

## MoCu<sub>3</sub>TeO<sub>7</sub>Cl<sub>2</sub>·0.5H<sub>2</sub>O

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Single crystals of molybdenum(VI) tricopper(II) tellurium(IV) heptaoxide dichloride hemihydrate, MoCu<sub>3</sub>TeO<sub>7</sub>Cl<sub>2</sub>·0.5H<sub>2</sub>O, were synthesized *via* a transport reaction in sealed evacuated silica tubes. All atoms occupy general positions within the triclinic (*P* $\bar{1}$ ) unit cell. The building units are irregular CuO<sub>4</sub>Cl and CuO<sub>3</sub>Cl<sub>2</sub> square pyramids, distorted TeO<sub>3+1</sub>*E* trigonal bipyramids (*E* is the lone pair of Te<sup>IV</sup>) and irregular MoO<sub>5</sub> pyramids. The TeO<sub>3+1</sub>*E*, CuO<sub>4</sub>Cl and CuO<sub>3</sub>Cl<sub>2</sub> polyhedra form (110) layers bridged by Mo atoms. The water molecules are located in [100] channels.

### Comment

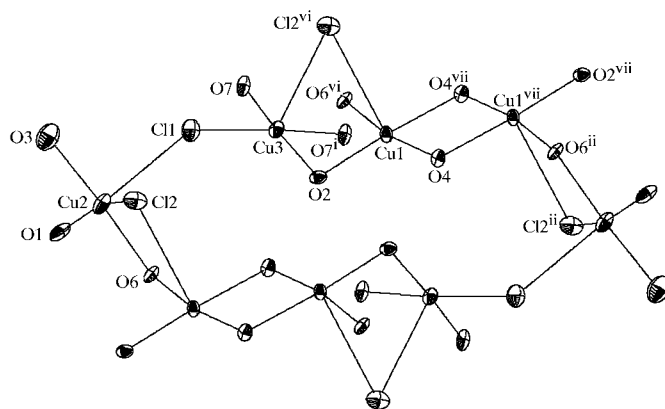
Transition metal oxohalogenides containing elements such as Te<sup>IV</sup>, Se<sup>IV</sup>, As<sup>III</sup> or Sb<sup>III</sup> with stereochemically active lone pairs form a family with a very rich structural chemistry in which there is a high probability of finding novel host–guest compounds and low-dimensional compounds with interesting physical properties (Johansson *et al.*, 2000, 2003, 2004; Becker *et al.*, 2005). In these oxohalogenides, the lone-pair cations are most often coordinated by oxygen, while the late transition metal ions are coordinated by both oxygen and halogen anions. The aim of the present work was to introduce a highly charged transition metal into oxohalogenides containing late transition metals and asymmetrically coordinated lone-pair elements. The idea was to use the Mo<sup>VI</sup> ion as a spacer to force the Cu<sup>II</sup> ions to adopt low-dimensional arrangements.

The Te atom has a threefold asymmetric coordination involving oxygen, with Te–O distances in the range 1.876 (4)–1.892 (4) Å. A fourth, longer, Te–O4 distance of 2.836 (4) Å completes a TeO<sub>3+1</sub> seesaw coordination. When the stereochemically active 5s<sup>2</sup> lone pair (*E*) is taken into account, the coordination becomes a distorted trigonal bipyramid, *viz.* TeO<sub>3+1</sub>*E*, where *E* is located in the equatorial plane. Assuming a Te–*E* distance of 1.25 Å (Galy *et al.*, 1975), the lone-pair centre is located at *x* = 0.7868, *y* = 0.7994, *z* = 0.1781.

