

The Layered Borate $\text{SrBe}_2(\text{BO}_3)_2$

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The compound $\text{SrBe}_2(\text{BO}_3)_2$ crystallizes in the monoclinic space group $P2_1/n$ in a cell of dimensions $a = 9.247(1) \text{ \AA}$, $b = 4.492(2) \text{ \AA}$, $c = 11.561(1) \text{ \AA}$, and $\beta = 112.17(1)^\circ$ with $Z = 4$. Least-squares refinement affords the final residuals $R = 0.034$ and $R_w = 0.045$. The structure consists of layers of composition $[\text{Be}_2(\text{BO}_3)_2]^{2-}$ that are interleaved by Sr atoms. Each layer contains two crystallographically inequivalent Be and B atoms; the Be atoms occupy distorted O tetrahedra while the B atoms occupy distorted triangular planar environments. Two Be atoms of one type share two O atoms to form a dimer of edge-shared tetrahedra. The Sr atom occupies a distorted monocapped 8-coordinate site. © 1990 Academic Press, Inc.

As part of our continuing studies of structural and optical characteristics of new borates (*I-3*) we have been involved in the synthesis of compounds having the formula $\text{XY}_2(\text{BO}_3)_2$ where X and Y are cations of disparate sizes with formal dipositive charges (4, 5). We have been particularly interested in new compounds with X or Y = Be since such materials are likely to exhibit structures and properties similar to those observed for polyborates containing an admixture of 3- and 4-coordinate B atoms.

Little information on anhydrous beryllium borates has been reported; only the borate fluorides $\text{Be}_2\text{BO}_3\text{F}$ (6) and $\text{KBe}_2\text{BO}_3\text{F}_2$ (7) have been described. In each of these compounds the larger size of the Be atom relative to that of the B atom renders a selective occupation of tetrahedral sites by Be atoms and triangular sites by B atoms even though triangular coordination of Be atoms is known to occur (8). We observe a similar distribution of the Be and B atoms

in the new compound $\text{SrBe}_2(\text{BO}_3)_2$ which we describe here.

Single crystals of the compound $\text{SrBe}_2(\text{BO}_3)_2$ were grown from a melt of composition 33 mol% SrO, 33 mol% BeO, and 33 mol% B_2O_3 that was cooled in a Pt crucible from 1100 to 900°C at 8°C/hr. Clear, colorless crystals were physically separated from the solidified melt.

A crystal of approximate dimensions $0.2 \times 0.2 \times 0.1 \text{ mm}$ was selected and mounted on a glass fiber with epoxy for X-ray structure determination. Diffraction data were collected with a Rigaku AFC6R diffractometer equipped with $\text{MoK}\alpha$ radiation. Unit-cell parameters were determined by automatic centering and least-squares refinement of 20 reflections in the range $30 < 2\theta < 36^\circ$. Intensity data were collected with ω - 2θ scans and a scanning speed of 16°/min in ω . Three standard reflections, monitored every 200 reflections, exhibited no significant fluctuations throughout the

TABLE I
CRYSTALLOGRAPHIC DATA FOR SrBe₂(BO₃)₂

Formula weight, amu	223.26
Crystal system	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>n</i> (No. 14)
<i>a</i> , Å	9.247(1)
<i>b</i> , Å	4.492(2)
<i>c</i> , Å	11.561(1)
β, °	112.17(1)
<i>V</i> , Å ³	444.7(2)
<i>Z</i>	4
<i>D</i> _{calcd} , g cm ⁻³	3.33
<i>F</i> (000)	416
Diffractometer	Rigaku AFC6
Radiation	MoKα (λ = 0.71069) graphite-mono- chromated
Data collection	± <i>h</i> , <i>k</i> , <i>l</i>
No. Observations (<i>F</i> ₀ ² > 3σ(<i>F</i> ₀ ²))	1222
<i>R</i>	0.034
<i>R</i> _w	0.045
Maximum shift in final cycle	0.01

