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REFINEMENT OF THE CRYSTAL STRUCTURE OF HYDROBORACITE

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ABSTRACT

Three-dimensional counter-diffractometer X-ray data and full-matrix least-squares have been used to refine the crystal structure of hydroboracite, $CaMg[B_3O_4(OH)_3]_2\cdot 3H_2O$, with *a* 11.769(2), *b* 6.684(2), *c* 8.235(4)Å, *β* 102.59(2)°, *Z*=2 in space group *P*2/*c*. The final *R* for 1428 reflections is 0.042. The structure proposed by Rumanova & Ashirov (1964) has been confirmed. The basic repeat unit of the structure is the $[B_3O_4(OH)_3]^{2-}$ group consisting of two tetrahedra and one triangle; these borate polyanions are polymerized into undulating chains along *c*. Chains of corner-shared $Mg(OH)_2(H_2O)_4$ octahedra are linked to boron–oxygen chains giving sheets parallel to (100). Chains of edge-shared $CaO_4(OH)_4$ polyhedra also run parallel to the *c* axis and connect the sheets to each other.

SOMMAIRE

Les données tridimensionnelles obtenues aux rayons X sur diffractomètre à compteur ont été utilisées pour affiner, par la méthode des moindres carrés à matrice entière, la structure de l'hydroboracite, $CaMg[B_3O_4(OH)_3]_2\cdot 3H_2O$: *a* 11.769(2), *b* 6.684(2), *c* 8.235(4)Å, *β* 102.59(2)° *Z* = 2, groupe spatial *P*2/*c*. Le résidu final pour 1428 réflexions est 0.042. La structure proposée par Rumanova & Ashirov (1964) est confirmée. Dans la structure, le groupement anionique $[B_3O_4(OH)_3]^{2-}$ est formé de deux tétraèdres et un triangle; ces polyanions sont polymérisés suivant *c* en chaînes ondulées. Des chaînes d'octaèdres $Mg(OH)_2(H_2O)_4$ à sommets communs sont reliées à des chaînes bore–oxygène formant ainsi des couches (100). Des chaînes de polyèdres $CaO_4(OH)_4$ à arêtes communes sont parallèles à *c* et relient les couches entre elles.

(Traduit par la Rédaction)

INTRODUCTION

As a part of the systematic investigation of the crystal structures of hydrated borate compounds, a refinement of hydroboracite, $CaMg[B_3O_4(OH)_3]_2\cdot 3H_2O$, was performed. Several occurrences of this mineral, commonly with other borates such as colemanite, inyoite, inderite and ulexite, are described in the literature. Recently, an occurrence of hydroboracite in Balikesir province, Turkey, was described by Demircioglu (1973); this author studied the changes occurring in the structure upon loss of water and found also that the hardness of the Turkish mineral is 5-6 according to Mohs' scale, whereas Palache *et al.* (1951) reported its hardness to range between 2 and 3.

An indexed powder pattern together with the unit-cell dimensions were given by Cipriani (1958), who also described the thermal behavior of hydroboracite. Rumanova & Ashirov (1964) gave a correct solution of the structure on the basis of photographic data.

EXPERIMENTAL

The crystals of hydroboracite used in this study come from the Bigadic mine, Balikesir, Turkey. Indexed X-ray powder data are given in Table 1; indexing was performed, through