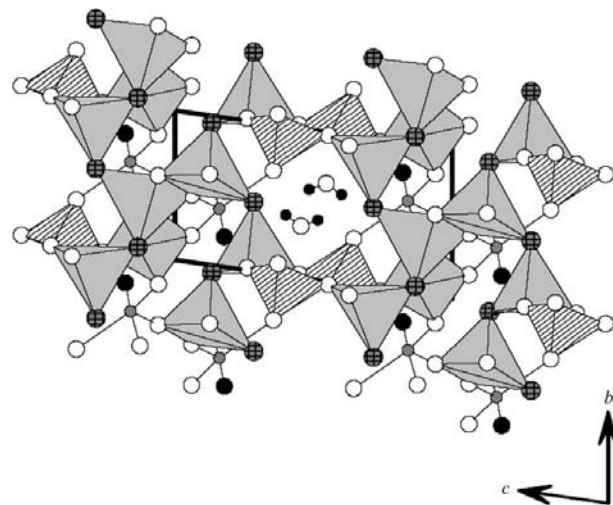
Atom Cu1 is coordinated by four O atoms in a square-planar configuration [Cu–O = 1.923 (4)–1.962 (4) Å] and by one Cl atom that completes a CuO<sub>4</sub>Cl square pyramid [Cu–Cl = 2.945 (2) Å]. Atoms Cu2 and Cu3 are coordinated by

three O atoms and one Cl atom in a square-planar geometry, with Cu–O distances in the range 1.914 (4)–1.992 (4) Å and Cu–Cl distances in the range 2.2474 (18)–2.2628 (17) Å. The distorted square pyramid is completed by Cu–Cl distances in the range 2.7192 (19)–2.7259 (19) Å. This unusual CuO<sub>3</sub>Cl<sub>2</sub> square-pyramidal coordination has been found previously in Cu<sub>5</sub>Se<sub>2</sub>O<sub>8</sub>Cl<sub>2</sub> (Galy *et al.*, 1979). The Mo atom is coordinated by five O atoms in a distorted square-pyramidal configuration, with Mo–O distances in the range 1.698 (5)–2.085 (4) Å.

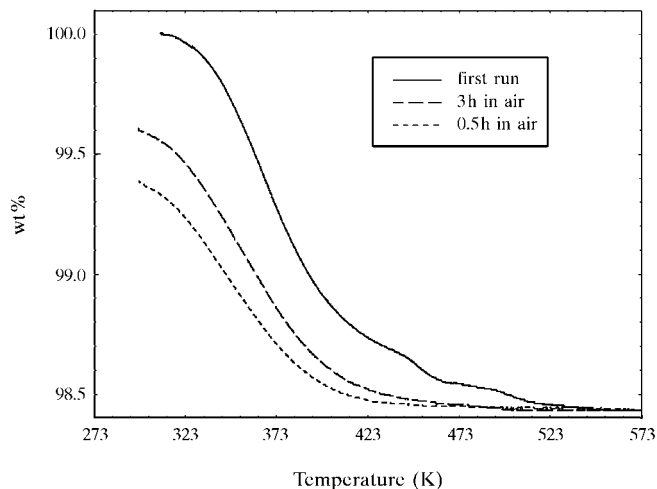
Each Cu1O<sub>4</sub>Cl polyhedron shares edges with one Cu1O<sub>4</sub>Cl, one Cu<sub>2</sub>O<sub>3</sub>Cl<sub>2</sub> and one Cu<sub>3</sub>O<sub>3</sub>Cl<sub>2</sub> polyhedron. Furthermore, it shares a corner with one MoO<sub>5</sub> polyhedron and three TeO<sub>3+1</sub>*E* polyhedra. The different Cu polyhedra form Cu<sub>8</sub>O<sub>20</sub>Cl<sub>6</sub> rings in the structure (Fig. 1). The TeO<sub>3+1</sub>*E* polyhedra are isolated and share corners with three Cu1O<sub>4</sub>Cl and three Cu<sub>2</sub>O<sub>3</sub>Cl<sub>2</sub> polyhedra. Two MoO<sub>5</sub> polyhedra share an edge and form



**Figure 1**  
The Cu<sub>8</sub>O<sub>20</sub>Cl<sub>6</sub> unit, with ellipsoids drawn at the 50% probability level. [Symmetry codes: (i)  $-x + 1, -y + 1, -z$ ; (ii)  $-x + 2, -y + 1, -z$ ; (vi)  $x, y + 1, z$ ; (vii)  $-x + 2, -y + 2, -z$ .]



**Figure 2**  
An overview of the structure of MoCu<sub>3</sub>TeO<sub>7</sub>Cl<sub>2</sub>·*x*H<sub>2</sub>O. CuO<sub>4</sub>Cl and CuO<sub>3</sub>Cl<sub>2</sub> polyhedra are light grey, and MoO<sub>5</sub> polyhedra are striped. The O, Te and Cl atoms are white, grey and grey checked spheres, respectively. The H atoms are shown as small black circles and the Te lone pairs (*E*) as large black circles.



