

## Structure of Lithium *catena*-Poly[3,4-dihydroxopentaborate-1:5- $\mu$ -oxo]

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**Abstract.**  $\text{LiH}_2\text{B}_5\text{O}_9$ ,  $M_r = 207.0$ , monoclinic,  $P2_1/a$ ,  $a = 13.576$  (4),  $b = 9.077$  (4),  $c = 5.543$  (3) Å,  $\beta = 91.47$  (1)°,  $V = 682.8$  (4) Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 2.013$  g cm<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.7107$  Å,  $\mu = 2.06$  cm<sup>-1</sup>,  $F(000) = 408$ ,  $T = 293$  K,  $R = 0.049$  for 1689 independent observed reflections. The structure contains chains of  $[\text{B}_5\text{O}_9\text{H}_2]^-$  anions linked through shared O atoms. In each anionic unit two  $\text{B}_3\text{O}_3$  rings, each incorporating two triangular  $\text{BO}_3$  units, are connected by a shared tetrahedral  $\text{BO}_4$  unit. The Li atom has four O-atom neighbours arranged in an approximately tetrahedral configuration. The Li polyhedra connect B–O polyanions to form a two-dimensional network. Further connections are provided by hydrogen bonds.

**Introduction.** Crystals of the title compound were prepared in teflon liners by a hydrothermal method using Morey-type autoclaves at 573 K and 10 MPa. A typical starting mixture consisted of  $\text{LiBO}_2$  (2 g),  $\text{B}_2\text{O}_3$  (4 g) and the solvent (6 ml of 1.5 M  $\text{HCOOH}$ ). After 8 d crystals of 0.2 to 4 mm in size were obtained. They were colourless with vitreous lustre and pseudo-orthorhombic symmetry. Details of the synthesis and properties of the title compound will be published elsewhere.

**Experimental.** A prismatic crystal (0.1 × 0.1 × 0.2 mm) was selected and mounted on a Philips PW 1100 diffractometer equipped with graphite monochromator. Unit-cell parameters were determined from automatic centring of 20 reflections with  $8 < \theta < 12^\circ$  and refined by a least-squares method. Intensities were measured from  $\omega/2\theta$  scans

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of rate  $0.03^\circ \text{ s}^{-1}$  and of width  $0.9^\circ$  in  $\theta$ . 1712 unique reflections were measured in the range  $4 < \theta < 30^\circ$  of which 23 were considered unobserved under the condition  $I < 2.5\sigma(I)$ . Range of  $hkl$ :  $-18 \leq h \leq 19$ ,  $0 \leq k \leq 9$ ,  $0 \leq l \leq 7$ . The reflections 221,  $\bar{2}2\bar{1}$  and  $2\bar{2}1$  were measured every 2 h as orientation and intensity controls; significant intensity decay was not observed. Lorentz-polarization factors were applied, but no absorption corrections were made. The structure was solved by Patterson synthesis using *SHELXS86* computer programs (Sheldrick, 1990) and refined by full-matrix least squares using *SHELX76* (Sheldrick, 1976). Scattering factors for neutral atoms and  $f'$ ,  $f''$  were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). The positions of all H atoms were obtained from a difference synthesis and refined with an overall isotropic temperature factor. Anisotropic displacement parameters were refined for non-H atoms.  $R = 0.049$  ( $wR = 0.056$ ) for all observed reflections. The number of refined parameters was 143. The function minimized was  $\sum w(|F_o| - |F_c|)^2$  where  $w = [\sigma^2(F_o) + 0.0104F_o^2]^{-1}$ . Maximum  $\Delta/\sigma = 0.057$ . Maximum and minimum peak heights in the final difference Fourier synthesis were 0.36 and  $-0.51 \text{ e \AA}^{-3}$ , respectively. Diagrams were drawn using *ORTEP* (Johnson, 1965) and *PLUTO78* (Motherwell & Clegg, 1978). Final atomic coordinates and  $B_{\text{eq}}$  values are reported in Table 1.†

**Discussion.** The basic unit of the present structure is the  $[\text{B}_5\text{O}_9\text{H}_2]^-$  anion, in which one tetrahedral  $\text{BO}_4$  group and four triangular  $\text{BO}_3$  groups form two

† Lists of structure factors, anisotropic thermal parameters and mean-planes data have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55619 (11 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: MU0290]

Table 1. Atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å<sup>2</sup>)

