Journal of Solid State Chemistry **161,** 205–213 (2001)
doi:10.1006/jssc.2001.9297, available online at http://www.idealibrary.com on IDEAL®

Crystal Structures of Three MB_5O_8 (M = Cs, Rb) Borates (α-CsB_5O_8, γ-CsB_5O_8, and β-RbB_5O_8)

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Received April 24, 2001; in revised form July 3, 2001; accepted July 12, 2001

Crystal structures of α-CsB_5O_8, γ-CsB_5O_8, and β-RbB_5O_8 have been determined from single-crystal X-ray diffraction data. α-CsB_5O_8 crystallizes in the monoclinic space group $P2_1/n$ with the following parameters: $a = 7.117(2)$ Å, $b = 9.634(3)$ Å, $c = 10.391(4)$ Å, $\beta = 101.160(4)°$; $Z = 4$; the structure was refined from 1392 reflections until $R_1 = 0.0489$. γ-CsB_5O_8 and β-RbB_5O_8 have been found to be isostructural with α-KB_5O_8 and β-KB_5O_8 (and TlB_5O_8), respectively. They crystallize with eight formula units in the *Pbca* space group. Unit cell parameters are $a = 8.697(3)$ Å, $b = 8.431(2)$ Å, $c = 21.410(6)$ Å for γ-CsB_5O_8 and $a = 7.553(2)$ Å, $b = 11.857(3)$ Å, $c = 14.813(4)$ Å for β-RbB_5O_8; their structures were refined from 1085 reflections until $R_1 = 0.0712$, and from 1271 reflections until $R_1 = 0.0290$, respectively. The structures of these compounds can be described on the basis of a new two- (α-CsB_5O_8) and three-dimensional (γ-CsB_5O_8, β-RbB_5O_8) network of pentaborate units $[B_5O_8]^-$; these units are formed by two B_3O_3 cycles linked by a boron atom, which contain two groups of two BO_3 triangles (Δ) on each side of a BO_4 tetrahedron (T); their shorthand notations are 5: ∞^2 (4Δ+T) for α-CsB_5O_8 and 5: ∞^3(4Δ+T) for γ-CsB_5O_8 and β-RbB_5O_8. Distortions of the $[B_5O_8]^-$ units found in these compounds are presented. © 2001 Academic Press

INTRODUCTION

Since the 1960s, the crystal structures of some MB_5O_8 compounds (M = K, Cs, Rb, Tl) have been studied. The known crystallographic data of these pentaborates are summarized in Table 1. In 1959, Krogh-Moe reported for the first time the existence of three KB_5O_8 polymorphs (1, 2) and later on resolved the structure of two of them, β-KB_5O_8 (3) and α-KB_5O_8 (4); the latter was simply characterized by its unit cell parameters (5) but since has been identified as the complex $K_5B_{19}O_{31}$ borate (6).

In 1966, Kocher showed the existence of three forms of RbB_5O_8 (7, 8), underlining the similarity between the potassium and rubidium pentaborates. Indeed, she reported that β-RbB_5O_8 was isostructural to β-KB_5O_8 (3). That was recently confirmed by Krzhizhanovskaya *et al.* (9) who solved the structure of β-RbB_5O_8 from X-ray powder diffraction data, using the crystallographic data of β-KB_5O_8. Recently, Touboul and Nowogrocki (10) solved the structure of TlB_5O_8 from single-crystal X-ray diffraction data, and showed that this compound was also isostructural to β-KB_5O_8 (3). In 1999, Bubnova *et al.* (11), describing the MB_5O_8 crystalline modifications (M = K, Rb), confirmed the similarity between these borates. These authors found that α-RbB_5O_8 was isostructural to α-KB_5O_8 (4) (see Table 1).

Concerning the Cs_2O–B_2O_3 binary system, Krogh-Moe (12, 13) reported the space group, the unit cell parameters, and the atomic coordinates of cesium atoms in CsB_5O_8. Later, Kocher (7, 8) showed the existence of three modifications of CsB_5O_8, and identified the form described by Krogh-Moe as being the high-temperature form (α) (see Table 1).

All the MB_5O_8 compounds (M = K, Rb, Tl) (3, 4, 9, 10) whose structures are known contain a three-dimensional network of $[B_5O_8]^-$ pentaborate groups which are formed by one tetrahedrally coordinated boron atom and four triangularly coordinated boron atoms.

In this paper, we will describe for the first time the structure of two of the three forms of CsB_5O_8 (α and γ) that involves, for the α form, the description of a new two-dimensional network of pentaborate groups $[B_5O_8]^-$. For the β-CsB_5O_8 form, a structural study carried out on X-ray powder diffraction showed that β-CsB_5O_8 is isostructural to β-KB_5O_8 (3), TlB_5O_8 (10), and β-RbB_5O_8 (9). Attempts to prepare single crystals of β-CsB_5O_8 remained unfruitful. Finally, we confirmed, by a single-crystal X-ray diffraction study, the results published for the β-RbB_5O_8 structure coming from X-ray powder diffraction data (9).

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TABLE 1
Crystallographic Data of MB_5O_8 (M = K, Rb, Cs, Tl)

	α-KB_5O_8	β-KB_5O_8	α-RbB_5O_8	β-RbB_5O_8	TlB_5O_8	α-CsB_5O_8
Formula weight (g/mol)	221.419		267.517		386.417	314.952
Space group	*Pbca*	*Pbca*	*Pbca*	*Pbca*	*Pbca*	$P2_1/a$
a (Å)	8.383	7.418	8.563	7.550	7.557	11.32
b (Å)	8.418	11.702	8.515	11.842	11.925	9.54
c (Å)	21.540	14.745	21.432	14.805	14.734	7.12
β(°)	—	—	—	—	—	117
V (Å^3)	1520	1280	1563	1324	1328	685
Z	8	8	8	8	8	2
Dx (g/cm^3)	1.93	2.29	2.29	2.68	3.865	—
Method	Single crystal	Single crystal	Powder	Powder	Single crystal	Single crystal
Structure resolved	Yes	Yes	No	Yes	Yes	No
References	(4)	(3)	(11)	(9)	(10)	(13)

EXPERIMENTAL

Synthesis

As for the study of other alkaline or pseudo-alkaline borates, for example β-$Tl_2B_4O_7$ (14), the anhydrous pentaborates were prepared by dehydration of their hydrated precursors which are easy to synthesize. The hydrated cesium and rubidium pentaborates $M[B_5O_6(OH)_4]\cdot 2H_2O$ (M = Cs, Rb) were obtained from an aqueous solution of dissolved M_2CO_3 (M = Cs, Rb) and H_3BO_3 in

TABLE 2
Crystal Data and Intensity Collection Conditions for γ-CsB_5O_8, α-CsB_5O_8, and β-RbB_5O_8

