

Redetermination of $\text{CaB}_8\text{O}_{11}(\text{OH})_4$ at low temperatureSeth B. Wiggin and
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Key indicators

Single-crystal X-ray study
 $T = 120 \text{ K}$
Mean $\sigma(\text{O}-\text{B}) = 0.003 \text{ \AA}$
 R factor = 0.034
 wR factor = 0.075
Data-to-parameter ratio = 11.2For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.

The structure of $\text{CaB}_8\text{O}_{11}(\text{OH})_4$ (calcium octaborate tetrahydroxide) [Zayakina & Brovkin (1978). *Kristallografiya*, **23**, 1167–1170] has been redetermined at 120 (2) K with improved precision. The $\text{O}-\text{H}\cdots\text{O}$ hydrogen-bonding arrangement has been established, based on freely refined H-atom positions.

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Comment

During the investigation of templated borosenate frameworks, single crystals of the known (Zayakina & Brovkin, 1978) title compound, (I) (Fig. 1), were obtained from a molten salt reaction of CaCl_2 , H_3BO_3 and $\text{NH}_4(\text{H}_2\text{AsO}_4)$. This redetermination at 120 (2) K offers a significantly better structural model and the H-atom positions and hydrogen-bonding scheme have been established. There is also an isostructural strontium material, strontioborite, reported by Brovkin *et al.* (1975).

The structure of (I) can be described in terms of linked triple six-rings of stoichiometry $\text{B}_6\text{O}_{12}\text{H}$ with a pendant $\text{H}_3\text{B}_2\text{O}_5$ group, as shown in Fig. 2. The three-coordinate O8 species (Table 1) is a distinctive feature of these units. Each of these triple-six-ring units have six O atoms that do not contribute to the ring formation. One of these forms a hydroxide grouping, four link to further similar units to form a sheet in the bc plane and the last bridges to an $\text{H}_3\text{B}_2\text{O}_5$ unit that is located outside the plane. The triple six-ring unit has two of the rings in the bc plane, while the third is below this plane. The out-of-plane ring has the hydroxide group

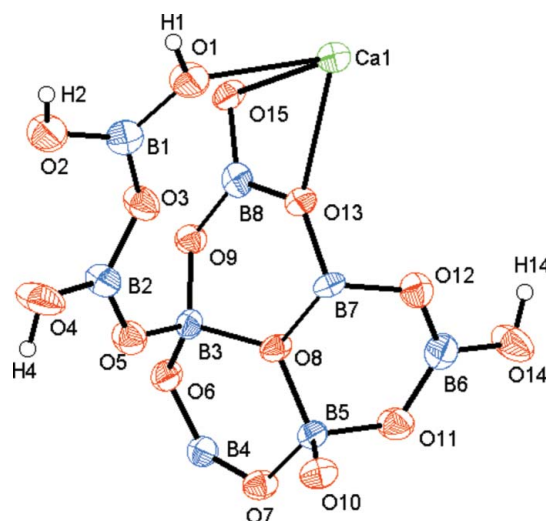


Figure 1
The asymmetric unit of (I), showing 50% probability displacement ellipsoids and arbitrary spheres for the H atoms. The mixture of trigonal (B1, B2, B4, B6 and B8) and tetrahedral (B3, B5 and B7) B atoms and the three-coordinate O8 species are evident.

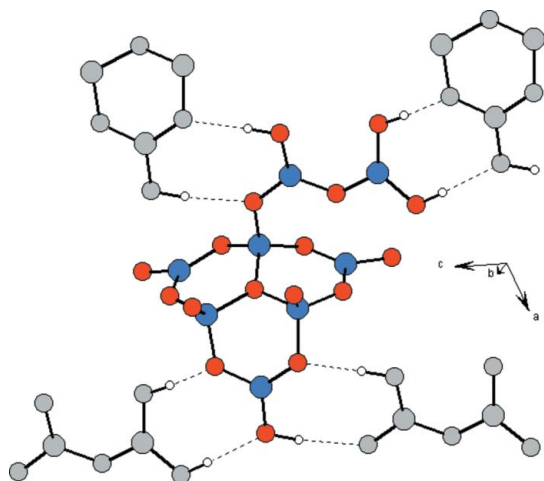


Figure 2
View of the borate unit in (I). Colour key: B blue, O red, and H white. Dotted lines signify hydrogen bonds.

