Journal of Solid State Chemistry **168,** 316–321 (2002)
doi:10.1006/jssc.2002.9704

Crystal Structure of a New Form of Sodium Octoborate β-$Na_2B_8O_{13}$

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Received March 4, 2002; in revised form June 4, 2002; accepted July 16, 2002

Single crystals of a new form of sodium octoborate, β-$Na_2B_8O_{13}$, were obtained fortuitously from a complex Na_2O–B_2O_3–P_2O_5 mixture, and studied. The compound is monoclinic, space group $P2_1/c$; the unit cell parameters are $a = 11.731(4)$ Å, $b = 7.880(3)$ Å, $c = 10.410(4)$ Å, $\beta = 99.883(3)°$; $Z = 4$. The crystal structure was solved from 1653 reflections until $R_1 = 0.0444$; it consists of two infinite, independent, and interleaved boron–oxygen networks containing a complex borate anion $(B_8O_{13})^{2-}$ formed by six BO_3 triangles (Δ) and two BO_4 tetrahedra (T), which can be viewed as a B_5O_{10} group linked to a B_3O_7 group; this leads to a Fundamental Building Block (FBB) with the shorthand notation: 8: ∞^3 $[(5:4\Delta + T) + (3:2\Delta + T)]$. This FBB is identical to that described in other octoborates such as α-$Na_2B_8O_{13}$ and $Ag_2B_8O_{13}$. However, some subtle differences exist in the interlinking of the octoborate anions found in these three compounds, which explains their different structure and unit cell parameters.

Key Words: **borate; sodium borate; sodium octoborate.**

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1. INTRODUCTION

Anhydrous sodium borates are known and have long been studied because they are the main constituents of borosilicate glasses (1). Several compounds were reported in the Na_2O–B_2O_3 binary system (2–4). Among them, the structures of Na_3BO_3 (5), $Na_4B_2O_5$ (6), $NaBO_2$ (7), $Na_2B_4O_7$ (8), α-NaB_3O_5 (9), β-NaB_3O_5 (10), and α-$Na_2B_8O_{13}$ (11, 12) were established. In the binary system Na_2O–B_2O_3 (2–4), the borate $Na_2O \cdot 4B_2O_3$ ($Na_2B_8O_{13}$), called octoborate, was reported to exist in two forms. This result was confirmed by the publication of their non-indexed powder patterns (13). The crystal structure of the stable α-form of this compound was studied in 1962 (11) and 1967 (12), and its indexed powder pattern was reported in powder diffraction file (12). Two other octoborates were simultaneously studied by Krogh-Moë (14) because of their similar structure: $Ag_2B_8O_{13}$ and $(Ag_{0.6}Na_{0.4})_2B_8O_{13}$. Despite a polyanion common to these three compounds, their structures are not identical. Single crystals of the second form of $Na_2B_8O_{13}$, β-$Na_2B_8O_{13}$, were obtained in a Na_2O–B_2O_3–P_2O_5 complex mixture, and they were identified after resolution of the structure. The subtle differences existing in all these octoborates will also be presented.

2. EXPERIMENTAL

2.1. Synthesis

In order to synthesize, by a ceramic route, a sodium phosphatoborate analogous to $Na_3[B_6O_9(VO_4)]$ sodium vanadoborate (15), a mixture of $Na_2CO_3 \cdot H_2O$, H_3BO_3 and $NH_4H_2PO_4$ in 3:12:2 proportions was heated until melting at 850°C. After melting, the mixture was slowly cooled down at 0.1°C/min for 50°C, annealed at this temperature (800°C) for 12 h. This last process was repeated five times until a temperature of 550°C was reached. Cooling led to a partially vitreous heterogeneous mixture, from which single crystals of the title compound were extracted.

