

# Proton-stabilized three-dimensional anionic framework in $\text{H}[\text{Zn}_6\text{O}_2(\text{BO}_3)_3]$

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A three-dimensional anionic framework built up from  $[\text{ZnO}_4]$  tetrahedra and planar  $[\text{BO}_3]$  groups, stabilized by H atoms, has been found for hydrogen zinc oxide borate,  $\text{H}[\text{Zn}_6\text{O}_2(\text{BO}_3)_3]$ . Boron and one of the borate O atoms are on 18e (2) positions. Triple units of  $[\text{ZnO}_4]$  tetrahedra sharing a common oxygen vertex on a 12c (3) site and strong asymmetrical linear hydrogen bonds with the H atom [on a 12c (3) position] disordered over a twofold axis are specific structural features of this zincoborate. There is evidence that the reported  $\text{Zn}_4\text{O}(\text{BO}_3)_2$  [Harrison, Gier & Stuky (1993). *Angew. Chem. Int. Ed. Engl.* **32**, 724–726] corresponds to this structure.

## Comment

Borates show a large structural diversity, from isolated anions to three-dimensional frameworks containing  $[\text{BO}_3]^{3-}$  and/or  $[\text{BO}_4]^{5-}$  units. Many of the framework structures are built in combination with mono- or bivalent metals. In the course of investigations on borate frameworks, such as  $\text{Na}_3(\text{NO}_3)(\text{B}_6\text{O}_{10})$  (Yakubovich *et al.*, 2002), we became interested in mixed anionic systems containing zinc. Interestingly, among more than 200 known borate minerals, no Zn compound is reported, but several synthetic Zn borates have been structurally characterized so far, namely  $\text{ZnB}_4\text{O}_7$  (Martinez-Ripoll

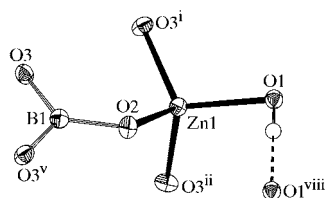


Figure 1

The main structural elements of the title compound, showing the atomic labelling scheme. Displacement ellipsoids are drawn at the 90% probability level and the H atom is shown in one of the alternative positions only and with arbitrary radius. [Symmetry codes: (i)  $y, -x + y, -z$ ; (ii)  $-x + y, -x, z$ ; (v)  $x - y + \frac{1}{3}, -y + \frac{2}{3}, -z + \frac{1}{6}$ ; (viii)  $y + \frac{1}{3}, x - \frac{1}{3}, -z + \frac{1}{6}$ ]

*et al.*, 1971),  $\text{Zn}_3(\text{BO}_3)_2$  (Baur & Tillmanns, 1970),  $\text{Zn}(\text{B}_3\text{O}_3)(\text{OH})_5 \cdot \text{H}_2\text{O}$  (Ozols *et al.*, 1971),  $\text{Zn}_2(\text{BO}_3)[(\text{OH})_{0.75}\text{F}_{0.25}]$  (Corbel *et al.*, 2001),  $\text{Zn}(\text{H}_2\text{O})(\text{B}_2\text{O}_4)(\text{H}_2\text{O})_{0.12}$  (Choudhury *et al.*, 2002),  $\text{Zn}_4\text{O}(\text{BO}_3)_2$  (Harrison *et al.*, 1993) and  $\text{Zn}_4\text{O}(\text{BO}_2)_6$  (Bondareva *et al.*, 1978; Smith-Verdier & Garcia-Blanco, 1980). The last is a borate analogue of the microporous aluminosilicate sodalite  $\text{Na}_4\text{Cl}(\text{AlSiO}_4)_3$ .  $\text{Zn}[\text{B}_3\text{O}_4(\text{OH})_3]$  is the most important commercial Zn borate today, used primarily as a polymer additive and preservative in wood composites, with a worldwide annual production exceeding 10 000 metric tons (Schubert *et al.*, 2003).

In the course of investigating the products of soft hydrothermal syntheses in the system  $\text{ZnO}-\text{B}_2\text{O}_3-\text{NaBr}-\text{H}_2\text{O}$ , we found crystals with the previously unreported composition  $\text{H}[\text{Zn}_6\text{O}_2(\text{BO}_3)_3]$ .

