D(1)–O(4)–D(2) is 352°. The coordination of the water molecule, O(5) D(3) D(4) is tetrahedral with one of the lone pairs pointing towards the Cd atom and the other acting as the negative end of the hydrogen bond from the water oxygen O(4). The relevant angles around O(5) are given in Table 4. It falls under the type H. The dimensions of the water molecules are normal. The angles D(1)–O(4)–D(2) and D(3)–O(5)–D(4) of 103·2°, 104·7° are not significantly different from the vapour value of 104·5°. This is consistent with the observation (Chidambaram, Sequeira & Sikka, 1964) that only in water molecules whose coordination is of type D (the group, metal $- OH_2$, is planar) is the HOH angle significantly greater than the value 104·5°.

Conclusion

The results of this study indicate that anomalous dispersion techniques can be successfully used in solving crystal structures directly from neutron diffraction data. In view of the difficulty in locating atoms which lie close to the antisymmetric axis in the sine function it would appear that the double phase Fourier method is superior in determining the atomic positions.

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The Crystal Structure of Ba[B(OH)4]2.H2O

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Crystals of $BaB_2O_4.5H_2O = Ba[B(OH)_4]_2.H_2O$ are monoclinic, space group $P2_1/c$, with four formula units in the unit cell of dimensions $a = 5·949 \pm 0·003$, $b = 8·535 \pm 0·004$, $c = 15·157 \pm 0·008$ Å and $\beta = 102·31 \pm 0·04°$. The structure consists of discrete tetrahedral $B(OH)_4^-$ groups. Each barium atom is bonded to ten oxygen atoms. Each barium polyhedron shares an edge each with two other barium polyhedra to form chains wound around the screw axis. The chains are linked in the [100] and [001] directions by boron tetrahedra. The water molecules and the hydroxyl groups form hydrogen bonds.

Introduction

The investigation of the structure was undertaken mainly to determine the configuration of the anion. From a study of two projections ($R_{h0l} = 0·21$, $R_{0kl} = 0·24$) Ozol, Vimba & Jevins (1960) suggested a structure with anions consisting of one tetrahedral and one triangular boron oxygen group each, with the two groups sharing an edge. The structure of the anion proposed by Ozol *et al.* is not in agreement with the results obtained by Kessler (1966), at the Institut für Anorganische und Anorganisch-Technische Chemie of the Technical University in Dresden, from an examination of infrared spectra. These indicate a structure containing isolated boron–oxygen tetrahedra and Kessler proposed the formula $Ba[B(OH)_4]_2.H_2O$. The structure determination

reported in the following confirmed these conclusions. When the manuscript of this paper had been prepared for publication a more recent note by Ozol, Jevins & Pech (1967) came to our notice. In this note the authors correct their earlier proposal for the structure and arrive at atomic positions fairly close to those obtained by us. The structure was solved from two projections only, therefore publication of our three-dimensional analysis still seems worth while.

Experimental

The crystals of $Ba[B(OH)_4]_2H_2O$ were kindly supplied by the Institut für Anorganische und Anorganisch-Technische Chemie of the Technical University Dresden. For preliminary studies multiple Weissenberg films of the layers $h0l$ and Hhl with $H=0,1,2,3$ were prepared with Cu $K\alpha$ radiation. No correction for absorption was applied although this effect was considerable because the irregular shaped crystals were fairly large. Thus the data were relatively inaccurate; a second set of intensity data was therefore collected. This set was obtained from equi-inclination Weissenberg films without integration, with the use of (a) Mo radiation instead of Cu radiation and (b) a spherically ground crystal with an average radius of about 0·005 cm instead of the irregularly shaped one. For Mo $K\alpha$ radiation the linear absorption coefficient, μ, is 49·5 cm⁻¹ while that for Cu $K\alpha$ is 378 cm⁻¹. The intensities of the Hkl layers, with $H=0,1,\ldots6$, were recorded on multiple Weissenberg films and a total of 2111 independent reflexions were measured photometrically without integration. Each reflexion was measured on

both halves of the film and the mean value was calculated to reduce errors in measurement. The intensities were corrected for background, Lorentz and polarization factors and for a factor allowing for the resolution of Mo $K\alpha_1$ and Mo $K\alpha_2$ at different θ-values; thus the relative structure factors were derived. Absorption correction was considered unnecessary because μr is less than 0·25. No corrections were made for primary or secondary extinction.

The unit-cell dimensions and standard deviations given in Table 1 together with those obtained by Ozol *et al.* (1960) were kindly determined by Schmittler in this institute from Guinier films and refined with a special least-squares program. The systematic absences $0k0$ with $k=2n+1$ and $h0l$ with $l=2n+1$ uniquely determine the space group $P2_1/c$. There are four formula units of $BaB_2O_4.5H_2O$ in the unit cell, and the calculated density of 2·77 g.cm⁻³ compares favorably with the measured density of $2·75\pm0·02$ g.cm⁻³ obtained by flotation.

Table 1. *Unit-cell dimensions*

	Ozol *et al.* (1960)	Present work
a	5·95780±0·00015 Å	5·949±0·003 Å
b	8·59743±0·00020	8·535±0·004
c	14·8775±0·0003	15·157±0·008
β	102°8′4″±15″	102°18′36″±3′

Structure determination and refinement

The approximate structure was determined from intensity data collected with Cu $K\alpha$ radiation. The coordinates of the Ba atom were derived from Patterson pro-

