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# Structure of the Borate $Li_{14}Be_5B(BO_3)_9$

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The new compound $Li_{14}Be_5B(BO_3)_9$ has been synthesized and structurally characterized by single-crystal X-ray methods. It crystallizes in the hexagonal system (space group $P6_3/m$, $Z = 2$) in a cell of dimensions $a = 7.730(2)$ Å, $c = 18.853(2)$ Å, and $V = 975.5(3)$ Å$^3$. The model has been refined with 1725 unique reflections to the final residuals $R = 0.048$ and $R_w = 0.067$. $LiO_3$ and $BO_3$ triangles, $LiO_4$ and $BeO_4$ tetrahedra, and $LiO_6$ trigonal prisms join by sharing vertices to form a unique, dense three-dimensional structure.

## Introduction

As part of our continuing efforts[1-3] to develop the structural chemistry of complex beryllium borates,[4,5] we have examined phase equilibria in the system $Li_2O$–BeO–$B_2O_3$. We have identified the title compound as a new member of this system and describe here its highly unusual arrangement of condensed polyhedra.

## Experimental Section

Single crystals of $Li_{14}Be_5B(BO_3)_9$ were prepared by decomposing $LiNO_3$ in a 6:1 molar ratio with $B_2O_3$ in an alumina crucible for 1 h at 875 K, followed by adding $BeF_2$ to achieve a 1:2 molar ratio with $B_2O_3$; this mixture was then heated at 900 K for 12 h and 1025 K for 16 h. The powder was melted in a Pt crucible at 1075 K, cooled to 475 K at 10 K/h, and rapidly cooled to room temperature by turning the power to the furnace off.

A colorless, transparent crystal of approximate dimensions 0.08 × 0.23 × 0.45 mm was isolated and mounted on a glass fiber with epoxy for structure analysis on a Rigaku AFC6R diffractometer equipped with Mo K$\alpha$ radiation. Unit-cell parameters were derived from automatic centering and least-squares refinement of 18 reflections in the range $30 \le 2\theta \le 35°$. From measurement of equivalent reflections, the Laue group was established as $6/m$ on the diffractometer. Intensity data spanning the indices $0 \le h \le 15, 0 \le k \le 15$, and $0 \le l \le 37$ were collected with $\omega$ scans to $(\sin\theta_{max})/\lambda = 0.995$. A total of 3530 reflections were measured, resulting in 1725 unique data with $F_o^2 \ge 3\sigma(F_o^2)$. Three standard reflections measured after each block of 200 data exhibited an average fluctuation in intensity of 2.1%.

Structure solution was accomplished by using computer programs from the TEXSAN crystallographic software package.[6] The systematic absence $00l$, $l = 2n + 1$, indicated that the compound crystallized in the centrosymmetric space group $P6_3/m$ or its noncentrosymmetric partner $P6_3$. Both the distributions of intensities[7] and $E$ values indicated that the structure was noncentrosymmetric. As a result, it was solved in the group $P6_3$. The B and O atoms were located by using the direct methods program SHELXS,[8] and the positions of the remaining Li and Be atoms were determined from subsequent examination of difference electron density maps. Analysis of the resulting structure, however, readily revealed the presence of an inversion center, so the positional parameters were directly transformed to the group $P6_3/m$. After refining the model with isotropic displacement coefficients on all atoms, we observed the coefficient of the Be site to be negative. To correct this parameter and achieve charge balance for the compound, the occupancy of this site was set to $^5/_6$ Be and $^1/_6$ B. Refinement of this model affords a reasonable displacement factor for the Be(B) site and reduced discrepancy factors. The data were corrected for absorption with the program DIFABS,[9] and equivalent reflections were averaged ($R_{int} = 0.026$). Final refinement on $F_o$ with those data having $F_o^2 \ge 3\sigma(F_o^2)$ and anisotropic displacement coefficients on all atoms, excluding the disordered Be site, affords the residuals $R = 0.048$ and $R_w = 0.067$. A correction for extinction was not applied. $F_c$ was derived from neutral-atom scattering factors corrected for anomalous dispersion with calculated $f'$ and $f''$.[10] The largest peak in the final difference electron density map corresponds to 6.4% of the atom O1. Crystallographic data and final atomic parameters are listed in Tables 1 and 2, respectively.