2.2. Single Crystal Structure Determination

The intensity data were collected on a Brucker AXS SMART three-circle diffractometer using a graphite monochromatized Mo$K\alpha$ radiation ($\lambda = 0.71073$ Å), and equipped with a CCD two-dimensional detector. Crystal data and conditions of intensity collections are given in Table 1. The structure was refined by full-matrix least-

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0022-4596/02 $35.00

TABLE 1
Crystal Data and Intensity Collection Conditions for β-$Na_2B_8O_{13}$

Formula	β-$Na_2B_8O_{13}$
Formula weight (g/mol)	340.46
Crystal system	Monoclinic
Space group	$P2_1/c$ (No. 14)
Unit cell dimensions (Å; deg)	$a = 11.731(4)$; $b = 7.880(3)$; $c = 10.410(4)$; $\beta = 99.883(6)$
V (Å^3); Z	948.0(6); 4
Density (g/cm^3)	$D_{calc.} = 2.385$
Crystal size (mm^3)	$0.20 \times 0.15 \times 0.10$
Diffractometer	Bruker AXS SMART
Radiation	Mo$K\alpha$, $\lambda = 0.71069$ Å
Collection method	$\varphi - \omega$
Temperature (K)	298
θ range (deg)	1.76−30.01
Range in h, k, l	$-16 \le h \le 16; -11 \le k \le 11; -14 \le l \le 14$
Absorption coefficient (mm^{-1})	μ(Mo$K\alpha$) = 0.298
Reflections collected	8154
Independent reflections	2510
Independent reflections with [$I > 2\sigma(I)$]	1653
R_{int}	0.0448
Refinement method	Full matrix least squares on F^2 SHELXTL-97 (16)
Number of variables	228
Goodness-of-fit on F^2 (GOF)	0.884
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0444, wR_2 = 0.0980$
R indices (all data)	$R_1 = 0.0711, wR_2 = 0.1037$
Largest difference map peak and hole (e Å^{-3})	0.407 and −0.399

squares techniques using the SHELXTL crystallographic software package (16). Fifteen nearly equivalent atoms were apparent by direct methods in the space group $P2_1/c$. As the formula was unknown, they were attributed to oxygen atoms. Refinement did not converge very well, but eight peaks on the difference map could be identified as boron atoms, and the reliability factors decreased to 0.21. At this stage, it became apparent that two of the previously named oxygen atoms were in fact sodium atoms, and that the two strongest peaks in the difference map were close to them. When each of these four positions was attributed to one half sodium atom, the reliability factor fell to 0.12. Going from isotropic to anisotropic thermal factors and refinement of occupation rates of sodium atoms, further decreased the reliability factor to $R_1 = 0.0444$ and $wR_2 = 0.0980$ for 1653 reflections [$I > 2\sigma(I)$]. No evidence for a doubling of a parameter was found that could account for this splitting of sodium atom positions. The atomic coordinates and the thermal motion parameters are reported in Table 2. Table 3 gives the anisotropic thermal factors for all atoms. Significant bond lengths and angles are listed in Table 4.

3. DESCRIPTION OF THE STRUCTURE AND DISCUSSION

3.1. Borate Anion

The borate anion found in β-$Na_2B_8O_{13}$ is formed by the association of BO_3 triangles and BO_4 tetrahedra linked by the vertices. All the oxygen atoms are common to two triangles or to one triangle and one tetrahedron. The B–O distances in this borate anion are comparable with those existing in other borates with shorter distances in BO_3 triangles (mean value: 1.366 Å) than in BO_4 tetrahedra (mean value: 1.467 Å). Figure 1 shows the octoborate anion that exists in this compound; it is formed by a triborate group (B_3O_7) constituted by two BO_3 triangles (B(6) and B(7)) and one BO_4 tetrahedron (B(8)) linked to a pentaborate group (B_5O_{10}), which consists of four BO_3 triangles (B(1), B(2), B(4), and B(5)) and one BO_4 tetrahedron (B(3)). These octoborate anions are linked together to form two symmetrically related independent networks (Fig. 2). Following the crystal chemical classification of borates proposed by Christ and Clark (17) and Heller (18), the shorthand notation of this complex

TABLE 2
Final Atomic Coordinates and Equivalent Isotropic Displacement Parameters U_{eq} (Å^2) of β-$Na_2B_8O_{13}$ with e.s.d.'s in Parentheses

