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The Crystal Structure of Pentapotassium Enneakaidekaborate, $5K_2O.19B_2O_3$

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Potassium borate glasses of the tetraborate composition, $K_2O.4B_2O_3$, may be crystallized to give a compound of the composition $K_2O.3{\cdot}8B_2O_3$ or $5K_2O.19B_2O_3$. This phase is monoclinic, space group $C2/c$, with unit-cell dimensions at 22°C: $a=17{\cdot}888\pm0{\cdot}002$, $b=11{\cdot}479\pm0{\cdot}001$, $c=12{\cdot}973\pm0{\cdot}002$ Å, $\beta=95{\cdot}52\pm0{\cdot}01°$. The calculated density is 2·247 g cm^{-3} with two formula units of $5K_2O.19B_2O_3$ in the cell. The structure was determined by direct methods from three-dimensional X-ray data taken with Mo $K\alpha$ radiation. A full-matrix least-squares refinement resulted in an R value of 0·030 (0·026 for the weighted R value). The borate anion polymer in this structure forms a three-dimensional framework consisting of interconnected pentaborate groups, triborate groups, BO_4 tetrahedra and BO_3 triangles. Boron–oxygen bond lengths (standard deviation 0·002 Å) are normal and with the usual differences depending on the location within the groups. The structure has three crystallographically different potassium atoms. The closest potassium–oxygen approach is 2·681 Å.

Introduction

A phase diagram of the system potassium oxide–boron was reported by Rollet (1935). The correctness of this phase diagram in the tetraborate ($K_2O.4B_2O_3$) region was questioned by Krogh-Moe (1961), who was unable to prepare a crystalline phase which he could unequivocally identify as a tetraborate. A monoclinic phase, with C-centring, was erroneously conjectured by Krogh-Moe (1961) to be γ-$K_2O.5B_2O_3$. One of the reasons for this assignment was the densities calculated from the unit-cell dimensions. A pentaborate with 8 formula units of $K_2O.5B_2O_3$ in the cell would correspond to a density of 2·216 g cm^{-3} for this phase, whereas a tetraborate with 8 formula units of $K_2O.4B_2O_3$ would only give 1·867 g cm^{-3}. The former density is close to the expected value, whereas the latter was considered too low. If a simple stoichiometry is assumed these remain the only two possibilities, since a tetraborate with 9 or 10 formula units in the cell requires positions of low multiplicity which are unavailable in the space group. As the present work has revealed, however, this phase actually has a composition $K_2O.3{\cdot}8B_2O_3$ with 10 formula units in the cell, giving a calculated density of 2·247 g cm^{-3}. The phase is therefore neither a pentaborate, nor a tetraborate, though it is closer in composition to the latter. Thus the presence of a tetraborate in the phase diagram for the system potassium oxide–boron oxide has not yet been confirmed.

The monoclinic C-centred potassium borate phase is the subject of the present crystal structure study. The rather unusual stoichiometry adds interest to a complete structure study of this phase.

Experimental

Crystalline $5K_2O.19B_2O_3$ was prepared by fusing in a platinum crucible potassium diborate tetrahydrate ($K_2O.2B_2O_3.4H_2O$, Riedel de Haen, A.G.) with boric acid (H_3BO_3, Merck, p.a.) in a stoichiometric ratio corresponding to the tetraborate composition. The $K_2O.4B_2O_3$ glass obtained, was crystallized at temperatures around 750°C.

A single crystal, approximately prismatic in shape with dimensions $0{\cdot}013\times0{\cdot}022\times0{\cdot}036$ cm, was used. Intensity data were obtained with an on-line Picker single crystal automatic diffractometer and Mo $K\alpha$ radiation. Measurements were made at 3325 different reciprocal lattice points, subject to the condition $h+k=2n$. 3078 reflexions not affected by systematic extinctions were observed larger than the background.

Unit-cell dimensions and standard deviations, $a=17{\cdot}888\pm0{\cdot}002$, $b=11{\cdot}479\pm0{\cdot}001$, $c=12{\cdot}973\pm0{\cdot}002$ Å, $\beta=95{\cdot}52\pm0{\cdot}02°$, were obtained by the method of least-squares from angle data recorded at 22°C for 12 high-angle reflexions (based on the wavelength 0·7093 Å for Mo $K\alpha_1$). With 2 formula units of $5K_2O.19B_2O_3$ in the cell, the calculated density is 2·247 g cm^{-3}.

