tene analogue. This is reflected in the physiological activities of the various analogues; the pentene analogue has a growth activity which is 50–60% of that of vitamine A, but the other analogues do not show any appreciable activity (Huisman & Baas, 1969; Skolnik, 1969).

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The Crystal Structure of Zinc Diborate, ZnB_4O_7

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Zinc diborate crystallizes in the orthorhombic system, space group *Pbca*, with eight formula units in a cell of dimensions $a=13{\cdot}714\pm0{\cdot}005$, $b=8{\cdot}091\pm0{\cdot}005$ and $c=8{\cdot}631\pm0{\cdot}005$ Å. The calculated density is 3·07 g.cm^{-3}, and all atoms are in general positions. The structure of ZnB_4O_7 has been solved by three-dimensional Fourier syntheses. The positional and isotropic thermal parameters were refined by the least-squares method based on 530 observed reflexions. The final conventional R index is 0·067. The structure consists of BO_3 triangles and BO_4 tetrahedra sharing a common vertex. Each zinc atom is surrounded by four close oxygen atoms, arranged in an irregular tetrahedron.

Introduction

The binary system ZnO–B_2O_3 has been studied by several workers (Harrison & Hummel, 1956; Bauer, 1963; Weir & Schroeder, 1964). Fayos, Garcia-Blanco & Rivoir (1966) investigated the system using calcined samples. Three compounds were reported: $Zn_3(BO_3)_2$ (Garcia-Blanco & Fayos, 1968), $Zn_4O(BO_2)_6$ (Smith, Garcia-Blanco & Rivoir, 1964), and a third compound having approximate composition $ZnO.2B_2O_3$. The purpose of the present paper is to report on the crystal structure of the last compound.

The structures of several compounds with a metal oxide to boron oxide ratio of 1 to 2 are known. The mineral borax, $Na_2O.2B_2O_3.10H_2O$ (Morimoto, 1956), contains a double ring polyion as an isolated unit. In anhydrous lithium diborate, $Li_2B_4O_7$ (Krogh-Moe, 1968), and in cadmium diborate, CdB_4O_7 (Ihara & Krogh-Moe, 1966), however, these double ring polyions are condensed into three-dimensional networks where half the boron atoms are fourfold coordinated. On the other hand, the structure of the isomorphous compounds SrB_4O_7 and PbB_4O_7 (Perloff & Block, 1966), contains a completely different type of network, having all the boron atoms in fourfold coordination. The unusual feature is the occurrence of an oxygen atom common to three BO_4 tetrahedra. In the barium compound BaB_4O_7 (Block & Perloff, 1965), the borate network can be described as a three-dimensional linkage of both six-membered and double rings. The former contain two tetrahedral boron atoms and one triangular boron atom, and the latter contain two tetrahedral boron atoms and three triangular boron atoms. Since structural data about other diborates are

highly desirable in order to explain the dependence of boron coordination on the cation, an investigation of the structure of zinc diborate has been undertaken.

Experimental

Single crystals of zinc diborate were prepared by fusion of a mixture of composition $ZnO.2B_2O_3$ with a small excess of boron oxide, and subsequent annealing at 850°C. Colourless crystals were extracted from the crystallized melt by washing with ethanol. Chemical analysis led to the formula ZnB_4O_7.

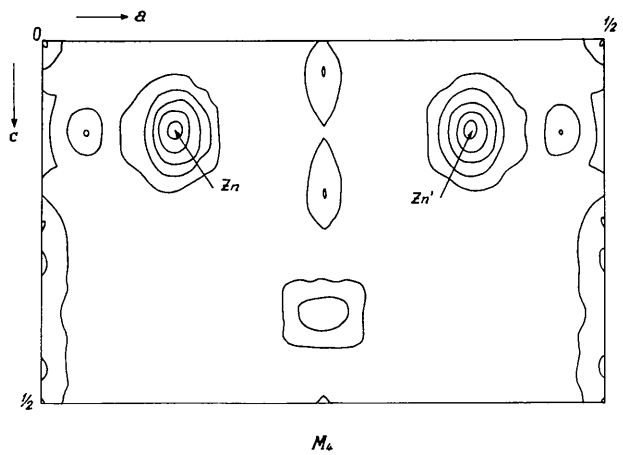

Fig. 1. Minimum function projection, M_4 (x,z).

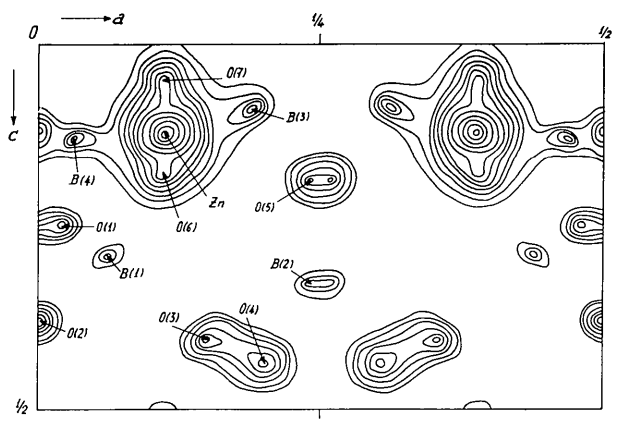

Fig. 2. (010) electron-density projection.

