

Acta Crystallographica Section E

Structure Reports

Online

ISSN 1600-5368

Zn₂(TeO₃)Br₂

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Received 5 April 2008; accepted 20 April 2008

Key indicators: single-crystal X-ray study; $T = 293$ K; mean $\sigma(\text{Zn}-\text{O}) = 0.003$ Å; R factor = 0.022; wR factor = 0.055; data-to-parameter ratio = 17.4.

Single crystals of dizinc tellurium dibromide trioxide, Zn₂(TeO₃)Br₂, were synthesized *via* a transport reaction in sealed evacuated silica tubes. The compound has a layered crystal structure in which the building units are [ZnO₄Br] distorted square pyramids, [ZnO₂Br₂] distorted tetrahedra, and [TeO₃E] tetrahedra (E being the 5s² lone pair of Te⁴⁺) joined through sharing of edges and corners to form layers of no net charge. Bromine atoms and tellurium lone pairs protrude from the surfaces of each layer towards adjacent layers. This new compound Zn₂(TeO₃)Br₂ is isostructural with the synthetic compounds Zn₂(TeO₃)Cl₂, CuZn(TeO₃)₂, Co₂(TeO₃)Br₂ and the mineral sphiite, Zn₂(SeO₃)Cl₂.

Related literature

For related literature, see: Becker *et al.* (2006); Johnsson & Törnroos (2003*a,b*, 2007); Semenova *et al.* (1992); Brown & Altermatt (1985); Galy *et al.* (1975).

Experimental

Crystal data

Zn₂(TeO₃)Br₂ $M_r = 466.18$ Orthorhombic, $Pccn$ $a = 10.5446$ (2) Å $b = 16.0928$ (2) Å $c = 7.7242$ (1) Å $V = 1310.74$ (3) Å³ $Z = 8$ Mo $K\alpha$ radiation
 $\mu = 23.79$ mm⁻¹ $T = 293$ (2) K
 $0.20 \times 0.16 \times 0.04$ mm

Data collection

Oxford Diffraction Xcalibur3
diffractometer
Absorption correction: analytical
(*CrysAlis RED*; Oxford
Diffraction, 2007);
 $T_{\min} = 0.05$, $T_{\max} = 0.35$ 15561 measured reflections
1290 independent reflections
1201 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.026$

Refinement

 $R[F^2 > 2\sigma(F^2)] = 0.022$
 $wR(F^2) = 0.055$
 $S = 1.09$
1290 reflections74 parameters
 $\Delta\rho_{\max} = 1.08$ e Å⁻³
 $\Delta\rho_{\min} = -0.82$ e Å⁻³

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, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Bergerhoff, 1996); software used to prepare material for publication: *enCIFer* (Allen *et al.*, 2004).

This work has been carried out with financial support from the Swedish Research Council.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: PK2093).

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supplementary materials

Acta Cryst. (2008). E64, i26 [doi:10.1107/S1600536808011252]

Zn₂(TeO₃)Br₂

D. Zhang and M. Johansson

Comment

The synthesis and crystal structure of the new compound Zn₂(TeO₃)Br₂ is a further result of an ongoing study investigating the rich chemistry of tellurium oxohalides. The tellurium atom has a typical one-sided threefold coordination due to the presence of its lone pair $5s^2$ (designated E) and the coordination polyhedron is that of a tetrahedron [TeO₃E].

Zn1 is coordinated by two oxygen atoms and two bromine atoms completing a distorted tetrahedron [Zn1O₂Br₂]. Zn2 is coordinated by four oxygen atoms and one bromine atom to complete a distorted square pyramid [Zn2O₄Br]. A distorted octahedron [Zn2O₄Br₂] is formed if Br1 is also taken into account. However, the distance Zn2–Br1 is long [3.3915 (8) Å] and Zn2 is located on the Br2 side of the oxygen plane. Bond valence sum calculations according to Brown & Altermatt (1985) gives a negligible contribution from Br1 suggesting that it should not be considered bonded to Zn2. The three different building units [Zn1O₂Br₂], [Zn2O₄Br] and [TeO₃E] are connected so that infinite layers are formed, see Figure 1.

