

## The Crystal Structure of Potassium Diborate, $K_2O \cdot 2B_2O_3$

By J. KROGH-MOE

Chemistry Department, University of Trondheim, Trondheim, Norway

(Received 28 April 1972)

Potassium diborate,  $K_2O \cdot 2B_2O_3$ , is triclinic, space group  $P\bar{1}$ , with unit-cell dimensions at 22°C:  $a = 6.484 \pm 0.002$ ,  $b = 9.604 \pm 0.004$ ,  $c = 10.413 \pm 0.005$  Å,  $\alpha = 89.28 \pm 0.07$ ,  $\beta = 102.75 \pm 0.05$ ,  $\gamma = 101.25 \pm 0.05^\circ$ . The calculated density is  $2.501 \text{ g.cm}^{-3}$  with four formula units in the cell. Three-dimensional X-ray intensity data were measured with a Picker automatic single-crystal diffractometer and Cu  $K\alpha$  radiation. The structure was determined by means of the heavy-atom method. A full-matrix least-squares refinement resulted in an  $R$  index of 0.032 (0.033 for the weighted  $R$  index). The structure contains a single three-dimensional borate anion framework, composed of mutually linked planar  $BO_3$  triangles, diborate groups and triborate groups, in which two of the three boron atoms are tetrahedrally coordinated. This combination of groups has not been previously encountered in a diborate compound. The average values of the boron–oxygen bond length, 1.477 Å and 1.369 Å for boron in fourfold and threefold coordination respectively, are normal. Significant differences in bond lengths and bond angles with location within the groups are observed. Some of these differences appear to be characteristic of the type of borate group considered. The potassium cations are coordinated in an unsymmetrical fashion by six or eight oxygen atoms at distances ranging from 2.631 to 3.106 Å.

### Introduction

The crystal structures of several anhydrous diborate compounds are known from earlier work. Lithium diborate,  $Li_2O \cdot 2B_2O_3$  (Krogh-Moe, 1968) and cadmium diborate,  $CdO \cdot 2B_2O_3$  (Ihara & Krogh-Moe, 1966) both exhibit interpenetrating double framework structures, built up from linked diborate groups. Ecker (1966) found that cadmium diborate is a member of an isomorphous series. Included in this series are diborates with divalent cations of the following elements: Mg, Mn, Fe, Co, Ni, Zn, Cd, Hg. The structure of the magnesium compound of this series has been refined with diffractometer data by Bartl & Schuckmann (1966) on the basis of parameters from cadmium diborate. The diborate group has also been found as isolated polyions of composition  $B_4O_5(OH)_4^{2-}$  in borax ( $Na_2O \cdot 2B_2O_3 \cdot 10H_2O$ ) by Morimoto (1956) and in potassium diborate tetrahydrate by Marezio, Plettinger & Zachariasen (1963).

Not all the anhydrous diborate compounds contain the diborate group, however. Barium diborate (Block & Perloff, 1965) has a single framework based on di-triborate groups and di-pentaborate groups. (The suggested notation for these groups is new. The prefix 'di' here refers to the presence of two tetrahedrally coordinated boron atoms in the group as opposed to the case for the normal triborate and pentaborate groups, each having only one fourfold coordinated boron. Another possibility for naming the groups makes use of the nomenclature recommended by IUPAC (1957) for complexes. The di-triborate group would then be

named cyclotri- $\mu$ -oxo-pentaoxotriborate which, however, is seen to be somewhat cumbersome.)

In strontium diborate,  $SrO \cdot 2B_2O_3$  (Krogh-Moe, 1964) there is a framework structure with anomalous coordination of boron and oxygen. The structures of the barium and strontium compounds show that the structural chemistry of the diborates is by no means simple. It is thus desirable to collect information about diborate structures for a variety of cations. Potassium diborate,  $K_2O \cdot 2B_2O_3$ , was previously studied by Krogh-Moe (1961), who determined unit-cell data. In the present work a full structure determination is reported.

### Experimental

The starting material for preparation of the anhydrous potassium diborate was potassium diborate tetrahydrate obtained commercially (Riedel de Haen AG, Hannover). By fusing the hydrate at 900°C in a platinum crucible the water was driven off and the viscous liquid was then crystallized at a temperature of  $\sim 700^\circ\text{C}$ .