In the structure (Fig. 1), the  $\text{Zn}^{2+}$  ions are surrounded by O atoms in tetrahedral coordination; the B atoms form only

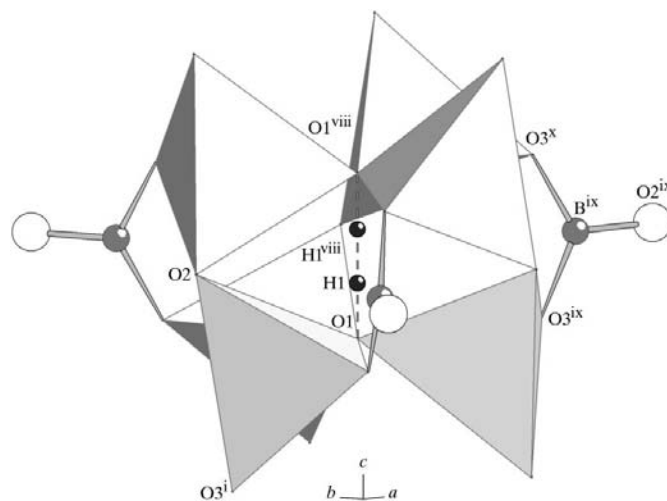


Figure 2

The cage of six  $[\text{ZnO}_4]$  tetrahedra, including the strong hydrogen bond. [Symmetry codes: (i)  $y, -x + y, -z$ ; (viii)  $y + \frac{1}{3}, x - \frac{1}{3}, -z + \frac{1}{6}$ ; (ix)  $x + 1, y, z$ ; (x)  $x - y + \frac{1}{3}, -y + \frac{2}{3}, -z + \frac{1}{6}$ ]

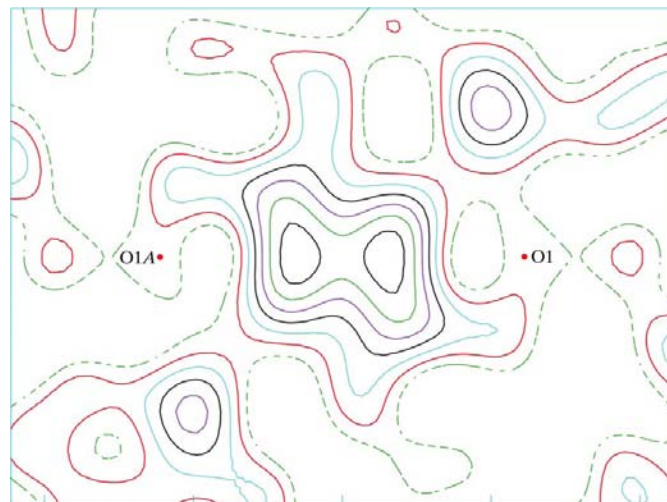
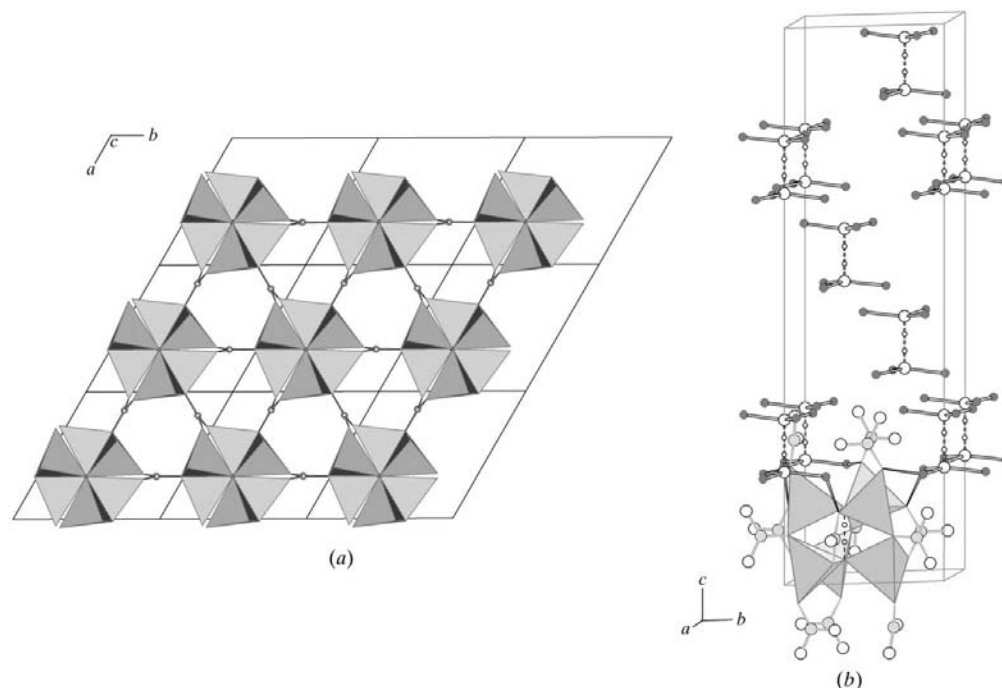


Figure 3

A difference electron-density map around the H-atom position. Isolines are at  $0.1 \text{ e } \text{\AA}^{-3}$ .



