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Refinement of the Calcium Metaborate Structure

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The structure reported for CaB_2O_4 in 1932 has been refined. The bond lengths have been determined to an accuracy of 0·005–0·010 Å.

The bond lengths in the BO_3 triangle are 1·326, 1·385 and 1·401 Å with the short B–O bond for the unshared oxygens in the infinite chain of triangles. The Ca–O bonds range in length from 2·347 to 2·727 Å.

Introduction

The crystal structure of calcium metaborate, CaB_2O_4, was reported from this laboratory many years ago (Zachariasen, 1931; Zachariasen & Ziegler, 1932), and it was found that the structure contained endless chains of BO_3 groups. However, the individual bond lengths were determined to no better than ±0·05 Å.

Recent work of this laboratory has shown that the B–O bond distance can vary appreciably within a given structure and from one structure to the next. Accordingly it became desirable to redetermine the atomic positions with greater accuracy.

Crystals of CaB_2O_4 are orthorhombic with space group symmetry *Pnca* and four molecules in a cell of dimensions

$$a=6{\cdot}214\pm0{\cdot}003,\ b=11{\cdot}604\pm0{\cdot}004,\ c=4{\cdot}285\pm0{\cdot}001\ \text{Å}\ .$$

The four calcium atoms lie on twofold axes, $\pm(\frac{1}{4}, 0, z)(\frac{1}{4}, \frac{1}{2}, \frac{1}{2}+z)$ while the boron atoms and two

Table 1. *Parameter values* (×10^4)

	Ca	B	O_I	O_{II}
x	2500	1258 ± 12	917 ± 7	1478 ± 8
y	0	1924 ± 8	862 ± 3	2078 ± 4
z	2726 ± 5	8296 ± 32	7268 ± 12	1485 ± 18
β_{11}	61 ± 4	63 ± 16	65 ± 10	146 ± 13
β_{22}	11 ± 1	24 ± 5	18 ± 3	11 ± 3
β_{33}	183 ± 13	108 ± 49	186 ± 30	205 ± 41
β_{12}	−2 ± 2	6 ± 8	−6 ± 5	6 ± 6
β_{13}	0	−30 ± 33	8 ± 22	−4 ± 25
β_{23}	0	−27 ± 24	−9 ± 10	0 ± 13