Structure determination

The observed intensities were converted to structure factors in the usual manner. A correction for absorption was also made, but since the linear absorption coefficient (~9 cm^{-1}) is small, the maximum correction amounted to only 1·5 per cent in the structure factors.

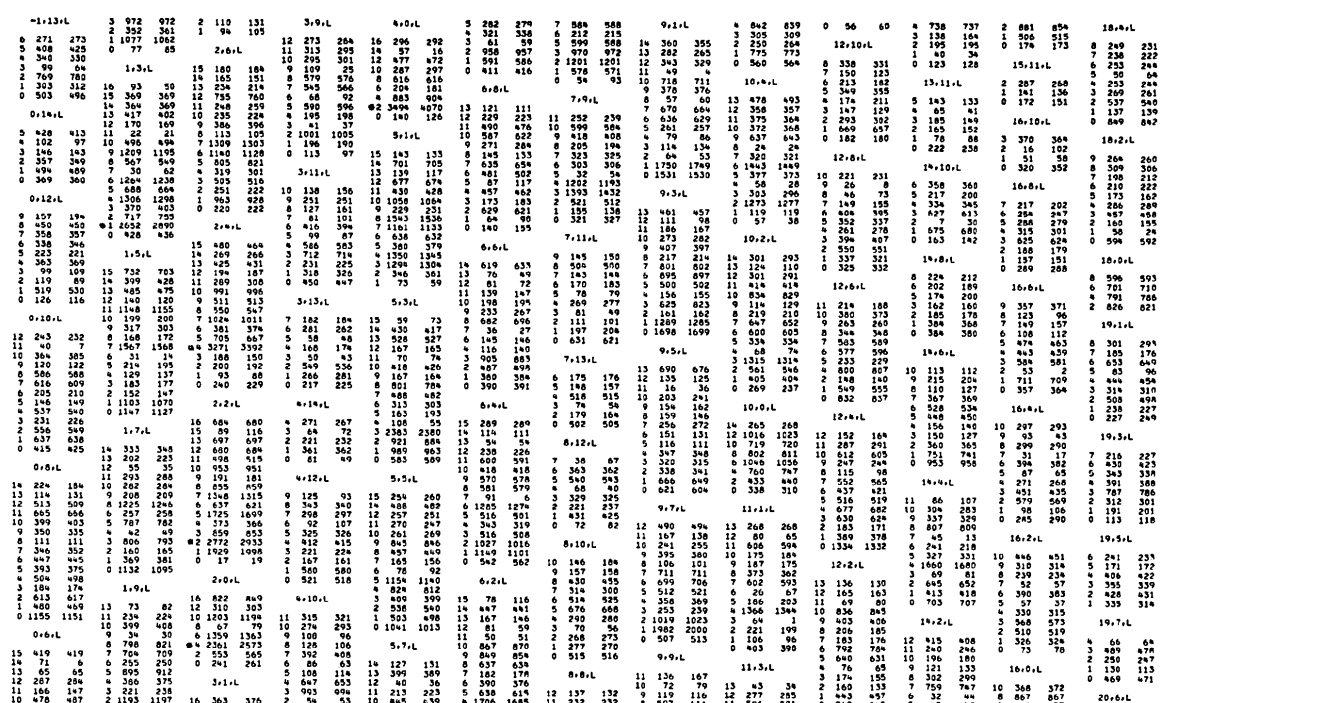
The observed systematic extinctions are those required by the space group $C2/c$. A statistical test of the distribution of normalized structure factors gave a strong indication of a centre of symmetry in agreement with the space group assignment. The structure was determined by direct methods, using the program system developed by Germain, Main & Woolfson (1971). The set of signs with the highest 'figure of merit' proved to give a sensible structure. The structure was refined by the method of least-squares, using the full-matrix *LSFIV*01 program by Borgen & Mestvedt

(1973). All the 3078 reflexions observed above the background were included in the refinement. The atomic scattering factors for B, O and K^+, used for calculating the 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 in-

Table 1. *Final observed and calculated structure factors.*

The columns are 1, $10F_o$ and $10F_c$. Reflexions affected by extinction are marked with an asterisk.

