A synthetic zinc tellurium oxochloride, $Zn_2(TeO_3)Cl_2$

Mats Johnsson[a]* and Karl W. Törnroos[b]

[a]Department of Inorganic Chemistry, Sockholm University, SE-106 91 Stockholm, Sweden, and [b]Department of Chemistry, University of Bergen, Allégaten 41, 5007 Bergen, Norway

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

Single crystals of dizinc tellurium dichloride trioxide, $Zn_2(TeO_3)Cl_2$, were synthesized *via* a transport reaction in sealed evacuated glass tubes. The compound has a layered structure in which the building units are $[ZnO_4Cl]$ square pyramids, distorted $[ZnO_2Cl_2]$ tetrahedra and $[TeO_3E]$ tetrahedra (E is the $5s^2$ lone pair of the Te^{IV} atom), joined through shared edges and corners to form charge-neutral layers. Cl atoms and Te-atom lone pairs protrude from the surfaces of each layer towards adjacent layers, and the layers are held together by dispersion forces only. The compound is isostructural with the synthetic compound $CuZn(TeO_3)Cl_2$ and the mineral sophiite, $Zn_2(SeO_3)Cl_2$.

Comment

The synthesis and crystal structure determination of the new compound $Zn_2(TeO_3)Cl_2$, (I), is a further result of an ongoing study investigating the chemistry of tellurium oxohalogenides. The Te atom in (I) has a typical one-sided threefold coordination because of the presence of its $5s^2$ lone pair (designated E), and the coordination polyhedron of the Te atom is therefore a $[TeO_3E]$ tetrahedron.

Atom Zn1 is coordinated by two O atoms and two Cl atoms, thus forming a distorted $[ZnO_2Cl_2]$ tetrahedron, and atom Zn2 is coordinated by four O atoms and one Cl atom, which complete a distorted $[ZnO_4Cl]$ square pyramid (Table 1). A distorted $[ZnO_4Cl_2]$ octahedron is also formed if atom Cl1 is taken into account. However, the Zn2—Cl1 distance is long [3.2904 (5) Å], and atom Zn2 is located on the Cl2-atom side of the O-atom plane. Furthermore, bond-valence sum calculations (Brown & Altermatt, 1985) indicate a negligible contribution from atom Cl1, suggesting that it should not be considered to be bonded to atom Zn2.

The three different building units, *viz.* the $[Zn1O_2Cl_2]$, $[Zn2O_4Cl]$ and $[TeO_3E]$ groups, are connected so that infinite layers extending in the *ac* plane are formed (Fig. 1). Each $[ZnO_4Cl]$ polyhedron is linked to two others by corner
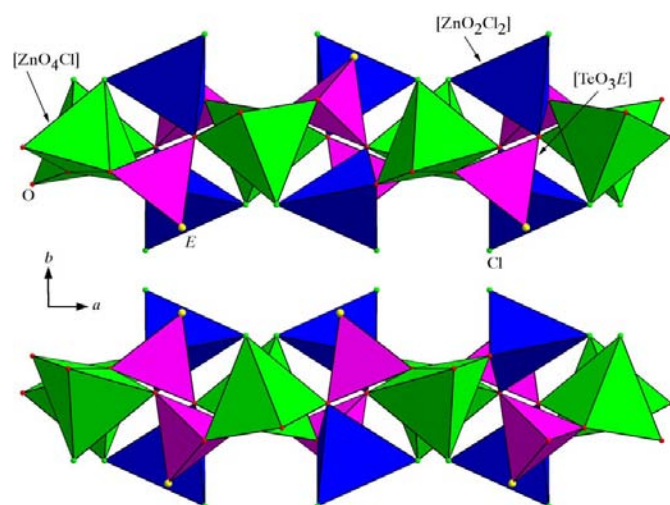

Figure 1
The layer features in (I) along [001].

sharing, so that infinite chains of $[ZnO_4Cl]$ polyhedra develop along the [001] direction in the layers. The chains are separated by $[ZnO_2Cl_2]$ and $[TeO_3E]$ groups. Each $[ZnO_4Cl]$ polyhedron shares two corners with two $[ZnO_2Cl_2]$ groups, as well as one corner and one edge with $[TeO_3E]$ groups (Fig. 2).

