

Monoclinic $\text{Cu}_3(\text{SeO}_3)_2\text{Cl}_2$: an oxo-halide with an unusual CuO_4Cl trigonal–bipyramidal coordination

Richard Becker,^{a*} Helmuth Berger^b and Mats Johansson^a

^aInorganic Chemistry, Stockholm University, S-106 91 Stockholm, Sweden, and

^bInstitut de Physique de la Matière Complexe, Ecole Polytechnique Fédérale de Lausanne, CH-1015 Lausanne, Switzerland

Correspondence e-mail: richard@inorg.su.se

Received 30 October 2006

Accepted 23 November 2006

Online 23 December 2006

In single crystals of a new monoclinic ($C2/m$) form of tricopper(II) diselenium(IV) dichloride hexaoxide, $\text{Cu}_3(\text{SeO}_3)_2\text{Cl}_2$, the Se atom is in the $4i$ position, while the two Cu atoms are in $2a$ and $4i$ positions. The structure is based on layers of CuO_4Cl trigonal bipyramids, CuO_4 square planes and SeO_3E tetrahedra. The Cu polyhedra are connected by edge- and corner-sharing to form $[010]$ chains and these chains are bridged by the Se atoms to form (001) layers. The compound is isostructural with $\text{Cu}_3(\text{TeO}_3)_2\text{Br}_2$.

Comment

The use of stereochemically active lone pairs as spacers to open up structures is a concept which has proved very successful for synthesizing novel low-dimensional compounds (Johansson *et al.*, 2000, 2003; Takagi *et al.*, 2006; Becker *et al.*, 2006). Cations such as Te^{IV} or Se^{IV} receive an asymmetric coordination due to their stereochemically active lone pair and may then function as a chemical scissor.

This work describes a new layered monoclinic $C2/m$ modification of $\text{Cu}_3(\text{SeO}_3)_2\text{Cl}_2$, (I), which was previously known in a triclinic form (Millet *et al.*, 2000). The structure of triclinic $\text{Cu}_3(\text{SeO}_3)_2\text{Cl}_2$ is three-dimensional with three crystallographically distinct Cu atoms in square-planar, octahedral and square-pyramidal coordinations. The structure is made up of layers of Cu polyhedra sandwiched by Se atoms, and the layers are connected *via* CuO_4 square planes. By contrast, monoclinic $\text{Cu}_3(\text{SeO}_3)_2\text{Cl}_2$ is isostructural with $\text{Cu}_3(\text{TeO}_3)_2\text{Br}_2$ (Becker *et al.*, 2005).

The Se atom in (I) shows a regular one-sided threefold coordination to one O2 and two O1 atoms. Its stereochemically active $4s^2$ lone pair (*E*) completes the tetrahedral SeO_3E coordination. The two crystallographically distinct Cu atoms have different coordinations (Fig. 1). Atom Cu1 has a square-planar coordination involving four O1 atoms, and two

further Cl atoms complete a distorted octahedral coordination. Atom Cu2 has a highly unusual distorted trigonal–bipyramidal CuO_4Cl coordination involving two apical O1 atoms and one Cl and two O2 equatorial atoms. To the best of our knowledge, (I) and $\text{Cu}_3(\text{TeO}_3)_2\text{Br}_2$ are the first compounds to show a trigonal–bipyramidal CuO_4X ($X = \text{Cl}$ or Br) coord-

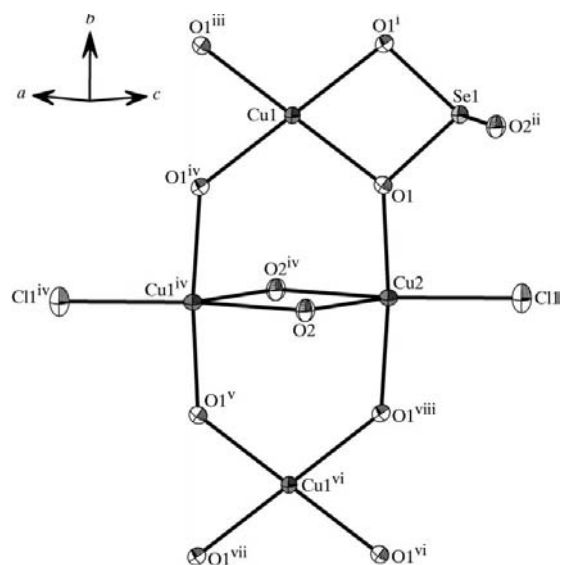


Figure 1

The asymmetric unit of $\text{Cu}_3(\text{SeO}_3)_2\text{Cl}_2$, with displacement ellipsoids drawn at the 50% probability level. [Symmetry codes: (i) $x, 1 - y, z$; (ii) $\frac{1}{2} - x, \frac{1}{2} + y, 2 - z$; (iii) $1 - x, 1 - y, 2 - z$; (iv) $1 - x, y, 2 - z$; (v) $1 - x, -y, 2 - z$; (vi) $x, -1 + y, z$; (vii) $1 - x, -1 + y, 2 - z$; (viii) $x, -y, z$.]