**Figure 4**

(a) The layer around  $z = \frac{1}{6}$  of  $[\text{BO}_3]$ -connected 'Zn<sub>6</sub> cages' in the [001] projection. (b) A sequence of layers along the  $c$  axis. In the higher layers, only the Zn1 and O1 atoms are drawn. Key: large grey spheres B, small grey spheres Zn, large white spheres O, small white spheres H and polyhedra  $[\text{ZnO}_4]$ .

triangular oxo complexes (Table 1). Each O atom is surrounded by three cations, *viz.* three Zn atoms for atom O1, and two Zn and one B atom for atoms O2 and O3. Thus, a three-dimensional framework is formed. The main feature is triple units of  $[\text{ZnO}_4]$  tetrahedra sharing one common O1 vertex that are connected by an equivalent unit over three corners (O2) and three  $[\text{BO}_3]$  units to form a cage, in the centre of which a disordered H atom is located (Fig. 2). This H atom was found in a difference Fourier map close to the  $6a$  position (site symmetry 32) and was refined with a free isotropic displacement parameter. It forms a strong asymmetric linear hydrogen bond between two  $\mu_3$ -bridging O1 atoms (Table 2). The O—H...O axis is on the threefold axis, and the H atom is disordered by operation of the twofold axis over both alternative positions of a double-minimum potential. An electron-density map calculated by a difference Fourier synthesis after removing the H atom from the model (Fig. 3) clearly shows a double maximum. The crystal chemical function of the H atoms seems to be the stabilization of the unusual cage unit shown in Fig. 2. Hydrogen bonds of similar strength [ $\text{O}\cdots\text{O} = 2.4853(5) \text{ \AA}$ ] have been reported for  $\gamma$ -metaboric acid (Freyhardt *et al.*, 2000) and are well known from structures of hydrogen sulfates, hydrogen phosphates and hydrogen arsenates. In a recent report (Schwendtner & Kolitsch, 2005), a similar example with split H-atom positions and an O...O distance of  $2.508(4) \text{ \AA}$  was found for  $\text{CsCr}(\text{H}_{1.5}\text{AsO}_4)_2(\text{H}_2\text{AsO}_4)$ .

The three-dimensional structure can be described as formed by layers of the aforementioned Zn<sub>6</sub> cages (Fig. 2), interconnected by  $[\text{BO}_3]$  units to form a porous net (Fig. 4a). Along

the  $c$  axis, equivalent layers are stacked according to the space-group symmetry in six orientations ('6L structure') and interconnected by sharing common vertices of  $[\text{ZnO}_4]$  tetrahedra and *via*  $[\text{BO}_3]$  units (Fig. 4b).

The title compound has similar unit-cell parameters and the same space-group type as the Zn borate  $\text{Zn}_4\text{O}(\text{BO}_3)_2$  published by Harrison *et al.* (1993). Its crystal structure was solved from powder data and corresponds roughly to our model, but the authors could achieve a charge-balanced formula for the compound only by assumption of vacancies in the position of one O atom, the occupancy of which was fixed at 0.833, giving a formula comparable to our setting  $[\text{Zn}_6\text{O}_{1.5}(\text{BO}_3)_3]$ . Probably, these authors had the same compound  $\text{H}[\text{Zn}_6\text{O}_2(\text{BO}_3)_3]$  in hand but, of course, were unable to detect the H atom by powder methods.

## Experimental

Colourless crystals of  $\text{H}[\text{Zn}_6\text{O}_2(\text{BO}_3)_3]$  with a rhombohedral shape up to 1 mm long were formed by hydrothermal synthesis in the system  $\text{ZnO}-\text{B}_2\text{O}_3-\text{NaBr}-\text{H}_2\text{O}$  (at a temperature of 553 K and a pressure of 70 bar, over a period of 20 d, with a  $\text{ZnO}/\text{B}_2\text{O}_3/\text{NaBr}/\text{H}_2\text{O}$  ratio of 2.2:1:30) in a PTFE-lined stainless steel autoclave. The presence of Zn in the samples was confirmed by qualitative X-ray spectral analysis.

