inorganic compounds

$Ca_2CuTe_4O_{10}Cl_2$, a new synthetic tellurium(IV) oxochloride

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Single crystals of dicalcium copper tetratellurium decaoxide dichloride, $Ca_2CuTe_4O_{10}Cl_2$, were synthesized *via* a transport reaction in sealed evacuated quartz glass tubes. The building units of the structure are irregular CaO_7 polyhedra, centrosymmetric CuO_4Cl_2 octahedra and two crystallographically distinct TeO_4E distorted bipyramids (E being the $5s^2$ lone pair of Te^{IV}). The TeO_4E and CuO_4Cl_2 polyhedra together form planes that are connected by the Ca atoms. The CuO_4Cl_2 octahedra are isolated from each other by the other building units.

Comment

Oxohalogenides comprising transition metals and elements having an asymmetric coordination due to the presence of stereochemically active lone pairs, such as Te^{IV}, Se^{IV}, As^{III} or Sb^{III}, have proved to be a very interesting family of compounds, in which there is a high probability of finding novel host–guest compounds, quantum spin systems and low-dimensional compounds (Johnsson *et al.*, 2000, 2003, 2004). The lone-pair elements and the halogens constitute 'structural scissors', hindering the development of three-dimensional networks. In these kinds of oxohalogenide compounds, the lone-pair elements are coordinated only by oxygen, and the metal ions are coordinated by both oxygen and halogens. The synthesis strategy involves the use of the halogens Cl, Br and I but not F, as the latter is so electronegative that it will also bond to the lone-pair elements; the F atom may then constitute a bridge directly between the lone-pair element and a transition metal ion and thus will not act as 'scissors', and therefore do not contribute in forcing the transition metal ions to take low-dimensional arrangements in the crystal structures.

The present work is the outcome of an ongoing investigation of transition metal oxohalogenides containing alkaline earth elements and asymmetrically coordinated lone-pair elements. The crystal structures of a few compounds in this family have been described before [*e.g.* $Ba_3Te_2O_6Cl_2$ (Hottentot & Loopstra, 1983), $Ba_2Co(SeO_3)_2Cl_2$ (Johnston &

Harrison, 2002), and $Ba_2Cu_4Te_4O_{11}Cl_4$ and $BaCu_2Te_2O_6Cl_2$ (Feger & Kolis, 1998)]. To our knowledge, the novel title compound, $Ca_2CuTe_4O_{10}Cl_2$, is the first oxohalogenide described with Ca^{II} in combination with Cu^{II} and Te^{IV}.

There are two crystallographically distinct Te atoms. Atom Te1 has a see-saw TeO_4 coordination to oxygen. When the stereochemically active $5s^2$ lone pair (designated E) is also taken into account, the coordination becomes a distorted TeO_4E trigonal bipyramid, where E is located in the equatorial plane. The bonding distances are in the range 1.841 (3)–2.206 (2) Å (Table 1). Atom Te2 has a threefold one-sided TeO_3 coordination, having Te—O bond distances in the range 1.867 (2)–1.932 (2) Å. A longer Te—O bond [Te2—O4 = 2.616 (3) Å] completes the see-saw coordination. Bond-valence-sum calculations (Brown & Altermatt, 1985) suggest that this long Te—O distance contributes to the bond valence and that these atoms therefore should be regarded as coordinated. Taking the stereochemically active lone pair into account, the coordination polyhedron becomes a $TeO_{3+1}E$ trigonal bipyramid for Te2, with the lone pair in the equatorial plane. Geometrically placing the lone pairs assuming a Te—E distance (radius) of 1.25 Å (Galy *et al.*, 1975) gives the fractional coordinates $E1$ ($x = 0.3175$, $y = 0.4855$, $z = 0.2878$) and $E2$ ($x = -0.3943$, $y = 0.6409$, $z = 0.4123$) for Te1 and Te2, respectively.

