inorganic compounds

$Sr_2Cu_2TeO_6Br_2$: honeycomb layers of copper(II) ions

Rie Takagi and Mats Johnsson*

Inorganic Chemistry, Arrhenius Laboratory, Stockholm University, S-106 91 Stockholm, Sweden
Correspondence e-mail: matsj@inorg.su.se

Single crystals of distrontium(II) dicopper(II) tellurium(VI) hexaoxide dibromide, $Sr_2Cu_2TeO_6Br_2$, were synthesized *via* solid state/gas phase reactions in sealed evacuated silica tubes. The building units are irregular SrO_4Br_3 polyhedra (a new type of coordination polyhedron around Sr^{II}), CuO_5 square pyramids and TeO_6 octahedra. The CuO_5 square pyramids and the TeO_6 octahedra together form layers in the *bc* plane bridged by Sr atoms. The Cu atoms are arranged to form puckered honeycomb layers. The Te atom lies on an inversion centre.

Comment

The title compound is the first tellurate halide compound in the system AE–Cu^{II}–Te^{VI}–O–X (AE = alkaline earth and X = halide). Very few compounds belonging to the family AE–Cu^{II}–Te^{VI}–O have been described before, *viz.* triclinic and tetragonal Ba_2CuTeO_6 (Koehl & Reinen, 1974; Iwanaga *et al.*, 1999) and tetragonal Sr_2CuTeO_6 (Reinen & Weitzel, 1976).

An overview of the structure of the title compound is shown in Fig. 1; selected interatomic distances are given in Table 1.
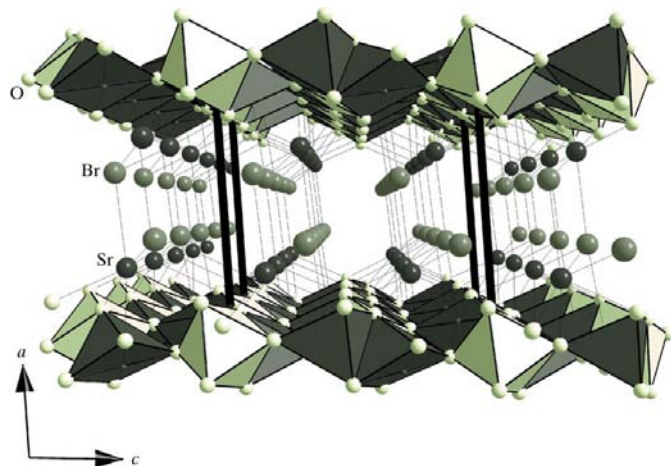

Figure 1
An overview of the structure of $Sr_2Cu_2TeO_6Br_2$. Key: CuO_5 square pyramids are grey and TeO_6 octahedra are white.

Atom Te1, which lies on an inversion centre, has an octahedral TeO_6 coordination, with Te—O bond distances in the range 1.915 (9)–1.943 (9) Å. Atom Cu1 is coordinated by five O atoms to form a CuO_5 square pyramid, with Cu—O bond distances in the range 1.933 (9)–2.022 (10) Å in the square plane and a distance of 2.355 (10) Å to the pyramid apex. A more distant Br atom, sitting in the opposite apical position, completes an elongated CuO_5Br octahedron with a Cu—Br distance of 2.974 (2) Å. However, bond-valence-sum (BVS) calculations (Brown & Altermatt, 1985; Brese & O'Keeffe, 1991) suggest that the primary coordination sphere around Cu is less than 2.93 Å, so this distant Br atom is just at the border and is not considered as bonded.