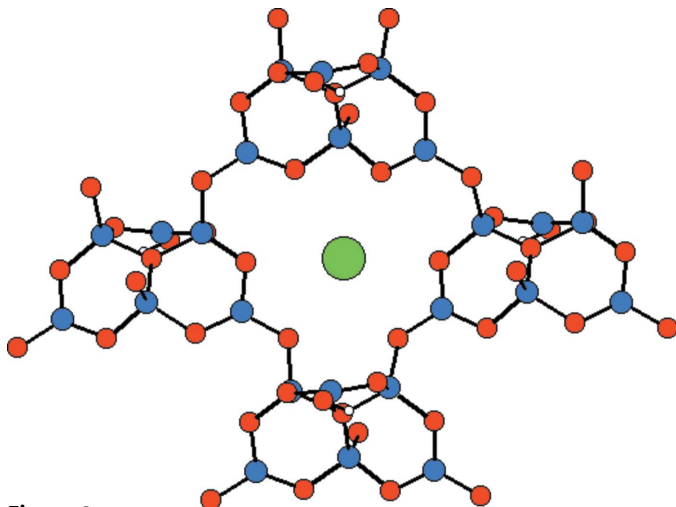


Figure 3
Detail of (I), showing the Ca^{2+} ion within its 18-atom ring. The $\text{H}_3\text{B}_2\text{O}_5$ units above and below the plane have been removed for clarity. Colour key: Ca green, other atom colours as in Fig. 2.

attached, forming, along with the pendant $\text{H}_3\text{B}_2\text{O}_5$ unit, an extensive hydrogen-bonding network between the borate sheets (Table 2). There are six distinct hydrogen bonds per unit, with $\text{O}\cdots\text{O}$ distances ranging from 2.585 (3) to 2.917 (4) Å. This network connects four adjacent $\text{B}_8\text{O}_{11}(\text{OH})_4$ units to a central unit, as shown in Fig. 2.

The calcium ion sits in the centre of an 18-atom ring formed by four of the triple six-ring units (Fig. 3). Nine O atoms coordinate to the calcium cation, with $\text{Ca}-\text{O}$ distances ranging from 2.482 (2) to 2.634 (2) Å (Table 1). Six of these $\text{Ca}-\text{O}$ bonds arise from the 18-atom ring, and two $\text{H}_3\text{B}_2\text{O}_5$ units that occur above and below the plane complete the Ca nine-coordination.

Experimental

Compound (I) was prepared using a molten salt technique. A typical reaction involved grinding H_3BO_3 (0.4637 g, 7.5 mmol),

$\text{NH}_4(\text{H}_2\text{AsO}_4)$ (1.1923 g, 7.5 mmol) and CaCl_2 (0.5549 g, 5 mmol) in a pestle and mortar before placing the powder in a 23 ml Parr Teflon-lined steel autoclave and heating to 513 K for 120 h. The product was washed with hot water to dissolve any remaining borate flux, leaving a white powder containing many colourless crystals of (I) in moderate yield (34% based on Ca). The material appears completely air- and water-stable.

