and Johnsson, M. (2007) Monoclinic  $\text{Cu}_3(\text{SeO}_3)_2\text{Cl}_2$ : an oxohalide with an unusual  $\text{CuO}_4\text{Cl}$  trigonal-bipyramidal coordination. *Acta Crystallographica*, **C63**, i4–i6.
- Berdonov, P.S., Olenev, A.V. and Dolgikh, V.A. (2009) Strontium–copper selenite–chlorides: synthesis and structural investigation. *Journal of Solid State Chemistry*, **182**, 2368–2373.
- Berdonov, P.S., Janson, O., Olenev, A.V., Krivovichev, S.V., Rosner, H., Dolgikh, V.A. and Tsirlin, A.A. (2013) Crystal structures and variable magnetism of  $\text{PbCu}_2(\text{XO}_3)_2\text{Cl}_2$  with  $X = \text{Se}, \text{Te}$ . *Journal of the Chemical Society, Dalton transactions*, **42**, 9547–9554.
- Breese, N.E. and O'Keeffe, M. (1991) Bond-valence parameters for solids. *Acta Crystallographica*, **B47**, 192–197.
- Burns, P.C. and Hawthorne, F.C. (1995a) Coordination-geometry pathways in  $\text{Cu}^{2+}$  oxysalt minerals. *The Canadian Mineralogist*, **33**, 889–905.
- Burns, P.C. and Hawthorne, F.C. (1995b) Mixed-ligand  $\text{Cu}^{2+}\Phi_6$  octahedra in minerals: observed stereochemistries and HartreeFock calculations. *The Canadian Mineralogist*, **33**, 1177–1188.
- Burns, P.C., Krivovichev, S.V. and Filatov, S.K. (2002) New  $\text{Cu}^{2+}$  coordination polyhedra in the crystal structure of burnsite,  $\text{KCdCu}_7\text{O}_2(\text{SeO}_3)_2\text{Cl}_9$ . *The Canadian Mineralogist*, **40**, 1587–1595.
- Burrows, A.D., Mahon, M.F., Sebestyen, V.M., Lan, Y. and Powell, A.K. (2012) Synthesis, structures, and magnetic behavior of new anionic copper(II) sulfate aggregates and chains. *Inorganic Chemistry*, **51**, 10983–10989.
- Christy, A.G. and Mills, S.J. (2013) Effect of lone-pair stereoactivity on polyhedral volume and structural flexibility: application to  $\text{Te}^{\text{IV}}\text{O}_6$  octahedra. *Acta Crystallographica*, **B69**, 446–456.
- Effenberger, H. and Pertlik, F. (1986) Die Kristallstrukturen der Kupfer(II)-oxo-selenite  $\text{Cu}_2\text{O}(\text{SeO}_3)$  (kubisch und monoklin) und  $\text{Cu}_4\text{O}(\text{SeO}_3)_3$  (monoklin und triklin). *Monatshfte für Chemie*, **117**, 887–896.
- Filatov, S.K., Semenova, T.F. and Vergasova, L.P. (1992) Types of polymerization of  $[\text{OCu}_4]^{6+}$  in inorganic compounds with 'additional' oxygen atoms. *Doklady Akademii Nauk SSSR*, **322**, 539–539.
- Kampf, A.R., Mills, S.J., Housley, R.M., Marty, J. and Thorne, B. (2010) Lead-tellurium oxysalts from Otto Mountain near Baker, California: VI. Telluroperite,  $\text{Pb}_3\text{Te}^{4+}\text{O}_4\text{Cl}_2$ , the Te analogue of perite and nadorite. *American Mineralogist*, **95**, 1569–1573.
- Krivovichev, S.V. and Filatov, S.K. (1999) Structural principles for minerals and inorganic compounds containing anion-centered tetrahedra. *American Mineralogist*, **84**, 1099–1106.
- Krivovichev, S.V., Shuvalov, R.R., Semenova, T.F. and Filatov, S.K. (1999a) Crystal chemistry of inorganic compounds based on chains of oxocentered tetrahedra. III. Crystal structure of georgbokiite,  $\text{Cu}_5\text{O}_2(\text{SeO}_3)_2\text{Cl}_2$ . *Zeitschrift für Kristallographie*, **214**, 135–138.