$B_{iso}$  for H atoms. For Li, O and B atoms,  $B_{eq} = (8\pi^2/3) (U_{11} + U_{22} + U_{33})$  for the orthogonalized  $U_{ij}$  tensor.

	x	y	z	$B_{iso}/B_{eq}$
Li	0.3038 (2)	0.4035 (3)	0.4778 (6)	1.52 (10)
O(1)	0.0940 (1)	0.4396 (2)	0.6497 (2)	1.67 (4)
O(2)	0.1200 (1)	0.6059 (2)	0.9602 (3)	1.91 (5)
O(3)	0.1440 (1)	0.7622 (2)	1.2960 (2)	1.74 (5)
O(4)	0.2513 (1)	0.5582 (1)	0.6943 (2)	1.24 (4)
O(5)	0.2749 (1)	0.7217 (1)	1.0398 (2)	1.47 (4)
O(6)	0.4129 (1)	0.6095 (1)	0.8606 (2)	1.29 (4)
O(7)	0.3195 (1)	0.8018 (1)	0.6461 (2)	1.25 (4)
O(8)	0.5793 (1)	0.5678 (1)	0.7410 (2)	1.61 (5)
O(9)	0.4825 (1)	0.7446 (1)	0.5418 (2)	1.74 (5)
B(1)	0.3139 (1)	0.6733 (2)	0.8132 (3)	1.10 (6)
B(2)	0.1575 (1)	0.5337 (2)	0.7656 (3)	1.26 (6)
B(3)	0.1805 (1)	0.6966 (2)	1.0958 (3)	1.23 (6)
B(4)	0.4903 (1)	0.6396 (2)	0.7204 (3)	1.20 (6)
B(5)	0.3986 (1)	0.8302 (2)	0.5157 (3)	1.19 (6)
H(1)	0.0865 (27)	0.7357 (35)	1.3329 (76)	4.08 (16)
H(2)	0.5759 (23)	0.5058 (35)	0.8722 (69)	4.08 (16)

Table 2. Main interatomic distances (Å) and bond angles (°)

Triangularly coordinated B				
B(2)—O(1)	1.362 (2)	O(1)—B(2)—O(2)	115.3 (1)	
B(2)—O(2)	1.372 (2)	O(1)—B(2)—O(4)	123.4 (1)	
B(2)—O(4)	1.361 (2)	O(2)—B(2)—O(4)	121.3 (1)	
B(3)—O(2)	1.373 (2)	O(2)—B(3)—O(3)	118.9 (1)	
B(3)—O(3)	1.364 (2)	O(2)—B(3)—O(5)	122.3 (2)	
B(3)—O(5)	1.346 (2)	O(3)—B(3)—O(5)	118.8 (2)	
B(4)—O(6)	1.351 (2)	O(6)—B(4)—O(8)	123.4 (1)	
B(4)—O(8)	1.374 (2)	O(6)—B(4)—O(9)	120.5 (1)	
B(4)—O(9)	1.376 (2)	O(8)—B(4)—O(9)	116.1 (1)	
B(5)—O(7)	1.347 (2)	O(7)—B(5)—O(9)	120.7 (1)	
B(5)—O(9)	1.382 (2)	O(7)—B(5)—O(1 <sup>1</sup> )	125.3 (1)	
B(5)—O(1 <sup>1</sup> )	1.357 (2)	O(9)—B(5)—O(1 <sup>1</sup> )	114.0 (1)	
Tetrahedrally coordinated B				
B(1)—O(4)	1.489 (2)	O(4)—B(1)—O(5)	112.4 (1)	
B(1)—O(5)	1.445 (2)	O(4)—B(1)—O(6)	108.0 (1)	
B(1)—O(6)	1.481 (2)	O(4)—B(1)—O(7)	107.8 (1)	
B(1)—O(7)	1.492 (2)	O(5)—B(1)—O(6)	108.4 (1)	
		O(5)—B(1)—O(7)	108.9 (1)	
		O(6)—B(1)—O(7)	111.3 (1)	
Hydrogen bonding				
O—H...X	O—H	O...X	H...X	O—H...X
O(3)—H(1)...O(9 <sup>ii</sup> )	0.85 (4)	2.611 (2)	1.86 (3)	148 (3)
O(8)—H(2)...O(6 <sup>iv</sup> )	0.92 (4)	2.732 (2)	1.82 (3)	172 (4)
Tetrahedrally coordinated Li				
Li	O(3 <sup>iv</sup> )	O(4)	O(7 <sup>v</sup> )	O(8 <sup>vi</sup> )
O(3 <sup>iv</sup> )	1.917 (2)	102.1 (1)	101.8 (2)	101.2 (1)
O(4)	3.039 (3)	1.991 (3)	103.0 (1)	124.4 (2)
O(7 <sup>v</sup> )	3.045 (3)	3.128 (2)	2.005 (2)	120.4 (2)
O(8 <sup>vi</sup> )	3.057 (3)	3.564 (2)	3.509 (4)	2.039 (3)