**Figure 3** Thermogravimetric analysis of  $\text{MoCu}_3\text{TeO}_7\text{Cl}_2 \cdot x\text{H}_2\text{O}$ . The sample was continuously dehydrated between room temperature and 543 K. One week of exposure to air in the laboratory gives a weight loss of about 1.5 wt% (first run) that corresponds to  $x \sim 0.5$ . The quick uptake of water is shown by subsequent experiments with exposure times of 0.5 and 3 h.

$\text{Mo}_2\text{O}_8$  units that connect the layers built by the  $\text{TeO}_{3+1}E$ ,  $\text{CuO}_4\text{Cl}$  and  $\text{CuO}_3\text{Cl}_2$  polyhedra. These connections create voids that host water molecules with a partial occupancy of 50% (Fig. 2). When the water molecule is present, it may form hydrogen bonds to atom O5 that weaken the  $\text{Mo}=\text{O}5$  double bond and cause the observed large anisotropic displacement parameter of O5.

Structural refinements and thermogravimetric analyses (TGA) on  $\text{MoCu}_3\text{TeO}_7\text{Cl}_2 \cdot x\text{H}_2\text{O}$  crystals that had been left in the laboratory for about one week support the fact that water is present in the channels of the crystal structure at the O8 position. During the refinements, the  $x$  value was found to be  $\sim 0.5$ . TGA gave a weight loss of 1.5 wt% that also corresponds to  $x \sim 0.5$ . The uptake of water is relatively rapid and was found to be approximately 0.3  $\text{H}_2\text{O}$  after exposing the crystals to air for 0.5 h and approximately 0.4  $\text{H}_2\text{O}$  after 3 h (Fig. 3). The  $\text{Mo}-\text{O}8$  distance of 2.495 (13) Å is close to the longest  $\text{Mo}-\text{O}$  distance in  $\text{MoTe}_2\text{O}_7$  [2.589 (6) Å], which displays a distorted octahedral coordination around  $\text{Mo}^{\text{VI}}$  (Arnaud *et al.*, 1976).

## Experimental

Single crystals of  $\text{MoCu}_3\text{TeO}_7\text{Cl}_2 \cdot x\text{H}_2\text{O}$  were synthesized using  $\text{MoO}_3$  (Chempur, 99.9%),  $\text{CuO}$  (Aldrich, 99.99%),  $\text{CuCl}_2 \cdot x\text{H}_2\text{O}$  (Aldrich, +99%) and  $\text{TeO}_2$  (Aldrich, 99.995%) as starting materials. The water in the  $\text{CuCl}_2 \cdot x\text{H}_2\text{O}$  powder was evaporated at 383 K before use. The preparation was carried out starting with  $\text{MoO}_3$ ,  $\text{CuO}$ ,  $\text{CuCl}_2$  and  $\text{TeO}_2$  in a 1:2:1:1 stoichiometric molar ratio, mixing the components in a mortar and placing the mixture in a Pyrex glass tube (length  $\sim 5$  cm) which was then evacuated. The tube was heated at 730 K for 65 h in a muffle furnace. The product formed as thin green plate-shaped crystals. The uptake of water upon exposure of the crystals to air was studied using thermogravimetry (Perkin-Elmer TGA7) at a heating rate of 10 K  $\text{min}^{-1}$ .

## Crystal data

$\text{MoCu}_3\text{TeO}_7\text{Cl}_2 \cdot 0.5\text{H}_2\text{O}$   
 $M_r = 606.06$   
 Triclinic,  $P\bar{1}$   
 $a = 6.1393$  (15) Å  
 $b = 6.386$  (2) Å  
 $c = 12.005$  (3) Å  
 $\alpha = 81.75$  (4)°  
 $\beta = 85.76$  (3)°  
 $\gamma = 86.18$  (3)°  
 $V = 463.8$  (2) Å<sup>3</sup>  
 $Z = 2$   
 $D_x = 4.34$  Mg  $\text{m}^{-3}$

Mo  $K\alpha$  radiation  
 Cell parameters from 1691 reflections  
 $\theta = 1.9\text{--}28.2^\circ$   
 $\mu = 11.77$   $\text{mm}^{-1}$   
 $T = 291$  (2) K  
 Plate, green  
 $0.08 \times 0.04 \times 0.01$  mm