The Cu atom, located at a centre of symmetry, is coordinated by four O atoms in a square-planar configuration, with Cu—O distances in the range 1.945 (2)–2.017 (3) Å, and two Cl atoms complete a CuO_4Cl_2 octahedron, with Cu—Cl distances of 2.738 (2) Å. The Ca atom is coordinated by seven O atoms to form an irregular CaO_7 polyhedron. The Ca—O distances are in the range 2.330 (3)–2.583 (3) Å, except for the Ca—O5 distance, which is only 2.266 (3) Å. A long Ca—Cl distance of 3.379 (2) Å does not contribute significantly to the bond valence sum and the Cl atom is therefore not regarded as bonded.
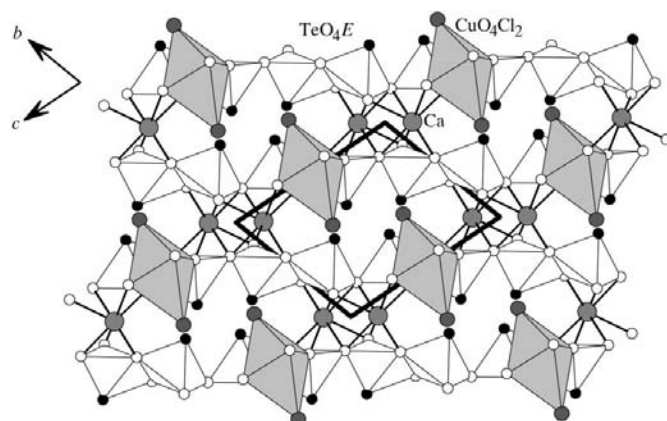
Figure 1
The structure of $Ca_2CuTe_4O_{10}Cl_2$ is composed of layers formed by CuO_4Cl_2 octahedra, and $Te1O_4E$ and $Te2O_{3+1}E$ trigonal bipyramids that are connected by the Ca atoms (medium grey). Colour key: O atoms are white, Cl atoms are dark grey and the positions of the $5s^2$ lone pairs (E) on the Te atoms are marked as black spheres. The lone pairs and the Cl atoms are located in channels in the structure.

An overview of the structure is shown in Fig. 1. The $Te1O_4E$ and $Te2O_{3+1}E$ polyhedra build infinite $[TeO_{2.5}]_n$ chains along [011] by corner sharing and edge sharing. The $[TeO_{2.5}]_n$ chains are linked by CuO_4Cl_2 octahedra *via* the $Te2O_{3+1}E$ polyhedra to form layers in the $(0\bar{1}1)$ plane (see Fig. 2). Each CuO_4Cl_2 octahedron shares edges with two CaO_7 polyhedra and with two $Te2O_{3+1}E$ bipyramids, and corners with two more such bipyramids (see Fig. 3). Each CaO_7 polyhedron shares edges with two $Te1O_4E$ and two $Te2O_{3+1}E$ bipyramids, and corners with two more of each kind of Te polyhedron. The CaO_7 polyhedra also each share edges with two more CaO_7 polyhedra to build up $[CaO_5]_n$ chains along [100]. The $[CaO_5]_n$ chains link the Te–O–Cu–Cl layers to build up the thre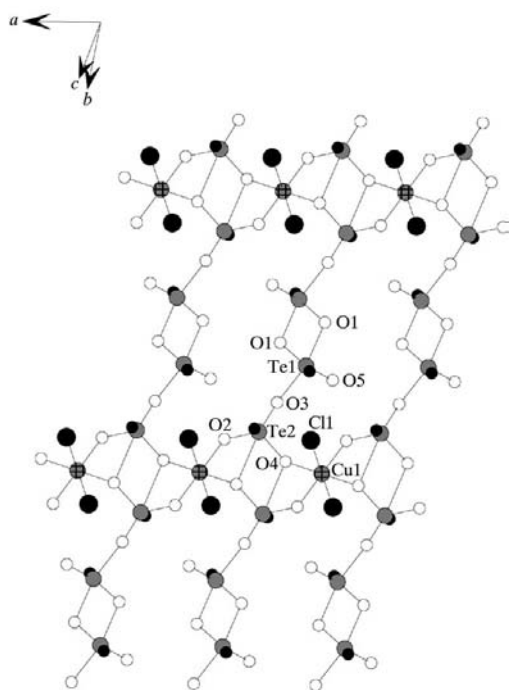e-dimensional structure and channels develop along [100], in which the Cl atoms and the lone pairs (E) are located (see Fig. 1).