Table 2. *Observed and calculated structure factors*

Reflections *HK*0 and *HK*1

HKL	F_o	$0{\cdot}236F_c$	*HKL*	F_o	$0{\cdot}236F_c$	*HKL*	F_o	$0{\cdot}236F_c$	*HKL*	F_o	$0{\cdot}236F_c$
020	6·3	5·4	0,12,0	5·6	5·4	071	5·8	−5·3	611	1·6	1·6
200	13·0	−12·9	650	nil	0·2	261	5·1	−4·9	621	1·1	1·1
210	20·3	−21·0	4,10,0	1·2	0·9	171	9·5	−9·5	3,10,1	2·3	2·3
040	14·4	14·1	2,12,0	4·0	−4·1	351	4·3	4·2	631	nil	0·1
220	8·9	−9·1	660	3·2	−3·1	411	2·1	−2·0	2,11,1	0·9	0·9
230	nil	−0·4	670	1·5	1·5	421	1·3	1·4	571	8·2	−7·9
240	16·0	−15·7	4,11,0	2·1	2·2	271	2·5	2·5	491	1·7	−1·6
060	5·7	5·8	2,13,0	0·8	1·0	431	1·7	1·7	641	1·8	−1·9
250	4·3	−4·1	680	5·3	−5·3	361	2·5	2·4	1,12,1	1·7	1·5
260	13·5	−13·2	0,14,0	8·1	8·3	181	2·5	−2·3	651	1·5	1·4
400	3·2	−2·6	4,12,0	6·5	6·5	441	0·9	−0·8	581	2·8	2·7
410	nil	0·6	690	3·5	−3·6	281	2·1	2·0	3,11,1	9·7	9·8
420	13·9	13·8	2,14,0	5·7	−6·0	371	4·6	4·6	4,10,1	nil	0·3
270	1·1	−0·9				451	4·7	−4·8	2,12,1	0·9	−0·8
080	1·6	1·3	011	0·6	−0·6	091	nil	0·4	661	1·6	1·6
430	6·6	−6·4	111	9·4	−9·6	191	9·7	−10·0	591	3·9	−4·0
440	8·5	8·5	121	8·0	7·9	511	6·2	−6·3	0,13,1	2·4	−2·5
280	9·0	−8·7	031	9·2	−9·0	521	4·5	−4·6	711	3·0	3·0
450	nil	−0·7	131	10·9	−11·6	461	1·2	1·2	1,13,1	5·0	−5·3
460	9·2	9·4	211	0·9	0·9	291	nil	0·4	671	nil	−0·4
290	10·1	9·8	221	3·1	−3·1	381	1·6	−1·6	721	1·2	−1·3
0,10,0	17·0	17·0	141	8·2	7·7	531	8·0	−7·9	3,12,1	0·9	−0·8
470	2·7	2·5	231	2·8	2·8	541	1·8	−2·0	4,11,1	0·9	−1·0
2,10,0	7·3	−7·3	051	7·1	6·4	1,10,1	4·3	−4·1	731	6·5	6·4
480	11·7	11·8	151	18·1	−18·4	471	1·1	1·0	2,13,1	0·8	0·8
600	7·7	−7·8	241	6·6	6·6	551	6·7	−6·7	741	1·1	−1·2
610	4·3	4·4	311	17·9	17·8	391	6·7	6·7	5,10,1	2·3	2·3
620	9·8	−9·7	321	nil	0·2	2,10,1	nil	−0·8	681	0·7	−0·7
630	1·3	−1·2	251	0·7	0·8	481	1·3	−1·4	751	5·4	5·3
2,11,0	4·0	−3·8	161	2·7	−2·5	0,11,1	1·2	−1·2	1,14,1	1·8	1·7
490	1·4	1·4	331	9·2	9·4	561	nil	−0·7	4,12,1	nil	0
640	3·6	−3·3	341	2·8	−2·9	1,11,1	3·3	−3·4	3,13,1	6·4	6·4

sets of oxygen atoms are in general positions, $\pm(xyz)(x,\ \tfrac{1}{2}-y,\ \tfrac{1}{2}+z)(\tfrac{1}{2}+x,\ y,\ \bar{z})(\tfrac{1}{2}+x,\ \tfrac{1}{2}-y,\ \tfrac{1}{2}-z)$.

The refinement

The crystals used in the investigation were prepared from the melt and were needle shaped along the *b*-axis with rectangular cross section. The intensities of all reflections *HK*0, *HK*1, 0*KL*, *H*0*L* and *H*1*L* were measured on a counter spectrometer using Cu *Kα* radiation. The absorption correction was made by direct integration procedure.

The least-square refinements were carried out on the IBM-704 computer of the Argonne National Laboratory using the Busing–Levi program. The McWeeny (1951) *f*-curve was assumed for boron and those of Berghuis *et al.* (1955) for calcium and oxygen. The parameter values reported in 1931 served as starting point in the refinement, and the 217 experimentally measured structure factors were assigned equal weight.

Table 3. *Observed and calculated structure factors*

Reflections 0*KL*

0*KL*	F_o	$0{\cdot}236F_c$	0*KL*	F_o	$0{\cdot}236F_c$
020	6·3	5·4	073	6·5	6·4
011	0·6	−0·6	004	4·7	4·3
040	14·4	14·1	024	10·3	9·6
031	9·2	−9·0	0,11,1	1·2	−1·2
002	23·4	−24·9	0,10,2	10·8	−10·6
051	7·1	6·4	044	2·4	2·2
022	10·7	−11·1	0,12,0	5·6	5·4
060	5·7	5·8	093	nil	1·0
042	7·7	−7·6	064	1·8	1·4
071	5·8	−5·3	0,12,2	6·5	−6·8
080	1·6	1·3	0,13,1	2·4	−2·5
062	4·5	−4·0	084	5·5	5·4
013	2·9	3·1	015	4·2	−4·0
033	9·6	9·2	0,11,3	2·3	2·5
091	nil	0·4	035	4·6	−3·7
053	5·6	−5·3	0,14,0	8·1	8·3
082	4·1	−3·9	055	nil	−0·4
0,10,0	17·0	17·0	0,10,4	2·8	2·8