Table 1 (*cont.*)



tensity. The structure initially refined to an R value of 0·031 (and 0·028 for the weighted R value). The 15 reflexions with the strongest intensities were systematically calculated larger than observed. They were therefore assumed to be affected by extinction and were removed from the data set. The structure now finally refined to an R value of 0·030 or 0·026 for the weighted R value. During the last cycle of refinement the largest shift to error ratio was 0·15. The observed and calculated structure factors are given in Table 1. The final atomic coordinates and the thermal parameters are given in Table 2.

Discussion of the structure

Fig. 1 shows a section of the three-dimensional borate framework in pentapotassium enneakaidekaborate, $5K_2O.19B_2O_3$, as a stereo-pair projected approximately along the *b* axis. (The seemingly cluttered stereo-pair becomes well resolved, when viewed in a stereoscope.) The framework consists of pentaborate and triborate

Table 2. *Final atomic parameters*

Positional parameters are expressed as a fraction of the cell edge, 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 10^5. Atoms K(3), O(10) and B(9) occupy special positions.

	x	*y*	*z*	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
K(1)	16416	45610	19611	99	809	252	57	60	161
K(2)	32477	26876	33243	91	307	203	8	26	14
K(3)	0	0	0	257	506	348	−203	−142	193
O(1)	38887	49123	33223	78	304	186	22	25	64
O(2)	8684	11377	30914	91	364	276	−54	77	−141
O(3)	20182	13754	23162	83	302	187	−37	45	−74
O(4)	14949	13634	5444	155	404	167	151	63	76
O(5)	26955	45204	5709	125	407	164	125	51	93
O(6)	26297	48578	38048	83	251	127	−41	22	−19
O(7)	8667	42095	36406	74	292	187	25	47	94
O(8)	2328	38306	5034	71	233	198	−16	43	−65
O(9)	8612	26616	49202	66	183	180	−4	27	37
O(10)	0	96934	25000	70	204	291	0	27	0
O(11)	31465	9811	49803	83	249	145	−47	20	−16
O(12)	17457	26533	36157	79	246	230	−15	46	−76
O(13)	35774	31658	12547	100	422	182	111	55	112
O(14)	47740	27373	6899	91	163	168	11	40	−10
O(15)	43329	18112	21765	70	228	159	36	20	39
O(16)	47649	3853	33476	68	200	146	4	12	38
B(1)	17640	6401	14337	85	248	144	19	26	−7
B(2)	6760	2481	24090	71	217	183	23	−3	27
B(3)	15439	17271	30182	82	230	166	5	13	4
B(4)	32680	37602	3951	73	265	202	20	21	45
B(5)	23818	47702	47603	61	218	155	7	15	−14
B(6)	13208	33756	42846	64	199	153	−13	28	0
B(7)	1455	29478	50453	80	178	123	−20	13	−36
B(8)	1568	44983	38214	84	194	118	−18	1	−13
B(9)	0	60911	25000	66	171	137	0	9	0
B(10)	42428	25268	13623	83	184	148	10	16	−35
Standard deviations									
K	2	4	3	1	4	3	2	1	3
O	5	9	8	3	8	6	4	4	6
B	9	15	13	5	13	9	6	5	9

