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Journal of Solid State Chemistry 175 (2003) 348–352

JOURNAL OF
SOLID STATE
CHEMISTRY

<http://elsevier.com/locate/jssc>

Refinement of α -CsB₉O₁₄ crystal structure

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Received 2 April 2003; received in revised form 28 May 2003; accepted 30 May 2003

Abstract

The structure of α -CsB₉O₁₄ was re-examined because the first determination corresponded to a poor reliability factor (12.9%). Single crystals were obtained by heating, melting and slow cooling a stoichiometric mixture (1:4) of β -Cs[B₅O₆(OH)₄]·2H₂O and H₃BO₃. This compound crystallizes in the non-centrosymmetric orthorhombic space group *P*222₁ (and not *P*4₁22) with the following parameters: $a = 8.732(2)$ Å, $b = 8.767(3)$ Å, $c = 15.736(4)$ Å, $V = 1204.6(6)$ Å³, $Z = 4$; after taking into consideration twinning, the structure was refined from 3188 reflections until $R_1 = 0.0304$. It consists of two infinite, interleaved three-dimensional boron-oxygen frameworks of the Fundamental Building Blocks formed by two B₃O₆ and one B₃O₇ groups; its shorthand notation is $9:\infty^3[(3:2\Delta+T)+2(3:3\Delta)]$ (Δ , triangle BO₃ and T, tetrahedron BO₄). Knowledge of the correct space group and the structure of α -CsB₉O₁₄ may help in the study of its physical properties, especially the non-linear optical ones.

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Keywords: Borate; Cesium borate; Enneaborate

1. Introduction

During the past few years, we focused our attention on the study of hydrated and anhydrous cesium borates [1–6]. This study mainly led to solve the structure of two new cesium borates of formula Cs₃B₁₃O₂₁ (B/Cs = 4.33) [5] and Cs₃B₇O₁₂ (B/Cs = 2.33) [6], compositions not reported in the different representations of the binary system Cs₂O–B₂O₃ [7–10], and to propose a new representation of this binary diagram [11].

The purpose of the present article is to report a refinement of the structure of the high-temperature form of CsB₉O₁₄. The existence of the cesium enneaborate was established for the first time by Krogh-Moë [7], during a study of the binary system Cs₂O–B₂O₃. The presence of two crystalline forms was reported, and the following crystallographic data were given: α -CsB₉O₁₄, tetragonal with $a = b = 8.74$ Å, $c = 15.72$ Å, $Z = 4$, space group *P*4₁, *P*4₃, *P*4₁22 or *P*4₃22; β -CsB₉O₁₄, monoclinic with $a = 8.56$, $b = 13.90$, $c = 9.32$ Å, $\beta = 92.0^\circ$, $Z = 4$ [7,12]. The existence of two forms of CsB₉O₁₄ was confirmed by Kocher [8,13]. In 1967, Krogh-Moë and Ihara [14] reported the refinement of

the structure of the tetragonal form of cesium enneaborate from visually estimated intensities coming from triple film Weissenberg exposures; the *P*4₁22 space group was proposed with the following unit-cell parameters $a = b = 8.768(5)$ Å, $c = 15.790(10)$ Å; that led to a reliability factor of 12.9%. The presence of twinning was pointed out, and the refinement of two oxygen atoms was carried out in another space group (*P*222₁) than the other atoms (*P*4₁22).

Due to all of the problems encountered in the resolution of this structure, we tried to prepare this compound in a single-crystal form, thus using better data to obtain better results.

2. Experimental section

2.1. Synthesis

The hydrated cesium pentaborate β -Cs[B₅O₆(OH)₄]·2H₂O [2] served as precursor for the synthesis of α -CsB₉O₁₄; it was obtained from an aqueous solution of dissolved Cs₂CO₃ and H₃BO₃ in stoichiometric proportions; CO₂ being released, the evaporation under constant stirring and heating led to the wanted compound. A stoichiometric mixture (1:4) of

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Table 1
Crystal data and intensity collection conditions for α -CsB₉O₁₄

