Oxocentered Cu(II) Lead Selenite Honeycomb Lattices Hosting Cu(I)Cl₂ Groups Obtained by Chemical Vapor Transport Reactions

Vadim M. Kovrugin,^{*a,b*} Marie Colmont,^{*b*} Olivier Mentré,^{*b*} Alexander Al-Shuray,^{*a*} Oleg I. Siidra,^{*a*} Vladislav V. Gurzhiy^{*a*} and Sergey V. Krivovichev*^{*a*}

^a Department of Crystallography, St. Petersburg State University, University Emb. 7/9, 199034 St. Petersburg, Russia.
 E-mail: s.krivovichev@spbu.ru
 ^b UCCS, UMR 8181, Université Lille Nord de France, USTL, F-59655 Villeneuve d'Ascq, France.

Electronic Supplementary Information

Experimental

Syntheses

SeO₂ (powder, 99%, Alfa Aesar), CuO (powder, 99%, Aldrich), CuCl₂ (powder, 99%, Aldrich), CuCl (powder, 90%, Sigma-Aldrich), PbO (powder, 99%, Aldrich), NaCl (powder, 99%, Alfa Aesar), and KCl (powder, 99%, Carlo Erba) were used as received.

Single crystals of three new Pb-containing mixed-valent copper oxoselenite chlorides have been prepared by the CVT reactions. The reagents were grounded in an agate mortar and loaded into a silica tube (*ca.* 15 cm), which was further evacuated to 10⁻² mbar and sealed. The tubes were placed horizontally into a tubular two-zone furnace, heated to 723K for 4 days (1) and 823 K for 3 days (2 and 3), and then slowly cooled to room temperature. The temperature difference between the hot zone with initial reagents mixture and cold zone of the tube in furnace was about 50 K. Likely, during these reactions the selenites and metal halides play the role of transport agent. The compounds obtained are only partially stable and deteriorate in air within several tens of hours, which prevented their detailed chemical characterization by electron microprobe analysis.

$(Pb_2Cu^{2+}_{9}O_4)(SeO_3)_4(Cu^+Cl_2)Cl_5(1)$

Red-brown prismatic crystals of **1** have been observed in the cold zone of the tube with a mixture of SeO_2 (0.111 g, 1 mmol), CuCl (0.124 g, 1.25 mmol), CuCl₂ (0.303 g, 2.25 mmol), PbO (0.167 g, 0.75 mmol), and NaCl (0.029 g, 0.50 mmol). Black block-shaped single crystals of synthetic georgbokiite, $[Cu_5O_2](SeO_3)_2Cl_2$, were found in all zones of the tube.

(PbCu²⁺₅O₂)(SeO₃)₂(Cu⁺Cl₂)Cl₃ (2)

Brown platy crystals of **2** were obtained by CTR from SeO₂ (0.111 g, 1 mmol), CuCl₂ (0.202 g, 1.5 mmol), CuO (0.159 g, 2 mmol), PbO (0.112 g, 0.5 mmol), and NaCl (0.059 g, 1 mmol). The crystals of **2** were found in association with dark-green prismatic crystals of Na₂[Cu₇O₂](SeO₃)₄Cl₄ in the hot zone of the tube. Black

block-shaped single crystals of synthetic georgbokiite, $[Cu_5O_2](SeO_3)_2Cl_2$, and orange needle-like crystals of synthetic chloromenite, $[Cu_9O_2](SeO_3)_4Cl_6$ were found in the middle part of the tube. Greenish transparent prismatic crystals of $Cu_2O(SeO_3)$ and Na_2CuO_2 were also observed in the cold zone of the tube.