Table 2. *Positional and isotropic thermal parameters*

	x/a	y/b	z/c	B
Ba	0·1250±0·0001	0·0237±0·0001	0·2118±0·0001	(0·93±0·02) Å²
O(1)	0·0153±0·0015	0·4844±0·0010	0·1220±0·0006	(1·27±0·12)
O(2)	0·5763±0·0014	0·0205±0·0010	0·3320±0·0005	(1·21±0·12)
O(3)	0·5819±0·0014	0·4044±0·0010	0·3949±0·0005	(1·33±0·13)
O(4)	0·7883±0·0015	0·0629±0·0011	0·0485±0·0005	(1·56±0·13)
O(5)	0·2334±0·0014	0·3416±0·0010	0·2484±0·0005	(1·37±0·13)
O(6)	0·6509±0·0015	0·1802±0·0010	0·4998±0·0005	(1·41±0·13)
O(7)	0·9524±0·0015	0·2911±0·0010	0·4404±0·0006	(1·56±0·13)
O(8)	0·2815±0·0015	0·2703±0·0010	0·1003±0·0006	(1·46±0·13)
O(9)	0·7367±0·0016	0·2192±0·0010	0·2227±0·0006	(1·67±0·14)
B(1)	0·2389±0·0020	0·4014±0·0013	0·1568±0·0008	0·83±0·15
B(2)	0·7402±0·0020	0·3261±0·0014	0·4701±0·0008	0·84±0·15

Table 3. *Anisotropic thermal parameters* ($\times 10^4$)

	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Ba	68±2	30±1	11±1	4±2	12±1	2±1
O(1)	80±26	44±11	16±3	−2±22	15±13	−9±9
O(2)	25±26	73±11	10±3	−14±22	−15±13	−7±9
O(3)	110±26	67±11	8±3	34±22	9±13	5±9
O(4)	123±26	57±11	13±3	−20±22	17±13	−5±9
O(5)	74±26	74±11	11±3	7±22	7±13	−1±9
O(6)	144±26	49±11	13±3	−45±22	41±13	−3±9
O(7)	107±26	54±11	23±3	4±22	55±13	−19±9
O(8)	138±26	32±11	18±3	−33±22	0±13	−29±9
O(9)	99±26	64±11	18±3	−10±22	9±13	−5±9

jections $P_0(u,w)$ and $P_0(v,w)$ and refined by Fourier and difference Fourier syntheses. With the help of the Ba atom most of the signs of the $F_{obs}(Hkl)$, with $H = 0,1,2,3$, could be determined. These calculations were performed on the ZRA1 by means of computer programs written by Weiss. From a three-dimensional Fourier synthesis approximate positions for all oxygen and boron atoms were determined.

Table 4. Observed and calculated structure factors

Headings are $h,k,\neq$. Columns refer to the running index.

Table 4 (*cont.*)