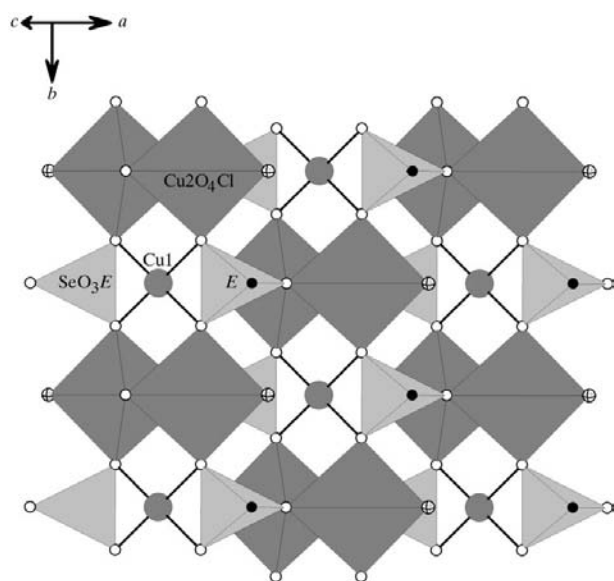


Figure 2

Chains of Cu-centred polyhedra and SeO_3E tetrahedra. O atoms, Cl atoms and Se lone pairs (*E*) are represented by open, crossed and solid circles, respectively.

dination polyhedron for Cu^{II} . Bond-valence sum calculations (Bresle & O'Keeffe, 1991) confirm the coordination and oxidation states of all ions. A low value of 0.6 v.u. is calculated for Cl if only the primary Cu—Cl bond is included (0.8 v.u. if longer interactions are included). This suggests that Cl^- acts more as a counter-ion than as part of the ionic/covalent bond network within the structure.

The structure of (I) is made up of pairs of $\text{Cu}_2\text{O}_4\text{Cl}$ trigonal bipyramids sharing an $\text{O}_2 \cdots \text{O}_2$ equatorial edge. These pairs are connected by sharing O1 atoms with two Cu_1O_4 square planes and form chains along the b axis (Fig. 1). The SeO_3E tetrahedra share an edge with the Cu_1O_4 square plane and a corner with the $\text{Cu}_2\text{O}_4\text{Cl}$ bipyramid, so that they bridge the chains into layers (Fig. 2). The layers are parallel to the ab plane and are separated from each other by the Cl atoms and the lone pairs of the Se atoms (Fig. 3). The absence of significant contacts between the layers implies that only van der Waals interactions connect the layers to each other in the structure. As the layers have no net charge, they can be considered as infinite two-dimensional molecules.

The structural difference between (I) and $\text{Cu}_3(\text{TeO}_3)_2\text{Br}_2$ is most obvious when looking at the $\text{Cu} \cdots \text{Cu}$ distances. Within a chain, the shortest distance ($\text{Cu}_2 \cdots \text{Cu}_2$) is actually shorter in $\text{Cu}_3(\text{TeO}_3)_2\text{Br}_2$ than in (I) [3.15 (2) versus 3.363 (12) Å], and this is also reflected in the smaller $\text{Cu}_2\text{—O}_2\text{—Cu}_2$ angle [96.09 (18) versus 101.72 (10)°]. These effects are probably due to the larger Br atom pushing the Cu_2 atoms closer together. The shortest inter-chain $\text{Cu} \cdots \text{Cu}$ distance ($\text{Cu}_1 \cdots \text{Cu}_2$) is shorter in (I) [3.607 (18) versus 3.71 (2) Å] due to the smaller size of Se^{IV} compared with Te^{IV} , thus allowing the chains to come closer. The shortest inter-layer $\text{Cu} \cdots \text{Cu}$ distance is substantially shorter in (I) [4.579 (16) versus 5.62 (3) Å], which again can be explained by the relatively smaller sizes of the Se and Cl atoms. The denser chain and layer packing in (I) can also be seen in the length of the a and c axes. The a axis, or the chain stacking direction, is reduced from 9.319 (2) to 8.933 (1) Å in (I), and the c axis, or the layer stacking direction, is reduced from 8.200 (2) to 7.582 (1) Å in (I).

