STRUCTURE AND HYDROGEN BONDING IN INDERBORITE, A HETEROPOLYHEDRAL SHEET STRUCTURE

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ABSTRACT

The crystal structure of inderborite, $CaMg[B_3O_3(OH)_5]_2(H_2O)_4 \cdot 2H_2O$, monoclinic, a 12.137(2), b 7.433(1), c 19.234(3) Å, β 90.29(1)°, V 1735.1(5) Å^3, $Z = 4$, space group $C2/c$, has been refined by full-matrix least-squares methods to an R index of 3.8% and a wR index of 4.8% for 2181 unique observed $[F \geq 5\sigma(F)]$ reflections measured with Mo$K\alpha$ X-radiation. The H-positions were located on difference-Fourier maps and were refined using the "soft" constraint that H–O distances are approximately 0.96 Å. The fundamental building block (FBB) of the inderborite structure is a boron–oxygen ring made up of two Bϕ_4 tetrahedra (ϕ: unspecified anion) and one Bϕ_3 triangle, with composition $[B_3O_3(OH)_5]^{2-}$. The borate FBBs do not polymerize, but share corners with Caϕ_8 square antiprisms and Mgϕ_6 octahedra to form complex heteropolyhedral sheets parallel to (100). Hydrogen bonds play three structural roles: (1) they link anions within the same structural units, (2) they link anions of adjacent structural units, and (3) they link to an interstitial H$_2$O group that is held in place solely by a network of hydrogen bonds.

Keywords: inderborite, borate, structure refinement, crystal structure, hydrogen bonding.

SOMMAIRE

Nous avons affiné la structure cristalline de l'inderborite, $CaMg[B_3O_3(OH)_5]_2(H_2O)_4 \cdot 2H_2O$, monoclinique, a 12.137(2), b 7.433(1), c 19.234(3) Å, β 90.29(1)°, V 1735.1(5) Å^3, $Z = 4$, groupe spatial $C2/c$, par méthodes des moindres carrés sur matrice entière, jusqu'à un résidu R de 3.8% ($wR = 4.8\%$) avec 2181 réflexions uniques observées $[F \geq 5\sigma(F)]$ (rayonnement Mo$K\alpha$). La position des atomes d'hydrogène a été précisée à l'aide des projections de Fourier par différence, et affinée en utilisant une contrainte "molle" que la distance H–O soit d'environ 0.96 Å. L'unité structurale fondamentale est un anneau de groupes bore–oxygène fait de deux tétraèdres Bϕ_4 (ϕ: anion non spécifié) et un triangle Bϕ_3, et de composition $[B_3O_3(OH)_5]^{2-}$. Ces unités structurales ne sont pas polymérisées; par contre, elles partagent leurs coins avec des antiprismes carrés de Caϕ_8 et des octaèdres Mgϕ_6 pour former des feuillets polyédriques complexes parallèles à (100). Les liaisons hydrogène jouent trois rôles structuraux: (1) elles lient les anions au sein d'une seule unité structurale, (2) elles lient les anions d'unités structurales adjacentes, et (3) elles assurent une connexion avec un groupe H$_2$O structurel interstitiel dont la position dépend uniquement de ce réseau de liaisons hydrogène.

(Traduit par la Rédaction)

Mots-clés: inderborite, borate, affinement de la structure, structure cristalline, liaison hydrogène.

INTRODUCTION

Inderborite, $CaMg[B_3O_3(OH)_5]_2(H_2O)_4 \cdot 2H_2O$, occurs with colemanite and ulexite in the Inder Lake borate deposits, western Kazakhstan, in the borate deposits of Sarikaya, in the Eskiçsehir district, Turkey, and at the Büyük Günevi mine, Turkey. The crystal structure of inderborite from Kazakhstan was reported by Kurkutova *et al.* (1966) based upon two-dimensional photographic X-ray data. Their refinement converged to $R_{h0l} = 19.6\%$ and $R_{0kl} = 19.9\%$ in space group $C2/c$, and the hydrogen-atom positions were not reported.

