

The Crystal Structure of Potassium Acid Dihydrionium Pentaborate $KH_2(H_3O)_2B_5O_{10}$, (Potassium Pentaborate Tetrahydrate).

By **W. H. Zachariasen**
(Ryerson Physical Laboratory, University of Chicago).

Introduction.

In connection with our work on the structure of oxygen-radicals in crystals we have undertaken investigations on some of the complex borates. In this article we shall report on the results of a complete structure determination of potassium pentaborate tetrahydrate. The chemical formula of this compound is usually given as $KB_5O_8 \cdot 4H_2O$. This investigation shows that the formula should be written $KB_5O_{10}H_2(H_3O)_2$.

Crystals of potassium pentaborate are described by Groth¹⁾ as orthorhombic bipyramidal with axial ratios $a : b : c = .9707 : 1 : .8054$. We prepared crystals in the manner described by Groth and determined the density to be 1.740. They were examined by the oscillating crystal method using $MoK\alpha$ radiation.

For the dimensions of the unit cell we found:

$$a = 11.08 \text{ \AA} \quad b = 11.14 \text{ \AA} \quad c = 8.97 \text{ \AA} \quad \text{Accuracy } \frac{1}{2}\%.$$

There are four (3.97) molecules per unit cell. Reflections occur only when $K + L$ is even, so the translation lattice is basecentered. Furthermore reflections $H0L$ and $0KL$ are absent unless H, K, L all are even integers, showing that the planes normal to the two zones are glide planes rather than reflection planes. The number of atoms per unit cell is so great that it is safe to assume that some of them occupy general positions. Accordingly the two space groups $Abam (V_b^{18})$ and $Aba (C_{2v}^{17})$ come into consideration. With the space group $Abam$ four of the boron atoms must be placed in centers of symmetry. This is unreasonable, and we proceeded therefore on the assumption that Aba is the correct space group. (It should be noted that inasmuch as Aba is a subgroup of $Abam$ we do not reject the latter space group as a possibility.)

The four potassium atoms and four of the boron atoms must be placed on the twofold axes with co-ordinates $(00z)$ $(\frac{1}{2}\frac{1}{2}z)$. The origin may

1) Groth, *Chemische Krystallographie* Vol. 2, S. 733. Leipzig 1904.

conveniently be chosen at a potassium atom (putting $z = 0$ for potassium). From considerations of interatomic distances it seems unlikely that further atoms can be placed on the twofold axes. However, the method of attack which we employed made such an assumption unnecessary. The co-ordinates of general positions are: (xyz) $(\bar{x}\bar{y}z)$ $(\frac{1}{2} - x, \frac{1}{2} + y, z)$ $(x + \frac{1}{2}, \frac{1}{2} - y, z)$.

Determination of the Parameters.

As we know the positions of the relatively heavy potassium atoms, the structure is excellently suited for the application of the Patterson analysis. In a two dimensional Fourier projection of the Patterson¹⁾ type the main peaks (apart from the known potassium-potassium peaks) will correspond to potassium-oxygen and potassium-boron vectors with slight modifications introduced by overlapping oxygen-oxygen, oxygen-boron and boron-boron vectors. Fig. 1 shows the projection of the c -face. In addition to the outstanding peak corresponding to the potassium-potassium separation there are prominent peaks at $2\pi x = 0^\circ, 2\pi y = 60^\circ, 30^\circ 30^\circ, 75^\circ 30^\circ, 90^\circ 0^\circ$ and an extensive one at $90^\circ 60^\circ$, and corresponding peaks at positions required by symmetry. Since, according to space group considerations, the potassium atoms are lying on the two-fold axes, the co-ordinates of the observed peaks will directly give us (apart from algebraic sign) the x - and y -co-ordinates of oxygen and boron atoms.