The Cu–Te–O layers extend in the *bc* plane and are arranged such that each TeO_6 octahedron has common edges with four and common corners with two CuO_5 polyhedra. Furthermore, each CuO_5 square pyramid has a common edge with one and common corners with two more such pyramids (Fig. 2*a*). The Cu atoms form a distorted pseudo-hexagonal puckered honeycomb network, with Cu—Cu distances of 3.067 (3) and 3.615 (2) Å (Fig. 2*b*).
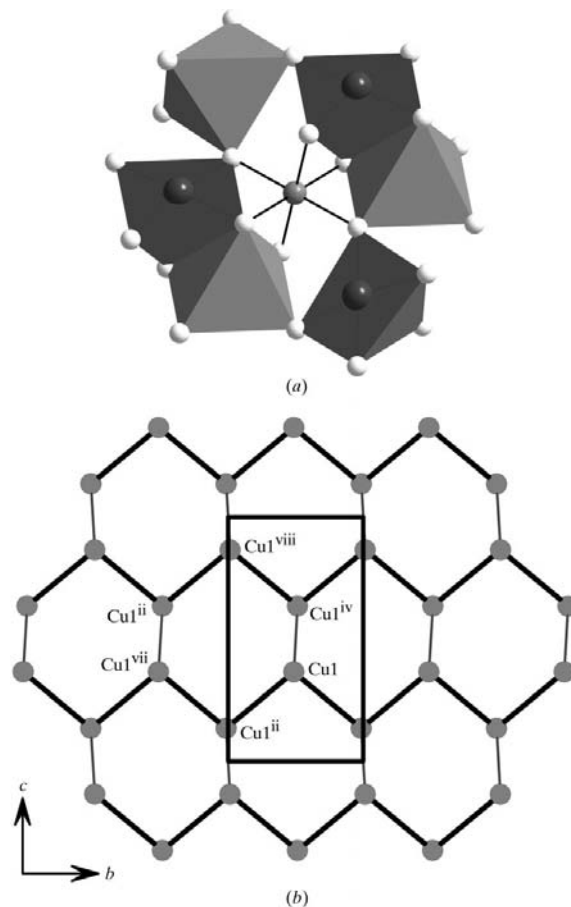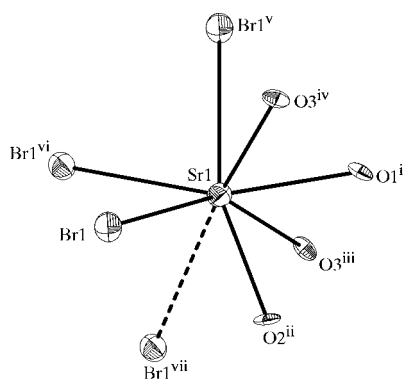

Figure 2
(*a*) The local coordination around a TeO_6 octahedron in a Cu–Te–O layer. Key: CuO_5 square pyramids are grey, and the Cu, Te and O atoms are dark grey, light grey and white, respectively. (*b*) The pseudo-hexagonal Cu honeycomb network in the Cu–Te–O layers. Two different Cu—Cu distances are present, *viz.* 3.615 (2) (thicker lines) and 3.067 (3) Å (thinner lines). The symmetry codes are as in Table 1.

Figure 3
The irregular SrO_4Br_3 polyhedron. There is also a long Sr—Br distance, marked with a dashed line. The symmetry codes are as in Table 1.

Atom Sr1 is coordinated by four O and three Br atoms to form an irregular SrO_4Br_3 polyhedron that, according to the best of our knowledge and a search of the Inorganic Crystal Structure Database (ICSD, 2005), actually constitutes a new coordination polyhedron for Sr^{II} (Fig. 3). The Sr—O distances are in the range 2.471 (9)–2.793 (10) Å and the Sr—Br distances are in the range 3.064 (2)–3.175 (2) Å. A fourth Br atom perches at a distance of 3.655 (2) Å, but does not contribute significantly to the BVS and is therefore not considered as bonded. It is common that BVSs give very low values for halide ions in oxohalides (0.3–0.4), thus indicating that such ions frequently have an unsaturated bond valence and take on the role of counter-ion rather than being integrated into the covalent/ionic network; an example is $Te_6O_{11}Cl_2$ (Giester, 1994). However, for the title compound, BVS calculations indicate that the bromide ions are well integrated into the covalent/ionic network, as they have a value of $\sim$0.9, which is near the expected value of 1 (see Table 2).

Each SrO_4Br_3 polyhedron is linked to four others by corner-sharing (two *via* Br and two *via* O) and to two others *via* Br–Br edge-sharing to form double layers that connect the Cu–Te–O layers (Fig. 1).