TABLE 1. X-RAY POWDER DIFFRACTION DATA FOR HYDROBORACITE*

h	k	l	d_{calc}Å	d_{obs}Å	I
1	0	0	11.486	11.45	11
0	1	0	6.683	6.69	85
1	1	0	5.777	5.78	100
0	1	1	5.139	5.14	1
-1	1	1	4.955	4.96	6
1	1	1	4.464	4.47	14
2	1	0	4.356	4.36	13
0	0	2	4.018	4.02	1
3	0	0	3.829	3.83	1
-2	0	2	3.692	3.69	2
2	1	1	3.589	3.59	5
1	0	2	3.559	3.56	1
0	1	2	3.444	3.45	3
3	1	0	3.322	3.32	74
-2	1	2	3.232	3.24	2
1	1	2	3.141	3.14	1
-1	2	1	3.045	3.05	1
2	0	2	3.000	3.00	1
1	2	1	2.919	2.921	1
3	1	1	2.884	2.887	4
4	0	0	2.871	2.873	3
-3	1	2	2.838	2.837	1
-4	1	1	2.670	2.670	1
4	1	0	2.638	2.637	5
2	2	1	2.628	2.630	1
-4	0	2	2.622		
3	2	0	2.518	2.517	2
0	1	3	2.487	2.486	1
-2	1	3	2.472	2.471	2
1	2	2	2.436	2.436	14
5	0	0	2.297	2.296	2
2	2	2	2.232	2.228	12
0	3	0	2.228	2.223	4
-5	1	1	2.215	2.215	7
-5	0	2	2.213		
1	3	0	2.187	2.187	1
4	2	0	2.178	2.181	1
5	1	0	2.172	2.172	6
1	3	1	2.089	2.088	3
-4	2	2	2.063	2.063	1
-1	0	4	2.057	2.057	1
4	1	2	2.027	2.027	1
1	2	3	1.998	1.996	1
5	1	1	1.996		
2	3	1	1.974	1.974	6
-3	0	4	1.964	1.968	2
0	3	2	1.949	1.948	1
-2	1	4	1.951		
3	3	0	1.926	1.926	7
6	0	0	1.914	1.914	16
-5	2	2	1.845	1.844	2
-4	0	4	1.846		
-6	1	2	1.824	1.827	1
2	3	2	1.789	1.788	1
-4	3	1	1.770	1.769	2
0	2	4	1.722	1.722	1
3	2	3	1.716	1.717	2
6	1	1	1.717		
0	4	0	1.671	1.671	7
6	2	0	1.661	1.661	2
1	4	0	1.654	1.653	2
-7	0	2	1.650		
7	0	0	1.641	1.641	2
3	0	4	1.638		
5	2	2	1.605	1.605	4
2	4	0	1.604		
7	1	0	1.594	1.593	3
2	4	1	1.555	1.555	2
6	1	2	1.554		
0	4	2	1.543	1.543	1
4	3	2	1.539	1.539	1

*Philips powder diffractometer, Co radiation, Fe filter, ¼° 2θ per min. range 5° ⩽ 2θ ⩽ 70°.

TABLE 2. CRYSTALLOGPAPHIC DATA AND OTHER INFORMATION

Formula unit: $CaMg\ [B_3O_4(OH)_3]_2 \cdot 3H_2O$

a = 11.769(2) Å	Crvstal size: 0.35x0.09x0.05 (mm)
b = 6.684(2) Å	Rad/filter: Mo/Zr
c = 8.235(4) Å	Total no. of |Fo| : 1846
β = 102.59(2)°	No. of |Fo|> 5σ : 1428
Space group P2/c	Z = 2
V = 632.3 $Å^3$	μ(MoKα) : 6.3 cm^{-1}
D obs = 2.15 gcm^{-3}	Final R (observed): 0.042
D calc= 2.170 gcm^{-3}	Final R (all data): 0.060

$$R = \sum(\|Fo| - |Fc\|)/\sum|Fo|$$

Temperature factor form used:

$$\exp[-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+2\beta_{12}hk+2\beta_{13}hl+2\beta_{23}kl)]$$

repeated cycles of cell-constant refinements, with the aid of single-crystal intensities. The refined parameters, based on 61 lines, are reported in Table 2. The observed density, determined by the flotation method, is 2.15g cm^{-3} and the calculated value, 2.170g cm^{-3}. Intensities were collected with a Philips PW 1100 4-circle computer-controlled diffractometer using MoKα radiation and the ω-2θ scan technique. A total of 1846 independent reflections in the range 3°<2θ<30° were measured; a reflection was considered to be observed if its intensity was greater than five standard deviations based on counting statistics. Application of this procedure gave 1428 observed reflections. Intensities were corrected for Lorentz-polarization effects, whereas absorption correction was considered negligible because of the crystal's thinness.