	γ-CsB_5O_8	α-CsB_5O_8	β-RbB_5O_8
Formula weight (g/mol)	314.96		267.52
Crystal system	Orthorhombic	Monoclinic	Orthorhombic
Space group	*Pbca*	$P2_1/n$	*Pbca*
Unit cell parameters (Å, °)	$a = 8.697(3)$ $b = 8.431(2)$ $c = 21.410(6)$	$a = 7.117(2)$ $b = 9.634(3)$ $c = 10.391(4)$ $\beta = 101.160(4)$	$a = 7.553(2)$ $b = 11.857(3)$ $c = 14.813(4)$
V (Å^3); Z	1569.8(8); 8	698.9(4); 4	1326.5(7); 8
Density (g/cm^3)	2.665	2.993	2.679
Crystal size (mm^3)	$0.35 \times 0.30 \times 0.20$	$0.45 \times 0.35 \times 0.20$	$0.40 \times 0.25 \times 0.15$
Collection method	φ and ω scans		
Temperature	298 K		
θ range (°)	1.90–30.05	2.91–30.03	2.75–30.01
Range in h, k, l	$-12 \leq h \leq 12$; $-11 \leq k \leq 11$; $-28 \leq l \leq 29$	$-9 \leq h \leq 9$ $-13 \leq k \leq 13$ $-14 \leq l \leq 14$	$-10 \leq h \leq 10$ $-16 \leq k \leq 16$ $-20 \leq l \leq 20$
Absorption coefficient (mm^{-1})	μ(Mo$K\alpha$) = 4.726	μ(Mo$K\alpha$) = 5.307	μ(Mo$K\alpha$) = 7.474
Reflections collected	10,872	6339	11,200
Independent reflections	2056	1881	1864
Independent reflections [$I > 2\sigma(I)$]	1085	1392	1271
R_{int}	0.0695	0.0437	0.0642
Refinement method	Full-matrix least squares on F^2—SHELXL-97 (17)		
Number of variables	127	127	127
Goodness-of-fit on F^2	1.002	0.912	0.871
Final R indices [$I > 2\sigma(I)$]^a	$R_1 = 0.0712$ w$R_2 = 0.1867$	$R_1 = 0.0489$ w$R_2 = 0.1276$	$R_1 = 0.0290$ w$R_2 = 0.0659$
R indices (all data)^a	$R_1 = 0.1384$ w$R_2 = 0.2025$	$R_1 = 0.0716$ w$R_2 = 0.1373$	$R_1 = 0.0497$ w$R_2 = 0.0683$
Largest difference map peak and hole (e.Å^{-3})	2.253 and -0.929	2.783 and -1.496	0.750 and -0.858

[a] $R_1 = \sum||F_o| - |F_c||/|F_o|$. w$R_2 = [\sum(\mathrm{w}(F_o^2 - F_c^2)^2)/\sum(\mathrm{w}F_o^2)^2)]^{1/2}$.

TABLE 3
Final Atomic Coordinates and Equivalent Thermal Isotropic Displacement U_{eq} (Å^2×10^3) with esd's in Parentheses of γ-CsB_5O_8, α-CsB_5O_8, and β-RbB_5O_8

Atoms	x	y	z	U_{eq}[a]
		γ-CsB_5O_8		
Cs	0.8568(1)	0.0336(1)	0.6190(1)	45(1)
O(1)	0.4987(11)	−0.0259(10)	0.6380(4)	51(2)
O(2)	0.5488(8)	0.1877(9)	0.5684(3)	43(2)
O(3)	0.2868(9)	0.1287(13)	0.5989(4)	64(3)
O(4)	0.4675(11)	0.2411(10)	0.6722(3)	56(2)
O(5)	0.8418(8)	0.2503(13)	0.4991(3)	51(2)
O(6)	0.9338(14)	0.0298(10)	0.7576(4)	63(3)
O(7)	1.0869(8)	0.1810(10)	0.5295(3)	47(2)
O(8)	0.5387(12)	−0.2175(13)	0.7132(4)	71(3)
B(1)	0.4470(17)	0.1320(18)	0.6194(6)	52(4)
B(2)	0.7428(14)	0.3126(17)	0.4562(6)	46(4)
B(3)	0.9530(20)	0.1850(20)	0.7687(6)	64(5)
B(4)	0.5009(14)	0.2455(19)	0.5155(5)	41(3)
B(5)	0.9820(20)	−0.0703(19)	0.8017(6)	63(5)
		α-CsB_5O_8		
Cs	0.0825(1)	0.4910(1)	0.7810(1)	23(1)
O(1)	0.5014(7)	0.7206(5)	0.5616(5)	20(1)
O(2)	0.2800(7)	0.8564(5)	0.4095(5)	21(1)
O(3)	0.2990(7)	0.6103(5)	0.3748(5)	23(1)
O(4)	0.1634(7)	0.6921(5)	0.5548(5)	21(1)
O(5)	0.8397(7)	0.7044(5)	0.5764(5)	20(1)
O(6)	0.6314(7)	0.6386(5)	0.3808(5)	24(1)
O(7)	0.0449(9)	1.0164(4)	0.2916(5)	24(1)
O(8)	−0.0512(7)	0.8455(5)	0.4212(5)	25(1)
B(1)	0.3108(12)	0.7193(8)	0.4775(8)	18(2)
B(2)	0.6540(11)	0.6897(7)	0.5084(8)	16(1)
B(3)	−0.0115(11)	0.7460(8)	0.5186(8)	20(2)
B(4)	0.1011(12)	0.9048(8)	0.3715(8)	20(2)
B(5)	0.4530(11)	0.5878(8)	0.3214(8)	18(1)
		β-RbB_5O_8		
Rb	0.0622(1)	0.2105(1)	0.1213(1)	24(1)
O(1)	−0.0727(2)	0.2042(2)	−0.0720(1)	17(1)
O(2)	−0.0952(2)	0.4882(2)	0.0911(1)	18(1)
O(3)	−0.0516(2)	0.1367(2)	0.3281(1)	18(1)
O(4)	0.1379(3)	0.2954(2)	0.3053(1)	17(1)
O(5)	−0.3186(2)	0.1781(2)	0.0639(1)	18(1)
O(6)	0.1978(2)	−0.0281(2)	0.0243(1)	16(1)
O(7)	0.0103(3)	−0.0340(2)	0.1509(1)	17(1)
O(8)	0.1124(3)	0.4433(2)	0.2029(1)	17(1)
B(1)	−0.4496(4)	0.2264(2)	0.1256(2)	14(1)
B(2)	0.0831(4)	0.4011(2)	0.2871(2)	13(1)
B(3)	−0.0937(4)	0.0926(3)	−0.0815(2)	14(1)
B(4)	−0.0225(4)	0.0271(3)	0.3439(2)	16(1)
B(5)	−0.3077(4)	0.0677(3)	0.0438(2)	15(1)

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

stoichiometric proportions; CO_2 being released, its evaporation under constant stirring and heating led to the desired compounds. The latter were characterized by X-ray powder diffraction (Siemens D5000 diffractometer; $\lambda CuK\alpha_1 = 1.54056$ Å). The X-ray powder pattern of $Rb[B_5O_6(OH)_4]\cdot 2H_2O$ is in good agreement with the ICDD cards 75-0693 and 43-0415 (15) whereas that of $Cs[B_5O_6(OH)_4]\cdot 2H_2O$ does not correspond to the single ICDD card with an indexed powder pattern (no. 75-0704) (16). The crystal structure determination of $Cs[B_5O_6(OH)_4]\cdot 2H_2O$ as well as a full study of its dehydration process will be reported in a forthcoming paper. Single crystals of α-CsB_5O_8 and γ-CsB_5O_8 were obtained after dehydration of $Cs[B_5O_6(OH)_4]\cdot 2H_2O$, melting approximately 30°C above the melting temperature (T = 700°C) (7),