Each [Zn2O₄Br] polyhedron is linked to two other [Zn2O₄Br] polyhedra by corner sharing so that infinite chains are formed along [001] throughout the layers. Those chains are separated by [Zn1O₂Br₂] and [TeO₃E] groups. Each [Zn2O₄Br] polyhedron further shares three corners with different [Zn1O₂Br₂] groups. The [Zn2O₄Br₂] polyhedra also share two corners and one edge with different [TeO₃E] groups, see Figure 2. The stereochemically active Te lone-pairs are located in the space in between the layers of the structure, pointing towards the space between the likewise protruding Br atoms of the opposite layer. The shortest cation-anion distances between adjacent layers, Zn1–Br1 3.8914 (8) Å, Zn1–Br2 5.3726 (8) Å, Zn2–Br1 4.6898 (8) Å and Te–Br1 3.3904 (6) Å, are similar to or larger than the cation-cation separation within the layers; Zn1[⋯]Zn1 4.2315 (11) Å, Zn1[⋯]Zn2 3.3127 (8) Å, Zn2[⋯]Zn2 3.8755 (1) Å, Te[⋯]Te 4.4788 (6) Å, Te[⋯]Zn1 3.4097 (6) Å and Te[⋯]Zn2 3.0815 (6) Å. This fact indicates the absence of strong contacts between the charge neutral layers and suggests that they are connected only *via* van der Waals interactions, see Figure 1. Each layer can thus be considered as an infinite two-dimensional molecule.

Assuming a Te–E radius of 1.25 Å, which is the average found for Te⁴⁺–E by Galy *et al.* (1975), the fractional coordinates for the lone-pair E are; $x = -0.0237$, $y = 0.6565$, $z = 0.1545$. This gives contacts E[⋯]Br1 and E[⋯]Br2 of ~2.96 and ~2.81 Å, respectively.

The present compound is isostructural with Zn₂(TeO₃)Cl₂ (Johansson & Törnroos, 2003a), CuZn(TeO₃)Cl₂ (Johansson & Törnroos, 2003b) and Co₂(TeO₃)Br₂ (Becker *et al.*, 2006). The mineral Sopihte Zn₂(SeO₃)Cl₂ (Semenova *et al.*, 1992) is also to be considered as isostructural with Zn₂(TeO₃)Br₂, although there is a difference in that the coordination around Zn2 in the mineral can be considered to form a distorted octahedron [Zn2O₄Cl₂] with Zn2 located in the oxygen square plane, rather than a square pyramid [Zn2O₄Br] as in Zn₂(TeO₃)Br₂. Related compounds are Co₂(TeO₃)Cl₂ (Becker *et al.*, 2006) that crystallizes in the monoclinic space group $P2_1/m$ and Zn₂(SeO₃)Cl₂ (Johansson & Törnroos, 2007) a synthetic monoclinic ($P2_1/c$) polymorph of the mineral sopihte.

Experimental

The synthesis of $\text{Zn}_2(\text{TeO}_3)\text{Br}_2$ was made by chemical transport reactions in sealed evacuated silica tubes. The compound appeared when searching for new compounds in the system $\text{Zn}^{2+}\text{—O—Br}$. The starting materials were ZnO (ABCR, +99%), ZnBr_2 (ABCR, +99%), and TeO_2 (ABCR, +99%). The preparation of crystals was made from a non stoichiometric mixture of $\text{ZnO} : \text{ZnBr}_2 : \text{TeO}_2 = 1:5:4$, which after mixing in a mortar was put into a silica tube (length ~ 6 cm) which was then evacuated. The tube was heated for 120 h at 830 K in a muffle furnace. The product appeared as colourless transparent plate-like single crystals and powder. The crystals were found to be hygroscopic. The synthesis product was characterized in a scanning electron microscope (SEM, Jeol 7000 F) equipped with an energy-dispersive spectrometer on 4 different single crystals giving a composition of 35.7 ± 2.0 at % Zn, 19.4 ± 0.9 at % Te, 44.1 ± 0.8 at % Br. No significant amount of Si originating from the silica tubes was detected; 0.80 ± 0.5 at% Si.

Refinement

The maximum residual peak (1.08) is located at 0.82 \AA from Te and the largest hole (-0.82) at 0.92 \AA from Te.

Figures

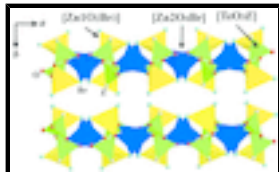


Fig. 1. The layer features in $\text{Zn}_2(\text{TeO}_3)\text{Br}_2$ along $[001]$.