- 1	32.7	33.9
0	58.8	-60.7
1	72.6	-78.1
2	75.2	81.7
3	93.5	100.7
4	85.3	-88.5
5	81.9	-90.8
6	78.1	77.6
7	40.4	41.9
8	34.0	-28.9
9	15.8	-19.0
10	8.5	1.0
11	9.2	-21.7
12	21.6	22.1
13	48.4	46.7
14	46.4	-45.3
15	48.0	-49.0
3 6	ł	
-17	53.4	51.0
-16	51.6	51.8
-15	34.2	-35.9
-14	27.9	-31.4
-13	45.3	47.9
-12	20.3	20.5
-11	16.1	-21.2
-10	8.0	-14.4
- 9	29.9	-28.3
- 8	8.9	-11.6
- 7	60.3	53.4
- 6	51.0	50.2
- 5	86.4	-86.4
- 4	75.1	-81.2
- 3	82.4	75.8
- 2	84.4	84.3
- 1	91.0	-93.5
0	37.1	-36.8
1	42.7	44.1
2	31.5	28.8
3	8.3	15.8
4	30.8	27.2
5	35.3	-31.0
6	26.2	-16.3
7	63.0	59.2
8	50.0	51.2
9	71.1	-71.3
10	34.5	-37.6
11	50.5	53.0
12	39.0	38.4
13	40.3	-39.3
3 7	ł	
-12	71.3	67.5
-11	43.5	41.3
-10	80.8	-76.1
- 9	44.4	-42.4
- 8	74.6	70.9
- 7	26.8	30.4
- 6	56.7	-54.7
- 5	19.0	20.2
- 4	17.7	22.1
- 3	17.7	-18.9
- 2	8.9	13.4
- 1	8.9	7.2
0	71.0	-69.2
1	32.5	-28.9
2	70.6	68.4
3	72.4	69.7
4	72.4	-62.2
5	35.7	-37.1
6	71.3	67.8
7	29.0	29.0
8	38.4	-35.9
9	8.1	-12.9
10	8.1	-8.1
11	8.2	-4.2
12	38.5	37.2
3 8	ł	
-17	44.6	46.1
-16	13.5	22.3
-15	56.5	-54.6
-14	12.9	-22.7
-13	58.6	52.7
-12	9.6	10.4
-11	25.1	-27.7
-10	9.2	-2.1
- 9	9.0	-10.9
- 8	8.8	-10.9
- 7	51.6	48.8
- 6	8.5	16.2
- 5	67.2	-66.2
- 4	51.1	-48.9
- 3	84.3	78.8
- 2	29.9	26.4
- 1	84.8	-78.8
0	20.1	-22.0
1	41.3	40.3
2	8.4	7.9
3	20.3	-13.0
4	8.7	3.0
5	38.2	-36.0
6	24.7	-24.9
7	59.1	55.0
8	25.7	21.8
9	57.6	-54.8
10	30.2	-30.0
11	50.0	57.5
3 9	ł	
-14	45.8	-40.7
-13	10.4	-4.2
-12	57.2	54.4
-11	10.3	21.8
-10	69.3	-69.3
- 9	32.0	-24.3
- 8	57.6	64.7
- 7	9.3	10.8
- 6	51.7	-47.2
- 5	9.1	1.0
- 4	24.6	22.5
- 3	12.2	14.3
- 2	24.4	28.0
- 1	17.1	18.0
0	57.6	-55.0
1	30.2	-19.1
2	61.0	60.0
3	9.2	14.7
4	66.2	-70.7
5	9.5	-6.9
6	58.8	59.5
3 10	ł	
- 7	54.3	51.0
- 6	9.8	0.5
- 5	61.0	-57.8
- 4	9.7	1.2
- 3	79.0	79.0
- 2	9.6	12.3
- 1	60.2	-62.1
0	9.7	3.2
1	41.9	43.7
2	9.8	0.2
3	9.9	11.8
4	10.0	-0.9
5	19.4	-26.8
6	10.3	-3.9
7	42.6	46.0
8	10.6	12.6
9	56.9	-61.0
10	10.5	-8.0
11	40.2	45.4
3 11	ł	
-12	48.5	46.2
-11	11.2	-7.5
-10	53.9	-55.3
- 9	10.9	-1.5
- 8	46.1	45.2
- 7	10.6	-8.6
- 6	40.4	-33.2
- 5	10.4	-9.8
- 4	10.4	5.1
- 3	9.8	-2.0
- 2	30.2	30.1
- 1	9.1	-6.5
0	34.5	-37.9
1	10.4	3.4
2	63.6	64.2
3	10.5	-6.8
4	63.0	-61.9
5	10.7	8.7
6	53.4	52.3
3 12	ł	
- 4	11.0	10.2
- 3	53.9	57.1
- 2	30.2	30.1
- 1	36.6	-46.2
0	11.0	8.3
4 0	ł	
-18	25.8	-30.8
-16	63.7	58.9
-14	125.0	-117.6
-12	68.4	75.0
-10	98.8	-100.8
- 8	45.4	49.8
- 6	5.0	-0.8
- 4	33.0	-39.4
- 2		
2	88.9	92.3
4	92.3	-95.2
6	18.1	-16.8
8	42.0	40.7
10	92.8	-85.0
12	73.5	71.9
14	59.3	-62.2
16	40.1	38.9
4 1	ł	
-21	49.7	56.4
-20	6.6	-7.4
-19	59.5	-64.2
-18	6.1	5.8
-17	55.5	57.0
-16	5.6	-5.5
-15	40.3	-39.3
-14	23.2	23.6
-13	4.5	3.0
-12	4.1	5.9
-11	17.4	17.6
-10	17.4	-17.6
- 9	95.9	-100.3
- 8	4.5	-3.5
- 7	135.2	138.3
- 6	19.8	-19.6
- 5	82.9	86.5
- 4	27.6	32.8
- 3	95.8	99.1
- 1	16.8	-21.8
0	11.6	8.0
1	35.8	-39.2
2	2.4	-5.2
3	99.2	101.2
4	15.7	16.5
5	92.3	-93.3
6	24.1	24.0
7	71.6	73.2
8	4.2	-0.2
9	95.3	-91.4
10	5.0	-1.3
11	56.0	55.9
12	5.7	2.1
13	5.9	-0.6
14	6.2	0.5
15	26.9	-26.9
16	18.3	16.7
17	45.9	47.3
18	7.2	-4.2
19	49.8	-49.4
20	7.6	3.8
21	44.6	40.9
4 2	ł	
-18	20.7	-22.1
-17	5.9	6.2
-16	69.9	75.1
-15	22.7	-20.2
-14	90.1	-83.4
-13	22.1	19.6
-12	80.1	76.8
-11	19.3	-19.7
-10	60.9	-58.7
- 9	3.3	-4.5
- 8	37.7	44.0
- 7	12.0	-10.1
- 6	40.8	36.3
- 5	13.4	-13.1
- 4	71.8	-78.2
- 3	23.2	28.3
- 2	101.8	104.2
- 1	52.8	-58.0
0	116.9	-129.4
1	34.4	37.9
2	125.7	133.5
3	35.4	-36.0
4	73.8	-68.3
5	12.3	16.3
6	27.7	22.6
7	4.1	-0.6
8	36.6	38.7
9	4.8	-11.0
10	77.6	-73.5
11	5.5	12.5
12	76.1	72.4
13	6.0	-14.1
14	48.0	-50.2
15	14.5	18.6
16	49.5	47.8
4 3	ł	
-21	49.6	47.6
-20	30.2	-24.8
-19	52.7	-52.4
-18	14.0	13.8
-17	37.6	37.9
-16	29.1	-28.4
-15	36.3	-36.5
-14	11.8	5.3
-13	12.3	7.3
-12	16.0	15.8
-11	48.7	49.7
-10	31.5	-29.2
- 9	98.5	-102.1
- 8	70.7	69.5
- 7	97.9	103.1
- 6	44.4	-49.4
- 5	112.9	-120.8
- 4	45.2	48.9
- 3	61.4	61.4
- 2	23.2	-24.4
- 1	32.5	-38.8
0	19.7	-23.6
1	38.5	-45.6
2	3.1	5.4
3	50.2	59.2
4	44.8	-45.8
5	86.8	-85.0
6	49.3	49.1
7	75.3	74.8
8	52.8	-46.9
9	76.4	-73.9
10	27.7	34.0
11	44.3	41.1
12	5.9	-2.3
13	6.1	-4.3
14	6.3	-2.6
4 4	ł	
-17	28.6	26.4
-16	49.2	45.9
-15	40.3	-44.0
-14	76.5	-69.7
-13	63.8	64.2
-12	74.4	63.5
-11	32.6	-34.6
-10	40.9	-37.5
- 9	45.2	44.5
- 8	30.3	25.4
- 7	14.0	13.2
- 6	13.4	-9.2
- 5	12.9	12.7
- 4	47.2	-49.1
- 3	50.3	56.1
- 2	87.7	103.2
- 1	75.2	-76.7
0	85.4	-83.5
1	45.9	47.2
2	78.0	76.6
3	59.0	-61.3
4	85.4	-74.1
5	9.2	15.4
6	9.8	8.7
7	22.1	21.3
8	45.9	41.7
9	27.6	-26.3
10	43.9	-41.0
11	44.3	42.8
12	46.5	42.2
13	35.9	-39.0
14	45.0	-45.1
15	40.0	40.2
16	40.6	37.2
4 5	ł	
-21	42.4	39.5
-20	37.1	-40.2
-19	30.6	-31.6
-18	34.8	32.3
-17	40.0	36.6
-16	37.4	-35.8
-15	31.4	-33.1
-14	15.8	18.5
-13	8.8	15.7
-12	8.4	14.2
-11	26.1	27.2
-10	32.5	-33.8
- 9	64.6	-64.1
- 8	60.4	58.6
- 7	82.5	80.2
- 6	66.5	-68.9
- 5	56.9	-52.4
- 4	58.9	65.3
- 3	57.2	61.7
- 2	25.2	-24.2
- 1	3.7	-2.5
0	18.9	-20.8
1	15.0	-15.7
2	12.6	12.8
3	49.3	45.1
4	55.8	-57.1
5	51.8	-49.8
6	55.2	58.0
7	59.9	62.4
8	59.1	-56.3
9	47.7	-48.6
10	30.7	30.1
11	32.5	29.1
4 6	ł	
-17	29.7	28.9
-16	38.9	38.8