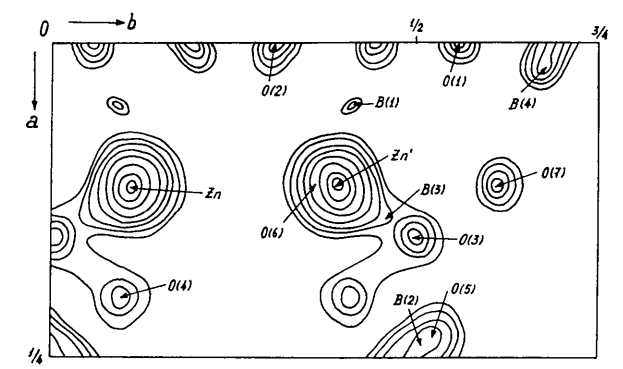

Fig. 3. (001) electron-density projection.

Unit-cell dimensions were obtained from indexed powder lines from a diffractometer recording. The following dimensions were found:

$a = 13{\cdot}714 \pm 0{\cdot}005$, $b = 8{\cdot}091 \pm 0{\cdot}005$, $c = 8{\cdot}631 \pm 0{\cdot}005$ Å

A list of interplanar spacings is given in Table 1. The observed reflexions led to the space group *Pbca*. The calculated and observed densities with 8 formula units in the cell are 3·07 and 3·09 g.cm^{-3} respectively.

Table 1. *Powder pattern of* ZnB_4O_7

hkl	d_o	*I*	*hkl*	d_o	*I*
200	6·825 Å	20	214	1·995 Å	30
111	5·416	25	041	1·972	10
210	5·228	100	612	1·960	10
102	4·114	45	141	1·953	10
020	4·051	30	423	1·936	50
112, 021	3·670	30	024, 432	1·904	10
121	3·542	20	233	1·894	15
220	3·488	25	711	1·859	25
400	3·426	50	042, 224	1·834	15
212	3·331	5	404	1·826	30
302	3·137	75	142, 341	1·818	50
312	2·926	45	532, 324	1·759	20
321	2·861	70	630	1·745	30
402	2·684	25	721	1·728	30
113	2·659	20	800	1·714	50
412	2·550	10	342	1·702	30
230	2·514	30			
511	2·488	25			
231	2·416	5			
023	2·347	15			
313	2·332	10			
502	2·315	15			
132	2·259	15			
422, 331	2·241	25			
512	2·225	60			
521, 610	2·198	25			
004	2·158	30			
611, 104	2·131	25			
323	2·088	10			
431, 114	2·061	15			
040	2·026	20			

Cu $K\alpha$ radiation ($\mu = 75$ cm^{-1}) and an integrating Weissenberg technique were used. The intensity data from seven reciprocal layers were measured photometrically. No absorption corrections were needed because of the small size of the crystal (0·001 × 0·006 × 0·010 cm). The intensities were corrected for Lorentz and polarization factors in the usual manner.

Determination of the structure

An (010) Patterson synthesis was calculated and minimum functions (Buerger, 1959) were obtained from the inversion peak. The x, z coordinates for the zinc atom were determined from the M_4 projection shown in Fig. 1. Several Fourier and difference Fourier syntheses were carried out; Fig. 2 shows the final synthesis, with a residual index R equal to 0·202. The y coordinate

for the zinc atom was obtained from the Patterson projection on (001). Several Fourier and difference Fourier syntheses gave the y coordinates of the other atoms. Fig. 3 shows the final Fourier synthesis, with an R value of 0·118. With these coordinates a coordination structure with (BO_3), (BO_4) and (ZnO_4) groups was obtained. Signs derived from these approximate coordinates together with the experimental structure factors were used for the calculation of a complete three-dimensional Fourier synthesis. Structure factors based on these coordinates, assuming isotropic temperature factors of 1·0 Å^2 correspond to $R=0{\cdot}117$. The f curves for neutral Zn, O and B were used.

After checking that the structural arrangement was reasonable from the crystal chemistry point of view, this structure was refined with the least-squares program *ORFLS* (Busing, Martin & Levy, 1962). Several cycles of isotropic refinement gave an R index of 0·067 including 530 reciprocal-lattice points. The weighting scheme chosen was: $w=1/(A+F_o+C.F_o^2)$ (Cruickshank, Pilling, Bujosa, Lovell & Truter, 1961). The final observed and calculated structure factors are given

Table 2. *Comparison of observed and calculated structure factors*

Asterisks denote unobserved reflexions.