We are currently studying the infrared spectra of borate minerals in the OH-stretching region (Burns & Hawthorne 1994) to ascertain the different roles of OH$^-$ and H$_2$O (Hawthorne 1992) in the structures of borate minerals. Here we report a crystal-structure refinement of inderborite, with the intent of obtaining a detailed description of the hydrogen bonding, which will be necessary in the interpretation of the infrared spectra of this mineral.

EXPERIMENTAL

A sample of inderborite from Kazakhstan was obtained from the Canadian Museum of Nature (sample 37367). A small crystal fragment was ground to a sphere with a radius of ~0.10 mm and was mounted on a Nicolet *R3m* automated four-circle diffracto-

TABLE 1. MISCELLANEOUS INFORMATION FOR INDERBORITE

a (Å)	12.137(2)	Crystal size (mm)	Sphere 0.20
b (Å)	7.433(1)	Total ref.	2793
c (Å)	19.234(3)	$|F_o| \geq 5\sigma(F)$	2181
β (°)	90.29(1)	Final R	3.8%
V (Å³)	1735.1(5)	Final wR	4.8%
F(000)	1040		

Space group   C2/c

Unit cell contents   4{CaMg[B₃O₃(OH)₅]₂(H₂O)₄.2H₂O}

$R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$

$wR = [\Sigma w(|F_o| - |F_c|)^2/\Sigma F_o^2]^{1/2}, \ w = 1/\sigma^2(F)$

TABLE 2. FINAL ATOMIC PARAMETERS FOR INDERBORITE

	x	y	z	*U_{eq}
Mg	0	0	0	130(3)
Ca	0	0.21603(6)	1/4	100(1)
B(1)	0.0996(1)	0.9579(2)	0.14969(9)	104(4)
B(2)	0.4049(1)	0.3513(2)	0.14216(9)	97(4)
B(3)	0.0553(1)	0.6367(2)	0.1669(1)	124(5)
O(1)	−0.01566(9)	−0.0147(2)	0.16342(6)	112(3)
OH(2)	0.1222(1)	0.0084(2)	0.07619(7)	173(3)
OH(3)	0.1610(1)	0.0704(2)	0.19957(6)	127(3)
O(4)	0.1330(1)	0.7674(2)	0.16103(7)	150(3)
O(5)	−0.0545(1)	0.6667(2)	0.15821(7)	155(3)
OH(6)	0.0862(1)	0.4595(2)	0.17832(7)	173(3)
OH(7)	0.29878(9)	0.3776(2)	0.17594(6)	144(3)
OH(8)	0.3881(1)	0.3633(2)	0.06469(6)	152(3)
OW(9)	0.4423(1)	0.7471(2)	0.03743(8)	299(5)
OW(10)	0.3604(1)	0.8276(2)	0.16832(7)	174(3)
OW(11)	0.1642(1)	0.4507(2)	0.02170(9)	307(5)
H(1)	0.196(1)	−0.020(4)	0.064(2)	**508(30)
H(2)	0.213(2)	0.158(3)	0.184(2)	508(30)
H(3)	0.1638(9)	0.444(6)	0.175(2)	508(30)
H(4)	0.307(3)	0.420(5)	0.2224(8)	508(30)
H(5)	0.367(3)	0.250(3)	0.045(2)	508(30)
H(6)	0.411(3)	0.748(5)	0.0827(9)	508(30)
H(7)	0.406(3)	0.849(3)	0.018(2)	508(30)
H(8)	0.2832(9)	0.806(5)	0.172(2)	508(30)
H(9)	0.369(3)	0.955(1)	0.168(2)	508(30)
H(10)	0.119(2)	0.399(4)	0.056(1)	508(30)
H(11)	0.231(2)	0.485(4)	0.045(1)	508(30)

