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$Zn_2(TeO_3)Br_2$

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Key indicators: single-crystal X-ray study; T = 293 K; mean σ(Zn–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, $Zn_2(TeO_3)Br_2$, were synthesized *via* a transport reaction in sealed evacuated silica tubes. The compound has a layered crystal structure in which the building units are [ZnO_4Br] distorted square pyramids, [ZnO_2Br_2] distorted tetrahedra, and [TeO_3E] tetrahedra (E being the $5s^2$ lone pair of Te^{4+}) 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 $Zn_2(TeO_3)Br_2$ is isostructural with the synthetic compounds $Zn_2(TeO_3)Cl_2$, $CuZn(TeO_3)_2$, $Co_2(TeO_3)Br_2$ and the mineral sophiite, $Zn_2(SeO_3)Cl_2$.

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

$Zn_2(TeO_3)Br_2$
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) Å^3
Z = 8
Mo $K\alpha$ radiation
μ = 23.79 mm^{-1}
T = 293 (2) K
0.20 × 0.16 × 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 $I > 2\sigma(I)$
$R_{\rm int}$ = 0.026

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.022
$wR(F^2)$ = 0.055
S = 1.09
1290 reflections
74 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).

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

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$Zn_2(TeO_3)Br_2$

Dong Zhang and Mats Johnsson

S1. Comment

The synthesis and crystal structure of the new compound $Zn_2(TeO_3)Br_2$ 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 5 s^2 (designated E) and the coordination polyhedron is that of a tetrahedron [TeO_3E].

Zn1 is coordinated by two oxygen atoms and two bromine atoms completing a distorted tetrahedron [$Zn1O_2Br_2$]. Zn2 is coordinated by four oxygen atoms and one bromine atom to complete a distorted square pyramid [$Zn2O_4Br$]. A distorted octahedron [$Zn2O_4Br_2$] 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 [$Zn1O_2Br_2$], [$Zn2O_4Br$] and [TeO_3E] are connected so that infinite layers are formed, see Figure 1.

Each [$Zn2O_4Br$] polyhedron is linked to two other [$Zn2O_4Br$] polyhedra by corner sharing so that infinite chains are formed along [001] throughout the layers. Those chains are separated by [$Zn1O_2Br_2$] and [TeO_3E] groups. Each [$Zn2O_4Br$] polyhedron further shares three corners with different [$Zn1O_2Br_2$] groups. The [$Zn2O_4Br_2$] polyhedra also share two corners and one edge with different [TeO_3E] 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 Te^{4+}–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 isostrucural with $Zn_2(TeO_3)Cl_2$ (Johnsson & Törnroos. 2003*a*), $CuZn(TeO_3)Cl_2$ (Johnsson & Törnroos, 2003*b*) and $Co_2(TeO_3)Br_2$ (Becker *et al.*, 2006). The mineral Sophiite $Zn_2(SeO_3)Cl_2$ (Semenova *et al.*, 1992) is also to be considered as isostructural with $Zn_2(TeO_3)Br_2$, although there is a difference in that the coordination around Zn2 in the mineral can be considered to form a distorted octahedron [$Zn2O_4Cl_2$] with Zn2 located in the oxygen square plane, rather than a square pyramid [$Zn2O_4Br$] as in $Zn_2(TeO_3)Br_2$. Related compounds are $Co_2(TeO_3)Cl_2$ (Becker *et al.* , 2006) that crystallizes in the monoclinic space group $P2_1/m$ and $Zn_2(SeO_3)Cl_2$ (Johnsson & Törnroos, 2007) a synthetic monoclinic ($P2_1/c$) polymorph of the mineral sophiite.

S2. Experimental

The synthesis of $Zn_2(TeO_3)Br_2$ was made by chemical transport reactions in sealed evacuated silica tubes. The compound appeared when searching for new compounds in the system Zn^{2+}—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 ZnO: $ZnBr_2$: 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.

S3. Refinement

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

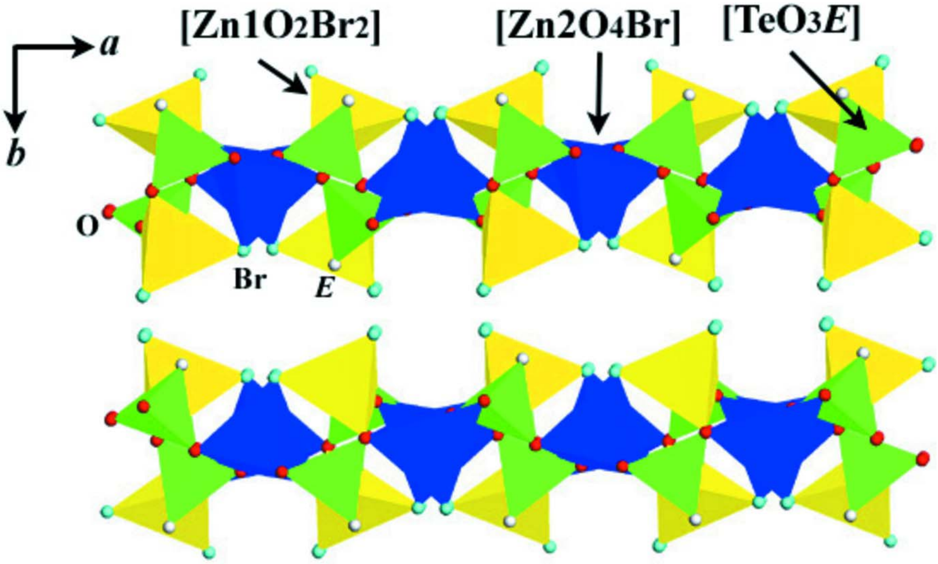

Figure 1

The layer features in $Zn_2(TeO_3)Br_2$ along [001].