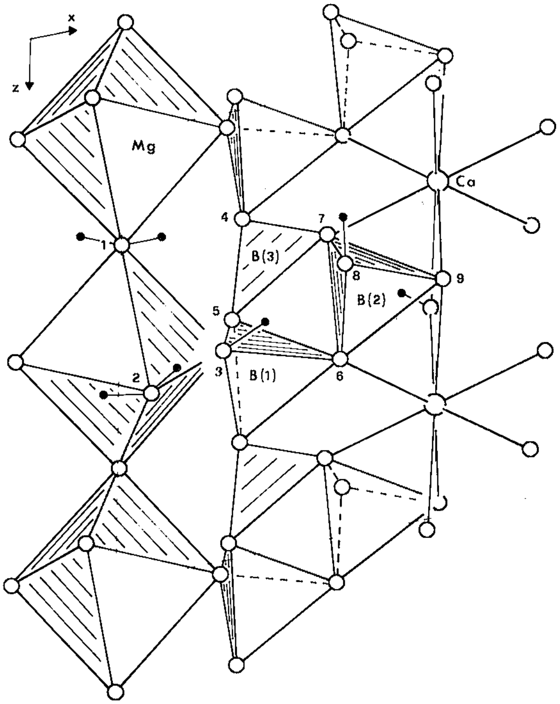

FIG. 1. Projection of the structure down the *b* axis. Half-cell in *x* is represented. Open circles and small black circles indicate oxygen and hydrogen atoms, respectively.

STRUCTURE REFINEMENT

The refinement of the structure was started using the atomic coordinates of Rumanova & Ashirov (1964) and giving each atom a *B* value obtained by averaging the *B*'s found by these authors for different layer-lines of Weissenberg data.

One least-squares full-matrix refinement cycle with isotropic thermal parameters and two subsequent full-matrix cycles with anisotropic thermal parameters led to a residual index *R*=0.048. At this stage of refinement a difference Fourier synthesis was computed in an attempt to directly locate the six hydrogen atoms of the structure. Since the O–O distance analysis showed an unambiguous hydrogen-bonding system, the resi-

TABLE 3. FRACTIONAL ATOMIC COORDINATES AND ISOTROPIC TEMPERATURE FACTORS

Atom	x	y	z	B ($Å^2$)
Mg	0	0	0	0.75
Ca	1/2	0.47388(9)	1/4	0.52
O(1)**	0	0.1238(3)	1/4	1.01
O(2)**	0.0504(2)	0.2772(3)	0.5966(2)	1.37
O(3)*	0.1667(1)	0.9061(2)	0.5359(2)	0.99
O(4)	0.1910(1)	0.3419(2)	0.2468(2)	0.80
O(5)	0.1758(1)	0.5515(2)	0.4678(2)	0.89
O(6)	0.3487(1)	0.7299(2)	0.6052(2)	0.80
O(7)	0.3266(1)	0.6114(2)	0.3209(2)	0.87
O(8)*	0.3544(1)	0.9672(2)	0.3936(2)	1.16
O(9)*	0.5093(1)	0.7160(2)	0.4717(2)	0.97
B(1)	0.2251(2)	0.7125(4)	0.5912(3)	0.66
B(2)	0.3848(2)	0.7614(3)	0.4480(3)	0.69
B(3)	0.2325(2)	0.5039(3)	0.3436(3)	0.63
H(1)	0.064	0.197	0.249	4.5
H(2)	0.092	0.370	0.554	4.5
H(3)	-0.025	0.335	0.575	4.5
H(4)	0.230	0.927	0.489	4.5
H(5)	0.353	1.069	0.298	4.5
H(6)	0.446	0.179	0.483	4.5

B's of the non-hydrogen atoms are the equivalent ones after Hamilton(1959). *O in OH; **O in water molecules.

TABLE 4. ANISOTROPIC TEMPERATURE FACTOR COEFFICIENTS *

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Mg	123(7)	363(22)	383(15)	-26(10)	62(8)	-16(14)
Ca	78(4)	359(13)	224(9)	0	64(5)	0
O(1)	176(16)	605(47)	439(34)	0	121(19)	0
O(2)	224(13)	619(34)	750(29)	49(16)	162(15)	80(25)
O(3)	154(11)	584(32)	482(26)	-75(15)	132(13)	-211(22)
O(4)	163(11)	513(32)	297(23)	-74(14)	131(13)	-48(20)
O(5)	149(11)	603(32)	351(23)	69(15)	116(15)	134(21)
O(6)	135(11)	541(31)	298(22)	-19(14)	73(12)	15(21)
O(7)	140(10)	570(32)	366(23)	-65(15)	113(12)	-109(22)
O(8)	262(12)	534(33)	433(24)	-21(16)	67(13)	145(23)
O(9)	144(12)	524(31)	496(26)	-72(15)	96(13)	-124(22)
B(1)	131(16)	408(45)	217(33)	-24(21)	36(18)	4(30)
B(2)	120(16)	397(46)	298(33)	-12(21)	70(18)	-15(31)
B(3)	111(15)	438(47)	205(30)	54(22)	41(17)	71(31)

* all values x 10^5.