* U_{eq} = 10⁴ x U_{eq}

** all H atom U's constrained to be equivalent

meter. Forty-eight reflections over the range $9° \leq 2\theta \leq 30°$ were centered using graphite-monochromated MoKα X-radiation. The unit-cell dimensions (Table 1) were derived from the setting angles of the forty-eight automatically aligned reflections by least-squares techniques. Data were collected using the θ–2θ scan method with a 2.2° 2θ scan range and a variable scan-rate ranging from 4 to 29.3° 2θ/min. A total of 2793 reflections was measured; the index ranges $-18 \leq h \leq 18$, $0 \leq k \leq 10$, $0 \leq l \leq 26$ were covered, and reflections forbidden by the C-centering were omitted. Two standard reflections were measured every fifty reflections; no significant change in their intensities occurred during data collection. An empirical absorption-correction based on 36 psi-scans for each of 11 reflections over the range $14° \leq 2\theta \leq 54°$ was applied, reducing R (azimuthal) from 1.86 to 1.82%. The data were corrected for Lorentz, polarization and background effects; of the 2793 reflections measured, there were 2181 classed as observed $[F \geq 5\sigma(F)]$.

STRUCTURE REFINEMENT

Scattering curves for neutral atoms, together with anomalous-dispersion corrections, were taken from Cromer & Mann (1968) and Cromer & Liberman (1970), respectively. The Siemens SHELXTL PLUS (PC version) system of programs was used throughout this study. R indices are of the form given in Table 1 and are expressed as percentages.

Refinement of the structure was carried out in the space group C2/c using the atomic parameters of Kurkutova et al. (1966) as the starting model. Refinement of the positional and isotropic displacement parameters gave an R index of 7.2%. Conversion to an anisotropic displacement model, together with refinement of all parameters, gave an R index of 5.3%. At this stage of the refinement, a difference-Fourier map was calculated, and the positions of eleven hydrogen atoms were determined. Subsequent cycles of refinement showed that the hydrogen positions were not realistic, as indicated by anomalously short O–H

bond lengths, a common feature of hydrogen positions refined using X-ray data. The "soft" constraint that O–H distances should be ~0.96 Å was imposed by adding extra weighted observational equations to the least-squares matrix. Only the O–H distance is constrained, and each H position is free to seek its

TABLE 3. ANISOTROPIC DISPLACEMENT PARAMETERS FOR INDERBORITE

	*U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Mg	149(5)	136(5)	104(5)	15(3)	−3(3)	−5(3)
Ca	96(2)	95(2)	110(2)	0	2(1)	0
B(1)	111(8)	103(8)	100(7)	6(6)	6(6)	−3(6)
B(2)	82(7)	93(7)	116(7)	10(6)	2(5)	3(6)
B(3)	125(8)	112(8)	133(8)	7(6)	2(6)	6(6)
O(1)	88(5)	101(5)	146(5)	−18(4)	4(4)	3(4)
OH(2)	151(6)	259(7)	110(5)	32(5)	17(4)	−10(5)
OH(3)	127(6)	111(5)	142(5)	−13(4)	0(4)	−40(4)
O(4)	101(6)	88(5)	260(7)	9(4)	3(5)	14(4)
O(5)	105(6)	94(5)	265(7)	31(5)	−14(5)	4(4)
OH(6)	119(6)	96(6)	303(7)	44(5)	−4(5)	15(4)
OH(7)	89(5)	195(6)	148(6)	−34(5)	12(4)	2(4)
OH(8)	180(6)	174(6)	102(5)	−7(4)	−10(4)	−36(5)
OW(9)	475(10)	228(7)	194(7)	18(6)	63(7)	137(7)
OW(10)	136(6)	136(6)	250(6)	14(5)	−25(5)	17(5)
OW(11)	303(8)	305(8)	313(8)	27(7)	−45(6)	31(7)

* U_{ij} = 10⁴ x U_{ij}

optimum position around the oxygen atom. We have found (Burns & Hawthorne 1993a, b) that this approach gives realistic hydrogen-bonding schemes for various borate minerals. Refinement of all parameters, including a refinable weighting scheme of structure factors and a correction for isotropic extinction, gave a final R index of 3.8% and a wR index of 4.8%. Final positional and equivalent isotropic-displacement parameters are given in Table 2, anisotropic displacement parameters in Table 3, selected interatomic distances and angles in Table 4, and a bond-valence analysis in Table 5. Observed and calculated structure-factors are available from the Depository of Unpublished Data, CISTI, National Research Council of Canada, Ottawa, Ontario K1A 0S2.