TABLE 4
Anisotropic Thermal Vibration Parameters (Å^2×10^3) (esd's in Parentheses) for All the Atoms of γ-CsB_5O_8, α-CsB_5O_8, and β-RbB_5O_8

Atoms	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Cs	45(1)	56(1)	35(1)	9(1)	−6(1)	3(1)
O(1)	70(6)	52(5)	30(4)	−1(4)	4(4)	12(4)
O(2)	30(4)	60(5)	38(4)	12(3)	6(3)	1(4)
O(3)	32(4)	116(8)	43(5)	37(5)	−4(4)	−11(5)
O(4)	91(7)	40(5)	37(4)	2(4)	12(4)	2(4)
O(5)	19(3)	99(7)	36(4)	23(4)	−6(3)	−2(4)
O(6)	116(8)	33(4)	40(5)	0(4)	−28(5)	6(5)
O(7)	22(3)	78(6)	41(4)	21(4)	−4(3)	−11(4)
O(8)	79(7)	91(8)	43(5)	−1(5)	2(5)	17(6)
B(1)	51(9)	49(9)	56(8)	31(7)	−16(7)	−21(7)
B(2)	16(5)	84(12)	37(6)	12(6)	3(5)	−13(6)
B(3)	83(13)	76(13)	32(7)	9(7)	8(7)	−15(10)
B(4)	23(6)	65(10)	35(6)	17(7)	15(5)	2(6)
B(5)	106(14)	54(11)	28(7)	−18(6)	−4(8)	7(9)
			α-CsB_5O_8			
Cs	19(1)	24(1)	24(1)	1(1)	3(1)	0(1)
O(1)	13(2)	22(2)	24(3)	−3(2)	0(2)	1(2)
O(2)	21(3)	20(2)	26(3)	5(2)	11(2)	−2(2)
O(3)	17(2)	25(3)	24(3)	−8(2)	−2(2)	−7(2)
O(4)	19(3)	19(2)	24(3)	7(2)	7(2)	3(2)
O(5)	17(2)	23(2)	19(2)	2(2)	3(2)	−2(2)
O(6)	14(2)	35(3)	24(3)	−13(2)	5(2)	−3(2)
O(7)	42(3)	10(2)	18(2)	5(2)	4(2)	5(2)
O(8)	19(3)	26(3)	31(3)	12(2)	5(2)	2(2)
B(1)	17(4)	17(3)	21(4)	−4(3)	7(3)	−1(3)
B(2)	18(4)	10(3)	21(4)	0(3)	4(3)	1(2)
B(3)	19(4)	14(3)	24(4)	1(3)	−2(3)	−4(3)
B(4)	27(4)	18(3)	15(4)	0(3)	1(3)	−3(3)
B(5)	19(4)	14(3)	19(4)	−3(3)	1(3)	−2(3)
			β-RbB_5O_8			
Rb	30(1)	21(1)	23(1)	−1(1)	−3(1)	−6(1)
O(1)	24(1)	10(1)	19(1)	−2(1)	5(1)	−2(1)
O(2)	24(1)	9(1)	20(1)	1(1)	−6(1)	−1(1)
O(3)	23(1)	11(1)	19(1)	0(1)	−6(1)	1(1)
O(4)	22(1)	11(1)	17(1)	2(1)	3(1)	4(1)
O(5)	23(1)	11(1)	19(1)	−2(1)	8(1)	−2(1)
O(6)	22(1)	11(1)	17(1)	−2(1)	5(1)	1(1)
O(7)	21(1)	11(1)	18(1)	−2(1)	5(1)	−2(1)
O(8)	22(1)	15(1)	15(1)	4(1)	2(1)	3(1)
B(1)	18(1)	10(1)	14(1)	−1(1)	1(1)	2(1)
B(2)	14(2)	11(1)	15(1)	0(1)	−1(1)	−1(1)
B(3)	16(2)	13(1)	13(1)	−1(1)	−1(1)	3(1)
B(4)	16(2)	16(2)	14(1)	−1(1)	2(1)	−2(1)
B(5)	16(2)	13(1)	14(1)	1(1)	−1(1)	0(1)

[a] The form of the anisotropic thermal parameters 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 5
Interatomic Distances (Å) and Angles (°) in γ-CsB_5O_8, α-CsB_5O_8, and β-RbB_5O_8

γ-CsB_5O_8

BO_4 Tetrahedron

B(1)–O(1)	1.46(2)	O(1)–B(1)–O(2)	108(1)
–O(2)	1.48(2)	O(1)–B(1)–O(3)	111(1)
–O(3)	1.46(2)	O(1)–B(1)–O(4)	109(1)
–O(4)	1.47(2)	O(2)–B(1)–O(3)	111(1)
Mean	1.47(2)	O(2)–B(1)–O(4)	107(1)
		O(3)–B(1)–O(4)	111(1)
		Mean	110(1)

BO_3 triangles

B(2)–O(3)$^{(i)}$	1.34(1)	O(3)$^{(i)}$–B(2)–O(5)	124(1)
–O(5)	1.36(1)	O(3)$^{(i)}$–B(2)–O(7)$^{(ii)}$	117(1)
–O(7)$^{(ii)}$	1.39(1)	O(5)–B(2)–O(7)$^{(ii)}$	119(1)
Mean	1.36(1)	Mean	120(1)
B(3)–O(4)$^{(iii)}$	1.36(2)	O(4)$^{(iii)}$–B(3)–O(6)	121(1)
–O(6)	1.34(2)	O(4)$^{(iii)}$–B(3)–O(8)$^{(iv)}$	124(1)
–O(8)$^{(iv)}$	1.45(2)	O(6)–B(3)–O(8)$^{(iv)}$	115(1)
Mean	1.38(2)	Mean	120(1)
B(4)–O(2)	1.30(1)	O(2)–B(4)–O(5)$^{(ii)}$	121(1)
–O(5)$^{(ii)}$	1.42(1)	O(2)–B(4)–O(7)$^{(ii)}$	128(1)
–O(7)$^{(ii)}$	1.37(1)	O(5)$^{(ii)}$–B(4)–O(7)$^{(ii)}$	112(1)
Mean	1.36(1)	Mean	120(1)
B(5)–O(1)$^{(iii)}$	1.35(2)	O(1)$^{(iii)}$–B(5)–O(6)	122(1)
–O(6)	1.33(2)	O(1)$^{(iii)}$–B(5)–O(8)$^{(iii)}$	116(1)
–O(8)$^{(iii)}$	1.37(2)	O(6)–B(5)–O(8)$^{(iii)}$	121(1)
Mean	1.35(2)	Mean	120(1)

Environment of Cesium Atoms (< 4 Å)

Cs–O(7)	3.036(7)	Cs–O(2)	3.168(7)
–O(6)	3.042(8)	–O(1)	3.181(10)
–O(8)$^{(iv)}$	3.048(9)	–O(2)$^{(v)}$	3.217(8)
–O(4)$^{(v)}$	3.117(8)	–B(4)$^{(v)}$	3.512(15)
–O(5)	3.153(8)	Mean Cs–O value	3.120(8)

Symmetry code: (i) $x+\frac{1}{2}, -y+\frac{1}{2}, -z+1$; (ii) $x-\frac{1}{2}, -y+\frac{1}{2}, -z+1$; (iii) $x+\frac{1}{2}, y, -z+\frac{3}{2}$; (iv) $-x+\frac{3}{2}, y+\frac{1}{2}, z$; (v) $-x+\frac{3}{2}, y-\frac{1}{2}, z$.