A single-crystal fragment of somewhat irregular shape was used. The specimen could be approximately described as a prismatic needle with the dimensions  $0.005 \times 0.005 \times 0.013$  cm.

Intensity data were collected with an on-line Picker single crystal automatic diffractometer. Cu  $K\alpha$  radiation was used and the X-ray reflexions were measured at 2063 different reciprocal lattice points.

Unit-cell dimensions and standard errors:  $a = 6.484 \pm 0.002$ ,  $b = 9.604 \pm 0.004$ ,  $c = 10.413 \pm 0.005$  Å,  $\alpha =$

89:28 ± 0.07, β = 102.75 ± 0.05, γ = 101.15 ± 0.05° were obtained by the method of least squares from angle data recorded at 22°C for 12 high-angle reflexions (based on the wavelength 1.5405 for Cu Kα₁). With 4 formula units of K₂O·2B₂O₃ in the cell, the calculated density is 2.501 g.cm⁻³.

Structure determination

The observed intensities were converted to structure factors in the usual manner. No correction for absorption was applied.

The linear absorption coefficient is 135 cm⁻¹. For a specimen of the size and shape used here, the absorption corrections are small.

A statistical test of the distribution of normalized structure factors gave a strong indication of the presence of a centre of symmetry. A three-dimensional Patterson map was used to locate the potassium atoms. The potassium-potassium vectors were sufficiently prominent in this map to allow the determination of a set of potassium positions that proved to be consistent with the presence of a centre of symmetry. The

Table 1. Final observed and calculated structure factors

The columns are I, 10F₀ and 10Fₑ respectively.

Table with multiple columns of numerical data representing structure factors. The data is organized into rows and columns, with some rows containing labels like '0,0,L', '0,1,L', '1,0,L', etc. The values are integers, some positive and some negative, representing the intensity and phase of various reflections.

potassium parameters were subsequently used to obtain preliminary signs for the structure factors. A three-dimensional electron-density map then revealed the structure. The structure was refined by the method of least squares using a version of the full matrix program *ORFLS* (Busing, Martin & Levy, 1962) revised by Borgen & Mestvedt (1966). 1936 independent non-zero reflexions were used in the refinement. Observed and calculated structure-factors are given in Table 1. The atomic scattering factors for O, B and K<sup>+</sup>, used for obtaining the calculated structure factors, were taken from *International Tables for X-ray Crystallography* (1962). The refinement was carried out with a weighting scheme based on the statistical counting errors compounded with errors assumed to be 1% of the observed intensity. With anisotropic temperature factors the structure was refined to an *R* value of 0.032 (or 0.033 for the weighted *R* value). The final atomic coordinates and the thermal parameters are given in Table 2.

### Discussion of the structure

The anion structure of potassium diborate consists of a single three-dimensional borate framework. The framework is composed of three different types of

groups: *viz.* planar BO<sub>3</sub> triangles, normal diborate groups and di-triborate groups. The groups and their mutual arrangement can be seen in Fig. 1, which shows a projection of the structure along the *a* axis. The diborate group, consisting of two BO<sub>4</sub> tetrahedra and two planar BO<sub>3</sub> triangles condensed in a double ring arrangement, is the only type of unit in most diborate compounds (see Introduction). The present structure is the first known instance of a diborate compound containing the diborate group accompanied by other groups. The additional groups are single planar BO<sub>3</sub> triangles and di-triborate groups. The di-triborate group is composed of two BO<sub>4</sub> tetrahedra and a planar BO<sub>3</sub> triangle linked in a single six-membered ring. According to Clark, Appleman & Christ (1964), the di-triborate group occurs as the basic unit in a series of hydrated calcium borates of composition 2CaO·3B<sub>2</sub>O<sub>3</sub>·*X*H<sub>2</sub>O (where *X* = 1, 5, 7, 9, 13).

The di-triborate group has also been found in anhydrous barium diborate (Block & Perloff, 1965), in which it is accompanied by a di-pentaborate group. In the present structure each di-triborate group is linked to two single planar BO<sub>3</sub> triangles and three diborate groups.

Boron-oxygen bond lengths are given in Table 3. The average boron-oxygen distance of fourfold coor-

Table 2. *Final atomic parameters*

Positional parameters are expressed as fractions of the cell edges, and temperature factors are of the form  $\exp [-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$ . All values are multiplied by 10<sup>4</sup>.