TABLE 5. SELECTED INTERATOMIC DISTANCES

Mg octahedron	
Mg-O(1),O(1^{iv})	2.219(1) Å
Mg-O(2^{vi}),O(2^{ix})	2.554(5)
Mg-O(3^{viii}),O(3^{x})	2.020(6)
Mean	2.098
Ca polyhedron	
Ca-O(6^{ii}),O(6^{viii})	2.351(4)
Ca-O(7),O(7^{v})	2.425(4)
Ca-O(9),O(9^{v})	2.424(3)
Ca-O(9^{ii}),O(9^{viii})	2.643(5)
Mean	2.461
B(3) triangle	
B(3)-O(4)	1.372(6)
B(3)-O(7)	1.367(4)
B(3)-O(5)	1.374(9)
Mean	1.371
O(4)-O(7)	2.398(8)
O(4)-O(5)	2.335(4)
O(7)-O(5)	2.390(9)
Mean	2.374
B-B distances	
B(1)-B(3)	2.519(4)
B(1)-B(2)	2.447(9)
B(1)-B(3)	2.498(9)
B(1) tetrahedron	
B(1)-O(3)	1.491(5) Å
B(1)-O(4^{vii})	1.469(8)
B(1)-O(5)	1.508(8)
B(1)-O(6)	1.440(4)
Mean	1.477
O(3)-O(4^{vii})	2.374(5)
O(3)-O(5)	2.446(2)
O(3)-O(6)	2.404(9)
O(4^{vii})-O(5)	2.374(4)
O(4^{vii})-O(6)	2.446(9)
O(5)-O(6)	2.419(9)
Mean	2.410
B(2) tetrahedron	
B(2)-O(6)	1.461(8)
B(2)-O(7)	1.502(9)
B(2)-O(8)	1.466(4)
B(2)-O(9)	1.470(5)
Mean	1.475
O(6)-O(7)	2.430(6)
O(6)-O(8)	2.469(3)
O(6)-O(9)	2.386(9)
O(7)-O(8)	2.458(2)
O(7)-O(9)	2.342(9)
O(8)-O(9)	2.460(9)
Mean	2.424

Symmetry code:

none	x	y	z
i)	1-x	2-y	1-z
ii)	1-x	1-y	1-z
iii)	-x	1-y	-z
iv)	-x	-y	-z
v)	1-x	y	$\frac{1}{2}$-z
vi)	-x	y	$\frac{1}{2}$-z
vii)	x	1-y	$\frac{1}{2}$+z
viii)	x	1-y	-$\frac{1}{2}$+z
ix)	x	-y	-$\frac{1}{2}$+z
x)	-x	-1+y	$\frac{1}{2}$-z
xi)	x	2-y	-$\frac{1}{2}$+z

dual peaks attributable to the six hydrogen atoms were recognized on this map. Unfortunately these maxima were rather diffuse and therefore did not give sufficiently reliable indications for an accurate positioning of the H atoms; it was considered preferable to locate H atoms at calculated positions ⅓ of the distance from the donor oxygen toward the acceptor oxygen along the hydrogen bridges previously recognized on the basis of O–O distances. Inclusion of these atoms in the structure factor calculations with rough coordinates and $B=4.5\text{Å}^2$ reduced R to 0.042 for observed reflections and to 0.060 for