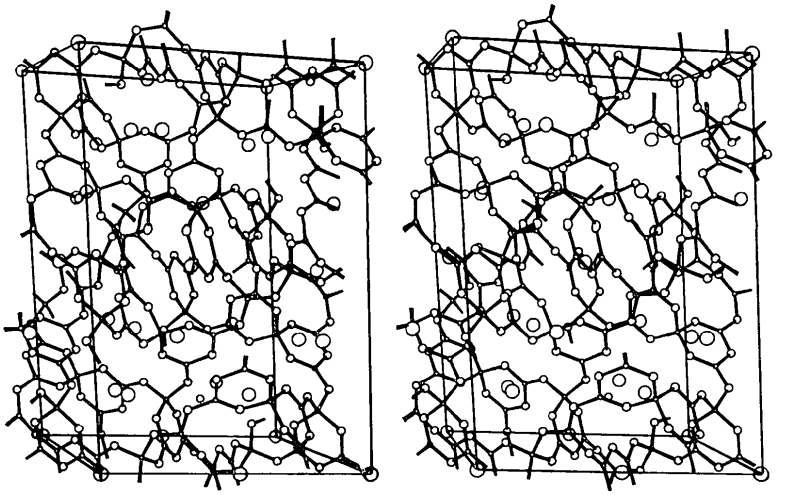


Fig. 1. Stereopair showing the boron–oxygen framework and the potassium atom positions in $5K_2O.19B_2O_3$. The large open circles, not connected by lines, represent the potassium atoms. Unit-cell edges are also shown. The *b* axis is approximately perpendicular to the paper plane; the *c* axis and the *a* axis are approximately horizontal and vertical respectively.

groups in equal amounts as well as BO_4 tetrahedra and BO_3 triangles which are not part of any larger groups.

Our 5:19 borate may be taken as a pseudotetraborate with an oxide ratio 1:3·8. The compound is actually found to be structurally related to some 1:4 tetraborates previously studied. Thus $Ag_2O.4B_2O_3$ (Krogh-Moe, 1965), $Na_2O.4B_2O_3$ (Hyman, Perloff, Mauer & Block, 1967) and $BaO.4B_2O_3$ (Krogh-Moe & Ihara, 1969) all have structures consisting of frameworks built up from alternating pentaborate and triborate groups. These frameworks are very space-demanding, however, and a normal packing density of the atoms is achieved by the interpenetration of two separate borate anion frameworks. In $K_2O.3{\cdot}8B_2O_3$, however, the borate anion forms a single framework. A normal packing density is here apparently achieved by an incorporation in the framework of BO_3 triangles and BO_4 tetrahedra. These additional units are perhaps crucial to obtaining the space filling required for the formation of a *single* framework consisting essentially of pentaborate and triborate groups. Each pentaborate group is now bonded to two triborate groups, one pentaborate group and a BO_3 triangle. The latter BO_3 triangle serves as a bridge to another triborate group. Each triborate group is bonded to two pentaborate groups, a BO_3 triangle and a BO_4 tetrahedron. This BO_4 tetrahedron similarly bridges to another triborate group.

The fraction of boron atoms in fourfold coordination should be $5/19 = 1/3{\cdot}8 = 0{\cdot}263$, according to the rule postulated by Krogh-Moe (1960). This rule is seen to be obeyed for the present structure. (Note that one of the fourfold-coordinated boron atoms, B(9), occupies a special position with half the multiplicity of a general position.)

The boron–oxygen bond lengths and bond angles are tabulated in Table 3. Reference can be made to Fig. 2, to identify the various bonds. The bond lengths show systematic variations, depending on adjacent boron–oxygen bonds. These variations were first brought to attention by Krogh-Moe (1972), and have since been

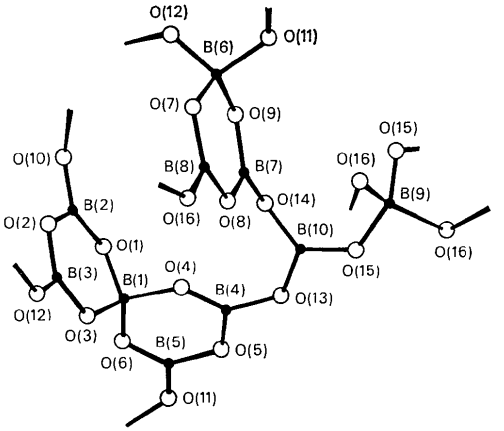


Fig. 2. Projection approximately along the *b* axis, showing the borate anion section included in the asymmetric unit. Open circles represent oxygen, filled circles represent boron. The numbering of the atoms is consistent with the tables.