Symmetry code: (i)  $-x + 0.5, y + 0.5, -z + 1$ ; (ii)  $x - 0.5, -y + 1.5, z + 1$ ; (iii)  $-x + 1, -y + 1, -z + 2$ ; (iv)  $-x + 0.5, y - 0.5, -z + 2$ ; (v)  $-x + 0.5, y - 0.5, -z + 1$ ; (vi)  $-x + 1, -y + 1, -z + 1$ .

interlinked approximately hexagonal rings (Fig. 1). These structural units are connected through O(1) to form infinite chains in which successive units are related by the operation of the  $2_1$  screw axis parallel to **b**. Two symmetrically equivalent infinite chains run along a single unit cell, as shown in Fig. 2. The structure can thus be described as made up of pentaborate chains linked to each other by hydrogen

bonds (see Table 2) in the directions  $[\bar{1}02]$  and  $[102]$  for H(1) and H(2), and by Li in the direction  $[100]$ . The pentaborate ion was first found by Zachariasen (1937) in  $\text{KB}_5\text{O}_6(\text{OH})_4 \cdot 2\text{H}_2\text{O}$ .

Table 2 reports the main interatomic distances and angles for  $\text{LiH}_2\text{B}_5\text{O}_9$ . The average B—O distance in the triangles is 1.364 (4) Å and in the tetrahedron is 1.477 (4) Å, in good agreement with the results previously found in other borates by various workers (Behm, 1983; Domenech, Solans & Solans, 1981). The average value of O—B—O bond angles involving the tetrahedrally coordinated B atom B(1) ( $109.5^\circ$ ) agrees with the ideal tetrahedral angle. The average O—B—O angle for all the triangularly coordinated B atoms is  $120.0^\circ$ , also equal to the ideal value.

The atoms of the pentaborate group lie approximately in two planes which are inclined to each other at an angle of  $89.7^\circ$ . The parameter  $\alpha$ , defined by Domenech & Solans (1982), is 0.991 and agrees with values in similar compounds.

There are four Li—O distances between 1.917 (2) and 2.039 (3) Å. The O—Li—O angles ( $101.2$ – $124.4^\circ$ ) suggest that Li coordination should be described as distorted tetrahedral. Each Li atom links through O atoms to three different polyanion

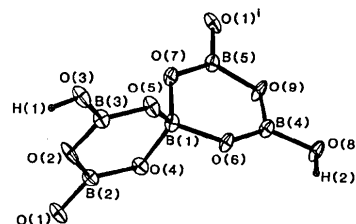


Fig. 1. The borate polyanion in  $\text{LiH}_2\text{B}_5\text{O}_9$ . The group is viewed along  $[001]$ . Thermal ellipsoids are shown at the 50% probability level. H atoms are of arbitrary size.

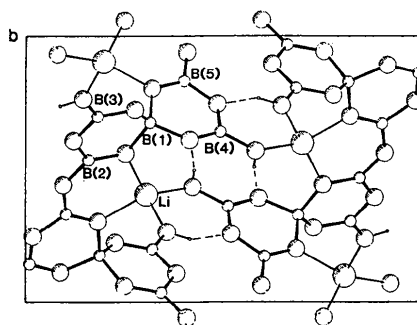


Fig. 2. Projection of the unit-cell structure of  $\text{LiH}_2\text{B}_5\text{O}_9$  viewed along  $[001]$ . Broken lines represent hydrogen bonds, thin lines indicate the tetrahedron around the Li atom.

units and may thereby perturb the chain structure. Each B—O polyanion is connected to two neighbouring Li atoms.