Atoms	Occ.	x	y	z	U_{eq}[a]
O(1)	1.0	−0.0286(1)	0.2826(2)	0.4854(1)	0.023(1)
O(2)	1.0	0.1151(1)	0.0824(2)	0.5562(1)	0.022(1)
O(3)	1.0	0.2646(1)	−0.1145(2)	0.6314(1)	0.023(1)
O(4)	1.0	0.2326(1)	−0.0309(2)	0.4120(1)	0.024(1)
O(5)	1.0	0.0886(1)	0.1807(2)	0.3365(1)	0.027(1)
O(6)	1.0	0.2492(1)	0.1294(2)	0.2237(1)	0.022(1)
O(7)	1.0	0.1776(1)	−0.0235(2)	0.0302(1)	0.024(1)
O(8)	1.0	0.5820(1)	0.2492(2)	−0.2706(1)	0.021(1)
O(9)	1.0	0.0935(1)	−0.0762(2)	0.2183(1)	0.027(1)
O(10)	1.0	0.3428(1)	0.1514(2)	0.0413(1)	0.024(1)
O(11)	1.0	0.4679(1)	0.1870(2)	−0.1083(1)	0.022(1)
O(12)	1.0	0.4462(1)	0.0312(2)	−0.3090(1)	0.019(1)
O(13)	1.0	0.3211(1)	−0.0221(2)	−0.1500(1)	0.021(1)
B(1)	1.0	0.0587(2)	0.1819(3)	0.4558(2)	0.019(1)
B(2)	1.0	0.2063(2)	−0.0197(3)	0.5327(2)	0.019(1)
B(3)	1.0	0.1677(2)	0.0520(3)	0.2968(2)	0.022(1)
B(4)	1.0	0.2569(2)	0.0855(3)	0.1012(2)	0.018(1)
B(5)	1.0	0.1002(2)	−0.1079(3)	0.0928(2)	0.020(1)
B(6)	1.0	0.3741(2)	0.1030(3)	−0.0748(2)	0.019(1)
B(7)	1.0	0.4977(2)	0.1573(3)	−0.2319(2)	0.017(1)
B(8)	1.0	0.3644(2)	−0.0868(3)	−0.2661(2)	0.017(1)
Na(1)	0.648(19)	0.1141(2)	0.0011(12)	−0.2157(2)	0.039(1)
Na(2)	0.352(19)	0.1155(5)	−0.0980(30)	−0.1973(7)	0.049(3)
Na(3)	0.498(9)	0.4254(3)	−0.1143(7)	0.4688(2)	0.035(1)
Na(4)	0.502(9)	0.3744(5)	−0.2110(8)	0.4669(2)	0.050(2)

[a] U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

TABLE 3
Anisotropic Displacement Parameters[a] (Å^2) (e.s.d's in Parentheses) for All Atoms of β-$Na_2B_8O_{13}$

Atoms	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O(1)	0.027(1)	0.032(1)	0.013(1)	0.000(1)	0.007(1)	0.006(1)
O(2)	0.025(1)	0.033(1)	0.009(1)	0.001(1)	0.005(1)	0.006(1)
O(3)	0.026(1)	0.027(1)	0.015(1)	0.002(1)	−0.003(1)	−0.002(1)
O(4)	0.026(1)	0.034(1)	0.012(1)	0.002(1)	0.006(1)	0.008(1)
O(5)	0.032(1)	0.038(1)	0.012(1)	0.005(1)	0.010(1)	0.012(1)
O(6)	0.028(1)	0.030(1)	0.010(1)	−0.004(1)	0.008(1)	−0.003(1)
O(7)	0.030(1)	0.031(1)	0.013(1)	−0.003(1)	0.009(1)	−0.010(1)
O(8)	0.024(1)	0.024(1)	0.015(1)	−0.004(1)	0.007(1)	−0.005(1)
O(9)	0.030(1)	0.041(1)	0.011(1)	−0.001(1)	0.008(1)	−0.008(1)
O(10)	0.028(1)	0.033(1)	0.014(1)	−0.008(1)	0.010(1)	−0.007(1)
O(11)	0.024(1)	0.032(1)	0.011(1)	−0.005(1)	0.007(1)	−0.006(1)
O(12)	0.024(1)	0.023(1)	0.011(1)	−0.001(1)	0.006(1)	−0.003(1)
O(13)	0.023(1)	0.026(1)	0.015(1)	−0.007(1)	0.009(1)	−0.004(1)
B(1)	0.022(1)	0.025(1)	0.012(1)	−0.000(1)	0.005(1)	0.000(1)
B(2)	0.020(1)	0.024(1)	0.011(1)	−0.002(1)	0.001(1)	−0.003(1)
B(3)	0.024(1)	0.033(1)	0.009(1)	0.001(1)	0.005(1)	0.004(1)
B(4)	0.024(1)	0.022(1)	0.009(1)	−0.000(1)	0.005(1)	0.002(1)
B(5)	0.023(1)	0.026(1)	0.011(1)	0.001(1)	0.005(1)	−0.001(1)
B(6)	0.021(1)	0.024(1)	0.011(1)	−0.002(1)	0.004(1)	−0.001(1)
B(7)	0.020(1)	0.020(1)	0.012(1)	0.000(1)	0.003(1)	0.002(1)
B(8)	0.022(1)	0.019(1)	0.010(1)	−0.002(1)	0.004(1)	0.002(1)
Na(1)	0.029(1)	0.071(4)	0.018(1)	−0.011(1)	0.005(1)	0.002(1)
Na(2)	0.037(2)	0.083(9)	0.028(2)	−0.022(3)	0.010(2)	−0.013(3)
Na(3)	0.037(2)	0.055(2)	0.012(1)	0.000(1)	0.005(1)	0.017(2)
Na(4)	0.070(3)	0.067(3)	0.013(1)	−0.002(1)	0.003(1)	0.042(3)

