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The Crystal Structure of Potassium Tetraborate Tetrahydrate

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The compound $K_2B_4O_7.4H_2O = K_2[B_4O_5(OH)_4].2H_2O$ is orthorhombic, space group $P2_12_12_1$, with four molecules in a cell of dimensions $a=12{\cdot}899$, $b=11{\cdot}774$, $c=6{\cdot}859$ Å. The positions of all atoms (including the hydrogen atoms) have been determined. The final R-index is 0·040, and the bond lengths have been determined to an accuracy of 0·006 Å for K–O bonds, 0·008 Å for B–O bonds and 0·11 Å for H–O bonds. The structure contains the complex ion $[B_4O_5(OH)_4]^{2-}$ consisting of two boron–oxygen triangles and two tetrahedra which have only corners in common. Detailed results are reported for bond distances, and bond angles and for the anisotropic thermal motions.

Introduction

This paper reports the results of a crystal structure examination of the compound $K_2B_4O_7.4H_2O = K_2[B_4O_5(OH)_4].2H_2O$. The investigation is part of a systematic study of borate structures which was begun in this laboratory in the nineteen thirties, was interrupted by the war, and has been resumed in recent years.

Single crystals were prepared by slow evaporation from aqueous solutions. The formula was confirmed by chemical analysis which gave the following result:

	Exp.	Theor.
K	24·4%	25·6%
B	14·7	14·2
H_2O	21·2	23·6

A direct density determination gave $\varrho=1{\cdot}919$ g.cm^{-3}.

The crystals were found to be orthorhombic with cell dimensions

$$a=12{\cdot}899\pm0{\cdot}002,\ b=11{\cdot}774\pm0{\cdot}002,$$
$$c=6{\cdot}859\pm0{\cdot}001\ \text{Å}.$$

The cell contains four molecules, the calculated density being 1·898 g.cm^{-3}.

The only systematic absences are the odd orders of pinacoidal reflections. Accordingly one is led to the space group symmetry $P2_12_12_1$ with all atoms in general positions:

$$(x, y, z)\,(\tfrac{1}{2}-x, \bar{y}, \tfrac{1}{2}+z)\,(\tfrac{1}{2}+x, \tfrac{1}{2}-y, \bar{z})\,(\bar{x}, \tfrac{1}{2}+y, \tfrac{1}{2}-z)$$

and 75 positional degrees of freedom.

With the aid of a counter spectrometer and Cu $K\alpha$ radiation the intensities were measured for all (867) reflections $HK0$, $HK1$, $H0L$, $H1L$, $0KL$, $1KL$. The specimen was a crystal ground into a nearly perfect sphere of radius $R=0{\cdot}0259\pm0{\cdot}0015$ cm.

Determination of the structure

According to the space group symmetry $P2_12_12_1$ the projection of the structure on each of the coordinate planes has a center of symmetry. Because of the relatively short c period, it was to be expected that the projection on the XY plane would give the best

resolution, and the first step towards the solution of the structure was therefore based on the ($HK0$) data.

By the statistical method introduced ten years ago (Zachariasen, 1952) a self-consistent set of signs for 62 large F_{HK0} terms was deduced. A Fourier synthesis carried out with these terms gave the approximate positions of all potassium, boron and oxygen atoms, and quite precise x and y coordinates were obtained by least-square refinements based on all experimental $|F_{HK0}|$ data.

An accurate projection of the structure having been deduced, it was a simple task to find the approximate z coordinates so that refinements utilizing the full set of three-dimensional data could be made.

The final least-square refinement provided for the simultaneous adjustment of 180 parameters: 3 scale factors, 75 position parameters, and 102 thermal parameters (the eight hydrogen atoms were assumed to have isotropic thermal motion with $B=5{\cdot}0$ Å^2). In the structure are eight short oxygen–oxygen distances which can be explained only in terms of O–H $\cdots$ O bonds. The midpoints of these short oxygen–oxygen connection lines were used as initial coordinates for the hydrogen atoms so as not to introduce preconceived ideas as to which oxygen atoms were hydroxyl or water oxygens.

The McWeeny (1951) f-curves were assumed for boron and hydrogen, those of Berghuis, Haanappel, Potters, Loopstra, MacGillavry & Veenendaal (1955) for potassium and oxygen.

The results of the final refinement, which gave $R=0{\cdot}040$, are shown in Tables 1 and 2, while Tables 3–5 illustrate the degree of agreement between observed and calculated structure factors.