## Results

The structure is a dense tangle of Li- and B-centered triangles, Li- and Be-centered distorted O tetrahedra, and Li-centered trigonal prisms. The overall connectivity of these polyhedra is best appreciated by considering Figures 1–3. Tubes comprised of Li- and Be-centered tetrahedra and B4-centered triangles parallel the $c$ axis along the center line 0, 0, $z$ (Figures 1 and 2). Each tube is characterized by Li-centered polyhedra that are grouped together in sets of four, i.e., pairs of edge-shared tetrahedra centered by atoms Li3 and Li4 are joined by sharing a common vertex (Figure 2). Adjacent to these Li–O units are two $BeO_4$ tetrahedra bridged by a $B4O_3$ triangle. Application of the $6_3$ screw axis to the combined groupings generates the tubes. The channels along the center line 0, 0, $z$ are occupied exclusively by B2 atoms in trigonal O3 planes. (The O3 atom also serves as a vertex for the $BeO_4$ tetrahedraon and as one member of the shared O···O edge of the fused $LiO_4$ units.)

The tubes join one to the other by sharing O vertices that are common to both the $BeO_4$ and $LiO_4$ tetrahedra. This results in a fully three-dimensional Li–Be–B–O framework. Moreover, additional channels that extend along the lines $^1/_3, ^2/_3, z$ and $^2/_3, ^1/_3, z$ are generated. These channels are occupied by atoms Li1, B1, and B3 in distinct O trigonal planes and atom Li2 in a trigonal prism. From consideration of the positional parameters and Figure 3, the atom sequence along the $c$ axis is seen to be ···B1–Li2–B3–B1–Li1–B3···.

Selected interatomic distances and angles are listed in Table 3. Three O4 atoms at a distance of 1.916(1) Å about atom Li1 form a trigonal plane having $D_{3h}$ symmetry. Similar planes are

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**Table 1.** Crystallographic Data for $Li_{14}Be_5B(BO_3)_9$

| | |
|---|---|
| chem formula | $Li_{14}Be_5B(BO_3)_9$ |
| fw | 680.52 |
| space group | $P6_3/m$ (No. 176) |
| $a$ | 7.730(2) Å |
| $c$ | 18.853(2) Å |
| $V$ | 975.5(3) Å$^3$ |
| $Z$ | 2 |
| $T$ | 296 K |
| $\rho_{calcd}$ | 2.317 g cm$^{-3}$ |
| λ | 0.710 69 Å |
| $\mu$ | 1.91 cm$^{-1}$ |
| $R_w(F_o)^a$ | 0.067 |
| $R(F_o)^a$ for $F_o^2 > 3\sigma(F_o^2)$ | 0.048 |

$^a$ $R = \sum||F_o| - |F_c||/\sum|F_o|$; $R_w = [\sum w(|F_o|^2 - |F_c|^2)^2/\sum w|F_o|^4]^{1/2}$.

**Table 2.** Atomic Parameters for $Li_{14}Be_5B(BO_3)_9$

| | $x$ | $y$ | $z$ | $B_{eq}{}^a$ |
|---|---|---|---|---|
| Li1 | $^1/_3$ | $^2/_3$ | $^3/_4$ | 1.8(1) |
| Li2 | $^2/_3$ | $^1/_3$ | $^3/_4$ | 3.0(2) |
| Li3 | 0.6496(4) | 0.6765(3) | 0.05361(1) | 1.29(6) |
| Li4 | 0.6732(4) | 0.6975(4) | 0.6706(1) | 1.45(6) |
| Be$^b$ | 0.6757(6) | 0.0234(5) | 0.6115(2) | 0.69(2) |
| B1 | $^1/_3$ | $^2/_3$ | 0.6072(1) | 0.78(3) |
| B2 | 0 | 0 | 0.5926(1) | 0.79(3) |
| B3 | $^2/_3$ | $^1/_3$ | 0.5523(1) | 0.78(3) |
| B4 | 0.6989(3) | 0.0198(2) | $^3/_4$ | 0.89(3) |
| O1 | 0.7339(1) | 0.1984(1) | 0.55063(4) | 0.99(2) |
| O2 | 0.4406(1) | −0.1279(1) | 0.60726(4) | 0.96(2) |
| O3 | 0.7958(1) | −0.0888(1) | 0.59290(4) | 0.97(2) |
| O4 | 0.6194(2) | −0.1823(2) | $^3/_4$ | 1.01(3) |
| O5 | 0.7382(1) | 0.1313(1) | 0.68812(4) | 1.10(2) |

$^a$ $B_{eq} = (8\pi^2/3)\sum_i\sum_j U_{ij}a_i^*a_j^*a_i{\cdot}a_j$. $^b$ Occupancy = 5/6 Be + $^1/_6$ B.