collection. A total of 1651 reflections was measured over the range $2 \leq 2\theta \leq 62^\circ$, affording 1285 unique reflections with $R_0^2 \geq 3\sigma(F_0^2)$. The systematic extinctions, $h0l$, $h + l = 2n + 1$, and $0k0$, $k = 2n + 1$, are consistent with the space group *P*2₁/*n* (No. 14). Computer programs from the TEX-SAN crystallographic software package (9) were used to determine the structure. The position of the Sr atom was located by application of the direct methods program SHELXS (10). The positions of the remaining atoms were determined by examining subsequent difference electron density maps. Following refinement of the model with isotropic thermal parameters, the data were corrected for absorption with the program DIFABS (11). Final least-squares refinement on *F* with those 1222 reflections having $F_0^2 \geq 3\sigma(F_0^2)$ and anisotropic thermal displacement coefficients on each atom affords the final residuals $R = 0.034$ and $R_w = 0.045$. Analysis of the final difference electron density map reveals a maximum

TABLE II
ATOMIC COORDINATES AND THERMAL
DISPLACEMENT COEFFICIENTS FOR SrBe₂(BO₃)₂

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> (Å ²) ^a
Sr	0.42743(4)	0.02664(8)	0.65652(3)	0.39(1)
Be(1)	0.6266(6)	-0.099(1)	0.0490(5)	0.5(2)
Be(2)	0.2164(6)	-0.062(1)	0.3077(5)	0.4(1)
B(1)	0.4501(5)	-0.437(1)	0.8549(4)	0.3(1)
B(2)	0.2948(5)	0.409(1)	0.4246(4)	0.4(1)
O(1)	0.2848(3)	-0.4868(6)	0.5315(3)	0.48(9)
O(2)	0.3442(3)	0.1210(7)	0.4217(3)	0.40(9)
O(3)	0.5401(3)	-0.5118(7)	0.7886(3)	0.6(1)
O(4)	0.4728(3)	-0.1635(7)	0.9127(3)	0.6(1)
O(5)	0.1635(3)	-0.1286(7)	0.6418(3)	0.7(1)
O(6)	0.7576(3)	-0.0814(7)	0.8177(3)	0.42(9)

$$^a B = (8\pi^2/3) \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j.$$

peak of density $1.5 e/\text{\AA}^3$ which corresponds to 0.79% of a Sr atom. Crystallographic data and final atomic parameters are listed in Tables I and II, respectively.

A labeled sketch of the contents of the unit cell is provided in Fig. 1. The nature of the structure is best appreciated by inspection of the perspective view along the *b* axis

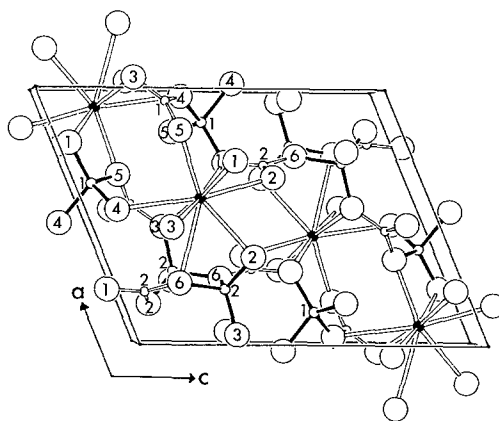


FIG. 1. Sketch of a labeled unit cell of the compound SrBe₂(BO₃)₂ viewed along the *b* axis. Large open circles represent O atoms, small solid circles represent Sr atoms. Open circles with open bonds represent B atoms, open circles with solid bonds represent Be atoms here, and in ensuing figures.

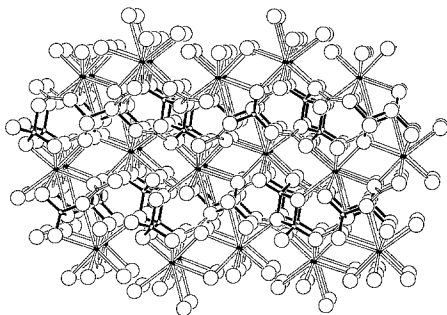


FIG. 2. Perspective view of the structure of $\text{SrBe}_2(\text{BO}_3)_2$ along the b axis.

given in Fig. 2. Layers of composition $[\text{Be}_2(\text{BO}_3)_2]^{2-}$ separated by planes of Sr atoms may be identified. A drawing of a single beryllium borate layer as viewed orthogonal to the b axis is given in Fig. 3. Each layer contains two crystallographically inequivalent Be atoms and two inequivalent B atoms. The Be atoms occupy distorted tetrahedral sites and the B atoms occupy triangular sites. The BeO_4 and BO_3 groups are connected one to the other by sharing O vertices. The tetrahedra occupied by atom Be(2) share vertices to form chains that extend along the b axis. This contrasts to the tetrahedra occupied by atom Be(1) that are present as isolated pairs sharing an edge.