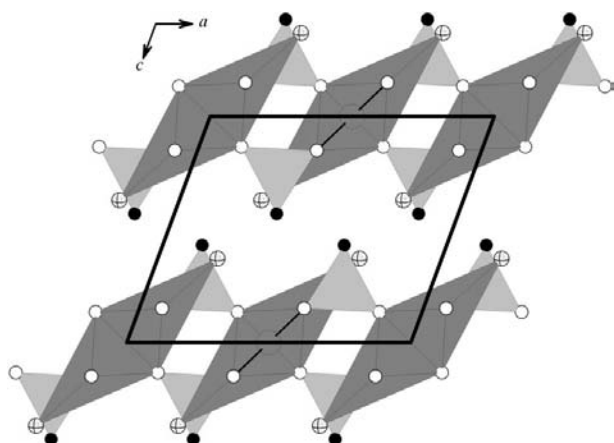


Figure 3
The (001) layers in $\text{Cu}_3(\text{SeO}_3)_2\text{Cl}_2$, viewed along the b axis. Atoms and polyhedra are drawn as in Fig. 2.

An atom should be positioned no further away than to contribute at least 4% of the bond valence to be regarded as bonded (Brown, 2002). For Se^{IV} and Te^{IV} , this means a longest primary bonding distance to O of 2.5–2.7 Å. The possibility of forming isostructural Se and Te analogues is largely dependent upon the coordination of these atoms. Se^{IV} has only been observed in SeO_3 coordination with bond distances of around 1.7 Å, while Te^{IV} may be coordinated by three, four or even five ligands, with the nearest three ligands at approximately 1.9 Å and additional ligands at more than 2 Å (Zemann, 1971). This means that a TeO_3 coordination environment is required for the formation of isostructural Te and Se analogues. This is the case in $\text{Cu}_3\text{Bi}(\text{TeO}_3)_2\text{O}_2\text{Cl}$ (Becker & Johnsson, 2005) and $\text{Cu}_3\text{Bi}(\text{SeO}_3)_2\text{O}_2\text{Cl}$ (Pring *et al.*, 1990), where the fourth Te—O and Se—O distances are both around 3 Å and thus clearly outside the primary coordination sphere. A different case is observed for $\text{Ni}_5(\text{TeO}_3)_4\text{Cl}_2$ (Johnsson *et al.*, 2003) and $\text{Ni}_5(\text{SeO}_3)_4\text{Cl}_2$ (Shen *et al.*, 2005), for which the fourth Te—O distance (2.65 Å) can be regarded as a bond, whereas the fourth Se—O distance (2.94 Å) clearly lies outside the primary coordination sphere.

Experimental

Single crystals of $\text{Cu}_3(\text{SeO}_3)_2\text{Cl}_2$ were synthesized *via* a chemical vapour transport reaction in a sealed evacuated silica tube. CuO (Alfa Aesar, 99.7%), SeO_2 (Alfa Aesar, 99.4%) and CuCl_2 (Alfa Aesar, 99%) were used as starting materials. The crystals were grown from the off-stoichiometric $\text{CuO}:\text{SeO}_2:\text{CuCl}_2$ molar ratio of 1:1:1. The powders were placed at one end of a silica tube which was then evacuated to 10^{-5} Torr (1 Torr = 133.322 Pa). Electronic grade HCl gas was introduced into the tube before sealing it off. The ampoule was then heated in a two-zone furnace with charge and growth zone temperatures of 733 and 623 K, respectively. After six weeks, two different kinds of single crystals were observed in the ampoule, namely yellow–green $\text{Cu}_3(\text{SeO}_3)_2\text{Cl}_2$ platelets with a maximum size of $10 \times 6 \times 0.2$ mm in the centre of the ampoule, and thin brown air-sensitive CuCl_2 needles with a maximum size of $20 \times 1 \times 0.1$ mm in the charge zone. The synthesis products were characterized using a scanning electron microscope (SEM, Jeol 820) with an energy-dispersive spectrometer (EDS, LINK AN10000), confirming the presence and stoichiometry of Cu, Se and Cl.