DISCUSSION

Borate fundamental building block

There are three distinct B positions in the inderborite structure. The B(1) and B(2) positions are each tetrahedrally coordinated by two oxygen atoms and two hydroxyl groups (Fig. 1a), with <B–ϕ> distances of 1.472 and 1.474 Å, respectively (ϕ: unspecified ligand). The B(3) position is triangularly coordinated by two oxygen atoms and a hydroxyl group, and the <B(3)–ϕ> distance is 1.369 Å.

The borate fundamental building block (FBB) in inderborite is a $[B_3O_3(OH)_5]^{2-}$ boron–oxygen ring (Fig. 1a) made up of two $B\phi_4$ tetrahedra and one $B\phi_3$ triangle. The borate FBBs are isolated (*i.e.*, are not

TABLE 4. SELECTED INTERATOMIC DISTANCES (Å) AND ANGLES(°) FOR INDERBORITE

Mg–OH(2),a	2.081(1) x2	Ca–O(1),h	2.397(1) x2
Mg–OH(8)b,c	2.107(1) x2	Ca–O(3),h	2.439(1) x2
Mg–OW(9)b,c	2.094(2) x2	Ca–OH(6),h	2.507(1) x2
<Mg–O>	2.094	Ca–OW(10)b,i	2.449(1) x2
		<Ca–O>	2.448
B(1)–O(1)d	1.440(2)		
B(1)–OH(2)e	1.489(2)		
B(1)–OH(3)e	1.472(2)	B(3)–O(4)	1.358(2)
B(1)–O(4)	1.489(2)	B(3)–O(5)	1.359(2)
<B(1)–O>	1.472	B(3)–OH(6)	1.389(2)
		<B(3)–O>	1.369
B(2)–O(1)f	1.444(2)		
B(2)–O(5)g	1.490(2)		
B(2)–OH(7)	1.458(2)		
B(2)–OH(8)	1.506(2)		
<B(2)–O>	1.474		

B(1) tetrahedron

O(1)d–OH(2)e	2.382(2)	O(1)d–B(1)–OH(2)e	108.8(1)
O(1)d–OH(3)e	2.338(2)	O(1)d–B(1)–OH(3)e	106.8(1)
O(1)d–O(4)	2.426(2)	O(1)d–B(1)–O(4)	111.8(1)
OH(2)e–OH(3)e	2.461(2)	OH(2)e–B(1)–OH(3)e	112.4(1)
OH(2)e–O(4)	2.426(2)	OH(2)e–B(1)–O(4)	109.1(1)
OH(3)e–O(4)	2.395(2)	OH(3)e–B(1)–O(4)	108.0(1)
<O–O>	2.405	<O–B(1)–O>	109.5

B(2) tetrahedron

O(1)f–O(5)g	2.416(2)	O(1)f–B(2)–O(5)g	110.9(1)
O(1)f–OH(7)	2.403(2)	O(1)f–B(2)–OH(7)	111.8(1)
O(1)f–OH(8)	2.402(2)	O(1)f–B(2)–OH(8)	109.0(1)
O(5)g–OH(7)	2.398(2)	O(5)g–B(2)–OH(7)	108.9(1)
O(5)g–OH(8)	2.417(2)	O(5)g–B(2)–OH(8)	107.6(1)
OH(7)–OH(8)	2.406(2)	OH(7)–B(2)–OH(8)	108.5(1)
<O–O>	2.407	<O–B(2)–O>	109.4

B(3) triangle

O(4)–O(5)	2.396(2)	O(4)–B(3)–O(5)	123.8(2)
O(4)–OH(6)	2.382(2)	O(4)–B(3)–OH(6)	120.2(2)
O(5)–OH(6)	2.330(2)	O(5)–B(3)–OH(6)	116.0(2)
<O–O>	2.369		120.0