Crystal data

$\text{CaB}_8\text{O}_{11}(\text{OH})_4$
 $M_r = 370.59$
Monoclinic, $P2_1$
 $a = 7.481$ (6) Å
 $b = 8.2693$ (12) Å
 $c = 9.859$ (3) Å
 $\beta = 108.76$ (6)°
 $V = 577.5$ (5) Å³
 $Z = 2$

$D_x = 2.131$ Mg m⁻³
Mo $K\alpha$ radiation
Cell parameters from 2430 reflections
 $\theta = 2.9\text{--}27.5^\circ$
 $\mu = 0.64$ mm⁻¹
 $T = 120$ (2) K
Plate, colourless
 $0.06 \times 0.06 \times 0.01$ mm

Data collection

Bruker–Nonius KappaCCD area-detector diffractometer
 φ and ω scans
Absorption correction: multi-scan (SADABS; Sheldrick, 2003)
 $T_{\min} = 0.732$, $T_{\max} = 0.994$
13192 measured reflections

2611 independent reflections
2430 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.059$
 $\theta_{\max} = 27.5^\circ$
 $h = -9 \rightarrow 9$
 $k = -10 \rightarrow 10$
 $l = -12 \rightarrow 12$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.034$
 $wR(F^2) = 0.075$
 $S = 1.05$
2611 reflections
233 parameters
All H-atom parameters refined

$w = 1/[\sigma^2(F_o^2) + (0.0314P)^2 + 0.2076P]$
where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.32$ e Å⁻³
 $\Delta\rho_{\min} = -0.40$ e Å⁻³
Absolute structure: Flack (1983),
1196 Friedel pairs
Flack parameter: 0.03 (3)

Table 1

Selected geometric parameters (Å, °).

$\text{Ca1}-\text{O1}$	2.619 (3)	$\text{Ca1}-\text{O7}^{\text{iii}}$	2.5610 (19)
$\text{Ca1}-\text{O13}$	2.5329 (18)	$\text{Ca1}-\text{O10}^{\text{iv}}$	2.621 (2)
$\text{Ca1}-\text{O15}$	2.634 (2)	$\text{Ca1}-\text{O2}^{\text{ii}}$	2.626 (3)
$\text{Ca1}-\text{O9}^{\text{i}}$	2.4806 (18)	$\text{Ca1}-\text{O6}^{\text{i}}$	2.6320 (18)
$\text{Ca1}-\text{O4}^{\text{ii}}$	2.528 (3)		
$\text{B5}-\text{O8}-\text{B7}$	116.33 (19)	$\text{B7}-\text{O8}-\text{B3}$	120.73 (18)
$\text{B5}-\text{O8}-\text{B3}$	122.88 (18)		

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

Table 2

Hydrogen-bond geometry (Å, °).

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
$\text{O14}-\text{H14}\cdots\text{O5}^{\text{ii}}$	0.98 (4)	1.93 (4)	2.900 (3)	173 (3)
$\text{O1}-\text{H1}\cdots\text{O14}^{\text{v}}$	0.86 (3)	1.95 (3)	2.817 (3)	177 (3)
$\text{O2}-\text{H2}\cdots\text{O11}^{\text{v}}$	0.87 (4)	1.72 (4)	2.585 (3)	172 (4)
$\text{O2}-\text{H2}\cdots\text{O7}^{\text{v}}$	0.87 (4)	2.50 (4)	2.917 (4)	110 (3)
$\text{O4}-\text{H4}\cdots\text{O12}^{\text{vi}}$	0.90 (4)	1.81 (4)	2.695 (3)	171 (4)
$\text{O4}-\text{H4}\cdots\text{O13}^{\text{vi}}$	0.90 (4)	2.27 (4)	2.751 (3)	113 (3)

Symmetry codes: (ii) $x + 1, y, z$; (v) $x - 1, y, z - 1$; (vi) $x - 1, y, z$.

The H atoms were found in a difference map and their positions and U_{iso} values were freely refined.

Data collection: *COLLECT* (Hooft, 1998); cell refinement: *DENZO* (Otwinowski & Minor, 1997) and *COLLECT*; data reduction: *DENZO* and *COLLECT*; method used to solve structure: coordinates taken from Zayakina & Brovkin (1978); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg, 1999); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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