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## Alkaline-Earth Beryllium Borate $\text{CaBe}_2\text{O}_5$

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**Abstract.** Beryllium calcium diborate,  $\text{CaBe}_2\text{O}_5$ ,  $M_r = 150.71$ , monoclinic,  $P2_1/n$ ,  $a = 5.167$  (2),  $b = 3.756$  (2),  $c = 17.160$  (2) Å,  $\beta = 98.12$  (2)°,  $V = 329.7$  (2) Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 3.036$  g cm<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.71069$  Å,  $\mu = 17.38$  cm<sup>-1</sup>,  $F(000) = 296$ ,  $T = 298$  K,  $R = 0.039$  for 508 reflections having  $F_o^2 \geq 3\sigma(F_o^2)$ . The structure is constructed from two intermingled networks – a  $\text{CaO}_9$  polyhedral system and a beryllium borate complex constructed from four-coordinate Be and three- and four-coordinate B atoms. The extended beryllium borate complex results from the unique condensation of six-membered rings containing the triangular and distorted tetrahedral beryllate and borate groups.

**Introduction.** The simple pyroborate group  $\text{B}_2\text{O}_5$  – two triangular planar  $\text{BO}_3$  units sharing an O atom – has been found to exist in the alkaline-earth materials  $\text{AE}_2\text{B}_2\text{O}_5$ , where  $\text{AE} = \text{Mg}$ ,  $\text{Ca}$  or  $\text{Sr}$  (Takéuchi, 1952; Schäfer, 1968; Bartl & Schuckmann, 1966) and in the mixed phase  $\text{CaMgB}_2\text{O}_5$  (Yakubovich, Yamnova, Shehedrin, Simonov & Belov, 1975). No data are available in the literature on a simple pyroborate with  $\text{AE} = \text{Be}$ .

In this contribution we describe the structure of the mixed alkaline-earth compound  $\text{CaBe}_2\text{O}_5$ . Although the formula indicates the structure could contain a pyroborate group, we have found instead an admixture of three- and four-coordinate B atoms in a complex beryllium borate network. So, a unique atomic arrangement is provided for addition to the small muster of known anhydrous beryllium borates:

$\text{SrBe}_2(\text{BO}_3)_2$  (Schaffers & Keszler, 1990),  $\text{BaBe}_2(\text{BO}_3)_2$  (Schaffers, 1992),  $\text{Be}_2\text{BO}_3\text{F}$  (Bajdina, Bakakin, Podberizskaja, Alekseev, Baconova & Pavlijuenko, 1978) and  $\text{KBe}_2\text{BO}_3\text{F}$  (Solov'eva & Bakakin, 1970).

**Experimental.** Crystals of  $\text{CaBe}_2\text{O}_5$  were grown in a Pt crucible from a melt consisting of 26.6 mol%  $\text{CaB}_2\text{O}_4$  prepared from  $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  (ALFA, reagent grade) and  $\text{B}_2\text{O}_3$  (ALFA, 99.98%), 43.2 mol%  $\text{BeO}$  made by heating  $\text{BeF}_2$  (CERAC, 99.5%) in air, and 30.2 mol%  $\text{LiBO}_2$  (AESAR, 99.9%). The melt was cooled from 1198 to 698 K at 6 K h<sup>-1</sup>. The crystals were washed in hot distilled water to remove excess flux. A clear block-shaped crystal of approximate dimensions 0.25 (2) × 0.22 (2) × 0.20 (2) mm was mounted on a glass fiber with epoxy for X-ray structure analysis. Data were collected by using a Rigaku AFC-6R single-crystal diffractometer and Mo  $K\alpha$  radiation. Sixteen automatically centered peaks in the range  $30 \leq 2\theta \leq 36^\circ$  were used for refinement of unit-cell parameters. The  $\omega$ -scan technique was used to collect a total of 762 data to  $\sin\theta/\lambda = 1.08$  Å<sup>-1</sup> with a scan speed of 16.0° min<sup>-1</sup> in  $\omega$  and a scan width of  $(4.50 + 0.30\tan\theta)^\circ$ ;  $0 \leq h \leq 6$ ,  $0 \leq k \leq 4$  and  $-20 \leq l \leq 20$ . From the 683 unique reflections measured, 508 reflections had  $F_o^2 \geq 3\sigma(F_o^2)$ . Three standard reflections were monitored throughout the data collection and an average fluctuation of 2.0% in intensity was detected.

The *TEXSAN* crystallographic software package (Molecular Structure Corporation, 1989) was used to solve the crystal structure. The position of the Ca

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