The height of the peak at $30^\circ 30^\circ$ strongly indicated that it had to be attributed to two sets of oxygen atoms. In order to get conclusive evidence on this point we proceeded in the following way:

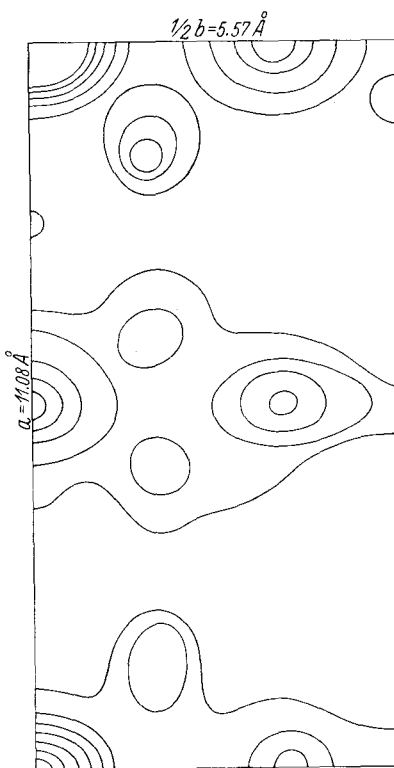


Fig. 1. Shows the Patterson Fourier projection on the c -face.

1) Patterson, A. L., Z. Kristallogr. **90** (1935) 517.

The peaks shown in the projection were partially accounted for by this atomic distribution: 4 *K* at $0^\circ 0^\circ$, 4 *B* at $0^\circ 0^\circ$, 8 *O* at $30^\circ 30^\circ$, 8 *O* at $90^\circ 0^\circ$. The remaining peaks must then be attributed to 16 *B* and 24 *O* atoms. We next calculated the contributions to the structure factor due to the atoms at the positions given above. Comparing these contributions with the estimated structure factor values, we were able to obtain values for the contributions made by the remaining atoms in the structure (i. e. by the 16 *B* and 24 *O*). Let the latter contributions be ψ_{HK0} . A Fourier analysis $\sigma_{xy} = \Sigma \Sigma \psi_{HK0} \cos 2\pi(Hx + Ky)$ naturally gave us a projection representing the electron distribution due to these 16 boron and 24 oxygen atoms. This new projection showed clearly that none of these atoms were lying on the two-fold axes, since the electron density practically vanished at the origin. It showed, however, well defined peaks at $30^\circ 30^\circ$, $75^\circ 30^\circ$ and an extensive peak at about $90^\circ 60^\circ$. By a similar procedure we were able to analyze the latter peak into two individual peaks at $80^\circ 50^\circ$ and $90^\circ 65^\circ$. We could find no evidence of further peaks. This was rather startling since we had expected to find five sets of peaks, rather than the four peaks of comparable volume. The only reasonable explanation was that two boron peaks were superimposed in the projection, thereby giving rise to a single peak of about the same volume as an oxygen peak.

Summarizing the results we obtained by direct methods we have:

4 <i>K</i> at $\pm 2\pi x = 0^\circ$	$\pm 2\pi y = 0^\circ$
4 <i>B</i>	0
8 <i>O</i> or 16 <i>B</i>	60
	30
	30
	75
	80
	90
	90
	65

It remained for us

1. to find which of the peaks was the "boron peak",
2. to determine the *z*-co-ordinates.

We found it to be too difficult to complete the last stages of the analysis by means of direct methods so far employed, and we tried therefore to arrive at the final structure by making reasonable guesses of the atomic arrangement based upon the information we already had to our disposal. By this procedure we found the following structure:

4 <i>K</i>	at	$2\pi x = 0^\circ$	$2\pi y = 0^\circ$	$2\pi z = 0^\circ$
4 <i>B</i> _I		0	0	140
8 <i>B</i> _{II}		70	35	115
8 <i>B</i> _{III}		70	-25	180
8 <i>O</i> _I		$27\frac{1}{2}$	30	105
8 <i>O</i> _{II}		$27\frac{1}{2}$	-30	175
8 <i>O</i> _{III}		80	-50	30
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8 <i>O</i> _V		90	65	90
8 <i>O</i> _{VI}		0	60	270

The amplitudes calculated on the basis of these parameter values are given in tables I and II. The agreement with observations is not perfect; but is as good as may reasonably be expected for a structure with 25 degrees of freedom. We have not found it worth our while to try to improve the agreement by slight changes in the parameter values.