- Krivovichev, S.V., Starova, G.L. and Filatov, S.K. (1999b) 'Face-to-face' relationships between oxocentered tetrahedra and cation-centred tetrahedral oxyanions in crystal structures of minerals and inorganic compounds. *Mineralogical Magazine*, **63**, 263–266.
- Krivovichev, S.V., Vergasova, L.P., Starova, G.L., Filatov, S.K., Britvin, S.N., Roberts, A.C. and Steele, I.M. (2002) Burnsite,  $\text{KCdCu}_7\text{O}_2(\text{SeO}_3)_2\text{Cl}_9$ , a new mineral species from the Tolbachik volcano, Kamchatka Peninsula, Russia. *The Canadian Mineralogist*, **40**, 1171–1175.

- Krivovichev, S.V., Filatov, S.K., Armbruster, T. and Pankratova, O.Y. (2004) Crystal structure of  $\text{Cu(I)Cu(II)}_4\text{O}(\text{SeO}_3)\text{Cl}_5$ , a new heterovalent copper compound. *Doklady Chemistry*, **399**, 226–228.
- Krivovichev, S.V., Filatov, S.K., Burns, P.C. and Vergasova, L.P. (2006) The crystal structure of allochalcocelite,  $\text{Cu}^+\text{Cu}_2^+\text{PbO}_2(\text{SeO}_3)_2\text{Cl}_5$ , a mineral with well-defined  $\text{Cu}^+$  and  $\text{Cu}^{2+}$  positions. *The Canadian Mineralogist*, **44**, 507–514.
- Krivovichev, S.V., Filatov, S.K., Burns, P.C. and Vergasova, L.P. (2007) The crystal structure of parageorgobokiite,  $\beta\text{-Cu}_5\text{O}_2(\text{SeO}_3)_2\text{Cl}_2$ . *The Canadian Mineralogist*, **45**, 929–934.
- Krivovichev, S.V., Filatov, S.K. and Vergasova, L.P. (2012) The crystal structure of ilinskite,  $\text{NaCu}_5\text{O}_2(\text{SeO}_3)_2\text{Cl}_3$ , and review of mixed-ligand  $\text{CuO}_m\text{Cl}_n$  coordination geometries in minerals and inorganic compounds. *Mineralogy and Petrology*, **107**, 235–242.
- Krivovichev, S.V., Mentré, O., Siidra, O.I., Colmont, M. and Filatov, S.K. (2013) Anion-centered tetrahedra in inorganic compounds. *Chemical Reviews*, **113**, 6459–6535.
- Mao, J.-G., Jiang, H.-L. and Kong, F. (2008) Structures and properties of functional metal selenites and tellurites. *Inorganic Chemistry*, **47**, 8498–8510.
- Melnik, M., Koman, M. and Ondrejovič, G. (2011) Tetramers  $\text{Cu}_4(\mu_4\text{-O})(\eta\text{-X})_6(\text{L}_4)$ : analysis of structural data. *Coordination Chemistry Reviews*, **255**, 1581–1586.
- Millet, P., Bastide, B., Pashchenko, V., Gnatchenko, S., Gapon, V., Ksari, Y. and Stepanov, A. (2001) Syntheses, crystal structures and magnetic properties of francisite compounds  $\text{Cu}_3\text{Bi}(\text{SeO}_3)_2\text{O}_2\text{X}$  ( $\text{X} = \text{Cl}, \text{Br}$  and  $\text{I}$ ). *Journal of Materials Chemistry*, **11**, 1152–1157.
- Pekov, I.V., Zelenski, M.E., Yapaskurt, V.O., Polekhovskiy, Y.S. and Murashko, M.N. (2013a): Starovaite,  $\text{KCu}_5\text{O}(\text{VO}_4)_3$ , a new mineral from fumarole sublimates of the Tolbachik volcano, Kamchatka, Russia. *European Journal of Mineralogy*, **25**, 91–96.
- Pekov, I.V., Zubkova, N.V., Zelenski, M.E., Yapaskurt, V. O., Polekhovskiy, Y.S., Fadeeva, O.A. and Pushcharovskiy, D.Y. (2013b): Yaroshevskite,  $\text{Cu}_9\text{O}_2(\text{VO}_4)_4\text{Cl}_2$ , a new mineral from the Tolbachik volcano, Kamchatka, Russia. *Mineralogical Magazine*, **77**, 107–116.