Table 3. *Interatomic distances and bond angles*: *boron–oxygen bond lengths* (*standard deviation* 0·002 Å), *potassium–oxygen distances below* 3·5 Å (*standard deviation* 0·001 Å) *and oxygen–boron–oxygen and boron–oxygen–boron bond angles* (*standard deviation* 0·1 °)

Distances listed for K(3) occur twice for each oxygen atom due to the symmetry centre.

B(1)—O(1)	1·494 Å	B(10)–O(13)	1·394 Å
B(1)—O(3)	1·459	B(10)–O(14)	1·372
B(1)—O(4)	1·465	B(10)–O(15)	1·336
B(1)—O(6)	1·464	K(1)–O(16)	2·682
B(2)—O(1)	1·341	K(1)–O(7)	2·723
B(2)—O(2)	1·373	K(1)–O(5)	2·732
B(2)—O(10)	1·382	K(1)–O(6)	2·855
B(3)—O(2)	1·396	K(1)–O(11)	3·054
B(3)—O(3)	1·364	K(1)–O(12)	3·060
B(3)—O(12)	1·345	K(1)–O(8)	3·117
B(4)—O(4)	1·336	K(1)–O(3)	3·245
B(4)—O(5)	1·381	K(1)–O(15)	3·367
B(4)—O(13)	1·377	K(2)–O(9)	2·681
B(5)—O(5)	1·404	K(2)–O(15)	2·748
B(5)—O(6)	1·360	K(2)–O(12)	2·749
B(5)—O(11)	1·346	K(2)–O(1)	2·799
B(6)—O(7)	1·464	K(2)–O(6)	2·820
B(6)—O(9)	1·469	K(2)–O(13)	2·857
B(6)—O(11)	1·479	K(2)–O(3)	2·875
B(6)—O(12)	1·465	K(2)–O(11)	2·926
B(7)—O(8)	1·378	K(3)–O(14)	2·789
B(7)—O(9)	1·347	K(3)–O(1)	2·805
B(7)—O(14)	1·366	K(3)–O(4)	3·120
B(8)—O(7)	1·355	K(3)–O(10)	3·262
B(8)—O(8)	1·399	K(3)–O(2)	3·315
B(9)—O(15)	1·479	K(3)–O(9)	3·428
B(9)—O(16)	1·460		

O(1)—B(1)—O(3)	110·4°	O(7)—B(8)—O(8)	120·4
O(1)—B(1)—O(4)	106·2	O(7)—B(8)—O(16)	124·1
O(1)—B(1)—O(6)	108·2	O(8)—B(8)—O(16)	115·5
O(3)—B(1)—O(4)	110·1	O(15)–B(9)—O(15)	112·0
O(3)—B(1)—O(6)	109·8	O(15)–B(9)—O(16)	103·9
O(4)—B(1)—O(6)	112·0	O(15)–B(9)—O(16)′	112·3
O(1)—B(2)—O(2)	122·9	O(16)–B(9)—O(16)	112·6
O(1)—B(2)—O(10)	120·0	O(13)–B(10)–O(14)	118·7
O(2)—B(2)—O(10)	117·0	O(13)–B(10)–O(15)	116·1
O(2)—B(3)—O(3)	120·0	O(14)–B(10)–O(15)	125·0
O(2)—B(3)—O(12)	122·0		
O(3)—B(3)—O(12)	118·0	B(1)–O(1)—B(2)	120·5°
O(4)—B(4)—O(5)	121·6	B(2)–O(2)—B(3)	118·8
O(4)—B(4)—O(13)	123·2	B(1)–O(3)—B(3)	121·9
O(5)—B(4)—O(13)	115·2	B(1)–O(4)—B(4)	123·3
O(5)—B(5)—O(6)	119·9	B(4)–O(5)—B(5)	119·5
O(5)—B(5)—O(11)	115·1	B(1)–O(6)—B(5)	123·5
O(6)—B(5)—O(11)	125·0	B(6)–O(7)—B(8)	122·6
O(7)—B(6)—O(9)	112·0	B(7)–O(8)—(B8)	118·5
O(7)—B(6)—O(11)	109·2	B(6)–O(9)—B(7)	121·4
O(7)—B(6)—O(12)	108·8	B(2)–O(10)–B(2)′	125·1
O(9)—B(6)—O(11)	106·1	B(5)–O(11)–B(6)	125·7
O(9)—B(6)—O(12)	111·5	B(3)–O(12)–B(6)	131·6
O(11)–B(6)—O(12)	109·0	B(4)–O(13)–B(10)	127·9
O(8)—B(7)—O(9)	122·9	B(7)–O(14)–B(10)	134·1
O(8)—B(7)—O(14)	119·7	B(9)–O(15)–B(10)	126·9
O(9)—B(7)—O(14)	117·2	B(8)–O(16)–B(9)	125·9