	<i>x</i>	<i>y</i>	<i>z</i>	$\beta_{11}$	$\beta_{22}$	$\beta_{33}$	$\beta_{12}$	$\beta_{13}$	$\beta_{23}$
K(1)	3694.4	1249.1	413.8	89	40	31	29	17	6
K(2)	3361.4	5200.3	1255.4	65	47	59	5	17	23
K(3)	7876.3	3742.6	4974.1	60	34	36	2	23	3
K(4)	2491.7	9987.6	4071.4	154	56	44	48	-8	-22
O(1)	9884	1977	9686	58	47	21	17	14	-3
O(2)	7982	985	1379	74	31	23	-5	13	2
O(3)	8290	3455	866	90	28	30	30	-5	-5
O(4)	1490	2554	1907	46	30	21	7	11	-1
O(5)	9554	1833	3610	64	25	27	-10	17	-2
O(6)	3197	3206	4147	46	34	19	4	10	4
O(7)	251	4310	3019	78	22	26	15	6	-1
O(8)	3238	121	6775	80	26	31	-9	24	-2
O(9)	6519	1313	8190	42	42	30	12	14	13
O(10)	3447	2313	8057	73	25	23	23	15	4
O(11)	2331	4467	8306	65	21	32	13	9	0
O(12)	4881	2300	6102	58	32	26	17	20	12
O(13)	1966	3501	6101	64	32	24	21	22	7
O(14)	9593	2381	7407	41	39	24	-4	13	4
B(1)	9431	2228	945	74	25	23	13	11	3
B(2)	1161	2978	3157	52	21	24	4	10	-1
B(3)	4502	1547	7321	44	25	28	9	15	7
B(4)	1866	3137	7492	69	23	26	11	16	4
B(5)	8088	888	2704	61	21	35	23	13	2
B(6)	8747	4434	1881	59	20	29	-1	21	7
B(7)	8668	1925	8438	67	20	27	16	15	0
B(8)	3315	3000	5461	56	14	34	-4	15	-1

Standard deviations

K	1.2	0.8	0.8	2	1	1	1	1	0.7
O	3	2	2	6	3	2	3	3	2
B	6	4	4	9	4	4	5	5	3

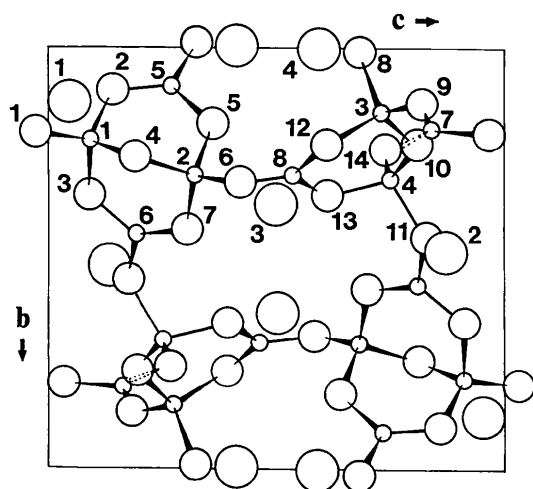


Fig. 1. View of the structure of  $K_2O \cdot 2B_2O_3$  along the  $a$  axis. The small circles represent boron, intermediate circles oxygen and large circles potassium. The numbering of atoms corresponds to Table 2.

minated borons [B(1), B(2), B(3) and B(4)] is  $1.477 \text{ \AA}$  as compared with  $1.369 \text{ \AA}$  for the average of the threefold coordinated borons. These values agree well with