-15	49.9	-48.5
-14	60.2	-56.1
-13	58.0	57.7
-12	44.6	44.0
-11	64.9	-60.3
-10	37.3	-36.6
- 9	44.4	40.3
- 8	23.8	22.4
- 7	4.7	-9.4
- 6	14.3	-10.5
- 5	31.7	-28.1
- 4	36.4	-35.7
- 3	35.4	32.6
- 2	48.9	51.3
- 1	60.3	-62.0
0	64.0	-61.8
1	74.2	81.2
2	52.4	51.0
3	48.8	-51.7
4	33.7	-31.9
5	5.2	14.4
6	5.4	2.2
7	5.6	1.3
8	38.6	30.8
9	39.8	-34.7
10	43.9	-41.2
11	52.0	53.4
12	31.8	32.1
13	46.4	-42.5
14	43.2	-42.5
4 7	ł	
-11	36.6	33.1
-10	40.0	-37.0
- 9	40.0	-40.0
- 8	75.1	74.9
- 7	45.3	39.9
- 6	85.1	-86.1
- 5	59.6	-54.2
- 4	68.2	64.4
- 3	20.1	19.9
- 2	36.1	-34.0
- 1	5.0	-8.0
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1	20.8	-19.4
2	52.6	46.3
3	37.8	34.5
4	56.6	-53.9
5	34.0	-36.3
6	59.6	61.7
7	55.8	49.1
8	50.9	-48.6
9	31.2	-29.2
10	50.3	49.9
4 8	ł	
-15	51.4	-50.4
-14	6.7	-16.6
-13	53.7	54.6
-12	31.9	32.4
-11	61.2	-59.7
-10	6.1	-8.7
- 9	29.9	29.8
- 8	18.5	13.8
- 7	5.8	6.7
- 6	5.7	-2.1
- 5	39.0	-35.8
- 4	28.7	-26.3
- 3	57.3	55.4
- 2	21.6	23.2
- 1	82.1	-83.2
0	28.1	-28.3
1	83.8	80.3
2	30.1	27.8
3	67.1	-70.2
4	18.7	-17.7
5	30.1	32.3
6	6.1	11.9
7	6.3	7.6
8	27.1	24.2
9	28.5	-27.3
10	6.7	-12.0
11	49.5	52.9
12	18.7	19.8
13	48.0	-49.7
4 9	ł	
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- 9	6.4	-15.6
- 8	65.6	64.7
- 7	6.2	13.7
- 6	78.4	-75.5
- 5	6.1	-15.6
- 4	67.0	62.7
- 3	6.0	4.5
- 2	28.0	-31.8
- 1	25.2	-20.2
0	9.5	-7.3
1	9.6	-12.7
2	31.6	29.0
3	6.2	10.6
4	47.9	-53.4
5	6.4	-6.1
6	57.6	58.8
7	6.6	-0.8
8	54.2	-53.8
4 10	ł	
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-12	7.1	-1.8
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-10	6.9	-6.4
- 9	40.9	37.8
- 8	6.7	-0.2
- 7	6.6	-3.6
- 6	6.5	8.1
- 5	14.5	-17.3
- 4	6.5	-7.7
- 3	36.9	38.2
- 2	6.4	-1.3
- 1	52.7	-54.4
0	6.5	-5.4
1	74.2	73.8
2	10.4	6.6
3	34.1	-40.2
4	6.7	-8.2
5	6.8	14.2
6	6.9	3.3
7	7.0	3.1
8	7.1	-1.4
9	32.5	-32.2
10	7.4	-3.8
11	40.4	44.1
12	7.6	4.2
13	41.8	-42.3
4 11	ł	
-10	30.4	-35.1
- 9	7.2	5.3
- 8	49.0	47.4
- 7	7.0	-0.4
- 6	66.8	-63.4
- 5	6.9	5.3
- 4	42.4	45.1
- 3	6.9	3.4
- 2	6.9	-16.1
- 1	6.9	3.5
0	6.9	-1.1
1	6.9	2.5
2	22.1	26.0
3	7.0	8.1
4	38.3	-40.2
5	7.2	6.7
6	50.3	50.1
7	7.4	-3.0
8	47.4	-50.4
4 12	ł	
- 3	34.7	36.7
- 2	7.3	-13.0
- 1	52.5	-54.0
0	7.3	13.4
1	47.3	51.2
5 0	ł	
-14	52.2	-49.9
-12	89.6	84.5
-10	141.2	-122.3
- 8	111.1	108.1
- 6	70.1	-74.0
0	49.7	-54.2
2	76.0	74.9
4	121.2	-117.1
6	90.7	83.3
8	44.5	-43.4
5 1	ł	
-19	37.7	-44.2
-18	6.8	14.0
-17	58.0	68.0
-16	5.9	-14.2
-15	77.0	-71.5
-14	4.8	6.5
-13	53.3	51.3
-12	37.4	-32.4
-11	21.9	-15.6
-10	2.6	-9.3
- 9	24.3	-26.8
- 8	2.6	1.4
- 7	55.5	51.1
- 6	12.6	-15.7
- 5	87.0	-97.5
- 4	11.8	15.2
- 3	120.2	131.0
- 2	15.3	-21.0
- 1	100.1	-105.8
0	14.5	15.9
1	67.2	69.8
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3	6.2	2.9
4	2.9	-2.7
5	51.1	-50.5
6	3.5	-3.7
7	64.5	60.6
8	38.9	-35.9
9	79.2	-70.5
10	5.5	7.9
11	62.5	57.7
12	17.8	-18.1
13	50.5	-46.9
5 2	ł	
-18	31.0	34.2
-17	6.6	-2.4
-16	6.1	0.0
-15	5.5	-9.7
-14	42.6	-41.6
-13	18.7	17.6
-12	64.6	67.2
-11	28.8	-28.6
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- 9	29.3	32.5
- 8	97.8	88.2
- 7	3.4	-4.6
- 6	73.0	-70.6
- 5	20.4	20.9
- 4	18.6	-22.5
- 3	9.2	11.4
- 2	28.7	37.5
- 1	3.9	-1.1
0	42.2	-41.6
1	53.3	56.9
2	95.8	93.5
3	29.8	-28.5
4	90.0	-85.3
5	26.1	25.6
6	70.3	74.4
7	28.0	-27.2
8	32.0	-31.4
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10	5.7	-3.2
11	6.3	4.6
12	29.7	32.0
13	7.0	-7.6
14	59.9	-58.9
15	7.6	13.0
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5 3	ł	
-19	49.0	-50.3
-18	20.3	21.8
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-16	35.6	-30.7
-15	62.6	-60.6
-14	19.1	17.2
-13	55.8	57.2
-12	25.1	-22.8
-11	33.6	-33.3
-10	21.7	18.7
- 9	19.9	-19.0
- 8	22.3	23.9
- 7	32.0	32.1
- 6	25.3	-27.0
- 5	77.0	71.1
- 4	37.0	43.6
- 3	83.4	86.5
- 2	29.2	-29.2
- 1	87.5	-84.0
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1	38.5	39.4
2	12.9	-18.7
3	24.4	25.0
4	18.5	-17.4
5	29.9	-32.5
6	18.1	17.1
7	70.3	67.2
8	22.4	-30.0
9	76.5	-69.7
10	45.0	37.4
11	61.9	59.8
12	22.2	-19.9
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5 4	ł	
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- 7	28.6	-28.5
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- 5	17.3	20.3
- 4	16.6	16.2
- 3	12.8	-16.0
- 2	32.4	31.1
- 1	40.4	-40.3
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1	31.9	30.5
2	66.1	72.5
3	54.0	-53.2
4	90.9	-78.9
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6	73.8	70.0
7	36.8	-34.8
8	34.5	-31.7
5 5	ł	
-16	37.5	-35.1
-15	48.1	-42.1
-14	32.8	33.7
-13	39.1	37.6
-12	21.9	-22.5
-11	16.8	-22.3
-10	4.7	-0.6
- 9	4.4	-12.1
- 8	34.6	32.5
- 7	50.8	56.2
- 6	46.3	-48.0
- 5	51.0	-54.7
- 4	85.7	81.6
- 3	82.8	82.6
- 2	59.7	-71.3
- 1	66.1	-76.7
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1	34.5	32.4
2	27.7	-23.8
3	4.3	-4.9
4	4.6	-4.4
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7	30.5	29.2
8	50.7	-47.2
9	61.0	-57.1
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11	54.7	50.9
5 6	ł	
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-12	42.2	42.4
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-10	42.0	-42.3