Formula	CsB ₉ O ₁₄
Formula weight (g mol ⁻¹)	454.20
Crystal system	Orthorhombic
Space group	<i>P</i> 222 ₁ (No. 17)
Unit cell dimensions (Å)	<i>a</i> = 8.732(2); <i>b</i> = 8.767(3); <i>c</i> = 15.736(4)
<i>V</i> (Å ³); <i>Z</i>	1204.6(6); 4
Density (g/cm ³)	<i>D</i> _{calc} = 2.504
Crystal size (mm ³)	0.065 × 0.140 × 0.320
Diffractometer	Bruker AXS SMART
Radiation	MoK α , λ = 0.71073 Å
Collection method	$\varphi - \omega$
Temperature (K)	293
θ range (deg)	1.29–31.16
Range in <i>h, k, l</i>	−12 ≤ <i>h</i> ≤ 12; −12 ≤ <i>k</i> ≤ 12; −22 ≤ <i>l</i> ≤ 22
Absorption coefficient (mm ⁻¹)	μ (MoK α) = 3.153
Reflections collected	13001
Independent reflections	3604
Independent reflections with [<i>I</i> > 2 σ (<i>I</i>)]	3188
<i>R</i> _{int}	0.0369
Refinement method	Full-matrix least squares on <i>F</i> ² SHELXTL-97 (15)
Number of variables	219
Goodness-of-fit (GOF) on <i>F</i> ²	0.990
Final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0304, <i>wR</i> ₂ = 0.0625
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0363, <i>wR</i> ₂ = 0.0646
Largest difference map peak and hole (e Å ⁻³)	0.982 and −1.032

Table 2
Final atomic coordinates and equivalent isotropic displacement parameters *U*_{eq} (Å²) of α -CsB₉O₁₄ with e.s.d.'s in parentheses

Atoms	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq} ^a
Cs(1)	0.5	0.5266(1)	0.25	0.03343(8)
Cs(2)	0.0072(1)	0	0	0.03725(10)
O(1)	0.8133(3)	0.5229(3)	0.1328(2)	0.0256(6)
O(2)	1.0155(4)	0.3292(2)	0.1156(2)	0.0264(5)
O(3)	0.7870(3)	0.2907(3)	0.2024(2)	0.0281(6)
O(4)	0.7781(3)	0.2933(3)	0.0496(2)	0.0282(6)
O(5)	1.0750(4)	0.5901(4)	0.1321(3)	0.0545(10)
O(6)	0.8972(4)	0.7783(3)	0.1502(2)	0.0380(7)
O(7)	0.2691(4)	0.4215(4)	0.1037(2)	0.0383(7)
O(8)	0.8398(4)	0.0304(3)	0.1749(2)	0.0377(7)
O(9)	0.7015(4)	0.1052(3)	0.2968(2)	0.0382(8)
O(10)	0.7245(4)	−0.1575(3)	0.2630(2)	0.0362(7)
O(11)	0.4002(5)	0.0715(4)	−0.1131(2)	0.0618(12)
O(12)	0.519(4)	0.3539(3)	0.0778(2)	0.0364(7)
O(13)	0.5858(4)	0.2008(4)	−0.0391(2)	0.0400(9)
O(14)	0.3234(4)	0.2336(4)	−0.0032(2)	0.0395(8)
B(1)	0.8481(5)	0.3616(5)	0.1248(3)	0.0220(7)
B(2)	0.9222(7)	0.6247(6)	0.1397(3)	0.0293(11)
B(3)	1.1137(6)	0.4429(6)	0.1169(3)	0.0307(10)
B(4)	0.7783(6)	0.1467(5)	0.2226(3)	0.0276(10)
B(5)	0.6780(6)	−0.0427(6)	0.3145(3)	0.0324(10)
B(6)	0.8189(6)	−0.1196(5)	0.1956(3)	0.0333(11)
B(7)	0.6329(6)	0.2847(6)	0.0314(3)	0.0264(10)
B(8)	0.3678(6)	0.3328(5)	0.0608(3)	0.0323(11)
B(9)	0.4361(17)	0.1721(6)	−0.0523(3)	0.0363(13)

^a *U*_{eq} is defined as one-third of the trace of the orthogonalized *U*_{*ij*} tensor.