Table I. Reflections *HK0*.¹⁾

<i>HK0</i>	Int. obs.	Ampl. calc.	<i>HK0</i>	Int. obs.	Ampl. calc.
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400	vs.	216	840	m-	73
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440	w.	46	860	m.	146
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160	w-	54	10.0.0	vw	51
260	nil	2	1.10.0	nil	- 2
620	nil	4	2.10.0	vwv	37
540	vw.	8	10.2.0	w-	36
360	w.	54	780	vw-	24
460	s-	148	3.10.0	nil	5
640	w.	48	4.10.0	vw-	25
720	nil	18	10.4.0	nil	2
560	w-	49	880	vw-	45
080	vwv	5	960	vw-	33
180	vw-	3	0.12.0	w-	95
740	vwv	5	12.0.0	w-	92

1) The following scale of estimated intensities is used: vs., vs, s., s, s-, m., m, m-, w., w, w-, vw., vw, vw-, vwv, nil.

Table II. Reflections HKL . Rotation around $[001]$.¹⁾

HK	$L = 0$	$L = 1$	$L = 2$	$L = 3$	$L = 4$
11		ms 44		s- 55	
02	vs 156		vs 181		vw 38
20	nil 15		m 18		s- 98
12	vw. 9		vs 148		w. 20
21		nil 11		m 52	
22	w. 53		m 42		ms 75
13		m 68		m 64	
31		m 64		m. 58	
23		wm 50		s- 76	
32	nil 11		w- 38		m 73
04	w- 34		s 96		m- 74
40	vs. 216		vw- 42		w. 51
14	w. 13		w. 20		wm 69
41		w- 20		w- 13	
33		s. 90		wm 61	
24	wm 39		s 78		w 50
42	w. 38		s. 120		w 39
34	nil 11		ms 95		w 49
43		w. 36		w- 27	
15		ms 98		w 64	
51		ms 72		wm 72	
52	w 15		ms 73		vw- 21

Description of the Structure.

Fig. 2 shows a projection of the structure on the c -face. According to the formula given in the literature, *viz.* $KB_5O_8 \cdot 4H_2O$, one should have expected to find complexes $(B_5O_8)^-$. No such group occurs in the structure; but there are radicals $(B_5O_{10})^{-5}$. (Since we have not yet found the positions of the hydrogen atoms, the possibility is open that some of the oxygen atoms actually are hydroxyl groups.) The structure of the B_5O_{10} group is shown in fig. 3. A BO_4 -tetrahedron forms the nucleus of the radical. Each tetrahedral corner is shared with a BO_3 triangle, and the four triangles are grouped together in two pairs by a common corner. Thus all but four of the ten oxygen atoms of the group are linked to two boron atoms each.

The distance from the central boron atom to its four neighboring oxygen atoms is 1.53 Å, which to us seems somewhat high.²⁾ Within

1) The columns for a given value of L contain observed intensity and calculated amplitude.

2) Schulze, G. E., Z. physik. Chem. (B) **24** (1934) 215 found the boron to oxygen distances in the tetrahedral groups of BPO_4 and $BAsO_4$ to be 1.44 Å and 1.49 Å.

the triangular groups the boron to oxygen distance is on the average 1.35 Å (individual values ranging from 1.28 Å to 1.42 Å). The same value has been found in other borates¹). The BO_3 -groups are plane. The