- 9	66.8	64.8
- 8	57.6	56.8
- 7	54.1	-56.4
- 6	23.7	-25.3
- 5	30.8	29.1
- 4	8.8	7.1
- 3	18.2	19.9
- 2	4.3	7.4
- 1	21.5	-20.6
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3	65.6	-60.5
4	54.5	-53.0
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6	27.7	27.3
7	45.7	-46.3
5 7	ł	
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-17	12.1	17.1
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-15	9.8	-16.0
-14	34.9	37.1
-13	30.0	29.7
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-10	6.3	1.9
- 9	6.0	-8.5
- 8	5.8	7.8
- 7	24.3	25.2
- 6	54.8	-51.8
- 5	31.2	-29.9
- 4	69.6	69.9
- 3	39.8	40.9
- 2	62.6	-59.5
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2	25.8	-26.8
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7	28.9	26.1
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9	24.5	-27.7
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-10	24.3	-23.3
- 9	63.7	64.9
- 8	23.5	25.6
- 7	34.5	-38.0
- 6	19.3	-16.8
- 5	21.8	27.4
- 4	6.2	-2.3
- 3	6.2	15.2
- 2	6.2	8.3
- 1	40.5	-39.1
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4	22.2	-24.1
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5 9	ł	
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-17	8.5	12.2
-16	46.9	-46.8
-15	15.6	20.9
-14	45.7	43.3
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-12	7.7	-18.2
-11	7.5	-2.9
-10	7.4	8.9
- 9	7.2	0.6
- 8	20.4	19.2
- 7	7.1	4.0
- 6	48.3	-43.2
- 5	6.9	-11.5
- 4	68.4	65.0
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- 2	67.3	-63.2
- 1	15.9	-18.0
0	47.6	42.7
1	7.1	10.0
2	18.8	-20.5
3	7.2	1.4
4	7.3	-11.8
5	7.5	-14.2
6	56.2	46.3
7	7.7	11.8
8	40.9	-43.3
9	8.1	-5.1
10	43.2	44.5
5 10	ł	
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-12	8.1	1.8
-11	62.9	-57.1
-10	7.9	-2.5
- 9	52.5	52.0
- 8	7.7	10.3
- 7	57.4	-54.3
- 6	7.5	-2.8
- 5	7.5	11.8
- 4	7.4	-5.8
- 3	7.4	-2.0
- 2	7.4	9.1
- 1	15.9	-18.0
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2	7.6	-2.5
3	61.2	-60.5
4	7.8	-12.8
5	48.2	44.6
6	8.1	5.1
7	37.1	-35.3
5 11	ł	
- 6	50.5	-51.3
- 5	8.0	9.8
- 4	55.8	53.8
- 3	7.9	-2.5
- 2	59.9	-53.7
- 1	8.0	1.6
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5 12	ł	
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-10	8.8	13.7
- 9	40.8	43.5
- 8	8.6	-5.6
- 7	26.2	-24.9
- 6	8.5	3.8
- 5	14.5	10.6
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- 3	8.4	-2.3
- 2	8.4	-3.1
- 1	20.8	-22.3
0	9.3	10.1
1	38.5	43.7
2	8.6	-13.0
3	35.6	-34.6
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5	44.3	38.3
6 0	ł	
2	53.9	52.7
4	62.2	-64.8
6	95.3	83.9
8	70.5	-61.6
10	47.5	50.7
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-16	7.0	-3.1
-15	67.0	-61.1
-14	6.0	8.5
-13	80.1	88.7
-12	11.2	3.1
-11	68.3	-69.6
-10	4.3	14.5
- 9	24.2	19.7
- 8	3.6	-4.6
- 7	5.6	-7.3
- 6	6.1	-6.2
- 5	22.1	-27.6
- 4	8.3	11.9
- 3	50.2	55.9
- 2	2.6	7.0
- 1	91.2	-104.1
0	18.2	19.8
1	82.0	83.2
2	3.8	1.2
3	71.6	-67.6
4	4.5	-4.0
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6	5.3	-3.5
7	7.3	9.5
8	7.9	-13.0
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11	62.2	57.4
12	7.8	-14.8
13	49.8	-46.9
6 2	ł	
-20	58.5	-56.8
-19	8.0	12.5
-18	49.5	44.8
-17	7.4	-14.2
-16	41.7	-35.2
-15	6.2	8.2
-14	17.7	18.0
-13	5.8	8.6
-12	17.8	17.9
-11	17.6	-19.9
-10	46.7	-49.8
- 9	15.8	15.9
- 8	76.0	79.8
- 7	32.4	-36.0
- 6	109.7	-117.7
- 5	24.3	26.4
- 4	67.2	73.5
- 3	11.6	-15.1
- 2	37.8	-42.7
- 1	19.7	19.1
0	3.5	4.3
1	3.8	0.8
2	40.7	35.6
3	22.1	-22.0
4	60.0	-58.8
5	13.0	16.1
6	78.6	71.4
7	24.1	-19.0
8	53.2	-51.4
9	7.0	3.4
10	34.8	38.4
11	7.6	-13.0
12	30.3	-32.6
6 3	ł	
-17	35.0	35.2
-16	29.5	-28.7
-15	60.8	-56.0
-14	37.6	30.0
-13	86.6	82.0
-12	33.8	-31.4
-11	56.5	-58.6
-10	29.3	28.3
- 9	45.2	43.6
- 8	28.3	-28.3
- 7	4.1	-5.9
- 6	3.9	-6.6
- 5	16.2	-15.8
- 4	30.3	29.7
- 3	56.3	56.6
- 2	29.2	-28.4
- 1	67.3	-69.6
0	40.4	31.3
1	83.6	83.9
2	43.0	-41.1
3	44.9	-42.7
4	28.2	28.4
5	41.1	39.3
6	5.9	-0.0
7	6.3	7.3
8	6.8	-2.7
9	36.6	-40.1
10	7.4	13.1
11	53.3	53.3
12	32.5	-32.9
13	48.8	-49.9
6 4	ł	
-20	31.2	-35.7
-19	30.3	33.6
-18	38.7	40.9
-17	37.4	-32.8
-16	33.4	-29.5
-15	18.5	16.6
-14	7.0	0.8
-13	6.6	-5.0
-12	6.2	7.4
-11	16.3	-17.9
-10	39.1	-40.6
- 9	31.9	35.0
- 8	71.5	73.8
- 7	43.4	-46.0
- 6	63.1	-71.3
- 5	42.5	43.8
- 4	57.8	54.6
- 3	37.5	-33.0
- 2	29.9	-30.3
- 1	23.0	18.9
0	8.2	3.8
1	20.9	21.0
2	34.3	34.2
3	28.5	-26.2
4	60.1	-58.6
5	46.2	45.6
6	58.8	49.6
7	30.2	-31.2
8	40.8	-41.5
9	37.9	36.6
10	29.4	27.5
6 5	ł	
-16	28.2	-32.0
-15	49.4	-45.6
-14	35.0	32.4
-13	41.5	40.0
-12	49.1	-47.2
-11	46.3	-44.1
-10	29.9	25.6
- 9	24.4	22.2
- 8	17.2	-19.0
- 7	9.5	-5.4
- 6	19.7	-21.1
- 5	28.1	-24.5
- 4	32.4	29.2
- 3	47.0	46.4
- 2	41.9	-40.5
- 1	59.3	-56.6
0	64.7	61.7
1	46.8	46.2
2	44.3	-44.4
3	42.5	-49.2
4	32.9	33.1
5	6.6	7.8
6	7.0	-7.5
7	7.2	-1.7
8	7.4	-17.5
9	24.1	-25.0
10	26.9	28.7
11	44.6	46.8
12	32.5	-33.4
13	38.7	-37.5
6 6	ł	
-19	42.4	33.3
-18	39.7	39.2
-17	21.4	-23.3
-16	20.8	-23.4
-15	20.2	23.4
-14	7.7	10.0
-13	7.5	-4.5
-12	7.2	9.9
-11	31.2	-29.6
-10	17.4	-17.1
- 9	27.8	31.9
- 8	36.2	45.3
- 7	59.8	-58.7
- 6	51.5	-48.8