β -Cs[B₅O₆(OH)₄] \cdot 2H₂O and H₃BO₃ was heated and melted at 650°C, slowly cooled down to 550°C at 0.1°C min⁻¹, and annealed at this temperature for 12 h. Then, the mixture was slowly cooled down at 0.1°C min⁻¹ for 50°C, and annealed at this temperature for 12 h. This last process was repeated three times until the sample temperature reached 350°C. Afterwards, the mixture was cooled down to room temperature by turning off the furnace. Part of the recovered sample was ground for a powder X-ray diffraction investigation (Siemens D5000 diffractometer; λ CuK α ₁ = 1.54056 Å). The X-ray powder pattern of the analyzed sample agrees with the ICDD card 72-0024 [14].

2.2. Single-crystal structure determination

A colorless single crystal was chosen from the preparation. The intensity data were collected on a Bruker AXS SMART three-circle diffractometer using graphite-monochromatized MoK α radiation (λ = 0.71073 Å), and equipped with a CCD two-dimensional detector. In a first step, the resolution of the structure of α -CsB₉O₁₄ was attempted in the tetragonal *P*4₁22 space group, as proposed by Krogh-Moë and Ihara [14]; the merging factor *R*_{int} was not very good (0.0797) but the refinement smoothly progressed to *R*₁ = 0.0570 and *wR*₂ = 0.1358. However, two oxygen atoms had high

displacement parameters: *U*_{eq} about 0.07 as compared to 0.02–0.03 for the other atoms. In a second step, the resolution was conducted in the orthorhombic *P*222₁ space group. The *R*_{int} was better (0.0369) and the refinement converged to *R*₁ = 0.0426 and *wR*₂ = 0.0912 for 3188 reflections with *I* > 2 σ (*I*). Finally, the pseudo-tetragonal symmetry and the proximity of *a* and *b* parameters compelled to consider the presence of twinning: a diagonal twinning *xyz*/*yx* − *z* was introduced; the batch scale factor (BASF) refined at 0.193(2) and *R*₁ lowered to 0.0304 and *wR*₂ to 0.0625. Crystal data and conditions of intensity collection are given in Table 1. The structure was refined by full-matrix least-squares techniques using the SHELXTL crystallographic software package [15]. Absorption correction was made using the SADABS program [16]. The atomic coordinates and the displacement parameters are reported in Tables 2 and 3; significant bond lengths and angles are listed in Table 4.

3. Description of the structure and discussion

3.1. Borate anion

It must be noted that the description of the structure remains close to that previously made by Krogh-Moë

Table 3
Anisotropic displacement parameters^a(Å²) (e.s.d's in parentheses) for all of the atoms of α -CsB₉O₁₄

Atoms	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Cs(1)	0.0343(2)	0.0381(2)	0.0279(2)	0	0.0009(2)	0
Cs(2)	0.0415(2)	0.0418(2)	0.0285(2)	0.0009(1)	0	0
O(1)	0.0242(14)	0.0177(12)	0.0348(15)	0.0019(10)	0.0028(12)	0.0026(11)
O(2)	0.0200(14)	0.0215(10)	0.0377(13)	-0.0020(9)	-0.0018(15)	0.0019(14)
O(3)	0.0374(17)	0.0193(12)	0.0274(14)	0.0015(10)	0.0072(13)	-0.0024(12)
O(4)	0.0232(15)	0.0349(14)	0.0264(14)	-0.0069(11)	0.0001(12)	0.0014(12)
O(5)	0.029(2)	0.0246(19)	0.110(3)	-0.011(2)	0.004(2)	-0.0056(13)
O(6)	0.049(2)	0.0191(13)	0.0460(18)	-0.0002(12)	0.0032(15)	-0.0003(13)
O(7)	0.0194(15)	0.0442(17)	0.0513(19)	0.0019(14)	0.0019(13)	0.0000(13)
O(8)	0.058(2)	0.0198(13)	0.0358(16)	0.0011(11)	0.0190(15)	-0.0042(13)
O(9)	0.050(2)	0.0326(16)	0.0320(15)	0.0029(12)	0.0129(15)	-0.0062(14)
O(10)	0.0410(17)	0.0251(11)	0.0424(19)	0.0144(13)	0.0053(16)	-0.0061(11)
O(11)	0.077(3)	0.048(2)	0.061(2)	-0.0208(18)	-0.037(2)	-0.0021(18)
O(12)	0.0179(17)	0.0506(15)	0.0406(14)	-0.0199(11)	-0.0037(14)	0.0003(15)
O(13)	0.042(2)	0.046(2)	0.0325(17)	-0.0185(15)	0.0011(15)	-0.00105(16)
O(14)	0.0312(16)	0.0380(18)	0.049(2)	-0.0015(13)	-0.0155(15)	-0.0082(14)
B(1)	0.020(2)	0.022(2)	0.0238(18)	-0.0001(16)	0.0024(18)	0.0013(14)
B(2)	0.035(3)	0.020(2)	0.033(3)	-0.0003(18)	0.003(2)	-0.0017(19)
B(3)	0.024(2)	0.028(2)	0.040(3)	0.003(3)	-0.004(2)	0.001(2)
B(4)	0.032(3)	0.023(2)	0.028(2)	0.0010(15)	0.0049(19)	-0.0005(17)
B(5)	0.031(2)	0.032(2)	0.034(2)	0.0091(19)	0.002(2)	-0.007(2)
B(6)	0.035(3)	0.022(2)	0.043(3)	0.0081(18)	-0.006(2)	-0.0045(18)
B(7)	0.025(2)	0.026(2)	0.028(2)	-0.0083(18)	-0.0006(19)	-0.0031(19)
B(8)	0.028(3)	0.027(2)	0.042(3)	0.001(2)	-0.008(2)	-0.0067(19)
B(9)	0.047(3)	0.028(2)	0.034(3)	0.001(2)	-0.017(3)	-0.014(2)