$(Pb_{x}Cu^{2+}{}_{(6-x)}O_{2})(SeO_{3})_{2}(Cu^{+}Cl_{2})K_{(1-x)}Cl_{(4-x)}, x = 0.20$ (3)

Ruby-red crystals of **3** were observed in the cold zone of the tube. The following mixture was used: SeO_2 (0.111 g, 1 mmol), CuCl (0.124 g, 1.25 mmol), CuCl₂ (0.303 g, 2.25 mmol), PbO (0.167 g, 0.75 mmol), and NaCl (0.029 g, 0.50 mmol). Black block-shaped crystals of synthetic georgbokiite, $[Cu_5O_2](SeO_3)_2Cl_2$, were also observed in all zones of the tube.

Chemical analysis

The electron-microprobe analyses (Hitachi TM 3000 EDS system) were performed for **1–3**. Qualitative electron microprobe analysis revealed no other elements, except Cu, Pb, Se, Cl and K (**3**), with the atomic number greater than 11 (Na). The compounds are unstable under en electron beam, which did not allow detailed chemical characterization.

X-ray crystallography

Single crystals of all compounds were mounted on thin glass fibers for X-ray diffraction analysis using Bruker APEX II DUO X-ray diffractometer with a micro-focus X-ray tube operated with MoK α radiation at 50 kV and 40 mA. The data were integrated and corrected for absorption using a multi-scan type model using the Bruker programs APEX and SADABS. More than a hemisphere of X-ray diffraction data were collected for each crystal. Crystallographic information for all obtained phases is summarized in Table 1. Atomic coordinates and additional structural information are provided in the Supporting Information (CIF).

Infrared spectroscopy

Infrared spectra of **2** and **3** were measured between 4000 and 400 cm⁻¹ with a Perkin–Elmer Spectrum Two spectrometer equipped with a diamond attenuated total reflectance (ATR) accessory. The vibrational bands of selenite groups and ethanol have been established in the studied range (Figs. S2–3). Stretching vibrations $v(SeO_3)$ and deformation modes $\delta(SeO_3)$ of selenite oxoanions appear in range 831–712, 665 cm⁻¹, and 571–411 cm⁻¹, respectively. The observed bands are in good agreement with those reported in the literature for similar natural and synthetic selenite phases^{1,2}. The presence of the bands of the ethanol molecules in the IR

spectra is a consequence of the use of ethanol for cleaning of the ATR accessory of the spectrometer between the measurements of the samples of different phases. Stretching and deformation modes of the ethanol molecules appear at 2988, 2901, 1490, 1250, and 1066 cm⁻¹. The observed positions of the bands are consistent with published data for ethanol³.

- 1 K. Nakamoto, in *Handbook of Vibrational Spectroscopy*, eds. J. M. Chalmers and P. R. Griffiths, John Wiley & Sons Ltd., 2006, vol. 3, pp. 1872–1892.
- 2 N. V. Chukanov, *Infrared spectra of mineral species*, Springer Netherlands, Dordrecht, 2014, vol. 1., 1726 p.
- 3 Coblentz Society Inc., in *NIST Chemistry WebBook, NIST Standard Reference Database Number 69*, eds. P. J. Linstrom and W. G. Mallard, National Institute of Standards and Technology, Gaithersburg MD, 2009.

Table S1 Bond-valence analysis (in valence units = v.u.) for the structure of 1 =

	01	O2	O3	O4	05	O6	Cl1	C12	C13	Cl4	Σ
Pb1		0.45			0.40 ^{2x→}		$\substack{0.28,\\0,08^{2x\to\downarrow}}$	0.21	0.06		1.96
Cu1		$0.51^{2x\downarrow}$		$0.56^{2x\downarrow}$	0.45	0.41			$0.06^{2x\downarrow}$	$0.05^{4x\downarrow}$	2.04
Cu2			$0.43^{2x \rightarrow}$	$0.58^{2x \rightarrow}$						$0.05^{2x \rightarrow \downarrow}$	2.12
Cu3	0.47, 0.40	0.55					0.44		$0.05^{2x \rightarrow \downarrow}$		1.96
Cu4			0.32	0.53		$0.34^{2x \rightarrow}$		0.57			2.10
Cu5									$0.51^{2x \rightarrow}$		1.02
Se1			1.39		$1.32^{2x \rightarrow}$						4.03
Se2	1.28					$1.44^{2x \rightarrow}$					4.16
Σ	2.15	2.02	2.14	2.23	2.17	2.19	0.88	0.78	0.79	0.30	