[a] The form of the anisotropic displacement factor is $\exp[-2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2hka^*b^*U_{12} + 2hla^*c^*U_{13} + 2klb^*c^*U_{23})]$.

TABLE 4
Interatomic Distances (Å) and Angles (deg) in β-$Na_2B_8O_{13}$

BO_3 triangles			
B(1)–O(5)	1.348(3)	O(5)–B(1)–O(1)	122.3(2)
–O(1)	1.371(3)	O(5)–B(1)–O(2)	121.8(2)
–O(2)	1.382(2)	O(1)–B(1)–O(2)	116.0(2)
〈B(1)–O〉	1.367(3)	〈O–B(1)–O〉	120.0(2)
B(2)–O(4)	1.347(3)	O(4)–B(2)–O(3)	120.3(2)
–O(3)	1.356(2)	O(4)–B(2)–O(2)	120.5(2)
–O(2)	1.394(3)	O(3)–B(2)–O(2)	119.1(2)
〈B(2)–O〉	1.366(3)	〈O–B(2)–O〉	120.0(2)
B(4)–O(6)	1.340(3)	O(6)–B(4)–O(10)	120.6(2)
–O(10)	1.375(3)	O(6)–B(4)–O(7)	121.3(2)
–O(7)	1.383(3)	O(10)–B(4)–O(7)	118.1(2)
〈B(4)–O〉	1.366(3)	〈O–B(4)–O〉	120.0(2)
B(5)–O(9)	1.346(3)	O(9)–B(5)–O(1)[a]	124.1(2)
–O(1)[a]	1.370(3)	O(9)–B(5)–O(7)	121.6(2)
–O(7)	1.376(3)	O(1)[a]–B(5)–O(7)	114.2(2)
〈B(5)–O〉	1.364(3)	〈O–B(5)–O〉	120.0(2)
B(6)–O(13)	1.343(3)	O(13)–B(6)–O(10)	123.3(2)
–O(10)	1.375(3)	O(13)–B(6)–O(11)	121.0(2)
–O(11)	1.379(2)	O(10)–B(6)–O(11)	115.7(2)
〈B(6)–O〉	1.366(3)	〈O–B(6)–O〉	120.0(2)
B(7)–O(8)	1.343(3)	O(8)–B(7)–O(12)	119.7(2)
–O(12)	1.352(3)	O(8)–B(7)–O(11)	119.7(2)
–O(11)	1.410(3)	O(12)–B(7)–O(11)	120.6(1)
〈B(7)–O〉	1.368(3)	〈O–B(7)–O〉	120.0(2)
BO_4 tetrahedra			
B(3)–O(6)	1.454(3)	O(6)–B(3)–O(4)	108.7(1)
–O(4)	1.459(3)	O(6)–B(3)–O(5)	111.0(1)
–O(5)	1.480(3)	O(6)–B(3)–O(9)	111.9(1)
–O(9)	1.484(3)	O(4)–B(3)–O(5)	109.9(1)
〈B(3)–O〉	1.469(3)	O(4)–B(3)–O(9)	108.8(1)
		O(5)–B(3)–O(9)	106.4(1)
		〈O–B(3)–O〉	109.4(1)
B(8)–O(3)[b]	1.459(2)	O(3)[b]–B(8)–O(8)[c]	108.4(1)
–O(8)[c]	1.459(3)	O(3)[b]–B(8)–O(12)	111.0(1)
–O(12)	1.461(3)	O(3)[b]–B(8)–O(13)	107.8(1)
–O(13)	1.480(3)	O(8)[c]–B(8)–O(12)	111.5(1)
〈B(8)–O〉	1.465(3)	O(8)[c]–B(8)–O(13)	106.5(1)
		O(12)–B(8)–O(13)	111.5(1)
		〈O–B(8)–O〉	109.4(1)
Environment of sodium atoms (<3.2 Å)			
Na(1)–O(13)	2.415(3)	Na(2)–O(7)	2.427(9)
–O(2)[b]	2.461(4)	–O(13)	2.451(7)
–O(9)[d]	2.501(4)	–O(5)[d]	2.659(7)
–O(7)	2.547(3)	–O(3)[b]	2.707(7)
–O(5)[e]	2.594(9)	–O(9)[f]	2.711(20)
–O(3)[b]	2.729(4)	–O(1)[a]	2.750(10)
–O(5)[d]	2.874(5)	–O(9)[d]	2.786(11)
		–O(2)[b]	2.933(12)
−B(2)[b]	3.006(4)		
		−B(5)	3.056(8)