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

and Ihara [14], which emphasizes the very good crystallographic work performed in 1967. The structure of α -CsB₉O₁₄ exhibits a framework of BO₃ triangles (Δ) and BO₄ tetrahedra (T) linked to each other, every oxygen atom being common to two polyhedra. The values for B–O bonds range between 1.302 and 1.394 Å for the eight BO₃ triangles, and between 1.452 and 1.471 Å for the unique BO₄ tetrahedron (Table 4). These values are in good agreement with those found in other anhydrous cesium polyborates such as Cs₃B₇O₁₂ [6], CsB₃O₅ [17], Cs₃B₁₃O₂₁ [5] and CsB₅O₈ (II) and (IV) [4,18]. With regard to the O–B–O angles, the mean values for BO₃ triangles and BO₄ tetrahedron are almost ideal: 120° for the triangles and 109.5° for the tetrahedron (Table 4).

α -CsB₉O₁₄ contains nine crystallographically independent boron atoms; the borate anion present in this compound is made of two sorts of triborate groups: two B₃O₆ and one B₃O₇ (Fig. 1). The B₃O₆ group consists of a six-membered planar ring in which the three boron atoms are surrounded by three oxygen atoms; all of these BO₃ triangles are linked by vertices; its shorthand notation is 3:3 Δ . An identical group is present alone in BBO, the low-temperature form of barium metaborate β -BaB₂O₄ [19]. The B₃O₇ group also consists of a six-membered ring in which two boron atoms are surrounded by three oxygen atoms, and one boron atom is surrounded by four oxygen atoms; these BO₃ and BO₄ groups are linked by vertices; its shorthand notation is 3:2 Δ +T. Such a group is frequently

encountered in anhydrous triborates as CsB₃O₅ [17]. This B₃O₇ group insures the connexion with the two independent B₃O₆ groups by two oxygen atoms, namely O3 and O4 (Fig. 1).

The structure of α -CsB₉O₁₄ consists of two infinite, interleaved three-dimensional networks of complex enneaborate groups; only one is reported in Fig. 2; the other is deduced from this one by the two-fold axes, and is not represented for the sake of clarity. Following the crystal chemical classification of borates proposed by Christ and Clark [20], Heller [21], which we have slightly modified [22], where fundamental building blocks (FBBs) are considered, the shorthand notation of the complex anion present in α -CsB₉O₁₄ is 9: $\infty^3[(3:2\Delta + T) + 2(3:3\Delta)]$.