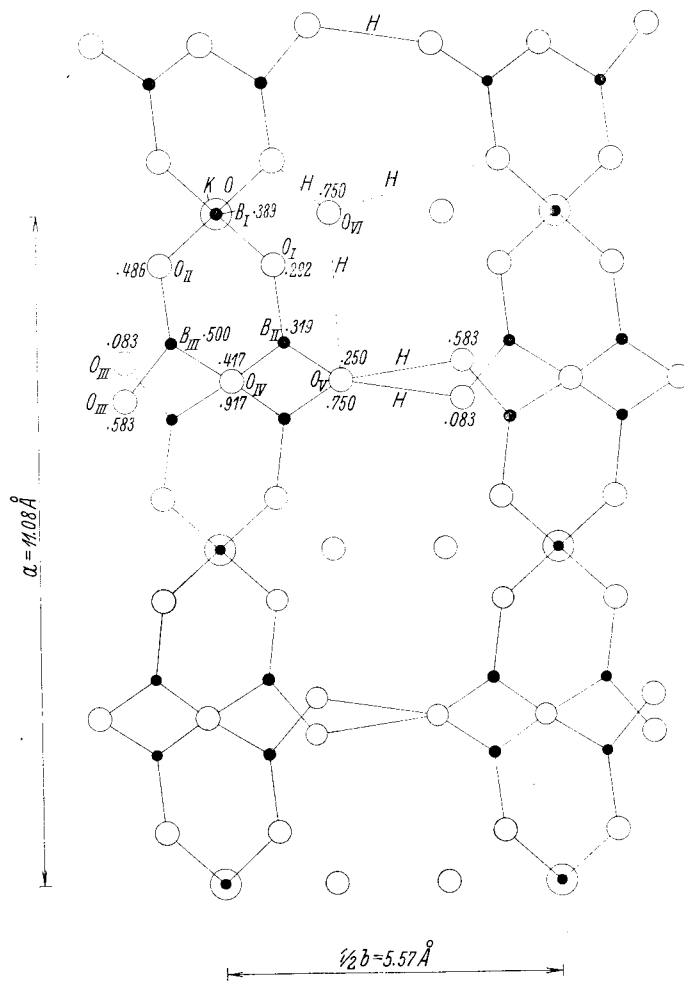


Fig. 2.

Represents a projection of the structure on the c -face. Boron atoms are indicated by small black circles. Large open circles immediately below or above boron atoms are potassium atoms. Medium sized open circles represent oxygen atoms. The numbers attached to the various atoms give the height in fractions of c -axis. The positions of the hydrogen atoms are indicated by their chemical symbol.

¹) Zachariasen, W. H., Z. Kristallogr. **76** (1931) 289; Zachariasen, W. H., and G. E. Ziegler, Z. Kristallogr. **83** (1932) 354.

bond angles for the oxygen atoms which are linked to two boron atoms each, O_I , O_{II} , O_{IV} , are 120° , 121° and 127° .

One set of oxygen atoms (O_{VI}) takes no part in the radical formation; these oxygen atoms are linked only to potassium (and hydrogen). Potassium has a co-ordination number of eight; the $K-O$ separation is on the average 2.92 \AA , with individual values ranging from 2.88 \AA to 3.00 \AA . The interatomic distance $K-O$ calculated from the ionic radii of the writer is 2.90 \AA .¹⁾

Naturally it is impossible to locate the hydrogen atoms from intensity considerations. Reliable results concerning the positions of

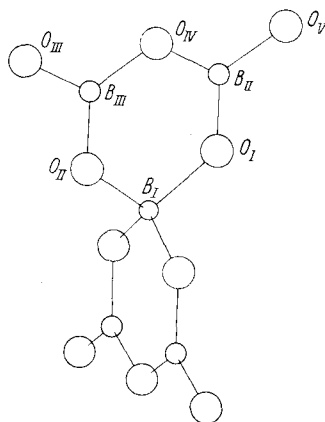


Fig. 3. Shows the structure of the pentaborate complex.

hydrogen atoms can as a rule be obtained from an inspection of the observed interatomic distances.

Two oxygen atoms of different radicals (O_{III} and O_V) have a separation of only 2.52 \AA . This value agrees well with the observed distance within the $O-H-O$ group²⁾, so we are led to believe that the atoms O_{III} and O_V are linked together by hydrogen bridges.

The oxygen atom O_{VI} has an O_{II} atom at a distance of 2.68 \AA , an O_V atom at 2.77 \AA and an O_I atom at 2.93 \AA . This suggests that O_{VI} is the oxygen atom of a hydronium ion with the three hydrogen atoms pointing towards the three close oxygens, O_I , O_{II} , O_V .

The chemical formula hence should be written: $KB_5O_{10}H_2(H_3O)_2$.

1) Zachariasen, W. H., Z. Kristallogr. **80** (1934) 137.

2) West, J., Z. Kristallogr. **74** (1930) 306 found 2.56 \AA in KH_2PO_4 ; Zachariasen, W. H., J. Chem. Physics **1** (1933) 634 found 2.55 \AA in $NaHCO_3$.

Table III gives a survey of the interatomic distances and bonds for the different atoms.

Table III. Interatomic Distances and Bonds.