association of BO_3 triangles (Δ) and BO_4 tetrahedra (T) can be written with the fundamental building block (FBB): 8: ∞^3 [(5 : 4Δ + T) + (3 : 2Δ + T)]. It is worth comparing this structure with the structure of previously reported octoborates, especially α-$Na_2B_8O_{13}$ (11, 12) and $Ag_2B_8O_{13}$ or better $(Ag_{0.6}Na_{0.4})_2B_8O_{13}$(14),[2] whose crystal data are reported in Table 5. All these borates contain the same complex borate anion, but some differences exist between them. Figure 3 reports the linkage of the octoborate anions found in the three compounds. In $Ag_2B_8O_{13}$, this is a BO_4 tetrahedron of the triborate group that is linked to a BO_3 triangle of the pentaborate group to form the octoborate anion (Fig. 3c). In the two forms of $Na_2B_8O_{13}$ (Figs. 3a and 3b), the linkage is made by two BO_3 triangles belonging to the triborate and the pentaborate groups of a same octoborate anion.

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[2] The structure was solved (14) for the mixed silver sodium borate $(Ag_{0.6}Na_{0.4})_2B_8O_{13}$ with a reliability factor of $R = 11\%$, and extended to the isostructural compound $Ag_2B_8O_{13}$; in the discussion only this last compound will be considered.

TABLE 4—*Continued*

BO_3 triangles			
Na(3)–O(8)^g	2.309(3)	Na(4)–O(4)	2.186(6)
–O(4)	2.332(4)	–O(8)^g	2.211(3)
–O(11)^h	2.345(4)	–O(11)^h	2.302(5)
–O(12)^g	2.515(4)	–O(3)	2.434(5)
–O(12)^i	2.556(3)	–O(13)^j	2.456(6)
–O(3)	2.743(4)		
–B(7)^g	2.788(3)	–B(2)	2.663(6)

Note. Symmetry code: $^a -x, y-\frac{1}{2}, \frac{1}{2}-z$; $^b x, y, z-1$; $^c 1-x, y-\frac{1}{2}, -z-\frac{1}{2}$; $^d -x, -y, -z$; $^e x, \frac{1}{2}-y, z-\frac{1}{2}$; $^f x, -y-\frac{1}{2}, z-\frac{1}{2}$; $^g 1-x, -y, -z$; $^h 1-x, y-\frac{1}{2}, \frac{1}{2}-z$; $^i x, y, 1+z$; $^j x, -y-\frac{1}{2}, \frac{1}{2}+z$.

In α-$Na_2B_8O_{13}$ (Fig. 3b), the pentaborate group of the octoborate anion is linked to three triborate groups belonging to other octoborate anions while the triborate group of the considered octoborate anion is linked to three pentaborate groups of other octoborate anions. In $Ag_2B_8O_{13}$ and in β-$Na_2B_8O_{13}$, the pentaborate group of the octoborate anion is linked to one triborate and two pentaborate groups belonging to other octoborate anions while the triborate group of the considered octoborate anion is linked to one pentaborate and two triborate groups of other octoborate anions. However, in β-$Na_2B_8O_{13}$, the groups are alternated, and the structure seems more symmetrical.