H	K	L	FOBS	FCAL
	2		202.0	208.0
	4		197.0	189.4-
	6		35.2	34.1-
	8		66.3	65.6
	10		57.7	57.2
2			44.3	40.9
2	1		170.5	181.2-
2	2		124.2	110.8-
2	3		200.6	203.5-
2	4		81.6	74.5-
2	5		24.7	23.8
2	6		19.7	17.4-*
2	7		83.3	78.2
2	8		51.5	52.2-
2	9		17.8	8.5-*
2	10		12.0	10.9-*
4			130.0	146.4-
4	1		11.0	4.0 *
4	2		12.3	16.2-*
4	3		14.1	7.7 *
4	4		190.0	189.4
4	5		18.4	9.8 *
4	6		59.6	63.2
4	7		21.3	16.1 *
4	8		114.4	109.3-
4	9		16.7	14.5 *
4	10		40.4	45.0-
6			22.3	23.9-
6	1		94.4	99.4
6	2		22.1	18.9-
6	3		96.9	100.9
6	4		54.8	50.3
6	5		42.6	36.8-
6	6		21.1	13.0 *
6	7		31.7	32.6-
6	8		51.0	51.8-
6	9		25.1	28.0
8			243.3	265.8
8	1		58.2	55.3
8	2		59.3	57.1
8	3		42.1	43.7
8	4		87.3	93.0-
8	5		59.5	53.4-
8	6		21.2	11.9-*
8	7		56.0	52.9-
8	8		47.0	52.0
8	9		25.0	22.3-
10			102.6	95.9
10	1		62.5	69.7-
10	2		44.2	37.8-
10	3		60.8	52.0-
10	4		118.7	121.8-
10	5		44.4	48.2
10	6		48.7	50.3-
10	7		71.4	73.3
10	8		13.0	9.6 *
12			77.0	73.1-
12	1		43.9	42.2-
12	2		21.3	14.1 *
12	3		21.2	26.5-*
12	4		122.5	124.3
12	5		34.2	35.5
12	6		42.7	44.4
12	7		20.6	22.7
14			58.4	52.5-
14	1		52.9	46.7
14	2		19.8	2.7 *
14	3		82.7	77.7
14	4		56.7	56.4
14	5		14.9	4.4-*
14	6		10.6	12.7-*
16			85.5	89.0
16	1		15.8	15.0 *
16	2		24.2	24.4
16	3		27.4	23.3
16	4		54.4	47.5-
	2	1	141.8	149.5-
	4	1	122.6	113.4-
	6	1	61.2	61.9
	8	1	48.2	47.9
	10	1	34.7	35.6-
1	1	1	66.8	70.5
1	2	1	73.4	79.9-
1	3	1	8.5	12.5-*
1	4	1	25.5	30.3-
1	5	1	29.0	28.9-
1	6	1	47.2	43.9
1	7	1	14.6	14.4-*
1	8	1	27.5	28.8
1	9	1	35.3	33.9
1	10	1	21.6	20.6-
2	1	1	5.7	6.6-*
2	2	1	10.6	6.3
2	3	1	40.5	45.4
2	4	1	22.6	21.3-
2	5	1	106.5	105.0
2	6	1	13.7	14.4 *
2	7	1	14.6	11.3 *
2	8	1	14.3	10.8 *
2	9	1	64.3	65.3-
2	10	1	8.0	14.3 *
3	1	1	16.0	20.6-
3	2	1	163.2	178.9-
3	3	1	41.9	31.9*
3	4	1	66.8	64.3-
3	5	1	31.4	32.7
3	6	1	75.7	72.1
3	7	1	16.7	12.2-*
3	8	1	49.4	51.3
3	9	1	25.2	24.8-
3	10	1	29.0	29.4-
4	1	1	14.7	8.1
4	2	1	44.0	52.3
4	3	1	46.3	41.4-
4	4	1	32.0	24.2-
4	5	1	12.8	10.7-*
4	6	1	100.5	99.3-
4	7	1	14.7	9.7-*
4	8	1	81.3	84.0-
4	9	1	16.8	18.6-
5	1	1	73.5	81.2-
5	2	1	64.7	67.2
5	3	1	10.5	3.0-*
5	4	1	40.3	42.2
5	5	1	92.6	94.6
5	6	1	42.4	41.6-
5	7	1	14.7	4.8 *
5	8	1	29.8	29.2-
5	9	1	55.4	52.5-
6	1	1	60.8	73.8
6	2	1	10.3	11.4 *
6	3	1	36.1	35.4-
6	4	1	12.5	7.1-*
6	5	1	72.7	69.8-
6	6	1	14.6	8.6 *
6	7	1	14.5	13.8-*
6	8	1	19.2	15.9
6	9	1	35.8	32.3
7	1	1	76.6	80.2
7	2	1	106.8	118.1
7	3	1	35.0	35.8-
7	4	1	67.8	70.6
7	5	1	27.8	25.3-
7	6	1	67.6	67.4-
7	7	1	14.7	3.0 *
7	8	1	45.9	52.8-
7	9	1	26.4	26.9
8	1	1	42.2	40.0
0	2	1	92.9	101.3-
8	3	1	12.9	5.3-*
8	4	1	95.4	101.6-
8	5	1	20.6	17.1-
8	6	1	28.8	26.8
8	7	1	13.7	4.4-*
8	8	1	40.3	40.5
8	9	1	18.4	14.3
9	1	1	59.5	56.2
9	2	1	74.2	76.0-
9	3	1	23.7	22.8-
9	4	1	18.5	18.7-
9	5	1	24.0	22.2-
9	6	1	14.3	18.1 *
9	7	1	12.9	2.9-*
9	8	1	10.3	4.7 *
10	1	1	43.6	42.1-
10	2	1	39.5	37.9-
10	3	1	14.3	19.3 *