found in several anhydrous borates. In the present structure the pentaborate rings have two relatively short boron–oxygen edges, with boron–oxygen bond lengths of 1·336 Å [B(4)–O(4)] and 1·341 Å [B(2)–O(1)]. These bond lengths occur typically with threefold-coordinated borons, such as B(1) and B(4), bonded to one BO_4 tetrahedron and two BO_3 triangles. The opposite edges [B(3)–O(3)] and [B(5)–O(6)] of the pentaborate rings are longer (1·364 and 1·360 Å) due to the circumstance that the boron atoms B(3) and B(5) are each bonded to two BO_4 tetrahedra and only one BO_3 triangle. A similar asymmetry, though less pronounced, is seen for the triborate ring.

The intergroup bond angles [in the present case the boron–oxygen–boron bond angles for oxygens O(10) to O(16)] are distributed in the range 125·1 to 134·1°. This is a normal range for such bond angles. The boron–oxygen–boron in-ring bond angles are significantly smaller, however, ranging from 118·5 to 123·5°.

Only the potassium atom K(2) has a fairly well defined coordination shell, with 8 oxygen atoms in the range from 2·681 to 2·926 Å. (Table 3). No further oxygen atoms are found within a distance of 3·5 Å. The atoms K(3) (which occupies a special position at the origin) and K(1) do not have an obvious upper limit for the coordination number. K(1) has 7 neighbours in the range from 2·682 to 3·117 Å and K(3) has 6 neighbours in the range from 2·789 to 3·120 Å.

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Thyroid Hormone Stereochemistry. I. The Molecular Structures of 3,5,3′-Triiodo-L-Thyronine (T_3) and L-Thyroxine (T_4)

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The crystal and molecular structures of the two thyroid hormones, 3,5,3′-triiodo-L-thyronine (T_3) and L-thyroxine (T_4) have been determined by X-ray crystallography. Crystals of T_3 hydrochloride trihydrate are monoclinic with $a=29{\cdot}080$, $b=5{\cdot}236$, $c=17{\cdot}047$ Å, $\beta=115{\cdot}85°$, space group $C2$ with $Z=4$. T_4 hydrochloride monohydrate also crystallizes in space group $C2$ with $a=17{\cdot}23$, $b=5{\cdot}14$, $c=25{\cdot}15$ Å, $\beta=90{\cdot}47°$, $Z=4$. Both structures were solved by Patterson and Fourier techniques and refined by full-matrix anisotropic least-squares methods. Final *R values* are 0·07 for T_3 and 0·107 for T_4. In both T_3 and T_4 the two phenyl rings are not mutually perpendicular and mutually bisecting. Angles between the plane of the inter-ring ether linkage and the planes of the α- and β-phenyl ring planes are 90° and −13° respectively for T_3 and 101° and −34° respectively for T_4. The four iodine atoms of T_4 are at the apices of a rather distorted tetrahedron. The conformation of the alanine side chain is very similar in both compounds. The conformation of T_3 is such that the 3′-iodine atom is *proximal* to the diiodo ring rather than *distal;* this conformation is opposite to that inferred from chemical studies. Theoretical calculations indicate this *proximal* conformation to be energetically favored over the *distal* one.

Introduction

The thyroid hormones L-thyroxine (T_4) and 3,5,3′-triiodo-L-thyronine (T_3) appear to exert an effect on nearly every organ and tissue of the body. They are essential for normal growth and development and the control of oxidative metabolism, and have a profound effect on protein synthesis in many tissues. Although their biological importance is well established, the mechanisms of thyroid-hormone action remain largely obscure.

* Investigator of the Howard Hughes Medical Institute.