α-CsB_5O_8

BO_4 Tetrahedron

B(1)–O(1)	1.464(10)	O(1)–B(1)–O(2)	108.0(5)
–O(2)	1.495(9)	O(1)–B(1)–O(3)	110.6(6)
–O(3)	1.488(9)	O(1)–B(1)–O(4)	110.7(6)
–O(4)	1.463(9)	O(2)–B(1)–O(3)	107.6(6)
Mean	1.476(9)	O(2)–B(1)–O(4)	111.3(6)
		O(3)–B(1)–O(4)	108.7(6)
		Mean	109.5(6)

BO_3 triangles

B(2)–O(1)	1.344(9)	O(1)–B(2)–O(5)	122.4(7)
–O(5)	1.380(9)	O(1)–B(2)–O(6)	121.0(7)
–O(6)	1.393(9)	O(5)–B(2)–O(6)	116.5(6)
Mean	1.372(9)	Mean	120.0(7)
B(3)–O(4)	1.334(9)	O(4)–B(3)–O(5)$^{(i)}$	121.3(7)
–O(5)$^{(i)}$	1.374(9)	O(4)–B(3)–O(8)	121.6(6)
–O(8)	1.383(9)	O(5)$^{(i)}$–B(3)–O(8)	117.2(6)
Mean	1.363(9)	Mean	120.0(6)

TABLE 5—*Continued*

BO_3 triangles

B(4)–O(2)	1.341(10)	O(2)–B(4)–O(7)	126.9(7)
–O(7)	1.370(9)	O(2)–B(4)–O(8)	120.3(6)
–O(8)	1.409(9)	O(7)–B(4)–O(8)	112.7(7)
Mean	1.373(9)	Mean	120.0(7)
B(5)–O(3)	1.338(9)	O(3)–B(5)–O(6)	120.7(6)
–O(6)	1.389(9)	O(3)–B(5)–O(7)$^{(ii)}$	125.8(7)
–O(7)$^{(ii)}$	1.363(9)	O(6)–B(5)–O(7)$^{(ii)}$	113.5(6)
Mean	1.363(9)	Mean	120.0(6)

Environment of Cesium Atoms (< 4 Å)

Cs–O(3)$^{(iii)}$	3.040(5)	Cs–O(5)$^{(i)}$	3.211(5)
–O(2)$^{(iv)}$	3.113(4)	–O(7)$^{(vi)}$	3.272(6)
–O(6)$^{(v)}$	3.140(5)	–O(2)$^{(vii)}$	3.429(5)
–O(8)$^{(vi)}$	3.151(5)	–B(1)$^{(vii)}$	3.603(8)
–O(4)	3.183(5)	Mean Cs–O value	3.192(5)
–O(1)$^{(vii)}$	3.193(5)		

Symmetry code: (i) $x-1, y, z$; (ii) $-x+\frac{1}{2}, y-\frac{1}{2}, -z+\frac{1}{2}$; (iii) $-x, -y+1, -z+1$; (iv) $x-\frac{1}{2}, -y+\frac{3}{2}, z+\frac{1}{2}$; (v) $-x+1, -y+1, -z+1$; (vi) $x+\frac{1}{2}, -y+\frac{3}{2}, z+\frac{1}{2}$; (vii) $-x+\frac{1}{2}, y-\frac{1}{2}, -z+\frac{3}{2}$.

β-RbB_5O_8

BO_4 tetrahedron

B(1)–O(1)$^{(i)}$	1.474(3)	O(1)$^{(i)}$–B(1)–O(3)$^{(ii)}$	108.8(2)
–O(3)$^{(ii)}$	1.481(3)	O(1)$^{(i)}$–B(1)–O(4)$^{(ii)}$	110.4(2)
–O(4)$^{(ii)}$	1.467(3)	O(1)$^{(i)}$–B(1)–O(5)	107.9(2)
–O(5)	1.464(3)	O(3)$^{(ii)}$–B(1)–O(4)$^{(ii)}$	108.2(2)
Mean	1.476(3)	O(3)$^{(ii)}$–B(1)–O(5)	111.2(2)
		O(4)$^{(ii)}$–B(1)–O(5)	110.4(2)
		Mean	109.5(2)

BO_3 triangles

B(2)–O(4)	1.347(3)	O(4)–B(2)–O(7)$^{(iii)}$	122.6(2)
–O(7)$^{(iii)}$	1.389(3)	O(4)–B(2)–O(8)	118.3(2)
–O(8)	1.362(3)	O(7)$^{(iii)}$–B(2)–O(8)	119.0(2)
Mean	1.366(3)	Mean	120.0(2)
B(3)–O(1)	1.340(3)	O(1)–B(3)–O(6)$^{(iv)}$	123.2(2)
–O(6)$^{(iv)}$	1.386(3)	O(1)–B(3)–O(7)$^{(iv)}$	121.1(2)
–O(7)$^{(iv)}$	1.391(3)	O(6)$^{(iv)}$–B(3)–O(7)$^{(iv)}$	115.7(2)
Mean	1.372(3)	Mean	120.0(2)
B(4)–O(2)$^{(v)}$	1.388(4)	O(2)$^{(v)}$–B(4)–O(3)	123.3(3)
–O(3)	1.339(4)	O(2)$^{(v)}$–B(4)–O(8)$^{(v)}$	114.9(3)
–O(8)$^{(v)}$	1.389(4)	O(3)–B(4)–O(8)$^{(v)}$	121.8(3)
Mean	1.372(4)	Mean	120.0(3)
B(5)–O(2)$^{(vi)}$	1.384(3)	O(2)$^{(vi)}$–B(5)–O(5)	121.2(2)
–O(5)	1.346(4)	O(2)$^{(vi)}$–B(5)–O(6)$^{(iv)}$	117.1(2)
–O(6)$^{(iv)}$	1.387(3)	O(5)–B(5)–O(6)$^{(iv)}$	121.7(2)
Mean	1.372(3)	Mean	120.0(2)

Environment of rubidium atoms (< 3.5 Å)

Rb–O(7)	2.959(2)	Rb–O(3)$^{(viii)}$	3.137(2)
–O(4)	2.961(2)	–O(5)$^{(vii)}$	3.175(2)
–O(5)	3.023(2)	–O(3)	3.300(2)
–O(1)$^{(vii)}$	3.027(2)	–O(6)	3.335(2)
–O(8)	3.037(2)	–B(2)	3.341(3)
–O(1)	3.040(2)	Mean Rb–O value	3.099(2)

Symmetry code: (i) $x-\frac{1}{2}, -y+\frac{1}{2}, -z$; (ii) $x-\frac{1}{2}, y, -z+\frac{1}{2}$; (iii) $-x, y+\frac{1}{2}, -z+\frac{1}{2}$; (iv) $-x, -y, -z$; (v) $-x, y-\frac{1}{2}, -z+\frac{1}{2}$; (vi) $-x-\frac{1}{2}, y-\frac{1}{2}, z$; (vii) $x+\frac{1}{2}, -y+\frac{1}{2}, -z$; (viii) $x+\frac{1}{2}, y, -z+\frac{1}{2}$.