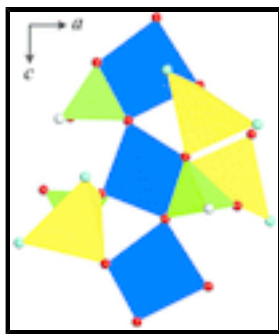


Fig. 2. Arrangement of coordination polyhedra around a central $[\text{Zn}_2\text{O}_4\text{Br}]$ square pyramid. The polyhedra and atom labels are as in Figure 1.

dizinc tellurium dibromide trioxide

Crystal data

$\text{Zn}_2(\text{TeO}_3)\text{Br}_2$

$M_r = 466.18$

Orthorhombic, $Pccn$

Hall symbol: $-P\ 2ab\ 2ac$

$a = 10.5446$ (2) \AA

$b = 16.0928$ (2) \AA

$c = 7.7242$ (1) \AA

$F(000) = 1648$

$D_x = 4.725$ Mg m^{-3}

Mo $K\alpha$ radiation, $\lambda = 0.71073$ \AA

Cell parameters from 13770 reflections

$\theta = 3.7\text{--}33.2^\circ$

$\mu = 23.79$ mm^{-1}

$T = 293$ K

$V = 1310.74 (3) \text{ \AA}^3$
 $Z = 8$

Block, colourless
 $0.21 \times 0.16 \times 0.04 \text{ mm}$

Data collection

Oxford Diffraction Xcalibur3 diffractometer	1290 independent reflections
Radiation source: fine-focus sealed tube graphite	1201 reflections with $I > 2\sigma(I)$
φ and ω scans	$R_{\text{int}} = 0.026$
Absorption correction: analytical (<i>CrysAlis RED</i> ; Oxford Diffraction, 2007)	$\theta_{\text{max}} = 26.3^\circ$, $\theta_{\text{min}} = 4.1^\circ$
$T_{\text{min}} = 0.05$, $T_{\text{max}} = 0.35$	$h = -12 \rightarrow 12$
15561 measured reflections	$k = -20 \rightarrow 20$
	$l = -9 \rightarrow 9$

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.022$	$w = 1/[\sigma^2(F_o^2) + (0.0333P)^2 + 5.0559P]$
$wR(F^2) = 0.055$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.09$	$(\Delta/\sigma)_{\text{max}} = 0.001$
1290 reflections	$\Delta\rho_{\text{max}} = 1.08 \text{ e \AA}^{-3}$
74 parameters	$\Delta\rho_{\text{min}} = -0.82 \text{ e \AA}^{-3}$
0 restraints	Extinction correction: <i>SHELXL97</i> (Sheldrick, 2008), $F_c^* = kFc[1 + 0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
	Extinction coefficient: 0.00342 (15)

Special details

Experimental. a multifaceted crystal model based on expressions derived by Clark & Reid (1995)]

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R -factor wR and goodness of fit S are based on F^2 , conventional R -factors R are based on F , with F set to zero for negative F^2 . The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R -factors(gt) *etc.* and is not relevant to the choice of reflections for refinement. R -factors based on F^2 are statistically about twice as large as those based on F , and R -factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
Te	0.02983 (3)	0.592957 (18)	0.21187 (3)	0.01207 (12)
Zn1	-0.00948 (6)	0.39234 (4)	0.34333 (7)	0.01639 (15)
Zn2	0.26526 (5)	0.52410 (4)	0.39968 (7)	0.01671 (16)

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Br2	0.20748 (5)	0.37261 (3)	0.43887 (7)	0.02286 (16)
Br1	-0.08838 (7)	0.29014 (3)	0.15586 (7)	0.03163 (18)
O2	0.1882 (3)	0.5524 (2)	0.1440 (4)	0.0160 (7)
O1	-0.0568 (3)	0.4903 (2)	0.1969 (4)	0.0155 (7)
O3	0.0906 (3)	0.5786 (2)	0.4378 (4)	0.0158 (7)