Mg octahedron

OH(2),a–OH(8)b,c	3.045(2) x2	OH(2),a–Mg–OH(8)b,c	93.3(1) x2
OH(2),a–OH(8)c,b	2.875(2) x2	OH(2),a–Mg–OH(8)c,b	86.7(1) x2
OH(2),a–OW(9)b,c	2.907(2) x2	OH(2),a–Mg–OW(9)b,c	88.3(1) x2
OH(2),a–OW(9)c,b	2.996(2) x2	OH(2),a–Mg–OW(9)c,b	91.7(1) x2
OH(8)b,c–OW(9)b,c	2.976(2) x2	OH(8)b,c–Mg–OW(9)b,c	90.1(1) x2
OH(8)b,c–OW(9)c,b	2.967(2) x2	OH(8)b,c–Mg–OW(9)c,b	89.9(1) x2
<O–O>	2.961	<O–Mg–O>	90.0

TABLE 4. continued

Ca polyhedron

O(1),h–OH(3),h	2.338(2) x2	O(1),h–Ca–OH(3),h	57.8(1) x2
O(1),h–OH(3),h	3.241(2) x2	O(1),h–Ca–OH(3),h	84.1(1) x2
O(1)–O(1)h	3.350(2)	O(1)–Ca–O(1)h	88.6(1)
O(1),h–OW(10)b,i	2.968(2) x2	O(1),h–Ca–OW(10)b,i	75.2(1) x2
OH(3),h–OH(6),h	3.058(2) x2	OH(3),h–Ca–OH(6),h	76.4(1) x2
OH(3),h–OW(10)b,i	3.191(2) x2	OH(3),h–Ca–OW(10)b,i	81.5(1) x2
OH(6)–OH(6)h	3.470(2)	OH(6)–Ca–OH(6)h	87.6(1)
OH(6),h–OW(10)b,i	2.916(2) x2	OH(6),h–Ca–OW(10)b,i	72.1(1) x2
OH(6),h–OW(10)i,b	3.172(2) x2	OH(6),h–Ca–OW(10)i,b	79.6(1) x2
<O–O>	3.035	<O–Ca–O>	78.8

H bonding

OH(2)–H(1)	0.95(2)	OW(11)b–H(1)	2.42(3)
OH(2)–OW(11)	3.226(2)	OH(2)–H(1)–OW(11)	142(3)
OH(3)–H(2)	0.95(3)	OH(7)–H(2)	1.94(3)
OH(3)–OH(7)	2.868(2)	OH(3)–H(2)–OH(7)	163(3)
OH(6)–H(3)	0.95(1)	OH(7)–H(3)	1.71(1)
OH(6)–OH(7)	2.651(2)	OH(6)–H(3)–OH(7)	169(3)
OH(7)–H(4)	0.95(2)	OH(3)j–H(4)	1.91(2)
OH(7)–OH(3)j	2.831(2)	OH(7)–H(4)–OH(3)j	162(3)
OH(8)–H(5)	0.96(2)	OW(11)b–H(5)	2.00(3)
OH(8)–OW(11)b	2.933(2)	OH(8)–H(5)–OW(11)b	163(3)
OW(9)–H(6)	0.95(2)	OW(10)–H(6)	1.85(2)
OW(9)–OW(10)	2.777(2)	OW(9)–H(6)–OW(10)	162(3)
OW(9)–H(7)	0.95(3)	OW(11)k–H(7)	1.88(3)
OW(9)–OW(11)k	2.827(3)	OW(9)–H(7)–OW(11)k	180(4)
H(6)–H(7)	1.46(4)	H(6)–OW(9)–H(7)	100(3)
OW(10)–H(8)	0.95(1)	O(4)–H(8)	1.86(1)
OW(10)–O(4)	2.798(2)	OW(10)–H(8)–O(4)	169(3)
OW(10)–H(9)	0.96(1)	O(5)f–H(9)	1.83(2)
OW(10)–O(5)f	2.731(2)	OW(10)–H(9)–O(5)f	155(3)
H(8)–H(9)	1.53(3)	H(8)–OW(10)–H(9)	106(3)
OW(11)–H(10)	0.95(3)	OH(6)–H(10)	2.42(2)
		OW(9)b–H(10)	2.45(3)
OW(11)–OH(6)	3.163(2)	OW(11)–H(10)–OH(6)	135(2)
OW(11)–OW(9)b	3.105(3)	OW(11)–H(10)–OW(9)b	126(2)
OW(11)–H(11)	0.95(2)	OH(8)–H(11)	2.15(2)
OW(11)–OH(8)	2.911(2)	OW(11)–H(11)–OH(8)	136(3)
H(10)–H(11)	1.51(4)	H(10)–OW(11)–H(11)	106(2)