There is a controversy about $Li_2B_8O_{13}$ that was characterized by its unit-cell parameters only:

- Song and Huang (1991) (19):$a = 15.506$ Å; $b = 5.723$ Å; $c = 7.521$ Å; $V = 1134$ Å^3.
- Bétourné and Touboul (1997) (20) (indexed powder pattern supplied):$a = 17.764$ Å; $b = 7.789$ Å; $c = 9.667$ Å; $\beta = 100.95°$; $V = 1312$ Å^3.

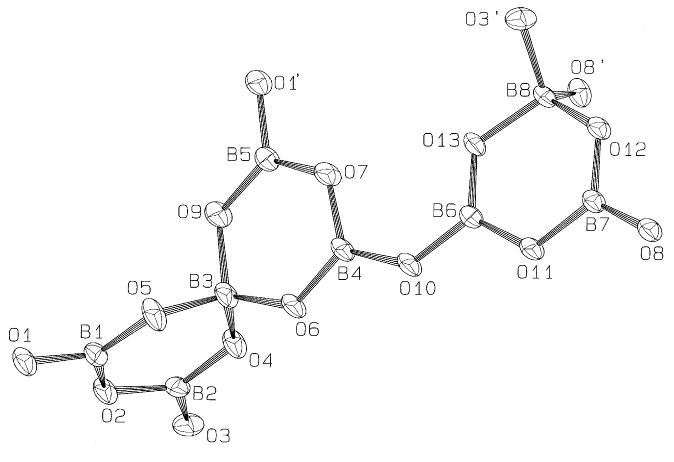

FIG. 1. Representation of the $(B_8O_{13})^{2-}$ borate anion constituted by the association of a (B_5O_{10}) pentaborate group with a (B_3O_7) triborate group.

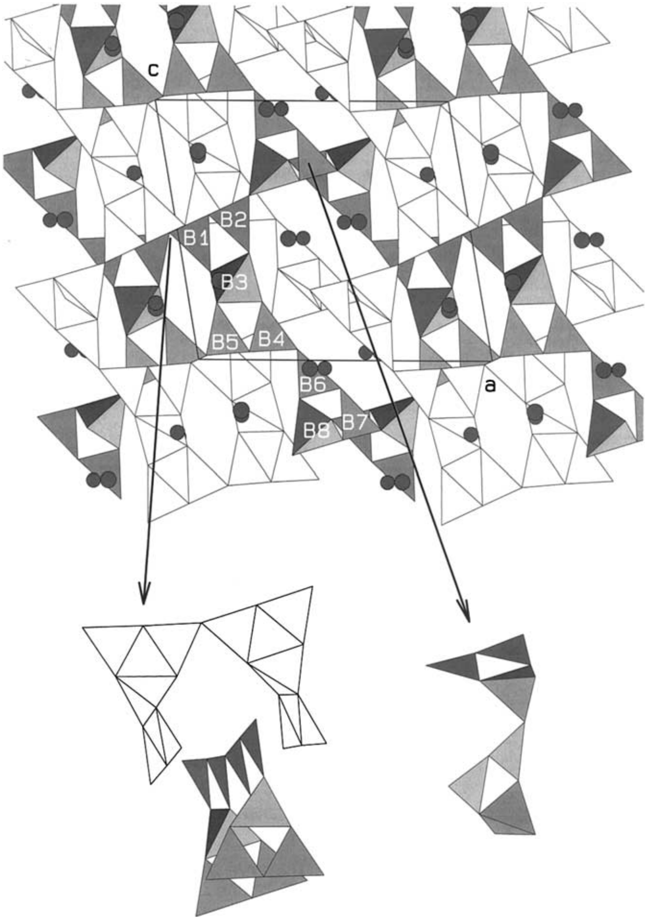

FIG. 2. Projection on (*a*,*c*) plane of the structure of β-$Na_2B_8O_{13}$; black circles are sodium atoms. The dark and light three-dimensional network of BO_3 and BO_4 polyhedra have no oxygen atoms in common. The projection creates some optical misunderstanding of the connectivity. At lower left, the pentaborate groups (near $x = 0$; $z = 0.5$) are shown after a rotation of about 60° to point out the non-connectivity. At lower right, the triborate groups (near $x = 0.5, z = 0.75$) are represented after a rotation of 90° (*b*-axis vertical) to better view the linkage.