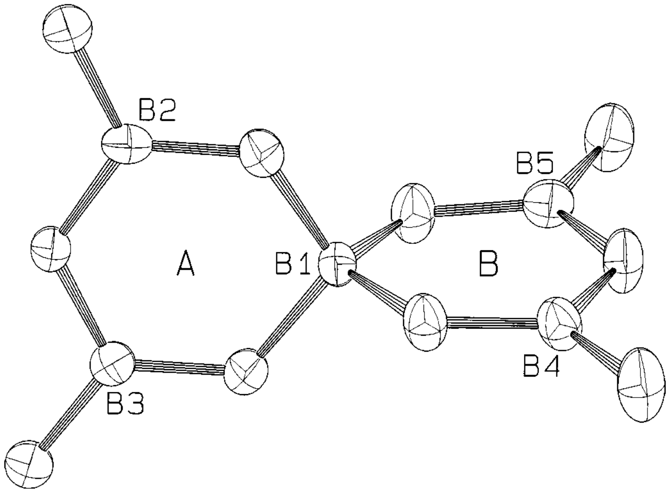

FIG. 1. Representation of the pentaborate unit $[B_5O_8]^-$ constituted by two B_3O_3 cycles linked by a boron atom; the two planes *A* and *B* are formed by two BO_3 triangles.

and cooling to 550°C and 460°C, respectively, at a rate of 10°C/min. Single crystals of β-RbB_5O_8 were obtained after dehydration of $Rb[B_5O_6(OH)_4]\cdot 2H_2O$, melting approximately 30°C above the melting point (7) ($T = 820$°C) and cooling to 550°C at a rate of 10°C/min. In each case, the cooling process was followed by an annealing for 96 h at 550°C (α-CsB_5O_8 and β-RbB_5O_8) or 460°C (γ-CsB_5O_8) and a quenching to room temperature.

Single-Crystal Structure Determination

Colorless single crystals were chosen from the various preparations; their forms are always irregular. The intensity data were collected on a Brucker AXS SMART three-circle diffractometer using 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 2. The positions of all the atoms were obtained using direct methods in the space groups *Pbca* (α-CsB_5O_8, β-RbB_5O_8) and $P2_1/n$ (γ-CsB_5O_8). The structures were refined by full-matrix least-squares techniques using the SHELXTL crystallographic software package (17). Absorption correction was made using the program SADABS (18). In the final cycles, all the positional parameters as well as the anisotropic displacement parameters of all the atoms were refined. The final refinement converged at $R_1 = 0.0712$ and w$R_2 = 0.1867$ using 1085 reflections $[I > 2\sigma(I)]$ for γ-CsB_5O_8; $R_1 = 0.0489$ and w$R_2 = 0.1276$ using 1392 reflections $[I > 2\sigma(I)]$ for α-CsB_5O_8; $R_1 = 0.0290$ and w$R_2 = 0.0659$ using 1271 reflections $[I > 2\sigma(I)]$ for β-RbB_5O_8. The atomic coordinates and the motion parameters are reported in Tables 3 and 4; significant bond lengths and angles are listed in Table 5.

DESCRIPTION OF THE STRUCTURES AND DISCUSSION

Borate Anions

From Table 5, it can be observed that the borate anions existing in these three pentaborates are constituted by BO_3 triangles (Δ) and BO_4 tetrahedra (T) sharing all their vertices. The B–O distances in BO_3 triangles range from 1.30 Å for B(4)–O(2) in γ-CsB_5O_8 to 1.45 Å for B(3)–O(8) in the same borate; in the BO_4 tetrahedra, the B–O distances are between 1.463 Å and 1.495 Å in α-CsB_5O_8 (Table 5). The mean values for B–O bonds are around 1.37(2) Å in the BO_3 triangles and around 1.47(2) Å in the BO_4 tetrahedra; these values are identical to those found in other borates such as α- and β-KB_5O_8 (4, 3), TlB_5O_8 (10), α- and β-RbB_3O_5 (19, 20), CsB_3O_5 (21), and $Rb_2B_4O_7$ (22). With regard to the O–B–O angles, the mean values for BO_3 triangles and BO_4 tetrahedra are almost ideal (Table 5). All the studied compounds are composed of $[B_5O_8]^-$ units, whose isolated scheme is represented in Fig. 1; it is formed by two B_3O_3 cycles linked by a boron atom, and it contains two groups of two BO_3 triangles (*A* and *B* planes) on each side of a BO_4 tetrahedron.

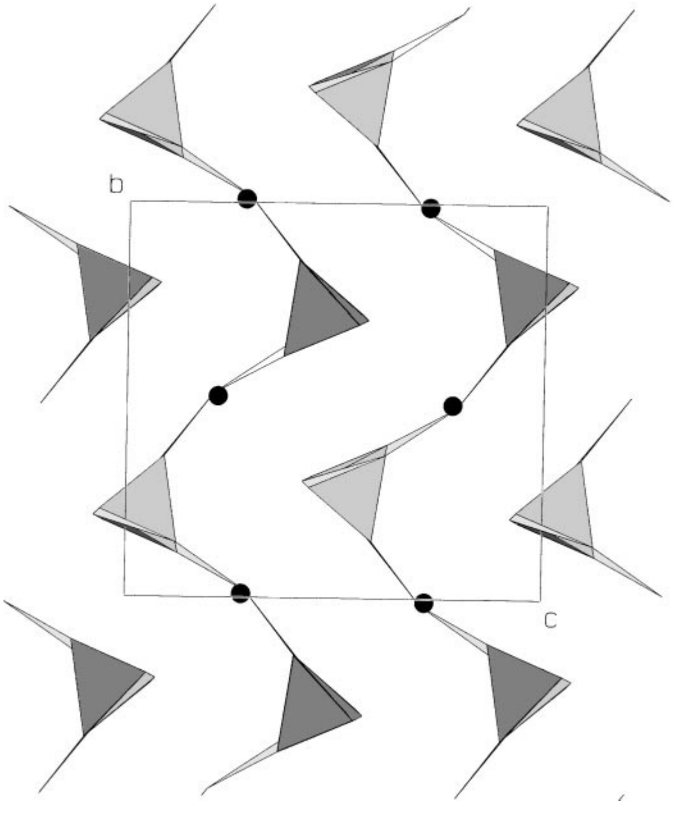

FIG. 2. Polyhedral representation of the structure of α-CsB_5O_8 on the (100) plane showing the infinite corrugated layers along the *c* direction; the black spheres represent cesium atoms.