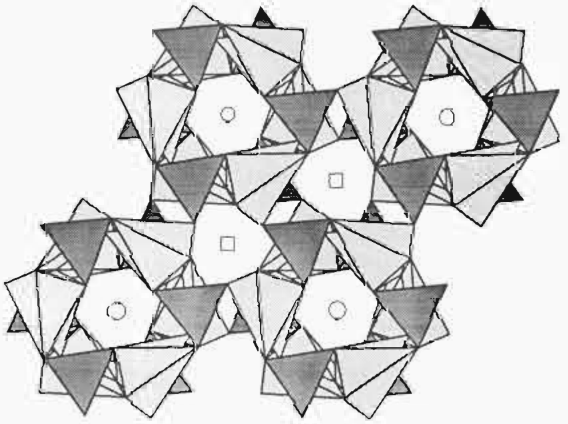

**Figure 1.** Polyhedral representation of the Li–Be–B–O framework of $Li_{14}Be_5B(BO_3)_9$ as viewed along [001]. Lightly shaded polyhedra represent Li sites, deeply shaded polyhedra B sites, and medium shading Be sites, here, and in all ensuing figures. The circles mark the line 0, 0, $z$, and the squares mark the lines $^1/_3$, $^2/_3$, $z$ and $^2/_3$, $^1/_3$, $z$.

found in the structures of $LiBa_3M_3Ti_5O_{21}$ (M = Nb, Ta, Sb) where the Li–O distances range from 1.88–1.99 Å.[11] Six O5 atoms at a distance of 2.230(1) Å define a trigonal prism about atom Li2; the edges of the prism that parallel the $c$ axis are significantly shortened by sharing with $BO_3$ triangles (Figure 4). This produces the compressed aspect ratio of 0.71 for the prism. The length 2.230 Å for Li2–O5 is also greater than the calculated distance of 2.12 Å for a 6-coordinate Li atom.[12] This longer distance likely arises from the rigidity of the surrounding Be borate matrix; the larger displacement coefficient of the Li2 atom (cf. Table 3) is also consistent with this distance. Atoms Li3 and Li4 approximately center distorted tetrahedra with average Li–O distances of 1.97(4) and 1.99(6) Å, respectively. The ranges of

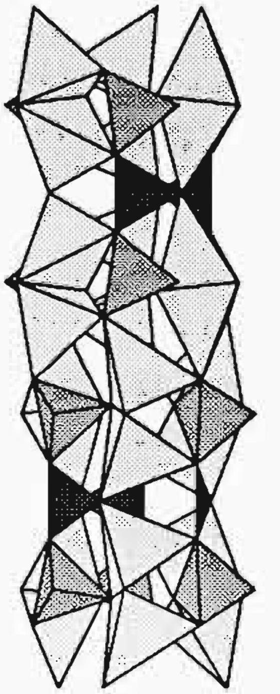

**Figure 2.** Portion of the Li–Be–B–O tube extending along the center line 0, 0, $z$.

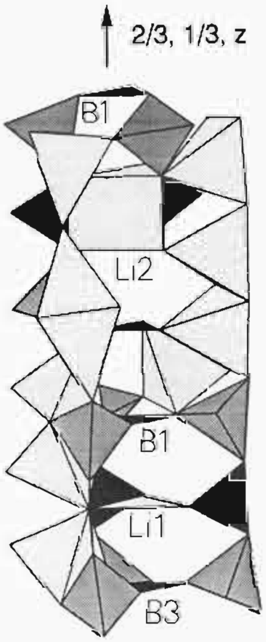

**Figure 3.** Occupancy of the Li–Be–B–O framework along the lines $^1/_3$, $^2/_3$, $z$ and $^2/_3$, $^1/_3$, $z$. A portion of the framework is drawn to illustrate the links between the framework and the central polyhedra.

angles 91.0(1)–132.9(1)° for O–Li3–O and 86.3(1)–125.4(1)° for O–Li4–O portray the degree of distortion from $T_d$ symmetry. As noted above, pairs of the Li3- and Li4-centered tetrahedra form $Li_2O_6$ dimers by sharing the edge O2···O3. The marked deviation from a Li3–O2–Li4–O3 square is deduced from the angles 78.9(1)° for Li3–O2–Li4 and 79.7(1)° for Li3–O3–Li4; the Li3···Li4 separation across the shared edge is 2.542(3) Å. All of the Li–O distances may be additionally compared to average distances of 1.90(8) Å in $Li_6Yb(BO_3)_3$,[13] 1.91(4) Å in $Ba_2LiB_5O_{10}$,[14] and 2.04(9) Å in $LiB_3O_5$[15] for 4-coordination; 2.13(7)