- Mathews *et al.* (1998) (21):$a = 8.619$ Å; $b = 8.756$ Å; $c = 7.151$ Å; $\alpha = 95.38°$; $\beta = 90.06°$; $\gamma = 92.32°$; $V = 537$ Å^3.
- Mathews *et al.* (1998) (22):$a = 4.584$ Å; $b = 11.07$ Å; $c = 22.44$ Å; $\beta = 114.05°$; $V = 1040$ Å^3.

No other octoborates were known with alkaline or pseudo-alkaline elements (*M*). However, compounds with a B/*M* ratio close to 4 were reported: isotypes $K_5B_{19}O_{31}$ (23) and $Rb_5B_{19}O_{31}$ (24) with B/*M* = 3.8 and $Cs_3B_{13}O_{21}$ (25) with B/Cs = 4.33. Their structures contain complex FBBs: 19: ∞^3 $2[(5:4\Delta+T)+(3:2\Delta+T)+(\Delta)+0.5(T)]$ for the first and 26: ∞^2 $[2\times(5:4\Delta+T)+4\times(3:2\Delta+T)+4\times(\Delta)]$ for $Cs_3B_{13}O_{21}$. It is interesting to note that all these compounds, including the sodium and silver octoborates,

TABLE 5
Crystallographic Data of $M_2B_8O_{13}$ Compounds

Formula	Parameters (Å, deg) ; V (Å^3); Z; D_x (g/cm^3)	S.G.	Ref.
α-$Na_2B_8O_{13}$	$a = 6.507, b = 17.796, c = 8.377, \beta = 96.57;\ V = 964;\ Z = 4;\ D_x = 2.32$	$P2_1/a$	(12)
β-$Na_2B_8O_{13}$	$a = 11.731(4), b = 7.880(3), c = 10.410(4), \beta = 99.883(6);\ V = 948;\ Z = 4;\ D_x = 2.385$	$P2_1/c$	This work
$Ag_2B_8O_{13}$	$a = 6.550, b = 8.671, c = 17.511, \beta = 90.18;\ V = 995;\ Z = 4;\ D_x = 3.41$	$P2_1/c$	(14)
$(Ag_{0.6}Na_{0.4})_2B_8O_{13}$	$a = 6.521, b = 8.624, c = 17.549, \beta = 90.20;\ V = 987;\ Z = 4;\ D_x = 2.98$	$P2_1/c$	(14)

are built from the same smallest borate anions with five and three boron atoms.

3.2. *Sodium Atom Environments*

The sodium atoms are located in four crystallographically independent positions, with occupancies of 0.65 (Na(1)), 0.35 (Na(2)), 0.5 (Na(3)) and 0.5 (Na(4)), respectively. This arrangement is different from that encountered in α-$Na_2B_8O_{13}$ (11, 12) and $Ag_2B_8O_{13}$ (14), in which the two M atoms (M = Na, Ag) occupy two crystallographically independent positions. In β-$Na_2B_8O_{13}$, the four crystallographically independent sodium atoms have different oxygen environments (Table 4), which are not regular. The Na–O distances show a considerable variation, ranging from 2.186(6) Å for Na(4)–O(4) to 2.933(12) Å for Na(2)–O(2). These values are close to those found in α-$Na_2B_8O_{13}$ (2.259–2.926 Å, coordination numbers eight for Na(1) and seven for Na(2)), and the calculated (26) bond-valence sums around sodium atoms are comparable in the two compounds. The shorter Na–O distance (2.186 Å) found in the studied compound is unusual; however, slightly shorter Na–O distances (2.178 and 2.171 Å) were reported in the borophosphate $Na_2[(BP_2O_7(OH)]$ (27). In the two forms of octoborate, the sodium atoms hold the two independent networks together.