Experimental

Single crystals of $Sr_2Cu_2TeO_6Br_2$ were synthesized by chemical transport reactions in sealed evacuated silica tubes. SrO (ABCR, 99.95%), $CuBr_2$ (Avocado Research Chemicals, +98%), CuO (Avocado Research Chemicals, +99%) and TeO_2 (ABCR, +99%) were used as starting materials and mixed in the molar ratio 1:1:3:1 in a mortar; the mixture was placed in a silica tube (length $\sim$5 cm), which was subsequently evacuated. The tube was heated for 72 h at 900 K in a muffle furnace. The product appeared as green single crystals, and as black and light-yellow powders. Chemical analysis for elements heavier than oxygen using a scanning electron microscope (JEOL820) equipped with an energy dispersive spectrometer (LINK AN10000) indicated that the black powder is unreacted CuO and that the light-yellow powder has a composition of 0.8 at% Sr, 75.3 at% Cu, 22.1 at% Te and 1.9 at% Br. The light-yellow colour indicates that this unknown phase contains Cu^{I} and not Cu^{II}. There must be a redox reaction taking place during the reactions so that Te^{IV} is transformed to Te^{VI} to form the title compound and Cu^{II} is transformed to Cu^{I} to form the light-yellow powder. The synthesis products were non-hygroscopic.

Crystal data

$Sr_2Cu_2TeO_6Br_2$	$Z = 2$
$M_r = 685.74$	$D_x = 4.990$ Mg m^{-3}
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation
$a = 9.422$ (3) Å	$\mu = 28.10$ mm^{-1}
$b = 5.1788$ (17) Å	$T = 291$ (2) K
$c = 9.388$ (3) Å	Plate, green
$\beta = 94.92$ (3)°	$0.07 \times 0.06 \times 0.02$ mm
$V = 456.4$ (3) Å^3	

Data collection

Stoe IPDS diffractometer	4112 measured reflections
φ scans	1099 independent reflections
Absorption correction: numerical	629 reflections with $I > 2\sigma(I)$
[*X-RED* (Stoe & Cie, 2001) and	$R_{int} = 0.113$
X-SHAPE (Stoe & Cie, 1999)]	$\theta_{max} = 28.0°$
$T_{min} = 0.045$, $T_{max} = 0.135$	

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0659P)^2]$
$R[F^2 > 2\sigma(F^2)] = 0.050$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.126$	$(\Delta/\sigma)_{max} < 0.001$
$S = 0.88$	$\Delta\rho_{max} = 3.79$ e Å^{-3}
1099 reflections	$\Delta\rho_{min} = -1.45$ e Å^{-3}
61 parameters	

Table 1
Selected geometric parameters (Å, °).

Te1—O2	1.915 (9)	Sr1—Br1^{vi}	3.175 (2)
Te1—O3	1.922 (9)	Sr1—Br1^{vii}	3.655 (2)
Te1—O1^i	1.943 (9)	Cu1—O1	1.933 (9)
Sr1—O2^{ii}	2.471 (9)	Cu1—O2	1.962 (9)
Sr1—O1^i	2.586 (10)	Cu1—O3^{viii}	1.988 (10)
Sr1—O3^{iii}	2.651 (10)	Cu1—O1^i	2.022 (10)
Sr1—O3^{iv}	2.793 (10)	Cu1—O2^{ii}	2.355 (10)
Sr1—Br1	3.064 (2)	Cu1—Cu1^{ii}	3.067 (3)
Sr1—Br1^v	3.146 (2)	Cu1—Cu1^{iv}	3.615 (2)
Cu1—O1—Cu1^{iv}	132.1 (5)	Cu1—O2—Cu1^{ii}	90.0 (4)

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

Table 2
Bond-valence-sum (BVS) values for the different atoms in (I).

Atom	BVS	Atom	BVS
Te1	5.85	O1	2.11
Sr1	1.97	O2	2.02
Br1	0.90	O3	1.82
Cu1	1.96		

The maximum residual electron density is at the fractional coordinates (0.7971, 0.0106, 0.7975) and the minimum is at (0.3424, 0.0672, 0.3253); the peak and hole are 0.88 and 1.68 Å, respectively, from atom Sr1.

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

inorganic compounds

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FA3009). Services for accessing these data are described at the back of the journal.

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