The stereochemically active Te-atom lone pairs are located in the space between the layers of the structure, pointing towards the space between the similarly protruding Cl atoms of the opposite layer. The shortest cation–anion distances between adjacent layers (Te···Cl1, Zn1···Cl1, Zn2···Cl1 and Zn1···Cl2) are similar to, or larger than, the cation–cation separations within the layers (Te···Zn2, Zn1···Zn2, Te···Zn1, Zn2···Zn2, Zn1···Zn1 and Te···Te; Table 2).

The long interlayer distances imply that the layers are held together only by attractive dispersion forces. Each layer can thus be considered as an infinite two-dimensional molecule.
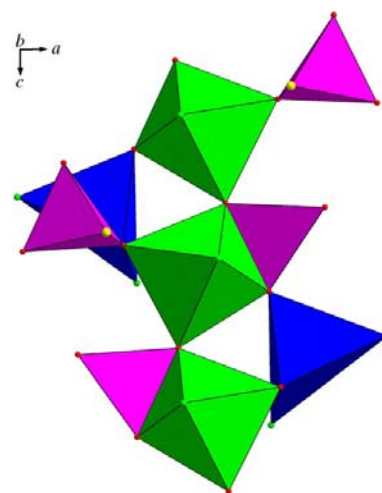

Figure 2
The arrangement of coordination polyhedra around a central $[ZnO_4Cl]$ square pyramid. The polyhedral and atom labels are as in Fig. 1.

inorganic compounds

Assuming a Te–E radius of 1.25 Å (Galy et al., 1975), the fractional coordinates for the lone pair E ($x = -0.02015$, $y = 0.33335$ and $z = 0.15126$) yield $E \cdots Cl1$ and $E \cdots Cl2$ contact distances of ~2.61 and 3.00 Å, respectively.

Compound (I) is isostructural with $CuZn(TeO_3)Cl_2$ (Johnsson & Törnroos, 2003). The mineral sophiite, $Zn_2(SeO_3)Cl_2$ (Semenova et al., 1992), can also be considered as isostructural with (I), although, in contrast to (I), the coordination around atom Zn2 in the mineral creates a distorted $[ZnO_4Cl_2]$ octahedron (Zn2—Cl1 = 2.68 Å and Zn2—Cl2 = 2.75 Å), with Zn2 located in the equatorial O-atom plane. In sophiite, the coordination of both atom Cl1 and atom Cl2 to atom Zn2 is supported by bond-valence sum calculations.

Experimental

Compound (I) was synthesized by chemical transport reactions in sealed evacuated soda-glass tubes. ZnO (ABCR, +99%), $ZnCl_2$ (Avocado Research Chemicals Ltd, +98%) and TeO_2 (ABCR, +99%) were used as starting materials. Equimolar amounts of $ZnCl_2$, ZnO and TeO_2 were mixed in a mortar and placed in a glass tube (length ~6 cm), which was then evacuated and heated for 140 h at 770 K in a muffle furnace. The product appeared as colourless transparent plate-like single crystals and powder. The crystals are hygroscopic. The synthesis product was characterized in a scanning electron microscope (Jeol 820) with an energy-dispersive spectrometer (LINK AN10000) on ten different single crystals. Analysis found Zn 41.2 (1.3), Te 20.4 (0.6), and Cl 38.3 (1.2)%. No Si originating from the glass tubes was detected.

Crystal data

$Zn_2(TeO_3)Cl_2$	Mo $K\alpha$ radiation
$M_r = 377.24$	Cell parameters from 5733
Orthorhombic, $Pccn$	reflections
$a = 10.4467\ (9)$ Å	$\theta = 2.4$–$32.5°$
$b = 15.4969\ (13)$ Å	$\mu = 13.14$ mm^{-1}
$c = 7.6471\ (6)$ Å	$T = 123\ (2)$ K
$V = 1238.00\ (18)$ Å^3	Plate, colourless
$Z = 8$	$0.33 \times 0.31 \times 0.03$ mm
$D_x = 4.048$ Mg m^{-3}	

Table 1
Selected geometric parameters (Å, °).