Table 1. *Atomic coordinates*

	x	σ	y	σ	z	σ
K_I	0·3587	±0·0001	0·3360	±0·0001	0·2139	±0·0003
K_{II}	0·7130	±0·0001	0·4001	±0·0001	0·5298	±0·0003
B_I	0·4484	±0·0006	0·2893	±0·0006	0·6514	±0·0014
B_{II}	0·4558	±0·0006	0·0846	±0·0006	0·6222	±0·0015
B_{III}	0·6281	±0·0005	0·0973	±0·0006	0·4691	±0·0014
B_{IV}	0·5940	±0·0006	0·1831	±0·0006	0·7920	±0·0013
O_I	0·5277	±0·0003	0·0579	±0·0004	0·4570	±0·0008
O_{II}	0·5174	±0·0003	0·0909	±0·0003	0·8025	±0·0007
O_{III}	0·3942	±0·0004	0·1056	±0·0005	0·1363	±0·0009
O_{IV}	0·6928	±0·0004	0·0653	±0·0004	0·3177	±0·0008
O_V	0·4047	±0·0003	0·1969	±0·0003	0·5830	±0·0009
O_{VI}	0·6633	±0·0003	0·1631	±0·0004	0·6177	±0·0007
O_{VII}	0·6575	±0·0004	0·1953	±0·0004	0·9648	±0·0007
O_{VIII}	0·3972	±0·0003	0·3920	±0·0004	0·6145	±0·0011
O_{IX}	0·3758	±0·0003	−0·0013	±0·0003	0·6326	±0·0009
O_X	0·5392	±0·0003	0·2921	±0·0003	0·7554	±0·0008
O_{XI}	0·5774	±0·0005	0·3443	±0·0005	0·2315	±0·0010
H_I	0·436	±0·008	0·485	±0·009	0·643	±0·021
H_{II}	0·277	±0·007	0·436	±0·009	0·663	±0·018
H_{III}	0·591	±0·008	0·423	±0·010	0·887	±0·020
H_{IV}	0·677	±0·008	0·149	±0·009	0·020	±0·018
H_V	0·489	±0·008	0·042	±0·009	0·202	±0·018
H_{VI}	0·436	±0·008	0·101	±0·009	0·994	±0·017
H_{VII}	0·594	±0·009	0·248	±0·008	0·194	±0·018
H_{VIII}	0·599	±0·008	0·429	±0·010	0·157	±0·017

Table 2. *Anisotropic thermal parameters* ($\times 10^4$)

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
K_I	32	41	157	7	−2	3
σ	1	1	4	1	2	3
K_{II}	29	39	162	−4	22	−3
σ	1	1	4	1	2	3
B_I	26	27	111	6	11	6
σ	4	4	18	4	11	11
B_{II}	24	24	150	0	−1	−15
σ	4	4	20	4	13	11
B_{III}	31	29	109	4	−4	−12
σ	4	4	17	4	10	13
B_{IV}	28	22	112	2	1	0
σ	4	4	17	4	10	11
O_I	27	38	114	−4	2	−32
σ	2	3	10	3	6	8
O_{II}	25	21	108	−1	−7	6
σ	2	2	11	3	6	6
O_{III}	43	65	163	2	−2	2
σ	3	4	13	4	7	9
O_{IV}	33	48	111	0	15	−21
σ	2	3	10	3	6	7
O_V	24	27	168	2	−22	3
σ	2	3	14	3	8	7
O_{VI}	29	35	135	−2	−7	−21
σ	2	3	10	3	6	8
O_{VII}	32	44	116	4	−19	3
σ	3	3	10	3	6	7
O_{VIII}	30	25	195	6	−9	−2
σ	2	3	15	3	9	9
O_{IX}	26	27	163	−4	−9	18
σ	2	3	13	3	7	7
O_X	28	18	152	3	−18	0
σ	2	2	12	2	7	7
O_{XI}	64	57	171	2	4	−15
σ	3	4	14	4	8	11

Discussion of the structure

The results of the final refinement correspond to the following standard errors for the various interatomic distances: 0·006 Å for K–O bond lengths, 0·007 Å for O–O separations, 0·008 Å for B–O bonds, and 0·11 Å for H–O and H $\cdots$ O distances.

In the course of the last refinement all of the eight hydrogen atoms moved from their initial positions towards one of the two oxygen atoms. The resulting interatomic distances are as follows:

$O_{VIII} \cdots O_{II}$	= 2·649 Å	O_{VIII}–H_I	= 1·22 Å
$O_{IV} \cdots O_{VIII}$	= 2·725	O_{IV}–H_{II}	= 1·09
$O_{IX} \cdots O_X$	= 2·777	O_{IX}–H_{III}	= 1·00
$O_{VII} \cdots O_{IV}$	= 2·900	O_{VII}–H_{IV}	= 0·72
$O_{III} \cdots O_I$	= 2·849	O_{III}–H_V	= 1·50
$O_{III} \cdots O_{II}$	= 2·791	O_{III}–H_{VI}	= 1·11
$O_{XI} \cdots O_{VII}$	= 2·737	O_{XI}–H_{VII}	= 1·18
$O_{XI} \cdots O_{IX}$	= 3·097	O_{XI}–H_{VIII}	= 1·15

$O_{II} \cdots H_I$	= 1·43 Å
$O_{VIII} \cdots H_{II}$	= 1·68
$O_X \cdots H_{III}$	= 1·91
$O_{IV} \cdots H_{IV}$	= 2·27
$O_I \cdots H_V$	= 1·83
$O_{II} \cdots H_{VI}$	= 1·69
$O_{VII} \cdots H_{VII}$	= 1·88
$O_{IX} \cdots H_{VIII}$	= 2·17