Table 4 (cont.)

```
- 5  61.0   56.0    - 5   6.8  -11.5     6  14.8   13.2    - 9  35.1   34.6
- 4  36.8   34.6    - 4  36.4   32.8     7  40.1  -48.3    - 8   8.6    8.1
- 3  36.8  -33.9    - 3  17.5   24.0     8   8.9  -20.5    - 7  52.4  -47.7
- 2   7.3  -12.4    - 2  46.5  -42.4     9  38.8   39.5    - 6   8.4   -4.1
- 1   5.9    6.4    - 1  40.9  -40.2   6  9   √              - 5  52.9   51.5
  0   6.0    6.1      0  56.5   57.4   -16  42.4  -38.7    - 4   8.4   11.8
  1  28.6   27.1      1  40.1   38.5   -15   9.0  -13.9    - 3  26.3  -32.2
  2  24.6   21.9      2  54.8  -55.2   -14  44.0   43.0    - 2   8.4    3.5
  3  39.3  -36.6      3  22.7  -24.1   -13   8.7   13.9    - 1   8.4    5.5
  4  54.8  -49.3      4  36.8   38.7   -12  52.6  -51.0      0   8.4   -2.6
  5  43.8   40.4   6  8   √            -11   8.4   -8.0      2  24.5   18.9
  6  45.1   41.2    -11  22.8  -22.1   -10  39.7   38.0      3   8.6   -2.6
  7  49.4  -49.9    -10   9.9  -13.9    - 9   8.2    1.1      3  31.5  -31.4
  8  24.4  -25.5    - 9  53.1   57.8    - 8   8.1  -13.3      4   8.8   -0.8
  9  29.0   31.9    - 8  19.3   25.9    - 7   8.0    5.4      6  36.2   45.1
 10  27.9   28.3    - 7  59.9  -57.3    - 6   7.9   -8.7      6   9.0   -0.3
6  7  √             - 6  18.9  -25.0    - 5   7.9   10.2      7  26.2  -37.3
-16  28.7  -32.3    - 5  69.4   66.3    - 4  24.7   24.3      8   9.1   -1.4
-15  25.4  -26.6    - 4  13.2   19.1    - 3  16.2   16.3      9  27.0   37.7
-14  58.4   57.2    - 3  54.8  -55.2    - 2  50.5  -48.2   6 11   √
-13  53.4   32.4    - 2   7.4   -8.9    - 1   7.9   -3.4    - 4  32.3   30.4
-12  49.1  -49.5    - 1   7.4    8.5      0  37.1   50.0    - 3   8.9   -9.9
-11  28.8  -28.3      0   7.5   -0.6      1   6.0   10.7    - 2  41.2  -38.2
-10  42.0   40.7      1   7.5   17.0      2  54.2  -54.1    - 1   8.9   -5.6
- 9  13.0   17.8      2   7.6   10.3      3   8.2   -8.1      1   9.0    1.2
- 8   7.2  -12.3      3  26.2  -29.5      4  32.1   33.6      2  43.0   44.3
- 7   7.0   -0.9      4  17.5  -19.4   6 10   √                1   9.0    1.2
- 6   6.9   -0.6      5  29.1   33.5                          2  43.6  -42.2
```