Selected interatomic distances and angles are listed in Table III. The mean Be–O distance, 1.63(4) Å, compares to that, 1.61 Å, computed for a 4-coordinate Be atom from crystal radii (12) and the mean B–O distance, 1.37(1) Å, is also similar to that, 1.36 Å, computed for a 3-coordinate B atom, suggesting there is little disorder among the Be and B sites. The sensitivity of the intensity data to the distribution of the Be and B atoms was examined in two ways. The refinement was repeated with the Be atoms on B sites and B atoms on Be sites. This procedure afforded larger residuals and equivalent temperature factors for the Be atoms that were not positive-definite and increased by a factor of three for the B

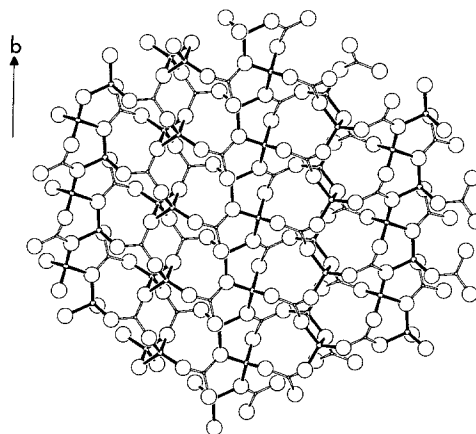


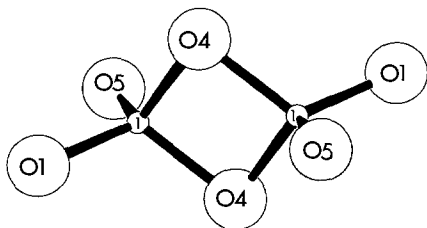
FIG. 3. Sketch of a single compositional layer $[\text{Be}_2(\text{BO}_3)_2]^{2-}$ viewed orthogonal to the b axis.

TABLE III
SELECTED INTERATOMIC DISTANCES (Å) AND
ANGLES (°) FOR $\text{SrBe}_2(\text{BO}_3)_2$

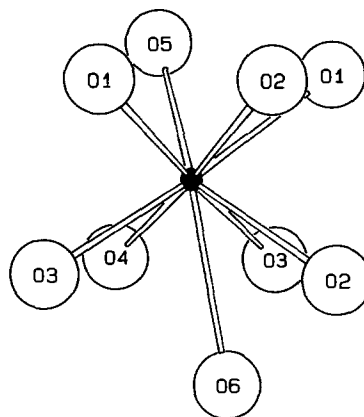
Sr–O(1)	2.677(3)	O(1)–Sr–O(1)	110.9(1)
Sr–O(1)	2.776(3)	O(1)–Sr–O(2)	84.19(9)
Sr–O(2)	2.562(3)	O(1)–Sr–O(4)	98.13(9)
Sr–O(2)	2.676(3)	O(1)–Sr–O(5)	85.5(1)
Sr–O(3)	2.840(3)	O(2)–Sr–O(3)	78.12(9)
Sr–O(3)	2.552(3)	O(2)–Sr–O(4)	115.81(9)
Sr–O(4)	2.957(3)	O(2)–Sr–O(5)	94.6(1)
Sr–O(5)	2.482(3)	O(3)–Sr–O(4)	76.34(9)
Sr–O(6)	2.955(3)	O(3)–Sr–O(6)	70.42(9)
		O(4)–Sr–O(5)	75.61(9)
		O(4)–Sr–O(6)	66.35(8)
Be(1)–O(1)	1.597(6)	O(1)–Be(1)–O(4)	114.2(3)
Be(1)–O(4)	1.653(6)	O(1)–Be(1)–O(5)	107.4(4)
Be(1)–O(4)	1.702(6)	O(4)–Be(1)–O(4)	90.3(3)
Be(1)–O(5)	1.580(7)	O(4)–Be(1)–O(5)	111.7(3)
		O(4)–Be(1)–O(5)	112.8(4)
Be(2)–O(2)	1.623(6)	O(2)–Be(2)–O(3)	113.6(3)
Be(2)–O(3)	1.595(6)	O(2)–Be(2)–O(6)	111.0(3)
Be(2)–O(6)	1.683(6)	O(3)–Be(2)–O(6)	114.2(4)
Be(2)–O(6)	1.641(6)	O(3)–Be(2)–O(6)	105.8(3)
		O(6)–Be(2)–O(6)	109.2(3)
B(1)–O(3)	1.369(5)	O(3)–B(1)–O(4)	118.5(4)
B(1)–O(4)	1.378(5)	O(3)–B(1)–O(5)	119.8(4)
B(1)–O(5)	1.369(5)	O(4)–B(1)–O(5)	121.6(4)
B(2)–O(1)	1.359(5)	O(1)–B(2)–O(2)	119.0(4)
B(2)–O(2)	1.374(5)	O(1)–B(2)–O(6)	122.5(4)
B(2)–O(6)	1.388(5)	O(2)–B(2)–O(6)	118.5(4)