10	4	1	63.9	64.8-
10	5	1	66.6	71.9
10	6	1	21.1	19.5
10	7	1	11.9	12.1 *
10	8	1	45.6	44.3
11	1	1	43.3	40.7-
11	2	1	72.3	74.1-
11	3	1	30.6	27.3-
11	4	1	14.7	15.4-*
11	5	1	20.8	17.1
11	6	1	47.6	46.2
11	7	1	10.5	10.8-*
12	1	1	42.0	39.9-
12	2	1	63.2	63.9
12	3	1	22.4	20.7-
12	4	1	14.2	7.9-*
12	5	1	31.6	28.3
12	6	1	12.9	9.6-
12	7	1	8.6	10.7 *
13	1	1	14.6	7.2-*
13	2	1	14.0	6.1 *
13	3	1	14.0	4.8 *
13	4	1	13.3	12.0 *
13	5	1	49.3	50.5
13	6	1	9.7	5.6 *
14	1	1	50.1	52.5
14	2	1	39.0	36.2
14	3	1	12.9	10.4-*
14	4	1	11.8	6.9 *
14	5	1	34.1	27.0-
14	6	1	11.5	11.0-
15	1	1	21.9	20.6
15	2	1	69.2	64.2
15	3	1	11.3	10.7-*
15	4	1	29.1	28.2
15	5	1	17.3	15.2
16	1	1	16.4	14.2
16	2	1	33.4	32.5-
16	3	1	8.9	1.8-*
16	4	1	30.6	32.0-
17	1	1	35.9	33.0
	2	2	47.0	39.0-
	4	2	51.9	45.7-
	6	2	15.4	7.0-*
	8	2	42.6	36.7
1		2	150.5	153.3-
1	1	2	22.4	29.0-
1	2	2	7.8	2.4-*
1	3	2	105.3	105.2-
1	4	2	119.2	113.0
1	5	2	31.2	28.3
1	6	2	23.7	22.6
1	7	2	9.3	9.1
1	8	2	54.6	50.8-
1	9	2	13.4	16.2-*
2		2	55.9	56.2-
2	1	2	30.6	24.3
2	2	2	21.8	19.2-
2	3	2	10.1	5.9 *
2	4	2	48.4	42.3
2	5	2	33.1	26.9-
2	6	2	48.5	45.3
2	7	2	16.4	13.2-*
2	8	2	24.9	21.5
2	9	2	13.1	4.7-*
3		2	197.6	209.7-
3	1	2	119.0	125.9
3	2	2	19.6	13.2
3	3	2	50.7	56.4
3	4	2	176.9	183.2
3	5	2	54.8	52.0-
3	6	2	49.9	47.0
3	7	2	20.8	22.9-
3	8	2	59.4	60.1-
3	9	2	12.8	9.0-*
4		2	109.4	113.3-
4	1	2	41.0	37.6
4	2	2	98.5	93.8-
4	3	2	58.0	50.6
4	4	2	23.6	19.5-
4	5	2	14.8	8.1 *
4	6	2	16.0	12.2 *
4	7	2	18.4	9.8-*
4	8	2	15.2	5.7-*
4	9	2	12.2	1 *
5		2	74.6	82.0
5	1	2	137.4	169.8
5	2	2	10.8	7.6-*
5	3	2	99.6	105.6
5	4	2	103.9	102.7-
5	5	2	89.1	80.0-
5	6	2	61.2	59.1-
5	7	2	75.0	73.4-
5	8	2	28.4	24.7
5	9	2	29.5	19.3-
6		2	34.1	32.2
6	1	2	45.6	41.9-
6	2	2	22.1	18.1
6	3	2	31.8	29.5-
6	4	2	32.0	30.3
6	5	2	29.9	22.9
6	6	2	34.2	33.6
6	7	2	16.1	12.2 *
6	8	2	14.2	11.5 *
6	9	2	10.6	6.4-*
7		2	176.9	199.2
7	1	2	22.8	27.0-
7	2	2	26.2	27.5
7	3	2	71.2	72.6-
7	4	2	129.1	137.2-
7	5	2	16.0	18.3 *
7	6	2	54.2	51.4-
7	7	2	76.2	76.0
7	8	2	63.9	66.2
7	9	2	12.5	14.5
8		2	35.1	29.0-
8	1	2	13.3	14.5-*
8	2	2	37.4	33.9-
8	3	2	14.7	6.6-*
8	4	2	23.1	22.7-
8	5	2	16.3	2.9 *
8	6	2	16.3	6.5-*
8	7	2	15.0	12.9-*
8	8	2	12.3	6.6 *
8	9	2	7.1	9.5-*
9		2	63.5	58.1-
9	1	2	73.1	73.9-
9	2	2	14.8	5.2-*
9	3	2	101.8	107.3-
9	4	2	61.7	60.2
9	5	2	30.8	29.6
9	6	2	27.5	28.2
9	7	2	64.5	65.8
9	8	2	17.3	20.1-
10		2	27.8	20.7
10	1	2	15.3	2.1-*
10	2	2	15.7	1-*
10	3	2	16.2	9.6-*
10	4	2	16.4	14.8-*
10	5	2	16.2	15.1-*
10	6	2	15.1	2.4-*
10	7	2	12.8	2.4-*
10	8	2	21.2	19.3
11		2	120.3	124.0-
11	1	2	19.7	21.3
11	2	2	16.3	9.6-*
11	3	2	16.4	12.7 *
11	4	2	107.5	112.0
11	5	2	15.5	7.8-*
11	6	2	34.2	38.7
11	7	2	25.9	22.2-
12		2	51.2	49.0-
12	1	2	16.4	2.6 *
12	2	2	32.2	31.9-
12	3	2	16.2	4.2-*
12	4	2	15.7	12.9 *
12	5	2	14.4	12.3-*
12	6	2	8.9	2.4-*
12	7	2	8.9	6.2 *
13		2	33.9	30.1-
13	1	2	66.6	69.1
13	2	2	36.4	32.2-
13	3	2	60.7	63.2