Table 4. *Observed and calculated structure factors*

Reflections *H*0*L* and *H*1*L*

HKL	F_o	$0{\cdot}227F_c$	*HKL*	F_o	$0{\cdot}227F_c$
200	13·0	−12·4	312	2·9	3·1
002	23·4	−24·0	411	2·1	−2·0
102	2·1	−1·9	013	2·9	3·0
202	7·3	7·6	113	4·8	4·8
400	3·2	−2·5	213	2·0	−2·1
302	3·5	−4·1	412	nil	0·9
402	2·0	−1·9	511	6·2	−6·1
502	2·8	2·9	313	9·2	−9·4
004	4·7	4·1	512	nil	−0·6
104	1·9	−2·3	114	nil	0·4
600	7·7	−7·5	413	3·4	3·1
204	2·5	−3·0	610	4·3	4·2
304	3·5	3·5	214	1·5	1·9
602	6·8	7·2	611	1·6	1·5
404	3·9	5·0	314	nil	0
702	2·3	−2·2	513	4·4	4·6
504	2·1	−1·7	612	1·8	−1·9
			414	1·4	−1·6
011	0·6	−0·6	711	3·0	2·9
111	9·4	−9·3	015	4·2	−3·8
210	20·3	−20·2	115	2·4	−2·5
211	0·9	0·9	613	3·0	−3·1
112	3·3	−3·2	215	2·5	2·2
311	17·9	17·1	712	nil	−0·2
212	7·2	6·8	514	nil	0·3
410	nil	0·6	315	3·9	4·0

The results for position coordinates and thermal parameters are shown in Table 1. The corresponding value for the traditional *R*-factor was 0·048 (0·038 with 'zeros' omitted). Tables 2–4 show the agreement between observed and calculated structure factors.

The structure

Except for the greater precision of the present study the results of the earlier work are confirmed. Fig. 1 shows a part of the structure with the endless $(BO_2)_\infty$ chain viewed along the *X*-direction.

The coordinates listed in Table 1 give the following interatomic distances:

$B-O_{I}$	$1{\cdot}326 \pm 0{\cdot}010$ Å	$Ca-2\ O_{I}$	$2{\cdot}347 \pm 0{\cdot}005$ Å
$-O_{II}$	$1{\cdot}385 \pm 0{\cdot}010$	$-2\ O_{I}$	$2{\cdot}399 \pm 0{\cdot}005$
$-O_{II}'$	$1{\cdot}401 \pm 0{\cdot}009$	$-2\ O_{I}$	$2{\cdot}727 \pm 0{\cdot}005$
		$-2\ O_{II}$	$2{\cdot}549 \pm 0{\cdot}005$
$O_{I}-O_{II}$	$2{\cdot}319 \pm 0{\cdot}008$ Å		
$-O_{II}'$	$2{\cdot}440 \pm 0{\cdot}006$		
$O_{II}-O_{II}'$	$2{\cdot}356 \pm 0{\cdot}004$		

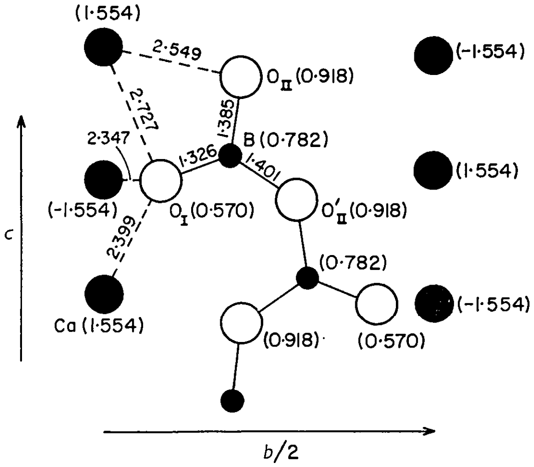

Fig. 1. Shows a part of the structure viewed along the *x*-axis. Numbers in parentheses give the height in Å above the plane $x=0$, and numbers on the bonds the lengths in Å.