Crystal data

$\text{Cu}_3(\text{SeO}_3)_2\text{Cl}_2$	$Z = 2$
$M_r = 515.44$	$D_x = 4.333 \text{ Mg m}^{-3}$
Monoclinic, $C2/m$	Mo $K\alpha$ radiation
$a = 8.9333$ (12) Å	$\mu = 17.88 \text{ mm}^{-1}$
$b = 6.2164$ (7) Å	$T = 292$ (3) K
$c = 7.5815$ (12) Å	Thin plate, green
$\beta = 110.238$ (13)°	$0.30 \times 0.12 \times 0.06 \text{ mm}$
$V = 395.03$ (10) Å ³	

Table 1
Selected bond lengths (Å).

Se1—O2 ⁱ	1.663 (2)	Cu2—O2 ⁱⁱ	2.099 (2)
Se1—O1	1.7379 (17)	Cu2—Cl1	2.2229 (15)
Cu1—O1	1.9468 (17)	Cu2—O2	2.236 (3)
Cu2—O1	1.9321 (18)		

Symmetry codes: (i) $-x + \frac{1}{2}, -y + \frac{1}{2}, -z + 2$; (ii) $-x + 1, -y, -z + 2$.

Data collection

Oxford Xcalibur3 diffractometer
 ω scans at different φ
 Absorption correction: Gaussian
 [CrysAlis CCD (Oxford Diffraction, 2006) and CrysAlis RED (Oxford Diffraction, 2006)]
 $T_{\min} = 0.113$, $T_{\max} = 0.554$

2959 measured reflections
 628 independent reflections
 610 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.051$
 $\theta_{\text{max}} = 30.0^\circ$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.026$
 $wR(F^2) = 0.076$
 $S = 1.65$
 628 reflections
 39 parameters
 $w = 1/[\sigma^2(F_o^2) + (0.0353P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\text{max}} = 0.001$
 $\Delta\rho_{\text{max}} = 1.34 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\text{min}} = -0.73 \text{ e } \text{Å}^{-3}$
 Extinction correction: SHELXL97 (Sheldrick, 1997)
 Extinction coefficient: 0.0254 (18)

The maximum residual electron density is located 0.58 Å from atom Cu2 and the minimum is located 0.72 Å from Cu2.

Data collection: CrysAlis CCD (Oxford Diffraction, 2006); cell refinement: CrysAlis RED (Oxford Diffraction, 2006); data reduction: CrysAlis RED; program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: DIAMOND (Brandenburg, 2001); software used to prepare material for publication: SHELXL97.

This work was carried out with financial support from the Swedish Research Council, the Swiss National Science Foundation (SNSF) and MaNEP.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BC3024). Services for accessing these data are described at the back of the journal.

References

- Becker, R., Berger, H., Johnsson, M., Prester, M., Marohnic, Z., Miljak, M. & Herak, M. (2006). *J. Solid State Chem.* **179**, 836–842.
- Becker, R. & Johnsson, M. (2005). *Solid State Sci.* **7**, 375–380.
- Becker, R., Johnsson, M., Kremer, R. K. & Lemmens, P. (2005). *J. Solid State Chem.* **178**, 2024–2029.
- Brandenburg, K. (2001). *DIAMOND*. Release 2.1e. Crystal Impact GbR, Bonn, Germany.
- Brese, N. E. & O'Keeffe, M. (1991). *Acta Cryst.* **B47**, 192–197.
- Brown, I. D. (2002). *The Chemical Bond in Inorganic Chemistry: The Bond Valence Model*, p. 43. New York: Oxford University Press Inc.
- Johnsson, M., Törnroos, K. W., Lemmens, P. & Millet, P. (2003). *Chem. Mater.* **15**, 68–73.
- Johnsson, M., Törnroos, K. W., Mila, F. & Millet, P. (2000). *Chem. Mater.* **12**, 2853–2857.
- Millet, P., Bastide, B. & Johnsson, M. (2000). *Solid State Commun.* **113**, 719–723.
- Oxford Diffraction (2006). *CrysAlis CCD* and *CrysAlis RED*. Versions 1.171.29.2. Oxford Diffraction Ltd, Abingdon, Oxfordshire, England.
- Pring, A., Gatehouse, B. M. & Birch, W. D. (1990). *Am. Mineral.* **75**, 1421–1425.
- Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
- Shen, Y.-L., Mao, J.-G. & Jiang, H.-L. (2005). *J. Solid State Chem.* **178**, 2942–2946.
- Takagi, R., Johnsson, M., Gnezdilov, V., Kremer, R. K., Brenig, W. & Lemmens, P. (2006). *Phys. Rev. B*, **74**, 014413.
- Zemann, J. (1971). *Monatsh. Chem.* **102**, 1209–1216.