Other compounds with FBBs containing nine boron atoms were known. In the two forms of NaB₃O₅, these FBBs exist: 9: $\infty^3[(5:4\Delta + T) + (4:2\Delta + 2T)]$ [20–22] in the α form [23] and 9: $\infty^3[(5:4\Delta + T) + (3:2\Delta + T) + (1:T)]$ [20–22] in the β form [24]. In the three compounds BaLiB₉O₁₅, BaNaB₉O₁₅ and SrLiB₉O₁₅ [25,26], the following FBB was found: 9: $\infty^3[(3:2\Delta + T)]$ [20–22]. At last, in two guanidinium and imidazolium borates [27], an isolated borate group [B₉O₁₂(OH)₆]³⁻ of shorthand notation 9:(6 Δ +3T) [20–22] with nine crystallographically independent boron atoms, was pointed out. As shown above, in all of the other cases, the structure is formed by the association of small borate groups with one, three, four, or five boron atoms.

Table 4
Interatomic distances (Å) and angles (deg) in α -CsB₉O₁₄

<i>BO₄ tetrahedron</i>			
B(1)–O(1)	1.452(5)	O(1)–B(1)–O(4)	112.4(4)
B(1)–O(4)	1.461(5)	O(1)–B(1)–O(3)	105.3(3)
B(1)–O(3)	1.470(5)	O(1)–B(1)–O(2)	113.6(3)
B(1)–O(2)	1.471(5)	O(4)–B(1)–O(3)	110.4(3)
⟨B(1)–O⟩	1.464(5)	O(4)–B(1)–O(2)	104.5(3)
		O(3)–B(1)–O(2)	110.8(3)
		⟨O–B(1)–O⟩	109.5(3)
<i>BO₃ triangles</i>			
B(2)–O(1)	1.308(6)	O(1)–B(2)–O(5)	123.2(5)
B(2)–O(5)	1.374(6)	O(1)–B(2)–O(6)	124.3(5)
B(2)–O(6)	1.374(6)	O(5)–B(2)–O(6)	112.4(5)
⟨B(2)–O⟩	1.352(6)	⟨O–B(2)–O⟩	120.0(5)
B(3)–O(2)	1.332(6)	O(2)–B(3)–O(5)	123.4(4)
B(3)–O(5)	1.355(7)	O(2)–B(3)–O(7) ^a	123.1(4)
B(3)–O(7) ^a	1.385(6)	O(5)–B(3)–O(7) ^a	113.5(4)
⟨B(3)–O⟩	1.357(6)	⟨O–B(3)–O⟩	120.0(4)
B(4)–O(3)	1.304(5)	O(3)–B(4)–O(8)	124.2(4)
B(4)–O(8)	1.376(5)	O(3)–B(4)–O(9)	119.0(4)
B(4)–O(9)	1.394(5)	O(8)–B(4)–O(9)	116.8(4)
⟨B(4)–O⟩	1.358(5)	⟨O–B(4)–O⟩	120.0(4)
B(5)–O(9)	1.342(5)	O(9)–B(5)–O(11) ^b	115.7(4)
B(5)–O(11) ^b	1.353(6)	O(9)–B(5)–O(10)	123.2(4)
B(5)–O(10)	1.354(6)	O(11) ^b –B(5)–O(10)	121.1(4)
⟨B(5)–O⟩	1.350(6)	⟨O–B(5)–O⟩	120.0(4)
B(6)–O(6) ^c	1.334(6)	O(6) ^c –B(6)–O(8)	116.7(4)
B(6)–O(8)	1.367(5)	O(6) ^c –B(6)–O(10)	123.6(4)
B(6)–O(10)	1.385(6)	O(8)–B(6)–O(10)	119.6(4)
⟨B(6)–O⟩	1.362(6)	⟨O–B(6)–O⟩	119.9(4)
B(7)–O(4)	1.302(6)	O(4)–B(7)–O(12)	124.3(4)
B(7)–O(12)	1.375(6)	O(4)–B(7)–O(13)	119.5(4)
B(7)–O(13)	1.393(5)	O(12)–B(7)–O(13)	116.2(4)
⟨B(7)–O⟩	1.357(6)	⟨O–B(7)–O⟩	120.0(4)
B(8)–O(7)	1.343(6)	O(7)–B(8)–O(12)	116.5(4)
B(8)–O(12)	1.360(6)	O(7)–B(8)–O(14)	123.3(4)
B(8)–O(14)	1.386(6)	O(12)–B(8)–O(14)	120.0(4)
⟨B(8)–O⟩	1.363(6)	⟨O–B(8)–O⟩	119.9(4)
B(9)–O(11)	1.338(6)	O(11)–B(9)–O(13)	117.4(5)
B(9)–O(13)	1.348(6)	O(11)–B(9)–O(14)	119.8(5)
B(9)–O(14)	1.363(7)	O(13)–B(9)–O(14)	122.6(4)
⟨B(9)–O⟩	1.350(6)	⟨O–B(9)–O⟩	119.9(5)
<i>Environment of cesium atoms (<4 Å)</i>			
Cs(1)–O(12)	3.108(3)	Cs(2)–O(8) ^g	3.127(3)
Cs(1)–O(12) ^d	3.108(3)	Cs(2)–O(8) ^h	3.127(3)
Cs(1)–O(7)	3.196(3)	Cs(2)–O(6) ⁱ	3.207(3)
Cs(1)–O(7) ^d	3.196(3)	Cs(2)–O(6) ^j	3.207(3)
Cs(1)–O(1)	3.299(3)	Cs(2)–O(4) ^g	3.350(3)
Cs(1)–O(1) ^d	3.299(3)	Cs(2)–O(4) ^h	3.350(3)
Cs(1)–O(3)	3.334(3)	Cs(2)–O(2) ^g	3.412(3)
Cs(1)–O(3) ^d	3.334(3)	Cs(2)–O(2) ^h	3.412(3)
Cs(1)–O(10) ^e	3.399(3)	Cs(2)–O(14)	3.438(3)
Cs(1)–O(10) ^f	3.399(3)	Cs(2)–O(14) ^k	3.438(3)
Cs(1)–B(8)	3.617(5)	Cs(2)–B(6) ^g	3.643(5)
Cs(1)–B(8) ^d	3.617(5)	Cs(2)–B(6) ^h	3.643(5)