## Data collection

Stoe IPDS diffractometer  
 $\varphi$  scans  
 Absorption correction: numerical (*X-RED*; Stoe & Cie, 2001)  
 $T_{\text{min}} = 0.37$ ,  $T_{\text{max}} = 0.524$   
 13580 measured reflections  
 2214 independent reflections

1677 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.094$   
 $\theta_{\text{max}} = 28.1^\circ$   
 $h = -8 \rightarrow 8$   
 $k = -8 \rightarrow 8$   
 $l = -15 \rightarrow 15$

## Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.027$   
 $wR(F^2) = 0.054$   
 $S = 0.85$   
 2214 reflections  
 131 parameters

H-atom parameters constrained  
 $w = 1/[\sigma^2(F_o^2) + (0.0218P)^2]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\text{max}} < 0.001$   
 $\Delta\rho_{\text{max}} = 1.18$  e Å<sup>-3</sup>  
 $\Delta\rho_{\text{min}} = -0.93$  e Å<sup>-3</sup>

**Table 1**

Selected bond lengths (Å).

Te—O7 <sup>i</sup>	1.876 (4)	Cu1—O4	1.962 (4)
Te—O4	1.887 (4)	Cu1—Cl2 <sup>vi</sup>	2.9452 (17)
Te—O2 <sup>ii</sup>	1.892 (4)	Cu2—O1	1.914 (4)
Te—O5 <sup>iii</sup>	2.836 (5)	Cu2—O3	1.927 (5)
Mo—O5	1.698 (5)	Cu2—O6	1.975 (4)
Mo—O3 <sup>iv</sup>	1.745 (4)	Cu2—Cl2	2.2474 (18)
Mo—O1	1.911 (4)	Cu2—Cl1	2.7192 (19)
Mo—O6 <sup>v</sup>	1.920 (4)	Cu3—O7	1.933 (4)
Mo—O1 <sup>v</sup>	2.085 (4)	Cu3—O2	1.934 (4)
Mo—O8 <sup>iv</sup>	2.495 (13)	Cu3—O7 <sup>i</sup>	1.992 (4)
Cu1—O6 <sup>vi</sup>	1.923 (4)	Cu3—Cl1	2.2628 (17)
Cu1—O2	1.933 (4)	Cu3—Cl2 <sup>vi</sup>	2.7259 (19)
Cu1—O4 <sup>vii</sup>	1.957 (4)		

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

**Table 2**

Hydrogen-bond geometry (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
O8—H8A $\cdots$ O5 <sup>viii</sup>	0.82	2.17	2.772 (14)	130
O8—H8B $\cdots$ O5 <sup>ix</sup>	0.97	2.29	3.126 (14)	144
O8—H8B $\cdots$ O8 <sup>x</sup>	0.97	1.75	2.47 (3)	129

Symmetry codes: (viii)  $-x + 1, -y + 1, -z - 1$ ; (ix)  $x - 1, y, z$ ; (x)  $-x, -y + 1, -z - 1$ .

Four different diffraction data sets were recorded with the crystal in different  $\varphi$  and  $\chi$  orientations. Scale factors for the individual data sets were computed with *SHELXL97* (Sheldrick, 1997) and finally the individual data sets were scaled and averaged with the program *REFLEX* (Eriksson, 2004). All atoms, except for those of the water molecule, were refined with anisotropic displacement parameters.

The H atoms were identified in a difference Fourier map in the final stage of the refinement by careful inspection of the electron-density peaks located at distances between 0.8 and 1.2 Å from the O atoms within the voids of the structure. These atoms were then

refined using a riding model with tetrahedral Mo—O—H angles. The displacement parameters of the H atoms were fixed at 1.5 times the  $U_{eq}$  value of the carrier O atom. The occupancy of each H atom was fixed at the same value as that of the carrier O atom.

Data collection: *EXPOSE* in *IPDS* (Stoe & Cie, 1997); cell refinement: *CELL* in *IPDS*; data reduction: *INTEGRATE* in *IPDS*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *DIAMOND* (Bergerhoff, 1996); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BC1088). Services for accessing these data are described at the back of the journal.

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