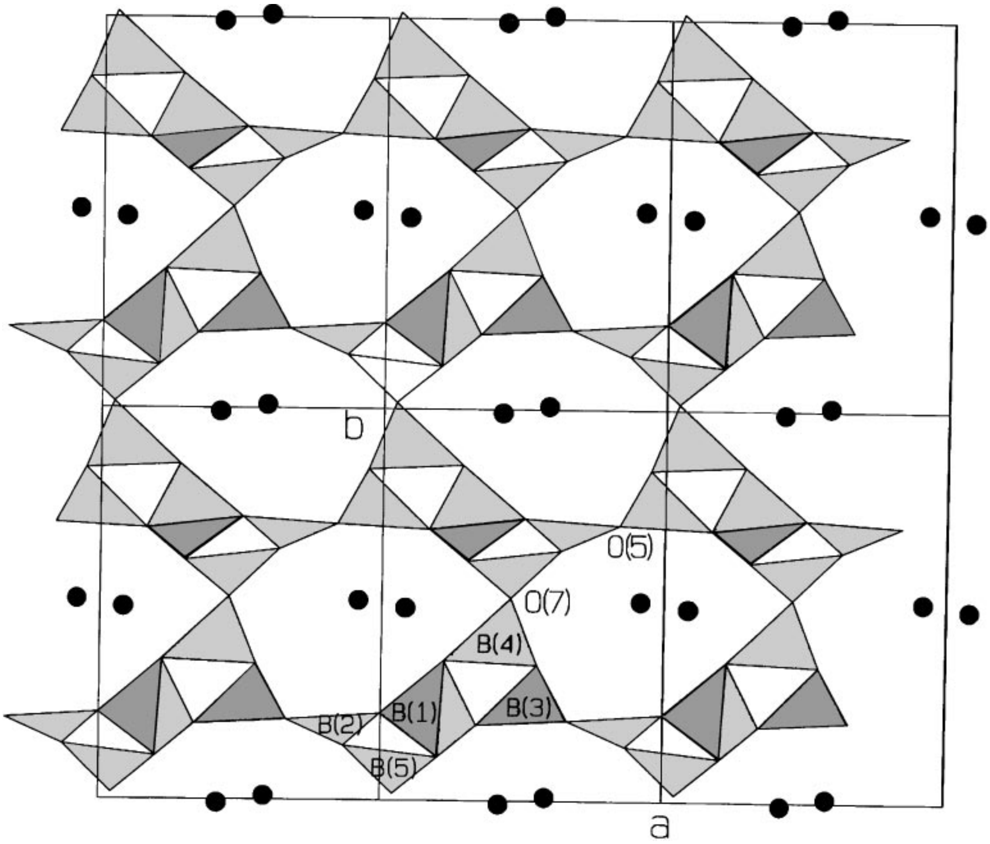

FIG. 3. Polyhedral representation of the structure of α-CsB_5O_8 on the (001) plane showing the connection of the pentaborate groups insured by the two O(5) in the *a* direction and the two O(7) in the *b* direction; for sake of clarity only half the cell content is drawn. The black spheres represent cesium atoms.

α-CsB_5O_8. Figures 2 and 3 give the representation of the α-CsB_5O_8 form in the (*b*, *c*) and (*a*, *b*) plane, respectively. It consists of infinite corrugated layers (Fig. 2) of $[B_5O_8]^-$ pentaborate groups linked to each other by the four external oxygen atoms of the four boron triangles along two different directions (Fig. 3). The connection of the pentaborate groups is insured by the two O(5) oxygen atoms in the *a* direction and by the two O(7) atoms in the *b* direction (Fig. 3) leading to a two-dimensional network in the (*a*, *b*) plane and to large tunnels perpendicular to the corrugated direction, along the *c* direction, in which Cs^+ ions are located (Fig. 3). The shorthand notation of this new borate anion is $5{:}\infty^2(4\Delta + T)$ (23, 24). The infinite corrugated layers are similar to those found in $SrKB_5O_9$ (25) and $CaNaB_5O_9$ (26). However, in these last compounds the layers are constituted of a two-dimensional network of other pentaborate groups $[B_5O_{11}]^{7-}$. The latter is built up from two tetrahedrally coordinated boron atoms and three triangularly coordinated boron atoms leading, in contrast to α-CsB_5O_8, to five terminal oxygen atoms. Four of them are shared with other $[B_5O_{11}]^{7-}$ groups to form a two-dimensional network and one of them remains as the terminal oxygen atom. The shorthand notation for this borate anion is $5{:}\infty^2(3\Delta + 2T)$ (23, 24).

γ-CsB_5O_8. Two projections of the structure of γ-CsB_5O_8 along the *b* and *a* axes are shown in Figs. 4 and 5, respectively. The γ-CsB_5O_8 form, isostructural to α-KB_5O_8 (4), differs from the α-CsB_5O_8 form in the mutual arrangement of the pentaborate groups, which in this compound leads to a three-dimensional network. The pentaborate groups $[B_5O_8]^-$ are connected through two groups of external oxygen atoms, O(7) and O(8), located on opposite ends of the pentaborate groups. In the neighborhood of O(7) and O(8) oxygen atoms, we note the presence of a two-fold screw axis along the *b* direction. The shorthand notation for the borate anion existing in γ-CsB_5O_8 is $5{:}\infty^3(4\Delta + T)$ (23, 24).

β-RbB_5O_8. Figure 6 shows a projection of the structure of β-RbB_5O_8 along the *a* axis. The structure of β-RbB_5O_8 is very close to that of TlB_5O_8 (10) and β-KB_5O_8 (3). As described for these two last compounds, the pentaborate groups $[B_5O_8]^-$ are attached to each other by common oxygen atoms, and form a three-dimensional network. Two-fold screw axes run near the center of the pentaborate groups; these groups run back in nearly the same direction, namely *b*, around the screw axes. These results are in good agreement with those recently published from an X-ray