13	4	2	21.3	20.9-
13	5	2	29.7	28.5-
13	6	2	10.2	13.6-*
14		2	15.4	5.7-*
14	1	2	15.3	4.2-*
14	2	2	14.9	8.5-*
14	3	2	14.1	7.1-*
14	4	2	12.7	13.9 *
14	5	2	10.6	10.8-*
15		2	117.4	133.6
15	1	2	13.7	15.8 *
15	2	2	27.4	28.2 *
15	3	2	12.1	14.7 *
15	4	2	63.8	64.8-
15	5	2	14.2	15.4
16		2	25.3	21.6-
16	1	2	15.3	16.8-
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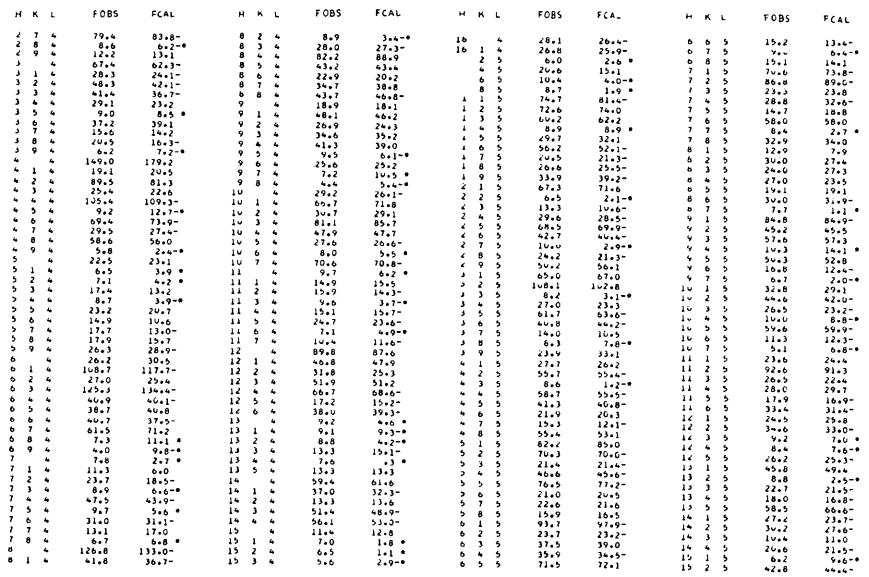
16	3	2	14.1	15.3-
17		2	30.0	30.1
17	1	2	44.6	45.3-
	2	3	137.2	141.1-
	4	3	30.4	33.3-
	6	3	149.9	160.1
	8	3	80.4	93.5
1		3	94.5	92.9-
1	2	3	66.8	67.5
1	3	3	13.0	13.9
1	4	3	51.1	48.0
1	5	3	76.0	77.7
1	6	3	28.3	28.1-
1	7	3	22.2	22.4
1	8	3	35.9	36.0-
1	9	3	50.6	52.0-
2	1	3	38.9	45.9-
2	2	3	52.6	45.4
2	3	3	65.4	64.7
2	4	3	7.5	4.4-*
2	5	3	120.6	124.7
2	6	3	15.5	10.6
2	7	3	19.3	18.0
2	8	3	13.0	16.4-
2	9	3	49.7	50.1-
3	1	3	57.4	71.5
3	2	3	38.5	43.3
3	3	3	10.2	15.2-*
3	4	3	40.2	35.5
3	5	3	59.9	60.1-
3	6	3	23.7	22.0-
3	7	3	9.8	9.8 *
3	8	3	36.2	38.2-
3	9	3	36.1	39.2
4	1	3	29.8	30.0-
4	2	3	167.3	173.4
4	3	3	45.5	41.2-
4	4	3	32.1	35.1
4	5	3	9.0	9.0-*
4	6	3	71.2	68.8-
4	7	3	9.8	1.7 *
4	8	3	53.7	61.8-
4	9	3	6.8	1 *
5	1	3	35.2	42.6
5	2	3	10.4	11.0-
5	3	3	13.6	14.7-
5	4	3	23.7	21.3-
5	5	3	76.3	76.6-
5	6	3	23.4	24.4
5	7	3	9.7	6.6-*
5	8	3	19.2	23.0
5	9	3	44.1	47.5
6	1	3	18.2	24.7
6	2	3	87.5	92.3
6	3	3	57.7	57.5-
6	4	3	37.0	35.0
6	5	3	48.3	50.2-
6	6	3	17.7	17.3
6	7	3	9.5	6.6 *
6	8	3	8.1	2.3-*
6	9	3	22.6	27.4
7	1	3	14.9	16.9-
7	2	3	16.1	18.2-
7	3	3	33.5	29.9
7	4	3	49.6	48.0-
7	5	3	17.0	13.4
7	6	3	22.1	21.7
7	7	3	9.1	8.4-*
7	8	3	39.2	41.2
8	1	3	68.9	65.4
8	2	3	44.5	48.0-
8	3	3	9.1	3.2-*
8	4	3	14.9	14.4-
8	5	3	14.0	8.8-
8	6	3	76.5	84.8
8	7	3	8.7	8.6 *
8	8	3	30.2	34.5
9	1	3	71.8	71.0-
9	2	3	32.0	29.7
9	3	3	26.8	27.4
9	4	3	9.8	5.5-*
9	5	3	48.6	50.8
9	6	3	9.3	6.6-*
9	7	3	8.0	1.8-*
9	8	3	9.2	11.1 *
10	1	3	48.1	51.8-
10	2	3	40.8	38.7-
10	3	3	21.6	18.0
10	4	3	37.6	33.4-
10	5	3	56.9	57.1
10	6	3	36.4	40.0
10	7	3	7.2	2.9-*
11	1	3	29.2	24.3
11	2	3	40.4	38.6
11	3	3	14.6	11.5
11	4	3	15.4	12.1
11	5	3	19.7	15.8-
11	6	3	38.5	35.2-
11	7	3	6.1	5.8 *
12	1	3	47.4	38.4-
12	2	3	114.1	113.6
12	3	3	15.5	9.4-
12	4	3	35.1	36.2
12	5	3	25.0	18.8
12	6	3	27.5	26.7-
12	7	3	4.2	7.6-*
13	1	3	22.7	22.0
13	2	3	29.8	27.3-
13	3	3	19.4	15.8-
13	4	3	8.3	7.4-*
13	5	3	82.8	65.5-
13	6	3	22.2	20.5
14	1	3	56.5	54.9
14	2	3	58.6	57.3
14	3	3	15.3	19.6-
14	4	3	14.1	7.2 *
14	5	3	35.5	33.6-
15	1	3	20.1	19.0-
15	2	3	38.3	31.5-
15	3	3	33.9	28.9
15	4	3	28.7	26.3-
16	1	3	12.9	7.9
16	2	3	30.7	28.3-
	2	4	5.1	5.1-*
	4	4	105.3	107.6
	6	4	9.6	11.2-*
	8	4	54.0	61.6-
1		4	41.2	49.1
1	1	4	47.7	40.9
1	2	4	21.1	23.1
1	3	4	11.6	9.7
1	4	4	19.2	15.1
1	5	4	23.7	22.6-
1	6	4	21.1	24.0
1	7	4	9.6	5.7 *
1	8	4	8.7	8.0 *
1	9	4	13.3	14.0
2		4	11.2	8.2-
2	1	4	120.7	129.4
2	2	4	76.4	68.3
2	3	4	141.8	150.9
2	4	4	32.6	31.8
2	5	4	35.8	37.4-
2	6	4	31.6	29.9-