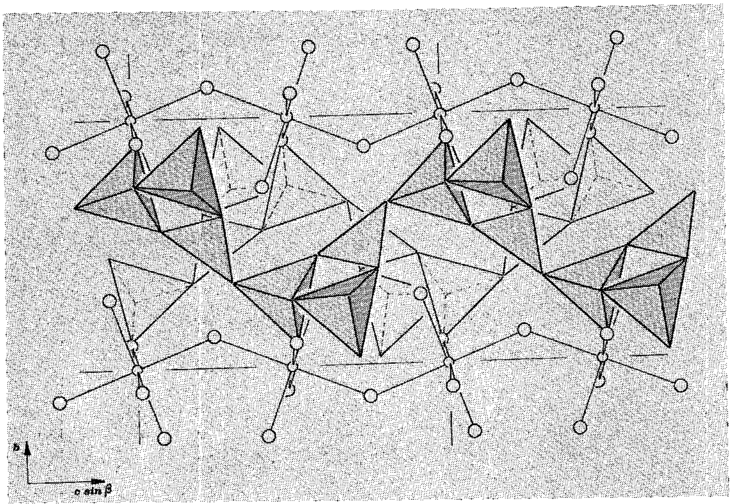

FIG. 2. An *a*-axis projection of two Mg–O chains connected with two overlaid B–O chains, to form a sheet parallel to *bc* plane.

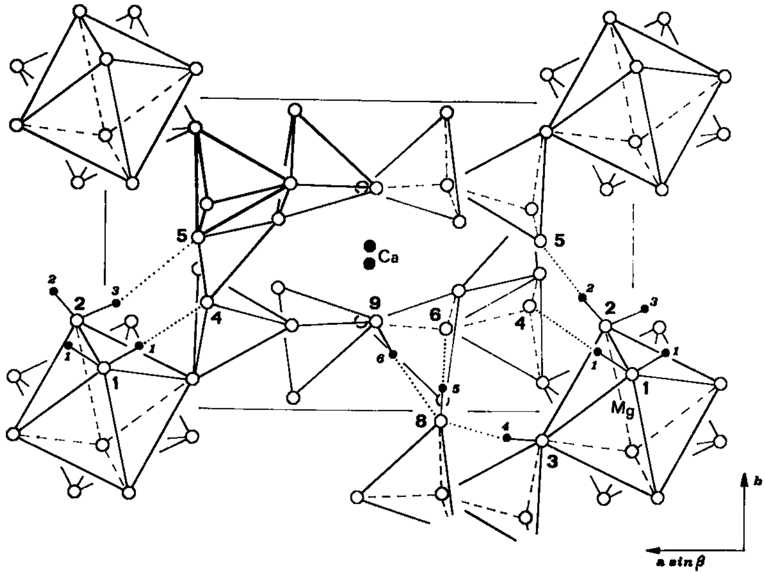

FIG. 3. A *c*-axis projection of the structure. Dotted lines indicate hydrogen bonds. Small numbers label the hydrogen atoms (small black circles); larger numbers designate the oxygens (open circles) belonging to two water molecules and to the three hydroxyl groups.

all data. Because of some inconsistencies in the shifts, the hydrogen atom parameters were not refined.

The structure refinement was performed with the CII 10070 computer using a modified version of the full-matrix least-squares program ORFLS (Busing *et al.* 1962). Neutral-atom scattering factors for Mg, Ca, O and B were taken from Cromer & Waber (1965), while for H the values by Stewart *et al.* (1965) were used. The positional and isotropic thermal parameters are given in Table 3; anisotropic thermal parameters appear in Table 4. A table of structure factors may be obtained at nominal charge from the Depository of Unpublished Data, CISTI, National Research Council of Canada, Ottawa, Ontario K1A 0S2.

DISCUSSION

Figures 1, 2 and 3 show the atomic arrangement in the structure of hydroboracite. Interatomic distances and angles are given in Tables 5 and 6 respectively.

The Mg atoms lie on symmetry centers and are octahedrally coordinated by four water molecules (O(1), O(2) and their symmetry equivalents) and two hydroxyls (O(3) and its sym-

TABLE 6. SELECTED INTERATOMIC ANGLES

Ca polyhedron	
$O(6^{viii})$-Ca-$O(6^{ii})$	109.1(1)°
$O(7)$	76.0(1)
$O(7^{v})$	133.1(1)
$O(9)$	132.4(1)
$O(9^{v})$	95.8(1)
$O(9^{ii})$	89.5(1)
$O(9^{viii})$	56.7(1)
$O(7)$ - Ca-$O(6^{ii})$	133.1(1)
$O(7^{v})$	135.4(1)
$O(9)$	57.8(1)
$O(9^{v})$	91.5(1)
$O(9^{ii})$	77.1(1)
$O(9^{viii})$	125.9(1)
$O(9)$ - Ca-$O(9^{v})$	96.2(1)
$O(9^{ii})$	70.8(1)
$O(9^{viii})$	165.9(1)