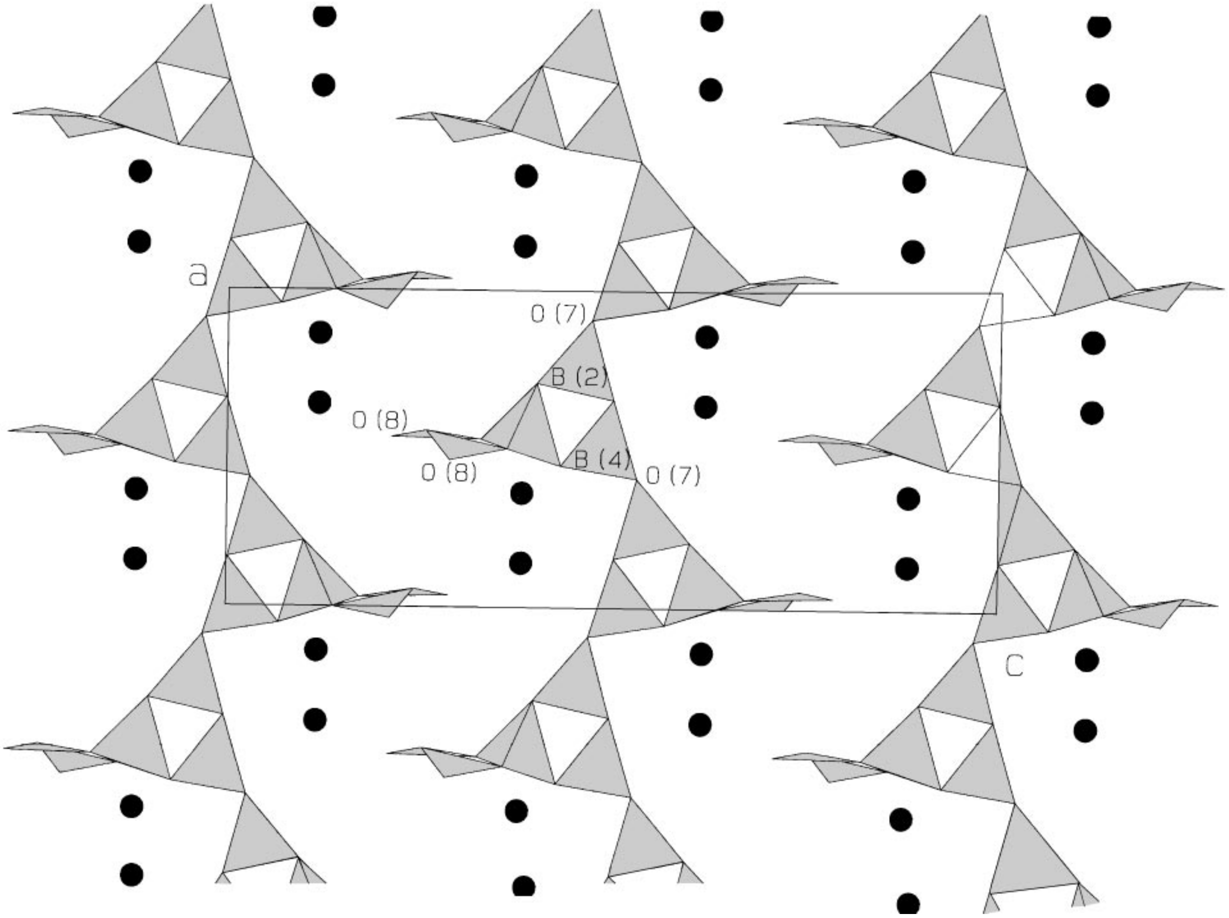

FIG. 4. Polyhedral representation of the structure of γ-CsB_5O_8 along the b axis. The networks connect through O(7) to pentaborate group above and below; for sake of clarity only half the cell content is drawn; the black spheres represent cesium atoms.

powder diffraction study (9). The shorthand notation for the borate anion existing in β-RbB_5O_8 is $5{:}\infty^3(4\Delta + T)$ (23, 24).

Whatever the M^+ cations (M = Cs, Rb), one can see that the structure of MB_5O_8 compounds can be described on the basis of a two- (α-CsB_5O_8) and three-dimensional (γ-CsB_5O_8, β-RbB_5O_8) network of pentaborate groups $[B_5O_8]^-$, with the shorthand notation $5{:}\infty^2(4\Delta + T)$ for α-CsB_5O_8 and $5{:}\infty^3(4\Delta + T)$ for γ-CsB_5O_8 and β-RbB_5O_8. It is interesting to note that the two forms of studied cesium pentaborates belong to two different space groups (Table 2) while the known forms of potassium and rubidium pentaborates crystallize in the same space group (Table 1). They are obtained by polymerization of the isolated pentaborate groups $[B_5O_6(OH)_4]^-$ (Fig. 1), where the terminal oxygens are OH groups found in hydrated cesium and rubidium pentaborates. Upon heating (i.e., formation and loss of water molecules), the four OH groups of the hydrated pentaborates are replaced by four terminal oxygen atoms that insure the connections between adjacent pentaborate groups (Fig. 1).

As we described above, the structures of α-CsB_5O_8, γ-CsB_5O_8, and β-RbB_5O_8 differ in the mutual arrangement of the pentaborate groups $[B_5O_8]^-$. These differences are associated with the angles between the two planes A and B (Fig. 1) formed by the two BO_3 triangles on each side of the BO_4 tetrahedron. To evaluate these angles, we defined a middle plane for A and B. In the case of hydrated cesium and rubidium pentaborates, we notice that this angle is of 77° and of 81° for $Cs[B_5O_6(OH)_4]\cdot 2H_2O$ (16) and $Rb[B_5O_6(OH)_4]\cdot 2H_2O$ (15), respectively; due to the small irregularity of the BO_4 tetrahedron, the angle between the two planes differs from the ideal value of 90°. In the case of α-CsB_5O_8, which is based on a two-dimensional network of pentaborate groups, the angle between the two planes is 80°. The latter value is close to the one found in the hydrated cesium pentaborate. In this case, due to the presence of a new network of pentaborate groups, we could not make any comparison with existing isostructural borates. In the three-dimensional network occurring in the γ-CsB_5O_8 form, the angle between the two planes is 81°. This value is not too far from that found in α-KB_5O_8 (72°) (4), which is