Table 3. *Interatomic distances and bond angles*

Boron-oxygen (e.s.d. 0.004 Å)		Potassium-oxygen (e.s.d. 0.002 Å)	
B(1)-O(1)	1.438 Å	K(1)-O(10)	2.631 Å
B(1)-O(2)	1.500	K(1)-O(1)	2.646
B(1)-O(3)	1.501	K(1)-O(2')	2.750
B(1)-O(4)	1.462	K(1)-O(4)	2.786
		K(1)-O(2)	2.800
B(2)-O(4)	1.441	K(1)-O(9')	2.838
B(2)-O(5)	1.508	K(1)-O(3)	3.245
B(2)-O(6)	1.465		
B(2)-O(7)	1.503	K(2)-O(3')	2.668
		K(2)-O(11')	2.684
B(3)-O(8)	1.499	K(2)-O(4)	2.740
B(3)-O(9)	1.472	K(2)-O(10')	2.822
B(3)-O(10)	1.428	K(2)-O(7)	3.016
B(3)-O(12)	1.497	K(2)-O(11)	3.056
		K(2)-O(9)	3.388
B(4)-O(10)	1.435		
B(4)-O(11)	1.485	K(3)-O(12)	2.643
B(4)-O(13)	1.498	K(3)-O(13)	2.706
B(4)-O(14)	1.495	K(3)-O(7')	2.726
		K(3)-O(7)	2.800
B(5)-O(2)	1.369	K(3)-O(5)	2.844
B(5)-O(5)	1.381	K(3)-O(13')	2.854
B(5)-O(8)	1.357	K(3)-O(6)	2.909
		K(3)-O(14)	2.934
B(6)-O(3)	1.366	K(3)-O(6')	3.325
B(6)-O(7)	1.379		
B(6)-O(11)	1.365	K(4)-O(14')	2.709
		K(4)-O(8)	2.749
B(7)-O(1)	1.359	K(4)-O(5)	2.809
B(7)-O(9)	1.371	K(4)-O(9')	2.927
B(7)-O(14)	1.369	K(4)-O(12)	3.022
		K(4)-O(6)	3.035
B(8)-O(6)	1.368	K(4)-O(12')	3.060
B(8)-O(12)	1.373	K(4)-O(8')	3.106
B(8)-O(13)	1.368	K(4)-O(5')	3.325

Table 3 (cont.)

Oxygen-boron-oxygen angles (e.s.d. 0.2°)	
O(1)-B(1)-O(2)	112.9°
O(1)-B(1)-O(3)	109.6
O(1)-B(1)-O(4)	107.7
O(2)-B(1)-O(3)	106.5
O(2)-B(1)-O(4)	109.9
O(3)-B(1)-O(4)	110.3
Boron-oxygen-boron angles (e.s.d. 0.3°)	
B(1)-O(1)-B(7)	132.2°
B(1)-O(2)-B(5)	116.8
B(1)-O(3)-B(6)	121.2
B(1)-O(4)-B(2)	110.2
B(2)-O(5)-B(5)	120.1
B(2)-O(6)-B(8)	123.3
B(2)-O(7)-B(6)	117.3
B(3)-O(8)-B(5)	130.7
B(3)-O(9)-B(7)	137.5
B(3)-O(10)-B(4)	124.9
B(4)-O(11)-B(6)	127.5
B(3)-O(12)-B(8)	116.9
B(4)-O(13)-B(8)	122.3
B(4)-O(14)-B(7)	126.8
Potassium-potassium less than 6 Å (e.s.d. 0.001 Å)	
K(3)-K(3')	3.281 Å
K(1)-K(1')	3.413
K(3)-K(4')	3.683
K(2)-K(2')	3.781
K(1)-K(2)	3.962
K(4)-K(4')	4.120
K(1)-K(2')	4.132
K(1)-K(4)	4.173
K(2)-K(3')	4.347
K(2)-K(3)	4.689
K(1)-K(3)	5.263
K(3)-K(4)	5.327
K(2)-K(4)	5.668
K(1)-K(4')	5.977
Oxygen-boron-oxygen angles (e.s.d. 0.2°)	
O(4)-B(2)-O(5)	109.7
O(4)-B(2)-O(6)	110.2
O(4)-B(2)-O(7)	110.0
O(5)-B(2)-O(6)	108.9
O(5)-B(2)-O(7)	107.7
O(6)-B(2)-O(7)	110.1
O(8)-B(3)-O(9)	107.2
O(8)-B(3)-O(10)	115.2
O(8)-B(3)-O(12)	102.1
O(9)-B(3)-O(10)	108.4
O(9)-B(3)-O(12)	112.2
O(10)-B(3)-O(12)	111.6
O(10)-B(4)-O(11)	107.6
O(10)-B(4)-O(13)	111.5
O(10)-B(4)-O(14)	113.8
O(11)-B(4)-O(13)	109.2
O(11)-B(4)-O(14)	110.1
O(13)-B(4)-O(14)	104.7
O(2)-B(5)-O(5)	121.9
O(2)-B(5)-O(8)	123.0
O(5)-B(5)-O(8)	115.0
O(3)-B(6)-O(7)	120.8
O(3)-B(6)-O(11)	116.6
O(7)-B(6)-O(11)	122.6
O(1)-B(7)-O(9)	119.7
O(1)-B(7)-O(14)	120.8
O(9)-B(7)-O(14)	119.3
O(6)-B(8)-O(12)	116.6
O(6)-B(8)-O(13)	121.2
O(12)-B(8)-O(13)	122.1