Mg octahedron	
$O(1)$ - Mg-$O(2^{vi})$	88.0(1)°
$O(3^{viii})$	86.8(1)
$O(2^{ix})$	92.0(1)
$O(3^{x})$	93.2(1)
$O(2^{vi})$-Mg-$O(3^{viii})$	88.0(1)
$O(1^{iv})$	92.0(1)
$O(3^{x})$	92.0(1)

B(1) tetrahedron	
$O(3)$ - B(1)-$O(4^{vii})$	106.6(2)°
$O(5)$	109.3(2)
$O(6)$	110.2(2)
$O(4^{vii})$-B(1)-$O(5)$	105.8(2)
$O(6)$	114.5(2)
$O(5)$ - B(1)-$O(6)$	110.2(2)

B(2) tetrahedron	
$O(7)$-B(2)-$O(8)$	111.8(2)°
$O(9)$	104.1(2)
$O(6)$	110.2(2)
$O(8)$-B(2)-$O(9)$	113.8(2)
$O(6)$	108.0(2)
$O(9)$-B(2)-$O(6)$	109.0(2)

B(3) triangle	
$O(4)$-B(3)-$O(7)$	122.2(2)°
$O(5)$	116.5(2)
$O(7)$-B(3)-$O(5)$	121.3(2)

metry equivalent). These $Mg(H_2O)_4(OH)_2$ octahedra are linked to each other through O(1) corners into chains that extend along *c*. An interesting feature is the greater length of the Mg–O(1) distance (2.219Å) in the *c* direction in relation to the Mg–O distances perpendicular to the chain (2.020 and 2.054Å). The mean value of 2.098Å is close to the values found for octahedrally coordinated magnesium in other structures. The coordination polyhedron is regular, the greatest deviation from 90° being 3.2°. The Mg–Mg distance in the chains is 4.12Å.

The Ca atom lies on a twofold axis and is 8-coordinated by four hydroxyls and four oxygen atoms. The Ca–O distances range from 2.351 to 2.643Å; the average is 2.461Å, slightly less than the sum of effective ionic radii given by Shannon (1976). The Ca polyhedron was well described by Rumanova & Ashirov (1964); in shape it is halfway between a right orthorhombic prism and an orthorhombic antiprism. Each Ca polyhedron lies on the two-fold axis and shares its hydroxyls (O(9) and its symmetry equivalents) with adjacent Ca polyhedra to form a chain of edge-shared polyhedra running parallel to the Mg chains and at ½*x*, ½*y* from them. The Ca–Ca distance is 4.13Å.

The structure of hydroboracite contains the $[B_3O_4(OH)_3]^{2-}$ polyanion consisting of two boron–oxygen tetrahedra and a boron–oxygen triangle, corner-linked in such a way as to build up a boron–oxygen ring. These groups are linked to each other to form infinite boron–oxygen chains. The structural unit, consisting of a pair of tetrahedra and one triangle (2t, Δ), is a very common B–O group found in polyborate structures and is evidently a particularly stable configuration. Examining the mutual arrangement of the boron tetrahedra in these rings, Rumanova (1972) stated that the boron–oxygen radicals belong to two forms defined on the basis of the respective orientations of the two tetrahedra in the ring, either both oriented in the same direction or alternating in direction. This fact can lead to a better description of borate compounds that contain this elementary unit either as an isolated polyanion or in polymerized forms. The radical found in hydroboracite and the one present in colemanite, which shows the same characteristic boron–oxygen chains (Christ *et al.* 1958), are close to the first limiting form in Rumanova's scheme. As seen especially in Figure 1 but also in Figures 2 and 3, both tetrahedra are oriented in the same direction; more than that, the distance (2.749Å) between the corners O(3) and O(8) of the two tetrahedra is very short compared with the same distance in other compounds with this arrangement of tetrahedra. In hydroboracite, indeed, this distance is indicative of a hydrogen bond, with O(3) as the donor and O(8) as the acceptor oxygens (Figs. 1 and 3). The interatomic distances and angles found in the present refinement agree well with those found for other similar borate compounds.