Note: symmetry codes: ^a1+x, y, z; ^b1-x, -y, 1/2+z; ^cx, y-1, z; ^d1-x, y, 1/2-z; ^ex, 1+y, z; ^f1-x, 1+y, 1/2-z; ^gx-1, -y, -z; ^hx-1, y, z; ⁱx-1, 1-y, -z; ^jx-1, y-1, z; ^kx, -y, -z.

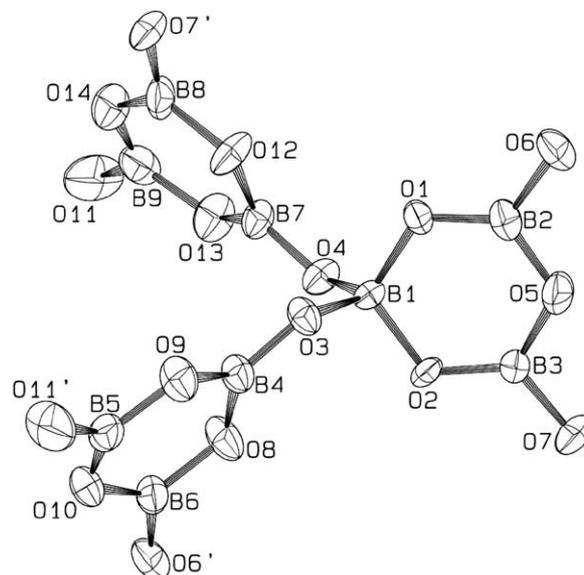


Fig. 1. Representation of the (B₉O₁₇) borate group existing in α -CsB₉O₁₄. It consists of the association of three triborate groups, two B₃O₆ (three BO₃ triangles) and one B₃O₇ (two BO₃ triangles and one BO₄ tetrahedron); the linkage is made by O3 and O4 oxygen atoms. Atoms are represented by 50% probability ellipsoids.