Table 3. *Reflections HK0 and HK1*

HK	L = 0			L = 1			
	F_o	A	B	F_o	$\|F_c\|$	A	B
10	0	0	0	47.4	46.4	0	46.4
01	0	0	0	62.2	63.0	0	-63.0
11	4.5	0	-5.3	51.9	53.1	24.4	-47.2
20	42.8	44.9	0	5.4	2.4	0	2.4
02	16.7	-13.1	0	51.5	53.4	53.4	0
21	10.1	-10.9	0	23.9	23.3	-20.0	11.9
12	28.9	0	-28.7	30.6	31.8	30.2	-9.9
22	17.7	-16.1	0	37.5	37.7	23.1	-29.8
30	0	0	0	69.7	70.9	0	70.9
31	16.9	0	-17.0	25.0	22.2	20.6	-8.2
03	0	0	0	86.7	91.2	0	-91.2
13	61.0	0	63.1	25.3	25.8	21.8	13.8
32	39.7	0	-39.7	61.3	63.5	-60.1	-20.4
23	15.0	-12.7	0	48.8	49.8	-15.9	47.3
40	95.1	-97.1	0	75.6	77.1	0	77.1
41	43.3	41.6	0	52.5	51.7	46.7	-22.2
04	116.4	-121.1	0	88.3	91.8	-91.8	0
33	23.9	0	24.9	6.9	6.0	-5.4	2.5
14	72.6	0	-72.6	41.7	41.4	-21.0	35.7
42	50.0	50.1	0	39.1	37.7	-37.7	0.4
24	28.5	29.9	0	72.6	74.2	51.6	53.4
50	0	0	0	17.4	16.2	0	16.2
51	46.3	0	44.8	49.0	49.1	-19.1	45.2
43	54.4	52.6	0	33.9	32.6	-17.6	-27.5
34	63.8	0	-64.8	61.8	62.3	-56.2	-26.9
52	10.4	0	-9.9	24.3	24.4	13.2	-20.5
05	0	0	0	26.8	26.7	0	-26.7
15	42.3	0	-42.5	57.3	58.2	31.1	49.2
25	31.7	-30.3	0	43.9	42.5	-39.9	-14.8
44	19.9	17.6	0	88.4	87.8	78.7	-38.9
53	115.3	0	-117.2	15.6	14.4	14.1	2.7
60	14.9	15.1	0	55.4	54.5	0	-54.5
61	87.2	-85.5	0	24.1	23.5	-0.9	23.5
35	57.8	0	54.2	34.8	32.5	-32.5	0.2
62	4.0	2.2	0	43.2	41.5	29.4	-29.3
06	3.6	-1.1	0	16.1	16.2	-16.2	0
54	19.3	0	-19.5	44.8	43.4	23.1	-36.8
16	20.3	0	-21.2	24.0	24.4	2.4	-24.3
45	13.1	13.3	0	30.9	29.0	-27.0	-10.6
63	72.8	-69.1	0	17.1	17.0	-8.9	-14.5

HK	L = 0			L = 1			
	F_o	A	B	F_o	$\|F_c\|$	A	B
14.5	7.4	6.6	0	3.6	3.5	-3.5	-0.5
15.1	3.9	0	-3.0	13.8	14.0	-0.3	-14.0
9.11	9.1	0	-9.8	12.9	14.6	-9.2	11.4
13.7	7.6	0	8.9	9.0	9.5	6.9	6.6
5.13	4.0	0	3.9	9.7	9.8	1.6	9.7
15.2	18.7	0	20.1	21.6	22.3	18.7	12.2
0.14	9.5	-9.1	0	23.0	22.8	22.8	0
15.3	4.0	0	3.4	8.5	8.7	0.4	-8.7
1.14	5.9	0	6.4	3.6	5.4	2.0	5.0
8.12	12.4	13.4	0	4.9	5.5	-4.7	2.9
6.13	9.5	-10.0	0	13.2	12.9	12.8	1.8
14.6	8.1	8.3	0	6.2	5.5	0.7	-5.5
2.14	13.5	14.8	0	11.3	11.2	7.3	8.5
11.10	8.2	0	7.6	10.9	10.7	-0.9	-10.7
12.9	0	-0.1	0	14.6	14.4	-2.8	-14.1
15.4	12.8	0	-13.0	10.0	9.6	0.2	9.6
3.14	20.4	0	-21.5	7.1	7.6	-7.0	2.9
10.11	18.3	-18.8	0	9.3	8.7	-2.2	-8.4
13.8	5.2	0	5.9	4.5	4.3	4.3	0.1
4.14	7.1	7.0	0	7.1	7.4	-1.8	-7.1
7.13	3.3	0	-3.9	3.2	2.7	2.6	-0.7
9.12	4.7	0	6.3	8.7	8.7	-5.0	7.1
14.7	7.3	-6.8	0	14.9	16.5	2.5	16.3
15.5	14.9	0	-15.5	3.8	3.9	-0.3	3.9
16.0	24.3	-24.5	0	13.8	14.0	0	-14.0
16.1	2.1	-1.6	0	8.9	8.6	-5.5	6.6
5.14	5.4	0	-4.7	12.1	11.5	11.5	-0.7
16.2	10.0	9.7	0	4.7	4.0	-3.1	-2.5
12.10	15.9	-15.6	0	8.1	8.8	1.0	8.8
11.11	12.7	0	13.0	7.5	8.1	-2.1	-7.8
13.9	13.0	0	-14.2	6.4	6.2	-1.6	6.0
16.3	18.5	-20.1	0	14.9	15.7	10.8	11.4
8.13	16.3	19.5	0	2.8	3.1	-1.3	2.9
15.6	2.7	0	2.7	9.5	9.3	-3.8	-8.4
1.15	3.1	0	3.1				
6.14	5.4	4.6	0				
14.8	4.2	4.9	0				
10.12	2.6	-3.5	0				
2.15	1.6	0.3	0				
16.4	10.4	12.0	0				