 $[Cu^+Cl_2][Cu^{2+}_9Pb_2O_4](SeO_3)_4Cl_5.$

Table S2 Bond-valence analysis (in valence units = v.u.) for the structure of 2 =

	01	02	O3	04	05	O6	Cl1	Cl2	C13	Cl4	C15	Σ
Pb1		0.39 ^{2x→}				0.44	0.23		$\begin{array}{c} 0.30, \\ 0.10^{2x \rightarrow \downarrow} \end{array}$			1.95
Cu1			0.32 ^{2x→}		0.53		0.56	0.32				2.05
Cu2	0.47, 0.41				0.56			0.49			$0.05^{2x \rightarrow \downarrow}$	2.03
Cu3				0.47, 0.42		0.55			0.45	$0.05^{2x \rightarrow \downarrow}$		1.99
Cu4		0.47	0.44		$0.52^{2x\downarrow}$	$0.51^{2x\downarrow}$				$0.07^{2x\downarrow}$	$0.12^{2x\downarrow}$	2.13
Cu5											$0.58^{2x ightarrow}$	1.16
Cu6										$0.50^{2x ightarrow}$		1.00
Se1	1.32	$1.37^{2x \rightarrow}$										4.06
Se2			1.42 ^{2x→}	1.29								4.13
Σ	2.20	2.23	2.18	2.18	2.13	2.01	0.79	0.81	0.95	0.74	0.92	

 $[Cu^+Cl_2][Cu^{2+}_5PbO_2](SeO_3)_2Cl_3.$

Table S3 Bond-valence analysis (in valence units = v.u.) for the structure of 3 =

 $K_{(1-x)}[Cu^+Cl_2][Cu^{2+}_{(6-x)}Pb_xO_2](SeO_3)_2Cl_{(4-x)}$ ($x \approx 0.20$). Site occupancy factors (s.o.f.) are shown in brackets. The Pb1 site is only 10% occupied and its bond-valence characteristics are omitted in the table.

	O1 (1.0)	O2 (1.0)	O3 (1.0)	Cl1 (1.0)	Cl2 (1.0)	Cl3 (0.9)	Σ
K1 (0.8)				0.08 ^{2x→}	$0.07^{4x \rightarrow 2x \downarrow}$	0.18 ^{2x→}	0.80
Cu1 (1.0)	0.50, 0.41		0.57	$0.05^{2x \rightarrow \downarrow}$	0.47		2.06
Cu2 (1.0)		$0.46^{2x \rightarrow}$	$0.54^{2x \rightarrow \downarrow}$	$0.07^{2x \rightarrow \downarrow}$			2.14
Cu3 (1.0)				$0.55^{2x \rightarrow}$			1.10
Cu4 (0.9)		$0.29^{2x \rightarrow}$	0.54		0.29	0.61	2.02
Se1 (1.0)	1.26	1.39 ^{2x→}					4.04
Σ	2.17	2.14	2.19	0.87	0.90	0.79	



Fig. S1 General representation of coordination environments of cations and additional oxygen atoms (O_a) coordination in the crystal structures of 1–3. The Pb–Cl and Cu²⁺–Cl bonds longer than 3 Å are shown as

dashed lines.



Fig. S2 Infrared spectrum of $(PbCu^{2+}_{5}O_{2})(SeO_{3})_{2}(Cu^{+}Cl_{2})Cl_{3}$ (2).



Fig. S3 Infrared spectrum of $(Pb_xCu^{2+}_{(6-x)}O_2)(SeO_3)_2(Cu^+Cl_2)K_{(1-x)}Cl_{(4-x)}, x = 0.20$ (3).