Table 2 (*cont.*)



in Table 2. The positional and thermal parameters are shown in Table 3.

Table 3. *Positional and thermal parameters*

Standard deviations, multiplied by 0·0001, are given in parentheses.

	x/a	*y/b*	*z/c*	*B*
Zn	0·1176 (1)	0·1094 (1)	0·1203 (2)	0·85 Å^2
O(1)	0·0035 (5)	0·5649 (9)	0·2546 (12)	0·23
O(2)	0·0057 (5)	0·3151 (9)	0·3938 (12)	0·57
O(3)	0·1438 (5)	0·4764 (9)	0·4077 (12)	0·62
O(4)	0·2034 (5)	0·1036 (8)	0·4442 (15)	0·62
O(5)	0·2499 (5)	0·5193 (9)	0·1895 (15)	0·67
O(6)	0·1087 (4)	0·3499 (9)	0·1637 (13)	0·19
O(7)	0·1131 (5)	0·6157 (8)	0·0482 (16)	0·44
B(1)	0·0652 (7)	0·4221 (12)	0·2980 (19)	0·10
B(2)	0·2309 (8)	0·5297 (14)	0·3426 (24)	0·54
B(3)	0·1683 (8)	0·4709 (14)	0·0825 (22)	0·46
B(4)	0·0375 (8)	0·6656 (14)	0·1419 (22)	0·56

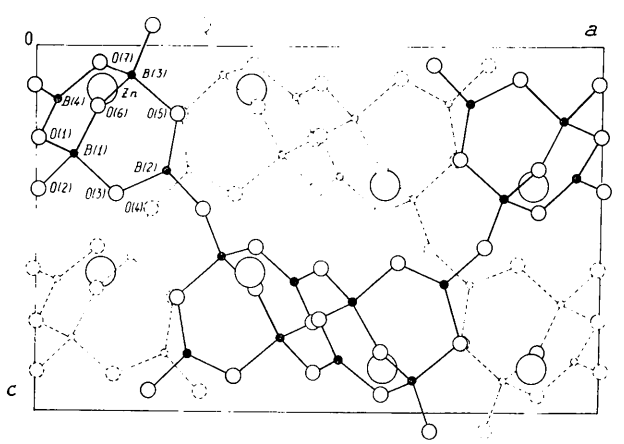


Fig. 4. The projection of the unit cell on (010).