Table 4. *Reflections 0KL and 1KL*

KL	H = 0			H = 1			
	F_o	A	B	F_o	$\|F_c\|$	A	B
10	0	0	0	4.5	5.3	0	-5.3
01	0	0	0	47.4	46.4	0	46.4
11	62.2	0	-63.0	51.9	53.1	24.4	-47.2
20	16.7	-13.1	0	28.2	28.7	0	-28.7
21	51.7	53.4	0	30.6	31.8	30.2	-9.9
30	0	0	0	61.0	63.1	0	63.1
02	33.0	-31.3	0	81.6	79.7	-79.9	0
31	86.7	0	91.2	25.3	25.8	21.8	13.8
12	34.6	0	-33.4	77.1	76.9	58.4	49.9
22	47.2	46.1	0	53.3	52.3	-15.6	-49.9
40	116.4	-121.1	0	72.6	72.6	0	-72.6
41	88.3	-91.8	0	41.7	41.4	-21.0	35.7
32	27.2	0	26.0	25.0	23.5	3.9	-23.2
50	0	0	0	42.2	42.5	0	-42.5
03	0	0	0	44.6	44.1	0	44.1
13	37.2	0	-35.1	4.6	5.0	2.8	4.1
42	0	-2.2	0	63.8	64.4	-9.1	63.8
51	26.8	0	-26.7	57.3	58.2	31.1	49.2
23	68.3	-66.7	0	53.6	52.7	49.6	-17.7
33	55.4	0	-54.6	23.4	21.7	10.8	-18.8
60	3.6	-1.1	0	20.3	21.2	0	-21.2
52	41.5	0	42.2	47.1	45.5	-32.0	-32.4
61	16.1	-16.2	0	24.8	24.4	2.4	-24.3
43	41.2	-39.0	0	35.6	33.5	28.0	-18.3
04	25.0	24.4	0	42.7	41.1	41.1	0
62	57.7	-56.3	0	32.6	32.4	-2.2	-32.3
14	5.9	0	5.2	6.9	6.8	-6.3	2.6
70	0	0	0	5.2	3.7	0	-3.7
24	24.7	-25.2	0	30.3	29.2	13.3	26.0
53	16.6	0	16.1	28.8	28.3	-27.7	-6.1
71	32.1	0	30.6	19.0	18.2	1.3	-18.2
34	33.8	0	32.1	8.2	7.2	3.1	-6.5
72	28.9	0	27.4	4.6	5.0	-4.9	-1.0
63	48.7	47.5	0	39.3	38.0	-7.1	37.3
44	19.0	-17.8	0	35.0	34.0	-23.2	-24.9
80	42.1	-41.7	0	22.6	22.2	0	22.2
81	59.9	57.8	0	23.3	23.7	-23.5	-3.2
54	29.1	0	28.7	29.1	27.9	7.6	-26.8
05	0	0	0	15.4	14.6	0	-14.6
15	42.9	0	43.0	20.3	18.9	-1.6	-18.8

KL	H = 0			H = 1			
	F_o	A	B	F_o	$\|F_c\|$	A	B
11.3	0	0	0.6	5.2	4.9	-2.9	-4.0
27	18.4	-18.1	0	13.4	12.9	-12.0	-4.8
37	4.1	0	-4.2	14.7	16.4	15.9	-4.0
95	5.9	0	-6.5	14.2	14.0	-9.0	10.7
76	3.7	0	1.8	10.3	11.6	8.4	8.0
12.2	13.8	-13.8	0	10.4	10.6	-0.6	10.6
47	15.4	-16.5	0	14.6	14.4	14.0	-3.4
11.4	3.3	0	2.6	10.4	10.8	10.3	-3.1
13.0	0	0	0	7.2	7.4	0	-7.4
57	13.9	0	13.6	6.1	6.0	-4.2	4.3
86	5.0	4.5	0	19.5	20.3	20.2	-2.4
12.3	5.9	-6.4	0	16.3	15.5	9.0	12.6
13.1	9.0	0	-8.7	19.1	18.7	10.5	-15.5
10.5	2.3	-1.7	0	12.7	12.7	-6.3	11.0
67	4.1	4.8	0	3.2	3.1	-1.6	2.7
13.2	7.9	0	6.7	5.9	5.7	4.4	3.7
96	9.4	0	10.0	16.1	16.6	16.1	4.2
08	3.6	2.8	0	9.9	9.7	9.7	0
18	5.6	0	-5.9	9.2	9.3	-5.9	7.2
12.4	2.5	2.2	0	13.6	14.1	13.7	-3.5
28	0	-1.5	0	5.7	6.2	-1.3	6.1
77	7.7	0	-8.4	8.0	9.4	0.3	9.4
11.5	9.8	0	-9.9	13.2	13.5	-12.4	-5.3
13.3	23.2	0	-24.8	11.2	11.5	-11.3	-2.0
14.0	9.5	-9.1	0	6.1	6.4	0	6.4
38	3.8	0	-4.0	3.3	2.8	-2.3	1.6
14.1	23.0	22.8	0	3.6	5.4	2.0	5.0
48	0	0.5	0	8.8	10.6	-10.6	0.3
10.6	4.2	4.7	0	15.0	16.2	16.2	-0.5
14.2	13.0	-13.2	0	5.0	4.9	-3.3	3.7
87	1.5	1.5	0	7.8	8.6	-7.8	3.5
58	4.6	0	5.4	4.5	4.9	4.9	-0.3
13.4	9.5	0	9.5	5.9	6.7	5.3	-4.1
12.5	2.2	-3.0	0	12.4	14.1	9.7	-10.2
14.3	16.3	-17.0	0	3.2	3.6	-2.2	-2.8
68	4.3	4.0	0	5.3	5.2	-0.2	5.2
15.0	0	0	0	3.1	3.1	0	3.1
97	2.3	0	1.6	6.5	7.0	2.8	6.4
11.6	21.3	0	-23.7	7.2	7.8	-6.2	4.8
15.1	0	0	0.3				