atoms. A partial disorder was imposed by altering the occupancy factors for the B and Be atoms to correspond to a 20% occupancy of B sites by Be atoms and Be sites by B atoms. The occupancy factor of each atom was then refined. All factors refined to within 5% of unity and their magnitudes were contraposed to values expected for any model of disorder among the Be and B sites.

The Be(1) atoms related by a center of symmetry across the shared edge O(4) ... O(4) of the tetrahedra are separated by 2.35(1) Å, Scheme 1. The angle between the plane of atoms Be(1), O(4), and O(4) and the plane of atoms Be(1), O(1), and O(5) is 87.7°. The four-membered ring Be(1)–O(4)–Be(1)–O(4) exhibits minimal deviations from a square as shown by consideration of the angles O(4)–Be(1)–O(4), 90.9(3)°, and Be(1)–O(4)–Be(1), 89.1(3)°. A dimer of tetrahedra formed by sharing an edge is relatively rare in oxides, although more common in chalcogenides and halides; a similar unit Be_2O_6 has been identified in the mineral epididymite, $\text{Na}_2\text{Be}_2\text{Si}_6\text{O}_{15} \cdot \text{H}_2\text{O}$ (13). The metrical data above may be compared to the four-membered Si–O–Si–O ring in the compound tetramesitylcyclodisiloxane (14). The Si–O bond lengths are 1.66 and 1.72 Å and the Si ... Si separation is 2.31 Å; evidence for greater deviation from a square is provided by the O–Si–O angle of 94°. The tetrahedron about atom Be(2) is only slightly distorted (cf., Table III).



SCHEME 1



SCHEME 2

The Sr atom occupies a distorted mono-capped 8-coordinate environment, Scheme 2, between layers. The Sr–O distances range from 2.552(3) to 2.957(3) Å with a mean of 2.72(6) Å. These distances compare to those observed for the 9-coordinate Sr atom in the compounds $\text{Sr}_3\text{Sc}(\text{BO}_3)_3$, 2.500(2)–2.857(2) Å (1), and SrNaBO_3 , 2.539(7)–2.93(2) Å (15).

Despite the existence of an extensive structural chemistry of simple anhydrous borates as well as polyborates exhibiting an admixture of 3- and 4-coordinate B atoms, only a limited number of chains, layers, and networks formed from combinations of tetrahedra and triangles selectively centered by atoms of different types are known. Examples include the aluminum orthoborates $\text{Sr}_2\text{Al}_2\text{B}_2\text{O}_8$ (16), $\text{Li}_6\text{Al}(\text{BO}_3)_3$ (17), CaAlBO_4 (18), and $\text{CaAl}_2\text{B}_2\text{O}_7$ (19); the zinc borates $\text{Zn}_3(\text{BO}_3)_2$ (20), LiZnBO_3 (21), $\text{KZn}_4(\text{BO}_3)_3$ (22), and $\text{BaZn}_2(\text{BO}_3)_2$ (23); and the beryllium borates mentioned here. Given the expectation and observation that Be atoms prefer in oxides tetrahedral sites in the presence of B atoms because of their larger size and greater electropositive nature, it is likely that many additional tetrahedral–triangular networks containing these atoms will be synthesized in the future.

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