Refinement was attempted by means of a three-dimensional difference Fourier synthesis, omitting reflexions with very large discrepancies between F_{obs} and F_{calc} and very strong F_{obs} with low $\sin\theta/\lambda$ values, followed by a block-diagonal least-squares procedure. The refinement stopped, however, at $R = 0.18$, evidently because the F values were rather inaccurate. The three-dimensional Fourier syntheses and the first set of least-squares calculations were carried out on an NE 503

computer by means of programs written by Weiss & Denner.

The final refinement was performed on the IBM 360/50 computer with the Zalkin full-matrix least-squares program with the use of the more accurate structure factors Hkl, with $H = 0, 1, \ldots 6$, collected from a spherical crystal with Mo $K\alpha$ radiation and scaled by comparison of the F_{obs} and F_{calc}. To obtain more reliable results the very strong F_{obs} with low indices which were relative inaccurately measured and influenced by extinction and all reflexions for which $I_{obs} \le 3$ in terms of the visual intensity scale were left out. The McWeeny (1951) f curve was assumed for boron, those of Berghuis, Haanappel, Potters, Loopstra, MacGillavry & Veenendaal (1955) for oxygen and those of Thomas & Umeda (1957) for barium. The parameters resulting from the least-squares refinement based on the first set of data recorded with Cu $K\alpha$ radiation were used as a starting point. As the first step, the positional parameters, the individual isotropic thermal parameters and the scale factors for the layers were refined. After three cycles the R index dropped from 0.108 to 0.068. The quantity minimized was
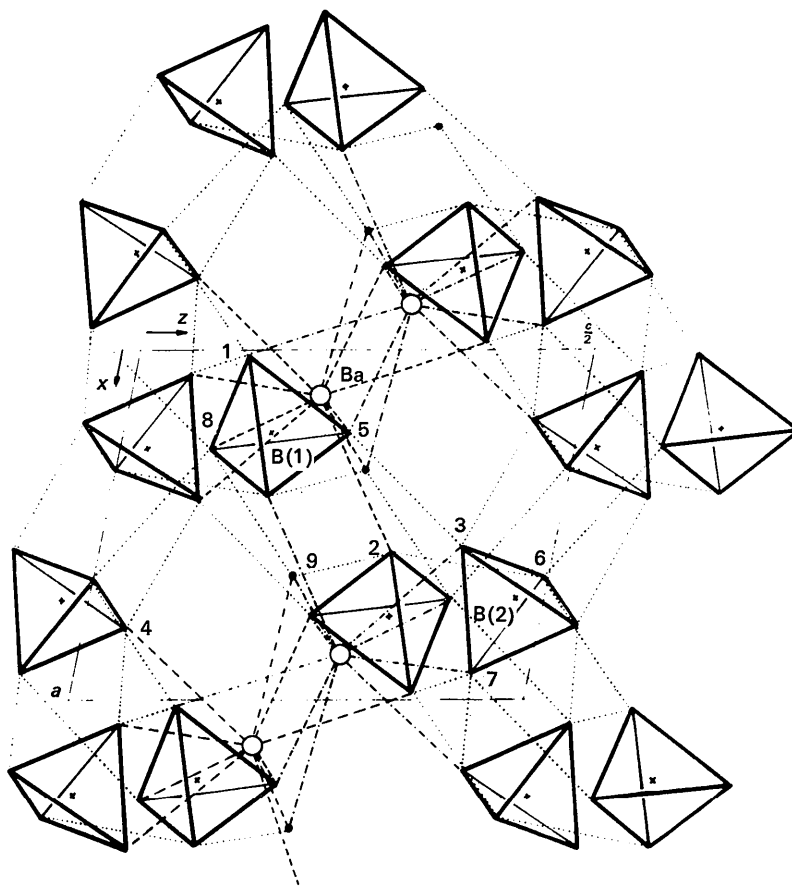