Table 5. *Reflections H0L and H1L*

HL	K = 0			K = 1			
	F_o	A	B	F_o	$\|F_c\|$	A	B
10	0	0	0	4.5	5.3	0	-5.3
01	0	0	0	61.3	63.0	0	-63.0
20	42.2	44.9	0	9.9	10.9	-10.9	0
11	46.7	0	46.4	51.1	53.1	24.4	-47.2
21	7.3	0	2.4	23.6	23.3	-20.0	11.9
30	0	0	0	16.7	17.0	0	-17.0
31	68.7	0	70.9	24.6	22.2	20.6	-8.2
02	32.5	-31.2	0	34.0	33.4	0	-33.4
12	80.4	-79.7	0	76.0	76.9	58.4	49.9
40	93.7	-97.1	0	42.7	41.6	41.6	0
22	67.8	-67.5	0	34.3	32.5	-31.1	9.5
41	74.5	0	77.1	51.7	51.7	46.7	-22.2
32	114.6	-117.7	0	63.2	60.5	-40.3	-45.0
50	0	0	0	45.6	44.8	0	44.8
51	17.2	0	16.2	48.3	49.1	-19.1	45.2
42	33.4	32.2	0	95.0	90.7	82.6	-37.4
03	0	0	0	36.6	35.1	0	-35.1
13	44.0	0	44.1	4.6	5.0	2.8	4.0
23	0	0	-2.8	5.5	5.4	3.6	-4.1
60	14.7	15.1	0	85.9	85.5	-85.5	0
52	7.2	5.6	0	39.2	37.8	-37.0	-7.6
61	54.5	0	-54.5	23.7	23.5	-0.9	23.5
33	98.2	0	-98.4	85.8	84.5	68.0	50.2
43	48.2	0	-48.0	20.4	19.7	-19.6	-1.0
70	0	0	0	43.8	43.7	0	-43.7
62	7.8	-7.7	0	27.5	26.3	24.4	-9.9
71	16.6	0	-15.4	45.3	44.7	41.0	-17.9
04	24.6	24.4	0	5.8	5.2	0	5.2
53	22.5	0	-23.3	29.5	27.8	-26.8	7.2
14	42.1	41.1	0	6.8	6.8	-6.3	2.6
24	9.7	-9.6	0	32.1	31.9	-30.9	8.0
72	23.2	22.4	0	8.2	8.4	-8.1	1.9
80	15.8	16.0	0	11.4	12.3	-12.3	0
34	23.6	-22.9	0	36.3	34.8	14.5	-31.7
81	9.8	0	8.8	21.1	20.1	-14.9	13.6
63	48.8	0	-47.7	32.0	31.2	-29.9	8.7
44	29.4	28.4	0	38.4	36.1	-34.0	-12.2
82	10.8	-9.6	0	20.2	19.6	-18.3	7.0
73	5.1	0	-4.2	17.6	17.2	16.2	-5.7
90	0	0	0	34.8	32.8	0	-32.8