As Figures 1 and 2 show, each B–O chain in hydroboracite runs parallel to *c* and undulates in the *b* direction. Each chain is joined through the hydroxyl O(3) to the Mg chain at $y=0$ and the adjacent Mg chain at $y=1$ in turn. As Figure 2 illustrates, the unit cell contains two B–O chains, placed one upon the other, connected to the same Mg chain; thus each Mg chain, having the Mg octahedra on symmetry centers, is linked to two B–O chains on one side and two more symmetrical B–O chains on the other side, making up O–B–O–Mg–O–B–O sheets in the *bc* plane. Each Ca chain, which also extends along *c* approximately at ½*y* (Fig. 1), provides the connections between the sheets bridging two adjacent B–O chains belonging to different sheets.

Further connections are also provided by the hydrogen-bond system in the following way (see Fig. 3): the hydrogens H(1) and its symmetry equivalent of the first water molecule and H(2) and H(3) of the second water molecule as well as H(4) and H(5) belonging to two hydroxyl groups make intra-sheet connections, whereas H(6), belonging to the third hydroxyl, is the only inter-sheet hydrogen bond.

The structure is in accordance with the observed (100) and (010) cleavages of hydroboracite: the first cleavage involves breaking of O(9)–H(6) . . . O(8) hydrogen bonds and of four out of the eight Ca–O bonds; the (010) cleavage breaks Mg–O(3) bonds and three of the remaining H bonds.

A water geometry test using the Ferraris & Franchini-Angela (1972) scheme was carried out. In the first water molecule the oxygen O(1), which lies on the two-fold axis, coordinates twice

TABLE 7. HYDROGEN-BONDING SYSTEM

Donor atom(D)	H	Acceptor atom(A)	D...A	D-H	H...A	A...D...A
O(1)	H(1)	O(4)	2.686(2)Å	0.90Å	1.79Å	114.2(1)°
O(1)	$H(1^{vi})$	$O(4^{vi})$	"	"	"	
O(2)	H(2)	O(5)	2.841(9)	0.91	1.81	102.8(1)
O(2)	H(3)	$O(5^{iii})$	2.712(9)	0.95	1.89	
O(3)	H(4)	O(8)	2.749(9)	0.92	1.83	
O(8)	H(5)	$O(6^{xi})$	3.112(3)	1.03	2.07	
$O(9^{i})$	H(6)	O(8)	2.743(9)	0.91	1.83	

TABLE 8. CHARGE BALANCE

Atom	Ca	Mg	B(1)	B(2)	B(3)	H—	...H	Sums
O(1)		0.24^{x2}				0.78		1.02
O(2)		0.37^{x2}				1.61		1.98
O(3)		0.39^{x2}	0.72			0.80		1.91
O(4)			0.76		1.00		0.22	1.98
O(5)			0.70		1.00		0.39	2.09
O(6)	0.32^{x2}		0.82	0.77			0.13	2.04
O(7)	0.26^{x2}			0.70	1.00			1.96
O(8)				0.77		0.87	0.40	2.04
O(9)	0.42^{x2}			0.76		0.80		1.98

Bond strengths of first line are to be doubled because O(1) is in special position.

the Mg cation along the two lone-pair orbitals with angles ϵ_2 and ϵ_3 of 42° and 43°, respectively; this water molecule therefore belongs to class 2, type B. The second water molecule, with the oxygen O(2) in general position and coordinating only one Mg cation along a lone-pair orbital, has a ϵ_1 angle of 37° and can be included in the class 1′, type J. In Table 7 the hydrogen-bonding system and the donor–acceptor, donor–hydrogen and hydrogen–acceptor distances are reported together with the two water angles.

An electrostatic valence balance was computed according to the method given by Brown & Shannon (1973). For the H bonds the curve by those authors quoted in Donnay & Donnay (1973) was employed. Table 8 shows the contributions of different atoms and the bond-strength sums (v.u.). As can be seen, the valence sum for O(1) is slightly positive in spite of the fact that the shortening of its hydrogen bond is balanced with the lengthening of the Mg–O(1) bond.

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