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Te	0.0105 (2)	0.01301 (18)	0.01267 (17)	0.00006 (11)	-0.00162 (10)	0.00168 (10)
Zn1	0.0188 (3)	0.0174 (3)	0.0130 (3)	0.0018 (2)	0.0002 (2)	-0.0011 (2)
Zn2	0.0110 (3)	0.0260 (3)	0.0132 (3)	0.0033 (2)	-0.0005 (2)	-0.0016 (2)
Br2	0.0163 (3)	0.0204 (3)	0.0318 (3)	0.0013 (2)	-0.00128 (19)	0.00377 (19)
Br1	0.0530 (4)	0.0191 (3)	0.0227 (3)	-0.0070 (3)	-0.0101 (2)	-0.0017 (2)
O2	0.0094 (17)	0.0266 (19)	0.0120 (14)	0.0012 (14)	0.0001 (12)	-0.0007 (13)
O1	0.0125 (18)	0.0165 (16)	0.0174 (15)	-0.0034 (14)	-0.0037 (13)	0.0013 (13)
O3	0.0138 (18)	0.0230 (18)	0.0105 (15)	0.0024 (15)	-0.0023 (12)	-0.0016 (12)

Geometric parameters (\AA , $^\circ$)

Te—O2	1.867 (3)	Zn1—Br2	2.4247 (8)
Te—O3	1.873 (3)	Zn2—O2 ⁱⁱ	2.002 (3)
Te—O1	1.891 (3)	Zn2—O1 ⁱⁱⁱ	2.033 (3)
Zn1—O3 ⁱ	1.952 (3)	Zn2—O3	2.061 (3)
Zn1—O1	2.004 (3)	Zn2—O2	2.184 (3)
Zn1—Br1	2.3438 (8)	Zn2—Br2	2.5310 (8)
O2—Te—O3	85.00 (14)	O2 ⁱⁱ —Zn2—O3	89.30 (13)
O2—Te—O1	96.31 (15)	O1 ⁱⁱⁱ —Zn2—O3	157.82 (14)
O3—Te—O1	96.55 (14)	O2 ⁱⁱ —Zn2—O2	153.62 (18)
O3 ⁱ —Zn1—O1	101.01 (14)	O1 ⁱⁱⁱ —Zn2—O2	92.03 (12)
O3 ⁱ —Zn1—Br1	123.23 (11)	O3—Zn2—O2	73.00 (12)
O1—Zn1—Br1	96.62 (10)	O2 ⁱⁱ —Zn2—Br2	99.54 (10)
O3 ⁱ —Zn1—Br2	100.43 (10)	O1 ⁱⁱⁱ —Zn2—Br2	98.97 (10)
O1—Zn1—Br2	120.65 (10)	O3—Zn2—Br2	100.22 (10)
Br1—Zn1—Br2	115.54 (3)	O2—Zn2—Br2	102.69 (10)
O2 ⁱⁱ —Zn2—O1 ⁱⁱⁱ	98.37 (13)		

Symmetry codes: (i) $-x, -y+1, -z+1$; (ii) $-x+1/2, y, z+1/2$; (iii) $x+1/2, -y+1, -z+1/2$.

Fig. 1

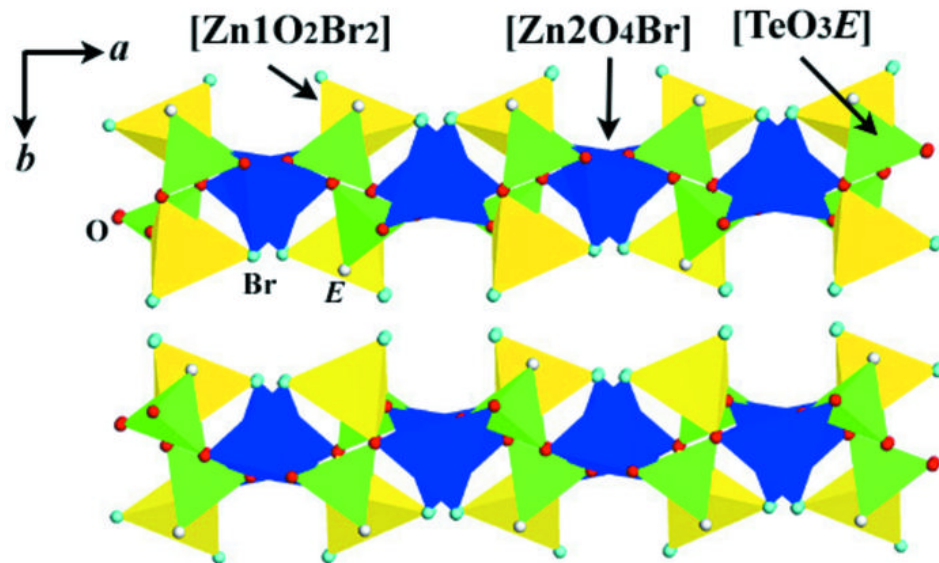


Fig. 2