### Crystal data

$\text{H}[\text{Zn}_6\text{O}_2(\text{BO}_3)_3]$   
 $M_r = 601.66$   
 Trigonal,  $R\bar{3}c$   
 $a = 8.1558(5) \text{ \AA}$   
 $c = 26.171(4) \text{ \AA}$   
 $V = 1507.6(3) \text{ \AA}^3$   
 $Z = 6$

$D_x = 3.976 \text{ Mg m}^{-3}$   
 Mo  $K\alpha$  radiation  
 $\mu = 14.14 \text{ mm}^{-1}$   
 $T = 193(2) \text{ K}$   
 Rhombohedron, colourless  
 $0.22 \times 0.15 \times 0.15 \text{ mm}$

## Data collection

Stoe IPDS-II diffractometer	3364 measured reflections
$\omega$ scans	541 independent reflections
Absorption correction: multi-scan (Blessing, 1995)	516 reflections with $I > 2\sigma(I)$
$T_{\min} = 0.047$ , $T_{\max} = 0.104$	$R_{\text{int}} = 0.026$
(expected range = 0.055–0.120)	$\theta_{\max} = 31.0^\circ$

## Refinement

Refinement on $F^2$	$w = 1/[\sigma^2(F_o^2) + (0.0276P)^2 + 4.2124P]$
$R[F^2 > 2\sigma(F^2)] = 0.019$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.047$	$(\Delta/\sigma)_{\max} < 0.001$
$S = 1.12$	$\Delta\rho_{\max} = 0.56 \text{ e } \text{\AA}^{-3}$
541 reflections	$\Delta\rho_{\min} = -0.72 \text{ e } \text{\AA}^{-3}$
35 parameters	Extinction correction: <i>SHELXL97</i>
All H-atom parameters refined	Extinction coefficient: 0.00133 (9)

Table 1

Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ ).

Zn1—O3 <sup>i</sup>	1.9383 (15)	Zn1—O2	1.9631 (13)
Zn1—O3 <sup>ii</sup>	1.9565 (16)	O2—B1	1.371 (4)
Zn1—O1	1.9616 (4)	B1—O3	1.379 (2)
O3 <sup>i</sup> —Zn1—O3 <sup>ii</sup>	106.38 (8)	B1—O2—Zn1	123.93 (5)
O3 <sup>i</sup> —Zn1—O1	113.99 (9)	Zn1 <sup>v</sup> —O2—Zn1	112.14 (11)
O3 <sup>ii</sup> —Zn1—O1	109.88 (5)	B1—O3—Zn1 <sup>vi</sup>	125.50 (15)
O3 <sup>i</sup> —Zn1—O2	111.66 (7)	B1—O3—Zn1 <sup>vii</sup>	125.21 (14)
O3 <sup>ii</sup> —Zn1—O2	108.86 (5)	Zn1—O3—Zn1 <sup>viii</sup>	108.33 (7)
O1—Zn1—O2	106.02 (9)	O2—B1—O3 <sup>v</sup>	120.23 (14)
Zn1 <sup>iii</sup> —O1—Zn1 <sup>iv</sup>	118.90 (3)	O3 <sup>ii</sup> —B1—O3 <sup>v</sup>	119.5 (3)
Zn1—O1—H1	96.05 (9)		

Symmetry codes: (i)  $y, -x + y, -z$ ; (ii)  $-x + y, -x, z$ ; (iii)  $-y + 1, x - y, z$ ; (iv)  $-x + y + 1, -x + 1, z$ ; (v)  $x - y + \frac{1}{3}, -y + \frac{2}{3}, -z + \frac{1}{6}$ ; (vi)  $x - y, x, -z$ ; (vii)  $-y, x - y, z$ .

For the disordered H atom, localized on a 12c position close to 6a, the  $z$  parameter and the isotropic displacement parameter were refined without any constraints. No significant correlations were observed for these parameters and the refinement converged well.

Data collection: *Win-XPOSE* in *X-AREA* (Stoe & Cie, 2000); cell refinement: *Win-CELL* in *X-AREA*; data reduction: *Win-INT-GRATE* in *X-AREA*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg, 2006); software used to prepare material for publication: *enCIFer* (Allen *et al.*, 2004).

Table 2

Hydrogen-bond geometry ( $\text{\AA}$ ,  $^\circ$ ).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
O1—H $\cdots$ O1 <sup>viii</sup>	0.82 (16)	1.63 (17)	2.450 (6)	180.0

Symmetry code: (viii)  $y + \frac{1}{3}, x - \frac{1}{3}, -z + \frac{1}{6}$ .

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SQ3040). Services for accessing these data are described at the back of the journal.

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