HL	K = 0			K = 1			
	F_o	A	B	F_o	$\|F_c\|$	A	B
37	4.3	0	-3.5	8.8	9.0	8.6	2.6
13.2	7.0	-7.1	0	15.4	15.5	2.1	-15.4
10.5	14.5	0	-14.9	19.8	19.3	-15.5	-11.5
47	5.4	0	-5.6	13.3	13.5	11.7	6.8
86	3.1	-2.8	0	11.0	11.4	8.6	-7.5
14.0	8.1	9.1	0	10.4	10.7	-10.7	0
57	9.0	0	9.1	0	2.0	1.8	-0.7
14.1	5.7	0	5.6	17.4	17.1	17.1	0
12.4	11.0	-11.3	0	15.1	15.0	-11.1	10.1
13.3	17.4	0	17.3	0	1.9	-1.9	0.3
96	23.5	-25.1	0	6.0	6.4	6.4	-0.8
67	8.4	0	-9.8	11.6	12.0	-9.3	-7.6
11.5	7.8	0	7.3	0	1.1	-0.8	-0.8
14.2	3.5	4.1	0	10.7	10.9	5.8	-9.3
77	9.3	0	-10.1	6.7	7.6	1.5	7.5
15.0	0	0	0	3.8	3.0	0	-3.0
13.4	16.6	-18.0	0	3.9	4.1	-3.3	-2.3
08	3.6	2.8	0	5.5	5.9	0	-5.9
10.6	7.0	7.5	0	2.1	2.1	-2.0	0.5
18	9.7	9.7	0	9.1	9.3	-5.9	7.2
14.3	5.3	0	5.0	13.0	13.8	-1.0	-13.7
15.1	23.5	0	-23.6	13.6	14.0	-0.3	-14.0
28	2.6	2.2	0	6.6	6.9	-1.5	6.8
12.5	5.6	0	6.3	10.2	10.3	1.5	10.2
3.8	4.2	-5.7	0	13.5	12.4	11.2	5.3
8.7	15.6	0	16.7	11.1	10.8	10.8	-0.9
15.2	9.6	9.0	0	14.4	14.5	-4.6	13.7
48	7.6	7.4	0	9.8	10.6	1.8	-10.4
11.6	12.2	12.2	0	13.1	13.2	13.1	2.0
58	0	-1.3	0	9.0	8.0	7.8	1.9
14.4	22.6	22.4	0	3.4	3.0	2.6	-1.5
97	6.9	0	7.4	6.4	5.8	0.4	5.8
16.0	23.9	-24.5	0	2.2	1.6	-1.6	0
15.3	4.8	0	4.9	13.3	12.5	-12.5	-0.9
13.5	3.4	0	3.3	14.0	12.8	-0.1	12.8
16.1	13.4	0	-14.0	8.8	8.6	-5.5	6.6
68	4.4	-4.8	0	0	1.3	1.3	-0.4
16.2	10.8	-11.6	0	14.0	11.9	-10.8	5.0
12.6	8.7	-10.0	0	14.4	12.7	-2.8	12.4
10.7	8.2	0	7.7				

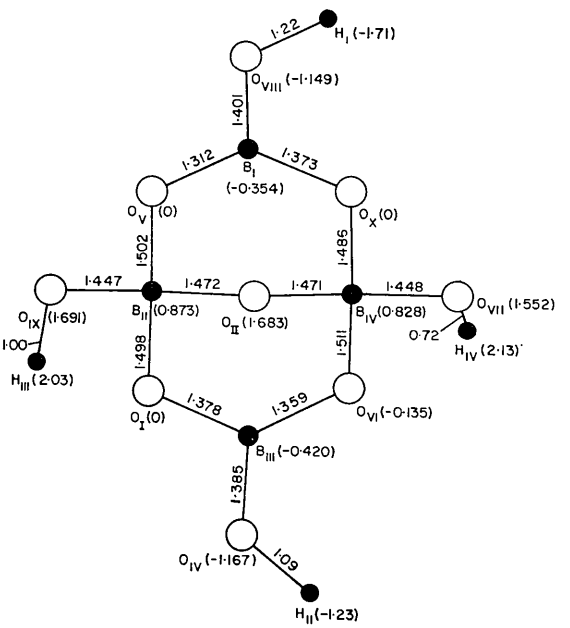

Fig. 1. A projection of the complex $[B_4O_5(OH)_4]^{2-}$. Numbers in parenthesis give the heights in Å above the projection plane. The lengths of the various bonds are shown.

Thus there are four hydroxyl groups in the structure ($O_{VIII}H_I$, $O_{IV}H_{II}$, $O_{IX}H_{III}$ and $O_{VII}H_{IV}$) and two water molecules ($H_VO_{III}H_{VI}$ and $H_{VII}O_{XI}H_{VIII}$).

The mean bond lengths are:

K–7O	= 2·862 Å	H–O	= 1·12 Å
B–3O	= 1·368	H · · · O	= 1·86
B–4O	= 1·480		

However, it is seen from Table 6, which lists all individual bond lengths, that there are large variations from the mean.

The structure contains complex ions $[B_4O_5(OH)_4]^{2-}$ consisting of two tetrahedral and two triangular boron oxygen groups as shown in Fig. 1. The same poly-ion has previously been observed in the mineral borax, $Na_2B_4O_7.10H_2O$ (Morimoto, 1956). The bond lengths within the boron–oxygen complex are given in Fig. 1, while the lengths of the triangular and tetrahedral edges are as follows:

Triangle about B_I		Triangle about B_{III}	
O_V–O_{VIII}	= 2·309 Å	O_I–O_{IV}	= 2·336 Å
O_V–O_X	= 2·380	O_I–O_{VI}	= 2·410
O_{VIII}–O_X	= 2·382	O_{IV}–O_{VI}	= 2·388
Tetrahedron about B_{II}		**Tetrahedron about B_{IV}**	
O_I–O_{II}	= 2·405 Å	O_{II}–O_{VI}	= 2·424 Å
O_I–O_V	= 2·438	O_{II}–O_{VII}	= 2·453
O_I–O_{IX}	= 2·403	O_{II}–O_X	= 2·407
O_{II}–O_V	= 2·437	O_{VI}–O_{VII}	= 2·412
O_{II}–O_{IX}	= 2·423	O_{VI}–O_X	= 2·401
O_V–O_{IX}	= 2·388	O_{VII}–O_X	= 2·385

These poly-ions, potassium ions and water molecules can be regarded as the units of which the structure