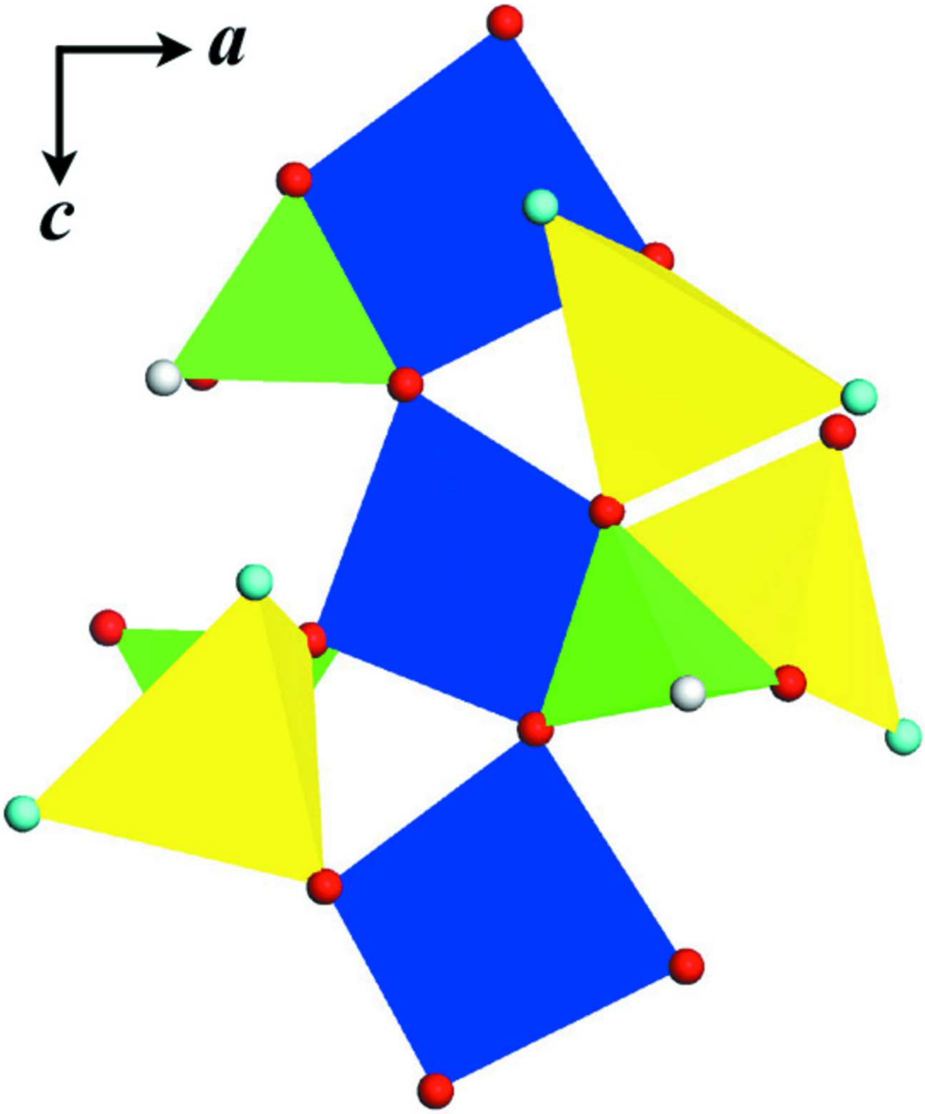

Figure 2

Arrangement of coordination polyhedra around a central [Zn2O_4Br] square pyramid. The polyhedra and atom labels are as in Figure 1.

dizinc tellurium dibromide trioxide

Crystal data

$Zn_2(TeO_3)Br_2$
$M_r = 466.18$
Orthorhombic, *Pccn*
Hall symbol: -P 2ab 2ac
$a = 10.5446$ (2) Å
$b = 16.0928$ (2) Å
$c = 7.7242$ (1) Å
$V = 1310.74$ (3) Å^3
$Z = 8$
$F(000) = 1648$
$D_x = 4.725$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 13770 reflections
$\theta = 3.7–33.2°$
$\mu = 23.79$ mm^{-1}
$T = 293$ K
Block, colourless
0.21 × 0.16 × 0.04 mm

Data collection

Oxford Diffraction Xcalibur3 diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
φ and ω scans
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 $I > 2\sigma(I)$
$R_{\text{int}} = 0.026$
$\theta_{\max} = 26.3°$, $\theta_{\min} = 4.1°$
$h = -12 \rightarrow 12$
$k = -20 \rightarrow 20$
$l = -9 \rightarrow 9$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.022$
$wR(F^2) = 0.055$
$S = 1.09$
1290 reflections
74 parameters
0 restraints
Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map
$w = 1/[\sigma^2(F_o^2) + (0.0333P)^2 + 5.0559P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 1.08$ e Å^{-3}
$\Delta\rho_{\min} = -0.82$ e Å^{-3}
Extinction correction: *SHELXL97* (Sheldrick, 2008), $Fc^* = kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
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 (Å^2)

	x	y	z	U_{iso}*/U_{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)
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 (Å^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 (Å, º)

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.