Were one to assign a bond strength of 1·00 to each B–O bond and a strength of 0·25 to each Ca–O bond, the O_{I} atom would be 'underbonded' and the O_{II} atom correspondingly 'overbonded'. However, this imbalance is in part removed by strengthening of the $B-O_{I}$ bond at the expense of the $B-O_{II}$ bonds. Using the length *versus* strength dependence for the B–O bond reported in a recent article (Zachariasen, 1963) and a linear relationship for the Ca–O bond, one finds the valence balance shown in Table 5.

It is obviously true that valence imbalance alone

Table 5. *Valence balance for the* CaB_2O_4 *structure*

	$O_{\rm I}$	$O_{\rm II}$	Σ
$\frac{1}{2}$ Ca	0·37 + 0·33 + 0·08	0·22	1·00
B	1·12	0·95 + 0·92	2·99
Σ	1·90	2·09	3·99

cannot explain all observed variations in bond lengths nor the observed distortions of the oxygen polyhedra about calcium and boron. For example, the short edge of the BO_3 triangle of 2·319 Å must be ascribed to next nearest neighbor interaction between calcium and boron since this edge is shared between the BO_3 triangle and the CaO_8 polyhedron.

Table 6. *Root mean square thermal displacements along principal axes,* Δ_i, *and direction cosines of principal axes,* $\alpha_1\alpha_2\alpha_3$

Atom	i	Δ_i (Å)	α_1	α_2	α_3
Ca	1	0·087 ± 0·004	0·21	0·98	0
	2	0·110 ± 0·004	0·98	−0·19	0
	3	0·131 ± 0·005	0	0	1·00
B	1	0·071 ± 0·038	0·33	0·42	0·85
	2	0·107 ± 0·016	0·87	−0·49	−0·09
	3	0·151 ± 0·021	0·37	0·76	−0·53
$O_{\rm I}$	1	0·101 ± 0·011	0·60	0·79	0·16
	2	0·116 ± 0·012	0·67	−0·47	−0·47
	3	0·137 ± 0·012	0·31	−0·39	0·87
$O_{\rm II}$	1	0·085 ± 0·012	−0·09	1·00	−0·02
	2	0·138 ± 0·014	0·05	0·02	1·00
	3	0·170 ± 0·007	1·00	0·09	−0·05

In Table 6 the thermal parameters of Table 1 are converted to root mean square displacements along principal axes. Also shown in Table 6 are the orientations of the principal axes expressed in terms of direction cosines, α_1, α_2, α_3, in a cartesian system with X, Y, Z axes along the vectors **a**, **b**, **c**. It is seen that the direction of maximum thermal displacement of the $O_{\rm II}$ atom is approximately normal to the two $O_{\rm II}$–B bonds.

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The Crystal Structure of Urea Ammonium Bromide

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Crystals of urea ammonium bromide were found to be monoclinic with two molecules in a unit cell of dimensions

$$a = 9{\cdot}03 \pm 0{\cdot}02,\ b = 4{\cdot}79 \pm 0{\cdot}01,\ c = 7{\cdot}10 \pm 0{\cdot}02 \text{ Å with } \beta = 101{\cdot}3^\circ \pm 0{\cdot}1^\circ\,.$$

The space group was found to be $P2_1$. The structure was determined from projections along the b and c axes by using the heavy-atom method. Interatomic distances were obtained which indicated the existence of hydrogen bonds between the ammonium ions and the oxygen atoms of the urea molecules. Examination of the structure also showed the presence of fairly strong electrostatic interactions between the amide groups of the urea molecules and the bromine ions.

Introduction

Little work has been published on the crystallography of the urea inorganic salt complexes, of which a large number exist.

The crystal structure of urea ammonium bromide was examined as part of a series of investigations on these compounds to obtain information on their structures and bonding. In preliminary work carried out in these laboratories it was found that some crystals of urea ammonium bromide appeared to be orthorhombic and others monoclinic. This ambiguity could be accounted for in terms of mimetic twinning (Catesby, 1960), which gave rise to a pseudo-ortho-

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