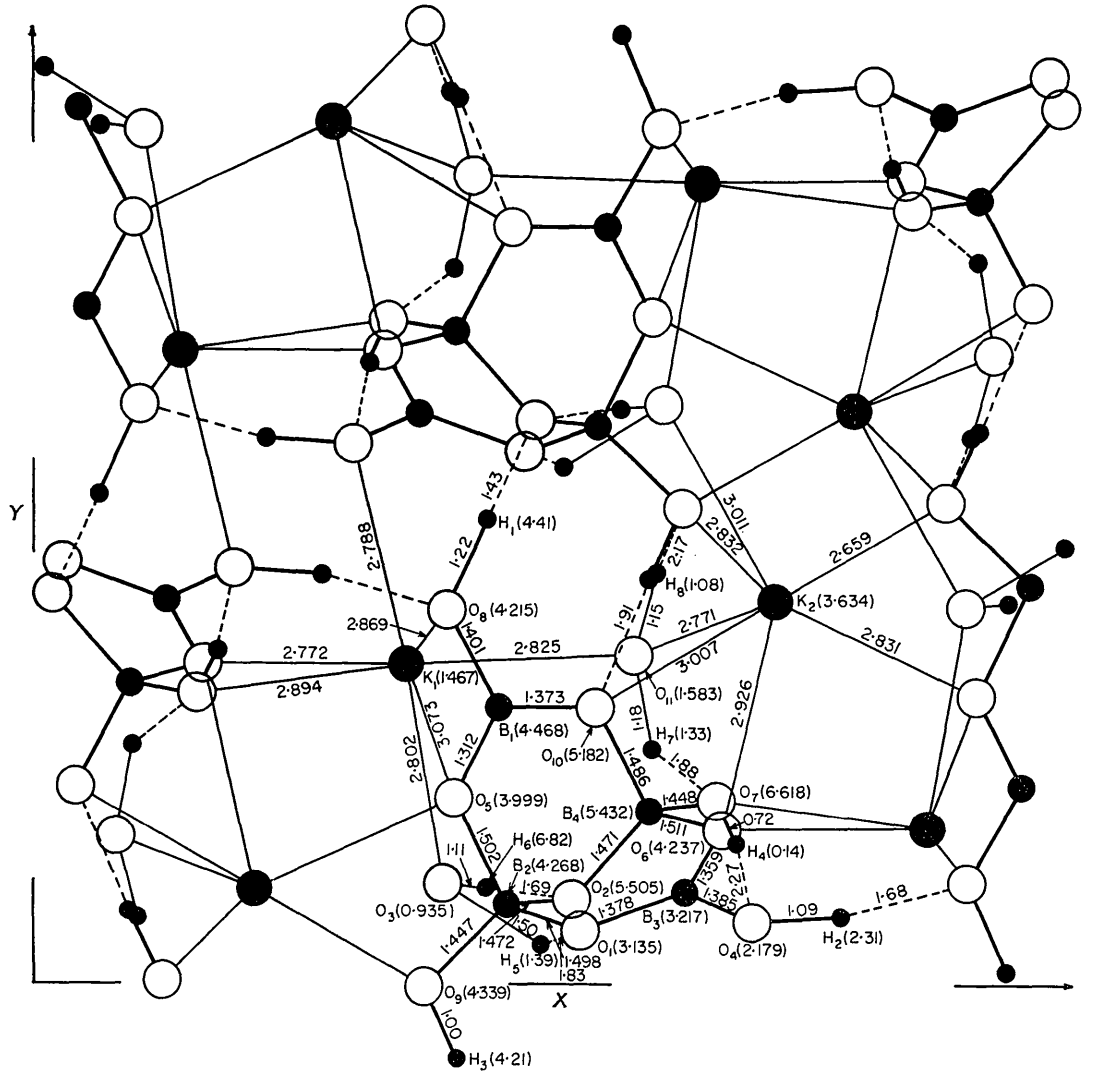

Fig. 2. The projection of one unit cell on the XY plane. The heights of the atoms in Å are given in parenthesis. The bond lengths are also shown.

Table 6. *Individual bond lengths*

	O_I	O_{II}	O_{III}	O_{IV}	O_V	O_{VI}	O_{VII}	O_{VIII}	O_{IX}	O_X	O_{XI}
K_I			2·802	2·788	3·073	2·772	2·894	2·869			2·825
K_{II}			3·011		2·831	2·926			2·659	3·007	2·771
									2·832		
B_I					1·312			1·401		1·373	
B_{II}	1·498	1·472			1·502				1·447		
B_{III}	1·378			1·385		1·356					
B_{IV}		1·471				1·511	1·448			1·486	
H_I		1·43						1·22			
H_{II}				1·09				1·68			
H_{III}									1·00	1·91	
H_{IV}				2·27			0·72				
H_V	1·83		1·50								
H_{VI}		1·69	1·11								
H_{VII}							1·88				1·18
H_{VIII}									2·17		1·15

is composed, and they are linked together by means of K–O and O–H · · · O bonds in the manner shown in Table 6 and in Fig. 2.

If one assigns a strength of 0·14 to each K–O bond, 1·00 to each triangular and 0·75 to each tetrahedral B–O bond, 0·80 to each H–O and 0·20 to each H · · · O bond, then the strength of the bonds ending on an oxygen atom ranges from 1·88 to 2·14 showing that there is nearly perfect valence balance in detail throughout the structure.

The oxygen atoms O_I, O_V, O_{VI} and O_X are each shared between a BO_3 triangle and a BO_4 tetrahedron. The B–O–B bond angles are 117·8° for O_I, 118·5° for O_V, 119·0° for O_{VI} and 118·3° for O_X. The corresponding bond angle is 111·0° for O_{II} which is shared between two BO_4 tetrahedra.