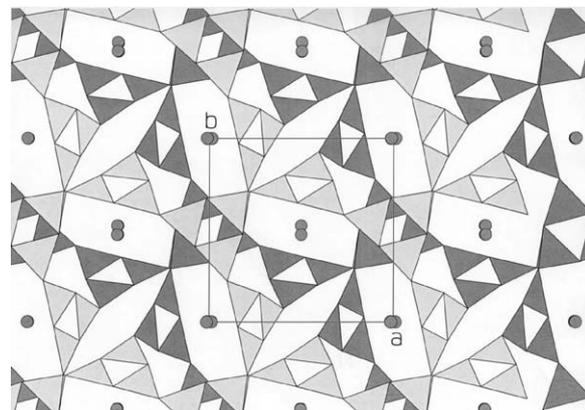


Fig. 2. Projection on (*ab*) plane of one of the interleaved three-dimensional frameworks existing in the structure of α -CsB₉O₁₄; the dark and light networks of BO₃ triangles and BO₄ tetrahedra are related by the helicoidal 2₁ axes. The other half of the structure is deduced from this one by the two-fold axes, and is not represented for the sake of clarity. Black circles represent cesium atoms.

3.2. Cesium environment

Fig. 2 shows the position of the cesium atoms; they are located in large tunnels along the three directions. There are two crystallographically independent cesium ions occupying particular positions in the space group $P222_1$, $2d$ for Cs1 and $2a$ for Cs2. In α -CsB₉O₁₄, the shortest Cs–B distance is 3.617 Å (Table 4). Therefore, only the oxygen atoms with shorter Cs–O bonds (i.e. Cs–O < Cs–B) will be considered for the oxygenated

Table 5
Bond valence analysis of α -CsB₉O₁₄^a

	O(1)	O(2)	O(3)	O(4)	O(5)	O(6)	O(7)	O(8)	O(9)	O(10)	O(11)	O(12)	O(13)	O(14)	$\Sigma_{s_{\text{calc.}}}$	$\Sigma_{s_{\text{theo.}}}$
Cs(1)	0.09		0.08				0.12			0.07		0.16			1.04	1
Cs(2)		0.07		0.08		0.12		0.15						0.06	0.96	1
B(1)	0.80	0.78	0.77	0.76											3.11	3
B(2)	1.19				0.99	0.99									3.17	3
B(3)		1.11			1.04		0.96								3.11	3
B(4)			1.20					0.99	0.94						3.13	3
B(5)									1.08	1.05	1.05				3.18	3
B(6)						1.11		1.01		0.96					3.08	3
B(7)				1.21								0.99	0.94		3.14	3
B(8)							1.08					1.03		0.96	3.07	3
B(9)											1.09		1.06	1.02	3.17	3
$\Sigma_{s_{\text{calc.}}}$	2.08	1.96	2.05	2.05	2.03	2.22	2.16	2.15	2.02	2.08	2.14	2.18	2.00	2.04		
$\Sigma_{s_{\text{theo.}}}$	2	2	2	2	2	2	2	2	2	2	2	2	2	2		

^aThe results refer to the equation $s = \exp[(r_0 - r)/B]$ with $r_0 = 1.371 \text{ \AA}$ and 2.42 \AA for B–O and Cs–O bonds, respectively, and $B = 0.37$ [30].

environment of Cs⁺ ions. Cs1 and Cs2 are surrounded by ten oxygen atoms. These environments and Cs–O distances are in good agreement with those found in other cesium borates [1–6,17,18,28,29].

The bond valence analysis [30] of the α -CsB₉O₁₄ structure is reported in Table 5; it leads to adequate bond valence sums with minor deviations, especially for the cesium atoms confirming their ten coordination number.

4. Conclusion

To complete the study of enneaborates, and as cesium, thallium and rubidium borates are often isotype for compounds with $B/M > 3$ as, for example, MB₅O₈ [4], we also focused our attention on the preparation of the compounds MB₉O₁₄ ($M = \text{Tl, Rb}$). Furthermore, these borates were reported in the previous studies of the binary systems Rb₂O–B₂O₃ (8) and Tl₂O–B₂O₃ [31]. Several attempts were realized but never led to the expected compounds. Note that three forms of sodium enneaborate were also reported in the Na₂O–B₂O₃ system [32]; they were only characterized by non-indexed powder patterns. Therefore, the only alkaline or pseudo-alkaline enneaborate with a known structure is α -CsB₉O₁₄; as its structure is non-centrosymmetric, experiments of crystal growth can be carried out to obtain large crystals allowing physical studies mainly linked to the non-linear optical properties.

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