Description and discussion of the structure

Fig. 4 shows a projection of the structure on (010). The structure consists of two infinite three-dimensional networks of boron–oxygen linkages, connected by the two-fold screw axes normal to the plane of the paper. Similar borate networks have previously been encountered in the structures of lithium diborate (Krogh-Moe, 1968), the mineral borax (Morimoto, 1956), and cadmium diborate (Ihara & Krogh-Moe, 1966), which is isomorphous with ZnB_4O_7. There are four types of boron atoms, two of which are tetrahedrally coordinated and two triangularly coordinated. The two tetrahedra and two triangles form a $[B_4O_7]^{2-}$ unit as shown in Fig. 5, and which is repeated throughout the structure. The mean boron–oxygen distances are 1·46 Å (BO_4) and 1·37 Å (BO_3), with individual lengths varying from 1·42 to 1·50 Å, and from 1·35 to 1·39 Å respectively. This result compares well with the corresponding mean bond distances given by Zachariasen (1963) (1·475 Å in BO_4, 1·365 Å in BO_3). The large variation of the individual B–O distances in the BO_4 groups found in this structure indicates that the tetrahedra are somewhat distorted.

Each zinc atom is surrounded by four close oxygen atoms at distances 1·984, 1·995, 2·014 and 2·045 Å. These four close oxygen atoms are arranged in a very distorted tetrahedron. The six O–Zn–O angles of this coordination polyhedron are 89·1, 91·3, 110·4, 120·8, 121·7 and 125·3°. The zinc atom seems to be essentially covalent-tetrahedrally bonded, though other oxygen atoms probably contribute to a smaller extent to the bonding.

All interatomic distances and their standard deviations are reported in Table 4. The individual valence angles O–B–O and O–Zn–O together with their standard deviations are shown in Table 5. The infrared

spectra of zinc diborate show two strong bands at 1·400 and 1·060 cm^{-1} respectively (Fig. 6). These results seem to be in good agreement with the existence of BO_3 and BO_4 groups in the crystal structure.

Table 4. *Interatomic distances*

	B(1)-tetrahedron		
B(1)–O(1)	1·48 (1) Å	O(1)–O(2)	2·35 (1) Å
–O(2)	1·45 (1)	O(2)–O(3)	2·30 (1)
–O(3)	1·50 (1)	O(3)–O(6)	2·39 (1)
–O(6)	1·43 (1)	O(6)–O(1)	2·39 (1)
Average	1·46	O(1)–O(3)	2·44 (1)
		O(2)–O(6)	2·45 (1)
	B(3)-tetrahedron		
B(3)–O(4)	1·42 (1) Å	O(4)–O(5)	2·42 (1) Å
–O(5)	1·50 (1)	O(5)–O(6)	2·38 (1)
–O(6)	1·45 (1)	O(6)–O(7)	2·37 (1)
–O(7)	1·43 (1)	O(7)–O(4)	2·34 (1)
Average	1·45	O(4)–O(6)	2·33 (1)
		O(5)–O(7)	2·37 (1)
	B(2)-triangle		
B(2)–O(3)	1·39 (1) Å	O(3)–O(4)	2·35 (1) Å
–O(4)	1·39 (1)	O(4)–O(5)	2·39 (1)
–O(5)	1·35 (1)	O(3)–O(5)	2·40 (1)
Average	1·37		
	B(4)-triangle		
B(4)–O(1)	1·35 (1) Å	O(1)–O(2)	2·40 (1) Å
–O(2)	1·38 (1)	O(2)–O(7)	2·35 (1)
–O(7)	1·38 (1)	O(1)–O(7)	2·37 (1)
Average	1·37		
	Zn-tetrahedron		
Zn–O(1)	2·014 (8) Å		
–O(3)	1·995 (9)		
–O(5)	2·045 (9)		
–O(6)	1·984 (8)		
Average	2·009		

Table 5. *Valence angles*

	B(1)-tetrahedron	
O(1)–B(1)–O(2)		107 (1)°
O(2)–	–O(3)	103 (1)
O(3)–	–O(6)	109 (1)
O(6)–	–O(1)	110 (1)
O(1)–	–O(3)	110 (1)
O(2)–	–O(6)	116 (1)
	B(3)-tetrahedron	
O(4)–B(3)–O(5)		112 (1)°
O(5)–	–O(6)	107 (1)
O(6)–	–O(7)	111 (1)
O(7)–	–O(4)	110 (1)
O(4)–	–O(6)	108 (1)
O(5)–	–O(7)	108 (1)
	B(2)-triangle	
O(3)–B(2)–O(4)		116 (1)°
O(4)–	–O(5)	121 (1)
O(3)–	–O(5)	123 (1)
	B(4)-triangle	
O(1)–B(4)–O(2)		122 (1)°
O(2)–	–O(7)	117 (1)
O(1)–	–O(7)	120 (1)

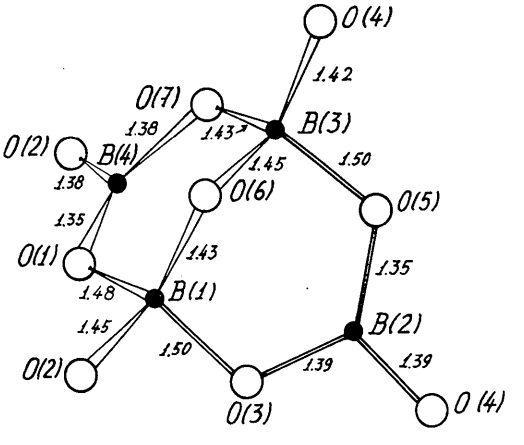


Fig. 5. A view of the $[B_4O_7]^{2-}$ unit. Bond lengths are given in Å. As can be seen from Fig. 4, these units are linked together to form a three-dimensional network.