Table 7. *Heat motion data*

	i	Δ_i (Å)	α	β	γ
K_I	1.	0·151±0·003	0·748	−0·655	0·104
	2.	0·182±0·003	0·663	0·743	−0·094
	3.	0·194±0·003	−0·016	0·173	0·990
K_{II}	1.	0·137±0·003	0·876	0·228	−0·426
	2.	0·166±0·002	−0·143	0·965	0·221
	3.	0·210±0·003	0·461	−0·132	0·878
B_I	1.	0·127±0·014	−0·617	0·781	0·096
	2.	0·142±0·018	−0·549	−0·514	0·659
	3.	0·177±0·017	0·564	0·354	0·666
B_{II}	1.	0·122±0·014	0·010	0·960	0·279
	2.	0·141±0·011	0·999	−0·016	0·017
	3.	0·194±0·013	−0·022	−0·279	0·960
B_{III}	1.	0·132±0·019	−0·213	0·865	0·454
	2.	0·156±0·015	0·805	−0·108	0·584
	3.	0·176±0·016	−0·553	−0·490	0·674
B_{IV}	1.	0·122±0·011	−0·179	0·984	−0·009
	2.	0·156±0·011	0·973	0·175	−0·148
	3.	0·163±0·013	0·143	0·036	0·989
O_I	1.	0·115±0·015	0·163	0·721	0·674
	2.	0·151±0·007	0·972	0	−0·235
	3.	0·201±0·010	0·169	−0·693	0·701
O_{II}	1.	0·120±0·008	0·074	0·981	−0·177
	2.	0·140±0·010	0·903	0·013	0·445
	3.	0·167±0·009	−0·439	0·192	0·878
O_{III}	1.	0·189±0·008	0·925	−0·176	0·336
	2.	0·198±0·009	−0·350	−0·056	0·935
	3.	0·215±0·007	0·146	0·983	0·113
O_{IV}	1.	0·132±0·012	−0·499	0·412	0·762
	2.	0·175±0·008	0·809	0·552	0·239
	3.	0·202±0·009	−0·311	0·736	−0·602
O_V	1.	0·123±0·011	0·820	−0·453	0·349
	2.	0·143±0·008	0·424	0·891	0·162
	3.	0·210±0·010	−0·384	0·015	0·923
O_{VI}	1.	0·134±0·012	0·411	0·742	0·530
	2.	0·160±0·008	0·902	−0·415	−0·118
	3.	0·195±0·009	−0·132	−0·527	0·840
O_{VII}	1.	0·135±0·011	0·707	−0·251	0·661
	2.	0·178±0·008	−0·054	0·913	0·405
	3.	0·191±0·009	0·705	0·321	−0·632
O_{VIII}	1.	0·125±0·008	−0·448	0·893	−0·037
	2.	0·163±0·009	0·875	0·447	0·185
	3.	0·218±0·008	−0·182	−0·050	0·982
O_{IX}	1.	0·127±0·009	0·268	0·927	−0·262
	2.	0·147±0·009	0·938	−0·188	0·291
	3.	0·206±0·009	−0·221	0·324	0·920
O_X	1.	0·111±0·008	−0·247	0·965	−0·093
	2.	0·141±0·011	0·862	0·262	0·433
	3.	0·201±0·009	−0·442	−0·027	0·897
O_{XI}	1.	0·185±0·012	−0·101	0·715	0·691
	2.	0·216±0·012	−0·051	−0·698	0·715
	3.	0·233±0·007	0·994	0·037	0·106

The heat motion

The results for the anisotropic thermal coefficients β_{ij} as obtained from the Busing–Levi refinement program are listed in Table 2. The corresponding values for the root mean square displacements, Δ_i, along principal axes are shown in Table 7 together with the direction cosines α, β, γ of the principal axes in the X, Y, Z system of the crystal.

A detailed study of the results of Table 7 reveals many features of physical interest and significance. One sees, for instance, that the water oxygens (O_{III} and O_{XI}) have larger thermal amplitudes than the hydroxyl oxygens, which in turn have larger displacements than the true oxygen atoms. Similarly one finds the smallest anisotropy of thermal motion for the water oxygens and for the oxygen (O_{II}) which is bonded to two tetrahedrally coordinated boron atoms.

The atoms O_V, O_{VIII}, O_X form a triangle about B_I, and the direction cosines for the normal to this plane are $\alpha=-0{\cdot}515$, $\beta=-0{\cdot}102$, $\gamma=0{\cdot}851$. Reference to Table 7 shows that this normal is nearly parallel to the direction of maximum displacement observed for these three oxygen atoms. In a similar manner atoms O_I, O_{IV}, O_{VI} form a triangle about B_{III}, the normal to the plane having direction cosines $\alpha=0{\cdot}261$, $\beta=-0{\cdot}821$, $\gamma=0{\cdot}508$, and again one finds this normal to be nearly parallel to the direction of maximum thermal displacement for the three oxygen atoms in question.

A detailed analysis of the data of Table 7 will not be presented. However, it can be stated that the results as to anisotropy of thermal motion and orientation of the tensor ellipsoid are physically reasonable when correlated with the directions and strengths of the chemical bonds.

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