K		B_I		B_{II}		B_{III}	
2 O_I	2.91 Å	2 O_I	1.53 Å	1 O_I	1.34 Å	1 O_{II}	1.33
2 O_{III}	3.00	2 O_{II}	1.53	1 O_{IV}	1.37	1 O_{III}	1.42
2 O_{IV}	2.88			1 O_V	1.28	1 O_{IV}	1.39
2 O_{VI}	2.90						
O_I		O_{II}		O_{III}			
1 K	2.91 Å .125	1 B_I	1.53 Å .75	1 K	3.00 .125		
1 B_I	1.53 .75	1 B_{III}	1.33 1.00	1 B_{III}	1.42 1.00		
1 B_{II}	1.34 1.00	1 $H(O_{VI})$	2.68 .333	1 $H(O_V)$	2.52 .50		
1 $H(O_{VI})$	2.93 .333		2.083		1.625		
	2.208						
O_{IV}		O_V		O_{VI}			
1 K	2.88 Å .125	1 B_{II}	1.28 Å 1.00	1 K	2.90 Å .125		
1 B_{II}	1.37 1.00	1 $H(O_{III})$	2.52 .50	1 $H(O_I)$	2.93 .667		
1 B_{III}	1.39 1.00	1 $H(O_{VI})$	2.77 .333	1 $H(O_{II})$	2.68 .667		
	2.125		1.833	1 $H(O_V)$	2.77 .667		
					2.126		

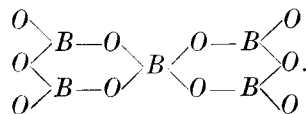
The third column gives the bond strengths.

The strength of bonds from hydrogen atoms of the hydrionium group is assumed to be $\frac{2}{3}$ and $\frac{1}{3}$ (rather than both equal to $\frac{1}{2}$) to allow for the stronger bonds within the ion.

Summary.

Crystals of potassium pentaborate tetrahydrate are orthorhombic with unit cell dimensions: $a = 11.08 \text{ \AA}$, $b = 11.14 \text{ \AA}$, $c = 8.97 \text{ \AA}$. There are four molecules per unit cell and the space group is $Aba (C_{2v}^{17})$. The four potassium atoms and four of the boron atoms are lying on twofold axes and all the remaining atoms in general positions. The 25 parameters involved were determined.

The structure contains complexes (B_5O_{10}). A BO_4 -tetrahedron forms the nucleus of the complex. Each of the four corners are shared with a BO_3 -triangle, and the four triangles are grouped together in two pairs by a shared corner, so that the structural picture of the complex becomes:



The $B-O$ distance is 1.53 Å within the tetrahedron and 1.36 Å within the triangular groups.

Potassium has eight oxygen neighbors at an average distance of 2.92 Å. There are hydrogen bonds between oxygen atoms of different B_5O_{10} groups. One set of oxygen atoms is not linked to boron atoms. The remaining hydrogen atoms appear to be linked to these latter oxygen atoms, so that hydronium ions are formed. The hydronium groups are not rotating; but are linked to three oxygen atoms by weak hydroxyl bonds and to one potassium atom each. Accordingly the formula of the compound should be written: $KH_2(H_3O)_2B_5O_{10}$.

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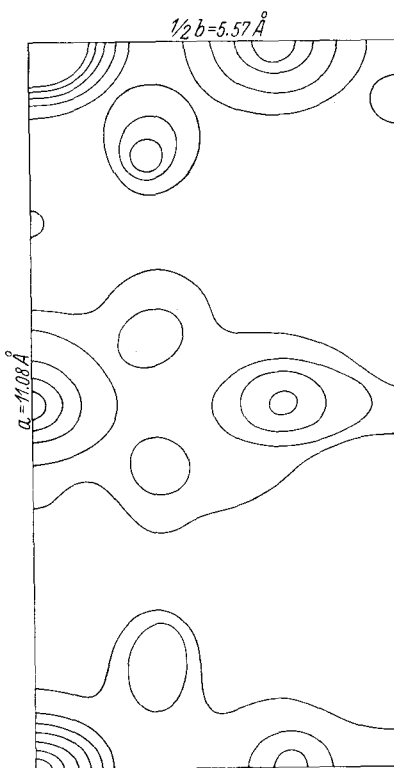


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