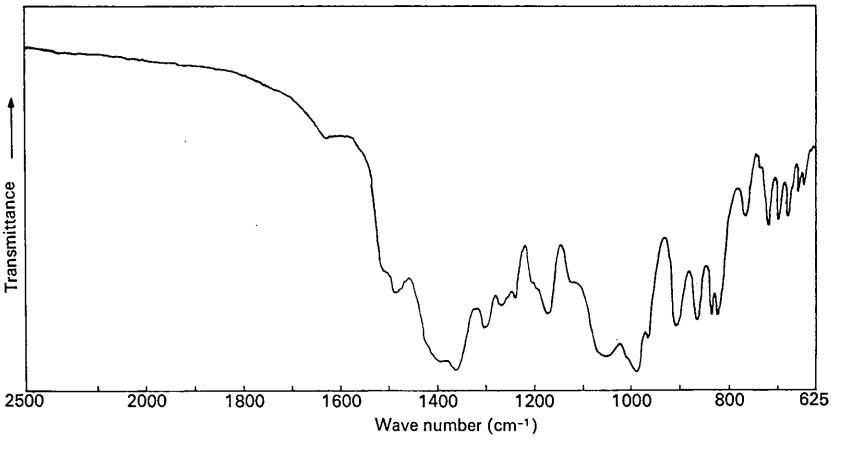


Fig. 6. Infrared spectrum of zinc diborate.

Table 5 (*cont.*)

Zn-tetrahedron	
O(1)–Zn–O(3)	125·3 (3)°
O(3)– –O(5)	89·1 (3)
O(5)– –O(6)	110·4 (3)
O(6)– –O(1)	91·3 (3)
O(1)– –O(5)	120·8 (3)
O(3)– –O(6)	121·7 (3)

The numerical calculations were carried out on the 7070 IBM computer of the Centro de Cálculo Electrónico del C.S.I.C., Spain, and on the 7090 IBM computer of the Centro de Cálculo de la Universidad de Madrid, Spain. This work forms part of the Ph. D. Thesis of one of us (M.M.R.) who also acknowledges the research grant given by Ministerio de Educación y Ciencia, Spain.

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The Crystal Structure of Copper Metaborate, CuB_2O_4

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Copper metaborate crystallizes in the tetragonal system, space group $I\bar{4}2d$, with twelve formula units in a cell of dimensions $a = 11{\cdot}484 \pm 0{\cdot}004$ and $c = 5{\cdot}620 \pm 0{\cdot}004$ Å. The calculated density is 4·02 g.cm^{-3}. The structure of CuB_2O_4 has been determined by three-dimensional Fourier syntheses. The positional and isotropic thermal parameters were refined by least-squares analysis, yielding a final R value of 0·053. All boron atoms are tetrahedrally coordinated. The structure consists of BO_4 tetrahedra sharing the four common oxygen atoms. Each copper atom is surrounded in a planar-square coordination by four oxygen atoms. All interatomic distances are of the usual order of magnitude.

Introduction

The binary system CuO–B_2O_3 has been treated by Weir & Schroeder (1964) in a preliminary study. In accordance with their results two copper borates were easily prepared by heating two mixtures of boron and copper oxides. Powder X-ray diffraction patterns of these compounds were taken. One compound apparently corresponds to the formula $3CuO \cdot B_2O_3$, and forms laminar green crystals. The other compound exactly corresponds to the formula $CuO \cdot B_2O_3$, and forms deep blue crystals. The purpose of the present paper is to report on the crystal structure of the phase $CuO \cdot B_2O_3$.

The structures of several anhydrous borates with a metal oxide to boron oxide ratio of 1:1 are known. In some of them, namely $NaBO_2$ (Marezio, Plettinger & Zachariasen, 1963*a*), CaB_2O_4(I) (Marezio, Plettinger & Zachariasen, 1963*b*), $LiBO_2$(I) (Zachariasen, 1964) and BaB_2O_4 (Mighell, Perloff & Block, 1966), all boron atoms have a coordination number 3. On the other hand, in the isomorphous SrB_2O_4(IV) (Dernier, 1969) and CaB_2O_4(IV) (Marezio, Remeika & Dernier, 1969*b*), and in $LiBO_2$(III) (Marezio & Remeika, 1966), all boron atoms are tetrahedrally coordinated. Finally, CaB_2O_4(III) (Marezio, Remeika & Dernier, 1969*a*), an isomorph of SrB_2O_4(III) (Dernier, 1969), contains BO_3 triangles and BO_4 tetrahedra. As part of a programme in progress aimed at achieving a better understanding of the structural principles of anhydrous borate compounds, the structure of CuB_2O_4 was selected for study.

Experimental

Single crystals of copper metaborate were prepared by annealing a melt of stoichiometry $CuO \cdot B_2O_3$ at