Fig. 1. The structure projected along the b axis. The B(OH)$_4^-$ tetrahedra are shown. The Ba atoms are marked by circles, the water molecules by points, and the boron atoms by crosses. The oxygen atoms coordinating a Ba atom are linked by dashed lines to the Ba atom. Hydrogen bonds are indicated by dotted lines.

$\Sigma w(|F_o| - |F_c|)^2$ and the weighting scheme was that of Cruickshank (1961). After correction of the weighting parameters the isotropic thermal parameters of the barium and oxygen atoms were transformed into the anisotropic B values and two further cycles were calculated. The final R index is 0·065 for the 1369 reflexions used in the refinement (very strong and unobserved hkl omitted). The R index for all 1671 observed reflexions is 0·067 and the R index for all 2111 reflexions (unobserved included) is 0·084.

Ozol *et al.* (1967) give, as R indices for their coordinates, 0·154 for $h0l$, 0·164 for $0kl$ and 0·133 and 0·143 respectively with zero reflexions excluded.

The positional parameters and standard deviations resulting from the final anisotropic refinement are listed in Table 2. The isotropic thermal parameters obtained before anisotropic refinement was started are given in brackets. The anisotropic thermal parameters are listed in Table 3, the B_{ij} being the coefficients in the expression

$$\exp[-(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + B_{12}hk + B_{13}hl + B_{23}kl)] .$$

The observed and calculated structure factors are compared in Table 4. This shows that the F_{obs} of a number of high intensity low angle reflexions were systematically too low, because of extinction, which was not allowed for, for most other reflexions there is much better agreement.

Description of the structure

The structure contains discrete tetrahedral $B(OH)_4^-$ groups; the appropriate formula is therefore

$$Ba[B(OH)_4]_2.H_2O .$$
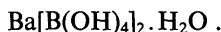
The Ba atom is coordinated by eight hydroxyl groups and two water molecules. Three $B(OH)_4^-$ tetrahedra share edges and two $B(OH)_4^-$ tetrahedra share corners with the Ba polyhedron. Each Ba polyhedron shares an edge each with two other Ba polyhedra. In this way chains wound around the screw axis are formed. The chains are linked in the [100] and [001] directions by boron tetrahedra. Additional bonding is provided by ten hydrogen bonds (Fig. 1). All hydrogen bonds are of the types OH–H₂O and OH–OH. There are no hydrogen bonds between the water molecules in the crystal. The positions of the hydrogen bonds were derived from

0·2 to each H…O bond, then the strength of the bonds ending at an oxygen atom add up to values ranging from 1·95 to 2·15. Thus the detailed balance of valences is nearly perfect throughout the structure. A study of the thermal coefficients shows that the amplitude of vibration of the water oxygen atom is larger than that of the hydroxyl oxygen atoms. As expected, the thermal motions of the barium and boron atoms are considerably smaller than those of the oxygen atoms. The mean B–O distances in the two independent tetrahedra are 1·483 and 1·474 Å respectively. The tetrahedra are fairly regular with angles ranging from 107·0 to 114·2°.

This structure conforms with theory proposed by Edwards & Ross (1960). The ratio of the number of tetrahedral boron atoms to the total number of boron atoms is equal to the ratio of the cation charge to the total number of boron atoms.

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Table 5. *Bond distances*

Tetrahedron about B(1)		Hydrogen bonds	
B(1)–O(1)	1·500 ± 0·015 Å	O(1)–O(6″)	2·897 ± 0·012 Å
B(1)–O(2′)	1·481 ± 0·015	O(1)–O(7′)	2·803 ± 0·012
B(1)–O(5)	1·485 ± 0·015	O(2)–O(6)	2·835 ± 0·012
B(1)–O(8)	1·466 ± 0·015	O(2)–O(9)	2·684 ± 0·012
		O(3)–O(4′)	2·868 ± 0·012
Tetrahedron about B(2)		O(3)–O(5)	2·748 ± 0·012
B(2)–O(3)	1·475 ± 0·015 Å	O(4)–O(7′)	2·771 ± 0·012
B(2)–O(4″)	1·498 ± 0·015	O(6)–O(8″)	2·956 ± 0·012
B(2)–O(6)	1·462 ± 0·015	O(7)–O(8″)	2·818 ± 0·012
B(2)–O(7)	1·459 ± 0·015	O(8)–O(9)	2·973 ± 0·012