Experimental

Single crystals of $Ca_2CuTe_4O_{10}Cl_2$ were synthesized by chemical transport reactions in sealed evacuated quartz glass tubes. CaO (ABCR, 99.95%), $CuCl_2$ (Avocado Research Chemicals, +98%), CuO (Avocado Research Chemicals, +99%) and TeO_2 (ABCR, +99%) were mixed in the non-stoichiometric molar ratio 1:1:1:2 in a mortar and placed in a quartz glass tube (length ~5 cm), which was then evacuated. The tube was heated for 72 h at 900 K in a muffle furnace. The product appeared as bright-green plate-like single crystals and a powder of undetermined composition. The product of the synthesis was non-hygroscopic.

Figure 2
The $Te1O_4E$ and the $Te2O_{3+1}E$ polyhedra build up infinite $[TeO_{2.5}]_n$ chains along [011] by corner and edge sharing. The $[TeO_{2.5}]_n$ chains are linked by CuO_4Cl_2 octahedra to form layers in the $(0\bar{1}1)$ plane.

Crystal data

$Ca_2CuTe_4O_{10}Cl_2$	$Z = 1$
$M_r = 885.00$	$D_x = 4.656$ Mg m^{-3}
Triclinic, $P\bar{1}$	Mo $K\alpha$ radiation
$a = 5.421$ (2) Å	Cell parameters from 1170
$b = 7.266$ (3) Å	reflections
$c = 8.717$ (5) Å	$\theta = 1.9$–28.1°
$\alpha = 71.60$ (6)°	$\mu = 12.07$ mm^{-1}
$\beta = 79.26$ (6)°	$T = 291$ (2) K
$\gamma = 77.63$ (5)°	Plate, green
$V = 315.6$ (3) Å^3	$0.16 \times 0.14 \times 0.12$ mm

Data collection

Stoe IPDS diffractometer	1487 independent reflections
φ scan	1381 reflections with $I > 2\sigma(I)$
Absorption correction: numerical	$R_{int} = 0.046$
[*X-RED* (Stoe & Cie, 2001) and	$\theta_{max} = 27.9°$
X-SHAPE (Stoe & Cie, 1999)]	$h = -7 \rightarrow 7$
$T_{min} = 0.136$, $T_{max} = 0.234$	$k = -9 \rightarrow 9$
4989 measured reflections	$l = -11 \rightarrow 11$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0269P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.018$	$+ 0.0814P]$
$wR(F^2) = 0.044$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.06$	$(\Delta/\sigma)_{max} = 0.001$
1487 reflections	$\Delta\rho_{max} = 1.03$ e Å^{-3}
88 parameters	$\Delta\rho_{min} = -0.83$ e Å^{-3}

Table 1
Selected interatomic distances (Å).

Te1—O5	1.841 (3)	Cu1—Cl1^v	2.738 (2)
Te1—O1^i	1.945 (3)	Ca1—O5^{vi}	2.266 (3)
Te1—O1	2.064 (3)	Ca1—O2	2.330 (3)
Te1—O3	2.206 (2)	Ca1—O1^v	2.353 (3)
Te2—O2	1.867 (2)	Ca1—O5	2.462 (3)
Te2—O4	1.910 (2)	Ca1—O3	2.575 (3)
Te2—O3^{ii}	1.932 (2)	Ca1—O4^{iv}	2.579 (3)
Te2—O4^{iii}	2.616 (3)	Ca1—O3^{vii}	2.583 (3)
Cu1—O2	1.945 (2)	Ca1—Cl1^v	3.379 (2)
Cu1—O4^{iv}	2.017 (3)		

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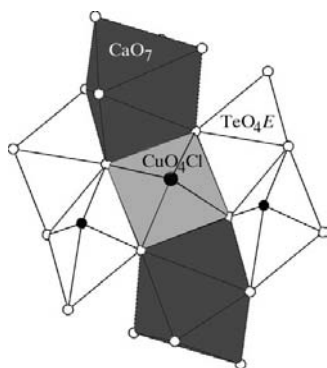

Figure 3
Each CuO_4Cl_2 octahedron shares edges with two $Te2O_{3+1}E$ bipyramids and corners with two more bipyramids of the same kind. Edges are also shared with two CaO_7 polyhedra.

Two different diffraction data sets were recorded with the same crystal in different χ 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). The O atoms were refined with isotropic displacement parameters.

Data collection: *EXPOSE* in *IPDS* (Stoe & Cie, 1997); cell refinement: *CELL* in *IPDS*; data reduction: *INTEGRATE* in *IPDS*;

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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: *SHELXL97*.

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