- Pertlik, F. and Zemann, J. (1988) The crystal structure of nabokoite,  $\text{Cu}_7\text{TeO}_4(\text{SO}_4)_5 \cdot \text{KCl}$ : the first example of a  $\text{Te(IV)O}_4$  pyramid with exactly tetragonal symmetry. *Mineralogy and Petrology*, **38**, 291–298.
- Pring, A., Gatehouse, B.M. and Birch, W.D. (1990) Francisite,  $\text{Cu}_3\text{Bi}(\text{SeO}_3)_2\text{O}_2\text{Cl}$ , a new mineral from Iron Monarch, South Australia: description and crystal structure. *American Mineralogist*, **75**, 1421–1425.
- Rosner, H., Johannes, M.D., Drechsler, S.-L., Schmitt, M., Janson, O., Schnelle, W., Liu, W., Huang, Y.-X. and Kniep, R. (2007)  $\text{Cu}^{\text{II}}$  materials – from crystal chemistry to magnetic model compounds. *Science and Technology of Advanced Materials*, **8**, 352–356.
- Scordari, F. and Stasi, F. (1990) The crystal structure of euchlorine,  $\text{NaKCu}_3\text{O}(\text{SO}_4)_3$ . *Neues Jahrbuch für Mineralogie, Abhandlungen*, **161**, 241–253.
- Sheldrick, G.M. (2008) A short history of SHELX. *Acta Crystallographica*, **A64**, 112–22.
- Shuvalov, R.R., Vergasova, L.P., Semenova, T.F., Filatov, S.K., Krivovichev, S.V., Siidra, O.I. and Rudashevskiy, N.S. (2013) Prewittite,  $\text{K Pb}_{1.5}\text{Cu}_6\text{Zn}(\text{SeO}_3)_2\text{O}_2\text{Cl}_{10}$ , a new mineral from Tolbachik fumaroles, Kamchatka peninsula, Russia: description and crystal structure. *American Mineralogist*, **98**, 463–469.
- Starova, G.L., Filatov, S.K. and Vergasova, L.P. (1991) The crystal structure of fedotovite,  $\text{K}_2\text{Cu}_3\text{O}(\text{SO}_4)_3$ . *Mineralogical Magazine*, **55**, 613–616.
- Varaksina, T.V., Fundamenskiy, V.S., Filatov, S.K. and Vergasova, L.P. (1990) The crystal structure of kamchatkite, a new naturally occurring oxychloride sulphate of potassium and copper. *Mineralogical Magazine*, **54**, 613–616.
- Vergasova, L.P., Semenova, T.F., Shuvalov, R.R., Filatov, S.K. and Ananiev, V.V. (1997) Ilinskite  $\text{NaCu}_5\text{O}_2(\text{SeO}_3)_2\text{Cl}_3$  – a new mineral of volcanic exhalations. *Doklady Akademii Nauk SSSR*, **353**, 641–644.
- Vergasova, L.P., Krivovichev, S.V., Semenova, T.F., Filatov, S.K. and Ananiev, V.V. (1999) Chloromenite,  $\text{Cu}_9\text{O}_2(\text{SeO}_3)_4\text{Cl}_6$ , a new mineral from the Tolbachik Volcano, Kamchatka, Russia. *European Journal of Mineralogy*, **11**, 119–123.
- Vergasova, L.P., Semenova, T.F., Krivovichev, S.V., Filatov, S.K., Zolotarev, Jr A.A. and Ananiev, V.V. (2014) Nicksobolevite,  $\text{Cu}_7(\text{SeO}_3)_2\text{O}_2\text{Cl}_6$ , a new complex copper oxoselenite chloride from Tolbachik fumaroles, Kamchatka Peninsula, Russia. *European Journal of Mineralogy*, **26**, 439–449.
- Zhang, D., Berger, H., Kremer, R.K., Wulferding, D., Lemmens, P. and Johnsson, M. (2010) Synthesis, crystal structure, and magnetic properties of the copper selenite chloride  $\text{Cu}_5(\text{SeO}_3)_4\text{Cl}_2$ . *Inorganic Chemistry*, **49**, 9683–9688.