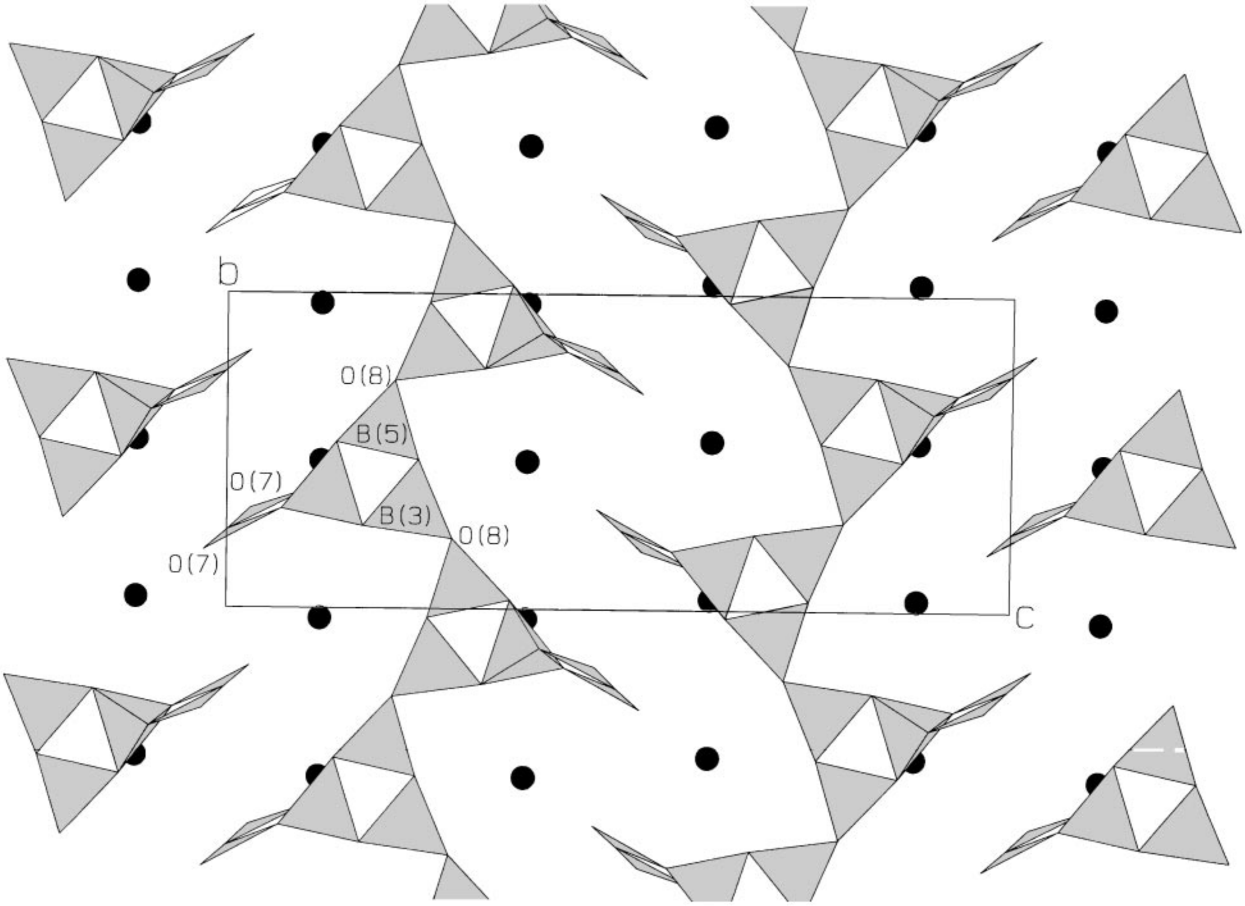

FIG. 5. Polyhedral representation of the structure of γ-CsB_5O_8 along the *a* axis. The networks connect through O(8) to pentaborate group above and below; for sake of clarity only half the cell content is drawn; the black spheres represent cesium atoms.

isostructural with γ-CsB_5O_8. The close values of angles in the two- and in three-dimensional networks indicate an absence of strain. For β-RbB_5O_8, where a three-dimensional network also exists, the angle is 56°. This value is in good agreement with that found in β-KB_5O_8 (56°) (3) and TlB_5O_8 (56°) (10). The smaller angle compared to the ones found in α-CsB_5O_8 and γ-CsB_5O_8 comes from a stronger strain in this three-dimensional network.

Four other pentaborate groups, different from those existing in MB_5O_8 ($M = K$ (α and β), Cs (α and γ), Rb (β) Tl), are reported. As discussed above, a two-dimensional network of $[B_5O_{11}]^{7-}$ anions is present in the structure of $SrKB_5O_9$ (25) and $CaNaB_5O_9$ (26); its shorthand notation is $5{:}\infty^2(3\Delta + 2T)$ (23, 24). Discrete $[B_5O_{10}]^{5-}$ anions form the structure of $CaNa_3B_5O_{10}$ (27), with the shorthand notation $5{:}(4\Delta + T)$ (23, 24). Several $MLnB_5O_{10}$ compounds (where M is a bivalent ion), for example $MgLnB_5O_{10}$ (28), have infinite two-dimensional boron–oxygen layers. Each of these infinite slabs consists of groups of three BO_4 tetrahedra and two BO_3 triangles that condense by sharing vertices, giving a boron–oxygen anionic complex $[B_5O_{10}]^{5-}$ with the shorthand notation $5{:}\infty^2(2\Delta + 3T)$ (23, 24). Finally, a fourth type of $[B_5O_{10}]^{5-}$ anion was found in $Ba_2LiB_5O_{10}$ (29) and $CuTbB_5O_{10}$ (30); it exhibits a unique one-dimensional polyborate anion built from two crystallographically independent BO_3 triangles and one distinct BO_4 tetrahedron that share vertices. The shorthand notation for this borate anion is $3{:}\infty^1(2\Delta + T)$ (23, 24).

M^+ *Environments*

For γ-CsB_5O_8, α-CsB_5O_8, and β-RbB_5O_8, the shortest M–B (M = Cs, Rb) distances are 3.512 Å, 3.603 Å, and 3.341 Å, respectively (Table 5). Therefore, only the oxygen atoms with shorter M–O bonds (i.e., $M\text{–O} < M\text{–B}$) will be considered for the oxygenated environment of Cs^+ and Rb^+ ions. The cations are eight-coordinated in γ-CsB_5O_8, nine-coordinated in α-CsB_5O_8, and ten-coordinated in β-RbB_5O_8. The M–O distances range from 3.036 Å to 3.153 Å in γ-CsB_5O_8, from 3.040 Å to 3.429 Å in α-CsB_5O_8, and from 2.959 Å to 3.335 Å in β-RbB_5O_8 with average values of 3.120 Å, 3.192 Å, and 3.099 Å, respectively. The

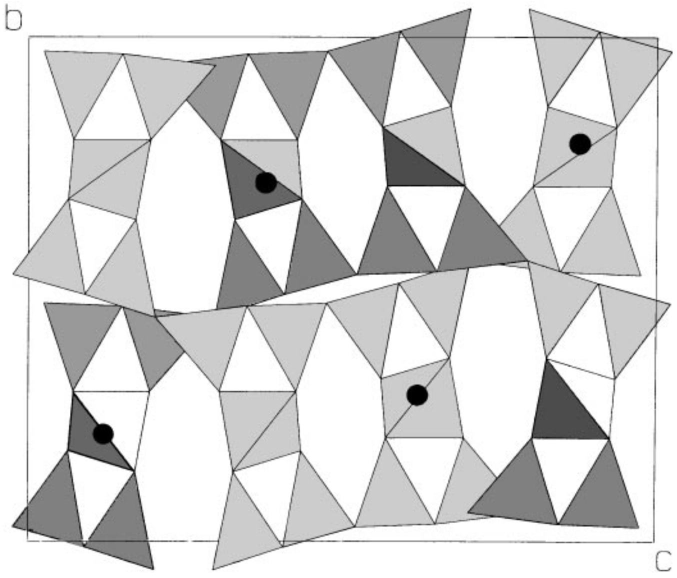

FIG. 6. Polyhedral representation of the structure of β-RbB_5O_8 showing the manner in which the pentaborate groups are interlinked in the two three-dimensional networks; the black spheres represent rubidium atoms.

mean values are consistent with the sum of the ionic radii ($r(Cs^+_{(8)}) = 1.74$ Å, $r(Cs^+_{(9)}) = 1.78$ Å, $r(Rb^+_{(10)}) = 1.66$ Å, $r(O^{2-}_{(4)}) = 1.38$ Å) (31) and in good agreement with those found in CsB_3O_5 (21), α- and β-RbB_3O_5 (19, 20), and $Rb_2B_4O_7$ (22).

CONCLUSION

In this paper, the structures of α-CsB_5O_8, γ-CsB_5O_8, and β-RbB_5O_8 were solved from single-crystal X-ray diffraction data. All these compounds are composed of $[B_5O_8]^-$ pentaborate units, formed by two groups of two BO_3 triangles on each side of a BO_4 tetrahedron. Their structures differ in the mutual arrangement of the pentaborate groups. In α-CsB_5O_8, the structure consists of infinite corrugated layers of $[B_5O_8]^-$ units linked to each other by the four external oxygen atoms of the four BO_3 triangles; its shorthand notation is $5{:}\infty^2(4\Delta + T)$. In contrast, the structures of γ-CsB_5O_8 and β-RbB_5O_8 can be described on the basis of a three-dimensional network of $[B_5O_8]^-$ units linked together; their shorthand notations are $5{:}\infty^3(4\Delta + T)$. The dehydration process of the $M[B_5O_6(OH)_4]\cdot 2H_2O$ (M = Cs, Rb, Tl) leading to several forms of MB_5O_8 (M = Cs, Rb, Tl) will be presented in a forthcoming paper.

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