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**Table 3.** Interatomic Distances (Å) and angles (deg) for $Li_{14}Be_5B(BO_3)_9$

| | | | |
|---|---|---|---|
| Li1–O4 × 3 | 1.916(1) | O4–Li1–O4 | 120 |
| Li2–O5 × 6 | 2.230(1) | O5–Li2–O5 | 63.11(4) |
| | | O5–Li2–O5 | 95.11(3) |
| | | O5–Li2–O5 | 129.57(1) |
| Li3–O1 | 2.009(2) | O1–Li3–O1 | 132.9(1) |
| Li3–O1 | 1.981(3) | O1–Li3–O2 | 106.6(1) |
| Li3–O2 | 1.985(3) | O1–Li3–O3 | 111.2(1) |
| Li3–O3 | 1.915(2) | O1–Li3–O2 | 104.9(1) |
| | | O1–Li3–O3 | 102.3(1) |
| | | O2–Li3–O3 | 91.0(1) |
| Li4–O2 | 2.016(3) | O2–Li4–O3 | 86.3(1) |
| Li4–O3 | 2.051(3) | O2–Li4–O4 | 110.6(1) |
| Li4–O4 | 1.914(3) | O2–Li4–O5 | 125.4(1) |
| Li4–O5 | 1.986(3) | O3–Li4–O4 | 107.0(1) |
| | | O3–Li4–O5 | 106.0(1) |
| | | O4–Li4–O5 | 115.4(1) |
| Be–O1 | 1.656(4) | O1–Be–O2 | 107.9(2) |
| Be–O2 | 1.597(4) | O1–Be–O3 | 107.3(2) |
| Be–O3 | 1.594(4) | O1–Be–O5 | 108.0(2) |
| Be–O5 | 1.616(4) | O2–Be–O3 | 110.4(2) |
| | | O2–Be–O5 | 111.1(3) |
| | | O3–Be–O5 | 111.9(3) |
| B1–O2 × 3 | 1.376(1) | O2–B1–O2 | 120 |
| B2–O3 × 3 | 1.371(1) | O3–B2–O3 | 120 |
| B3–O1 × 3 | 1.379(1) | O1–B3–O1 | 120 |
| B4–O4 | 1.363(2) | O4–B4–O5 | 122.93(7) |
| B4–O5 × 2 | 1.391(1) | O5–B4–O5 | 114.1(1) |

Å in $Sr_2InLi(B_2O_5)_2$[16] for 5-coordination; and 2.15(9) Å in $LiNbO_3$[17] and 2.17(5) Å in $LiMnPO_4$[18] for 6-coordination.

The Be atom is surrounded by atoms O1, O2, O3, and O5 at the vertices of a distorted tetrahedron. Although the site is $^1/_6$ occupied by B atoms, no significant shortening of the Be–O distance is expected, and the average Be–O bond distance of 1.62(3) Å compares to 1.63(6) and 1.64(4) Å for $SrBe_2(BO_3)_2$,[1] 1.63(4) Å for $BaBe_2(BO_3)_2$,[2] and 1.597(6) Å for $CaBeB_2O_5$,[3] all describing 4-coordinate Be sites.

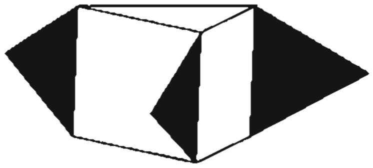

**Figure 4.** Edge sharing between the $LiO_6$ prism and $BO_3$ triangles.

Four types of B atoms occupy triangular planar environments. Atoms B1, B2, and B3 reside in sites having $D_{3h}$ symmetry with B–O distances of 1.376(1) Å for B1–O2, 1.371(1) Å for B2–O3, and 1.379(1) Å for B3–O1. The atom B4 bonds to O4 and O5 × 2 in a distorted triangular planar site having bond lengths of 1.363(2) and 1.391(1) Å, respectively, and angles of 122.93(6) × 2 and 114.1(1)°.

The five chemically and crystallographically different O atoms in the structure occupy distorted tetrahedral environments. Connectivity with the Li, Be, and B atoms can be discerned from consideration of Table 3.

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**Supplementary Material Available:** Tables listing complete crystallographic and data collection information and anisotropic displacement coefficients (2 pages). Ordering information is given on any current masthead page.

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