3.3. *Powder Patterns*

First reflections of the calculated powder pattern of the studied compound are reported in the Table 6. The 2θ values are in good agreement with those given by Bouaziz (13) for a modification of a sodium octoborate (PDF No. 16-0199); this form, metastable, has been noted β in this paper. The indexed powder pattern (12) (PDF No. 20-0257) of the stable form of the sodium octoborate, noted α,

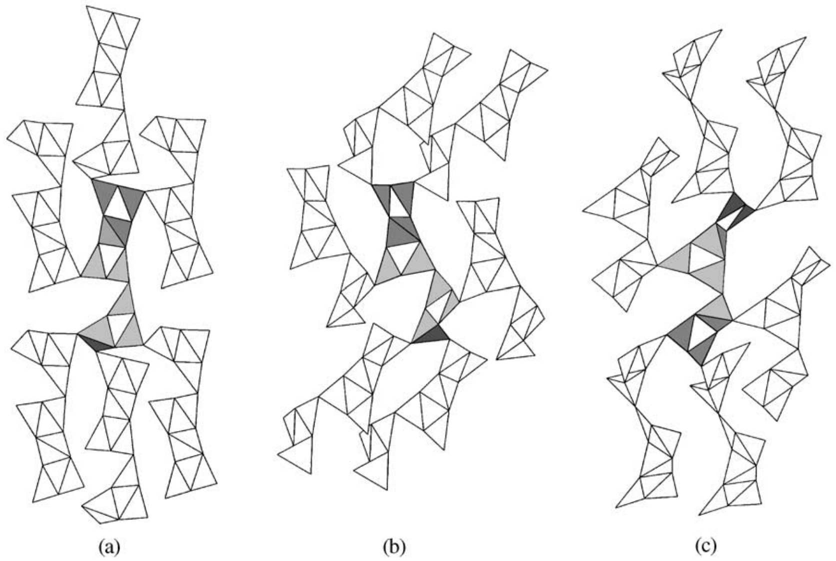

FIG. 3. Representation of the interlinking of the octoborate anions found in (a) β-$Na_2B_8O_{13}$, (b) α-$Na_2B_8O_{13}$, and (c) $Ag_2B_8O_{13}$.

TABLE 6
Powder Diffraction Patterns of β-$Na_2B_8O_{13}$

2θ (deg)[a]	Int.[a]	*hkl*	2θ (deg)[b]	Int.[b]
15.386	1	11−1		
17.662	5	10−2	17.723	10
19.029	5	210	18.987	10
19.789	23	21−1	19.756	80
20.097	2	102	19.935	30
20.648	8	012	20.493	20
20.973	4	11−2	20.883	30
			21.289	30
21.998	18	211	21.818	80
22.547	15	020	22.375	80
23.068	3	300	22.961	60
23.073	2	112		
23.840	7	120	23.578	60
23.940	1	21−2		
24.178	3	021	24.097	30
25.097	3	202		
25.719	2	310	25.575	60
25.847	13	121	25.954	60
27.374	37	220	27.248	100
27.566	10	212	27.856	60
27.918	3	22−1		
28.437	13	311	28.307	80
28.546	3	022		
28.786	2	12−2		
29.556	100	221	29.256	100
			30.062	10
30.666	2	113		
30.924	3	400		
31.058	3	22−2		
31.318	10	302	31.247	10
32.477	10	320	32.290	80
32.581	16	32−1		
32.732	1	4−11	32.900	30
33.365	5	312		
33.988	6	222	33.795	30
34.477	3	10−4		
34.712	3	023		
34.804	1	41−2		
34.966	5	004		
35.539	1	411	35.522	80
35.763	15	20−4		
36.446	6	131	36.265	60
37.582	3	230	37.359	30

[a] Calculated from our structural data.

[b] Reported in the PDF database, file no. 16-0199 (13).

corresponds to the non-indexed pattern reported by Bouaziz (13) (PDF No. 16-0306).

4. CONCLUSIONS

The structure of a new form of sodium octoborate, β-$Na_2B_8O_{13}$, was resolved from single crystals obtained during an attempt to synthesize a sodium borophosphate. We note that the compounds α-$Na_2B_8O_{13}$, β-$Na_2B_8O_{13}$ and $Ag_2B_8O_{13}$ contain the same polyborate anion, but have different unit-cell parameters; this is probably due to the difference between the association of the (B_5O_{10}) and (B_3O_7) groups and the linkage between octoborate anions.

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