Te—O1	1.8738 (11)	Zn1—Cl2	2.2919 (5)
Te—O2	1.8708 (12)	Zn2—O1	2.0680 (13)
Te—O3	1.8962 (13)	Zn2—O2	2.1488 (12)
Zn1—O1^i	1.9430 (12)	Zn2—O2^{ii}	1.9965 (12)
Zn1—O3	2.0021 (12)	Zn2—O3^{iii}	2.0223 (12)
Zn1—Cl1	2.2235 (5)	Zn2—Cl2	2.3941 (5)
O2—Te—O1	85.08 (5)	O2^{ii}—Zn2—O1	89.19 (5)
O2—Te—O3	96.59 (5)	O3^{iii}—Zn2—O1	159.71 (5)
O1—Te—O3	95.15 (5)	O2^{ii}—Zn2—O2	152.57 (7)
O1^i—Zn1—O3	101.51 (5)	O3^{iii}—Zn2—O2	92.76 (5)
O1^i—Zn1—Cl1	121.85 (4)	O1—Zn2—O2	73.77 (5)
O3—Zn1—Cl1	95.55 (4)	O1—Zn2—Cl2	99.61 (4)
O1^i—Zn1—Cl2	101.15 (4)	O2^{ii}—Zn2—Cl2	102.52 (4)
O3—Zn1—Cl2	117.92 (4)	O2—Zn2—Cl2	101.45 (4)
Cl1—Zn1—Cl2	118.575 (19)	O3^{iii}—Zn2—Cl2	97.88 (4)
O2^{ii}—Zn2—O3^{iii}	96.98 (5)		

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

Table 2
Inter- and intralayer distances (Å).

Te$\cdots$Cl1^{iv}	3.1841 (5)	Zn1$\cdots$Zn2^{vii}	3.2992 (3)
Zn1$\cdots$Cl1^v	3.7923 (5)	Te$\cdots$Zn1	3.4166 (4)
Zn2$\cdots$Cl1^{iv}	4.4850 (6)	Zn2$\cdots$Zn2^{viii}	3.8329 (3)
Zn1$\cdots$Cl2^{vi}	5.2262 (6)	Zn1$\cdots$Zn1^i	4.2162 (5)
Te$\cdots$Zn2	3.0613 (3)	Te$\cdots$Te^{ix}	4.4186 (3)

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

Data collection

Bruker SMART 2K CCD diffractometer	2119 reflections with $I > 2\sigma(I)$
ω scans	$R_{int} = 0.036$
Absorption correction: numerical [SHELXTL/PC (Sheldrick, 2001a) and PLATON (Spek, 2003)]	$\theta_{max} = 32.6°$
	$h = -15 \rightarrow 15$
	$k = -23 \rightarrow 23$
	$l = -11 \rightarrow 11$
	440 standard reflections
$T_{min} = 0.035$, $T_{max} = 0.709$	remeasured after 28 h
20 130 measured reflections	intensity decay: none
2248 independent reflections	

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0156P)^2]$
$R[F^2 > 2\sigma(F^2)] = 0.016$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.039$	$(\Delta/\sigma)_{max} = 0.002$
$S = 1.26$	$\Delta\rho_{max} = 0.78$ e Å^{-3}
2248 reflections	$\Delta\rho_{min} = -0.85$ e Å^{-3}
73 parameters	

The maximum residual peak is located 0.76 Å from the Te atom and the largest hole is 0.73 Å from the same atom.

Data collection: SMART (Bruker, 1999); cell refinement: SAINT (Bruker, 2001); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 1990); program(s) used to refine structure: SHELXL97 (Sheldrick, 2001b); molecular graphics: DIAMOND (Brandenburg, 2000); software used to prepare material for publication: SHELXTL/PC (Sheldrick, 2001a) and PLATON (Spek, 2003).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BC1017). Services for accessing these data are described at the back of the journal.

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