previously obtained averages for comparable structures. The individual bond lengths exhibit systematic differences from these averages, however, depending on the location of the bond within its group. In the diborate group each of the two tetrahedra has two short ( $\sim 1.45 \text{ \AA}$ ) and two long ( $\sim 1.50 \text{ \AA}$ ) B-O bonds. The long bonds within the group connect the  $BO_3$  triangles to the pair of fourfold coordinated borons. The same bond lengths for the equivalent tetrahedral bonds have been found in other diborate compounds. The long and short bonds respectively are about  $1.50$  and  $1.45 \text{ \AA}$  in the compounds  $Li_2O \cdot 2B_2O_3$ ,  $MgO \cdot 2B_2O_3$  and  $K_2O \cdot 2B_2O_3 \cdot 4H_2O$ . The systematic nature of the above differences in bond length with the location of the bond within the group apparently has not been previously noted. In the di-triborate group there is also a similar distribution of the bond lengths. Again the boron-oxygen bonds in the bridge between the two

fourfold coordinated borons are noticeably shorter ( $\sim 1.43$  Å) than the remaining boron–oxygen bonds from the fourfold coordinated boron atoms ( $\sim 1.49$  Å). This effect is also to be seen, though less pronounced, in other compounds such as the dicalcium triborates (Clark *et al.*, 1964).

Table 3 also presents the O–B–O and B–O–B bond angles. The three O–B–O bond angles for each threefold coordinated boron atom sum up to values within  $0.3^\circ$  of  $360^\circ$ , consistent with a planar  $\text{BO}_3$  group. The O–B–O bond angle for the tetrahedrally coordinated boron is on average  $109.47^\circ$ , consistent with the tetrahedral arrangement. However, many of the individual O–B–O bond angles for each of the two coordination types differ significantly from the corresponding average values.

The B–O–B bond angle is exceptionally small ( $110.2^\circ$ ) for the oxygen atom linking the two tetrahedrally coordinated boron atoms in the diborate group. Similar small values for the corresponding bond angle are found in lithium diborate ( $108.0^\circ$ ), magnesium diborate ( $110.5^\circ$ ) and potassium diborate tetrahydrate ( $111.0^\circ$ ). The analogous B–O–B bond angle for the oxygen atom bridging the two tetrahedrally coordinated boron atoms in the di-triborate is considerably larger ( $124.9^\circ$ ). The B–O–B bond angles for the oxygen atoms linking different groups range from  $123.3$  to  $137.5^\circ$ . This is a normal range for intergroup bond angles (Krogh-Moe, 1972*a, b*).

The four crystallographically non-equivalent potassium atoms have individual unsymmetrical oxygen coordinations. If the upper limit of the coordination sphere is taken (somewhat arbitrarily) as  $3.11$  Å, two of the potassium atoms have six close oxygen neighbours and the other two have eight close oxygen neighbours (see Table 3). The shortest potassium–oxygen distance is  $2.631$  Å. In comparison, in  $\alpha$ -potassium pentaborate there are eight close oxygen neighbours

surrounding potassium, the potassium–oxygen distances of these oxygen atoms ranging from  $2.770$  to  $3.139$  Å (Krogh-Moe, 1972*a*). The potassium–potassium distances are fairly evenly distributed from  $3.281$  Å upwards, whereas the shortest potassium–potassium distance in  $\alpha$ -pentaborate (Krogh-Moe, 1972*a*) is  $4.856$  Å.

Financial support for this work from the Norwegian Research Council for Science and Humanities, and the technical assistance of Mrs Slaattelid are acknowledged.

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