a = $\bar{x}$, $\bar{y}$, $\bar{z}$; b = x–½, y–½, z; c = $\bar{x}$+½, $\bar{y}$+½, $\bar{z}$; d = x, y–1, z; ℈ = x, y+1, z;
f = x+½, y+½, z; g = x+½, y–½, z; h = $\bar{x}$, y, ½–z; i = $\bar{x}$+½, y–½, $\bar{z}$+½;
j = $\bar{x}$+½, y+½, $\bar{z}$+½; k = $\bar{x}$+½, $\bar{y}$+1½, $\bar{z}$

TABLE 5. BOND-VALENCE* ANALYSIS FOR INDERBORITE

	Ca	Mg	B(1)	B(2)	B(3)	H(1)	H(2)	H(3)	H(4)	H(5)	H(6)	H(7)	H(8)	H(9)	H(10)	H(11)	Σ
O(1)	0.313×2↓		0.831	0.821													1.965
OH(2)		0.350×2↓	0.727			0.93											2.007
OH(3)	0.279×2↓		0.761				0.87		0.13								2.040
O(4)		0.727		1.036									0.18				1.943
O(5)				0.725	1.033									0.18			1.938
OH(6)	0.232×2↓				0.953			0.77							0.05		2.005
OH(7)				0.780			0.13	0.23	0.87								2.020
OH(8)		0.327×2↓	0.694							0.89						0.10	2.011
OW(9)		0.338×2↓									0.85	0.86			0.05		2.098
OW(10)	0.272×2↓										0.15		0.82	0.82			2.062
OW(11)						0.07				0.11		0.14			0.90	0.90	2.120
Σ	2.192	2.030	3.046	3.030	3.022	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	

* Bond-valence parameters from Brown & Altermatt (1985)

polymerized), and the FBB is fully hydrated, *i.e.*, all oxygen atoms that are not shared between two boron atoms are protonated. According to the rules of Christ & Clark (1977), the shorthand notation for this FBB is $3:1\Delta + 2T$. The fully hydrated form of the FBB also occurs in inderite, kurnakovite, meyerhofferite, and inyoite. The same FBB is polymerized into chains in the structures of hydroboracite and colemanite, and a partly hydrated form of this FBB occurs as an isolated cluster in the structure of solongoite.

Mg and Ca polyhedra

The single magnesium site has $\bar{1}$ symmetry, and the atom is octahedrally coordinated by four hydroxyl groups and two H_2O groups. Bond lengths range from 2.081(1) Å to 2.107(1) Å, with $<Mg-\phi> = 2.094$ Å, a value within the typical range observed for $Mg\phi_6$ octahedra. The Ca position has two-fold symmetry, and the atom is coordinated by two oxygen atoms, four hydroxyl groups, and two H_2O groups (Fig. 1b) in a distorted square antiprism arrangement. Bond lengths range from 2.397(1) Å to 2.507(1) Å, and $<Ca-\phi> = 2.448$ Å.

Heteropolyhedral sheets

The borate rings (Fig. 1a) are oriented perpendicular to the c axis (Fig. 2). The two borate tetrahedra in the FBB each share one corner with a single $Mg\phi_6$ octahedron; one tetrahedron shares a non-bridging anion, and both tetrahedra share a bridging anion with
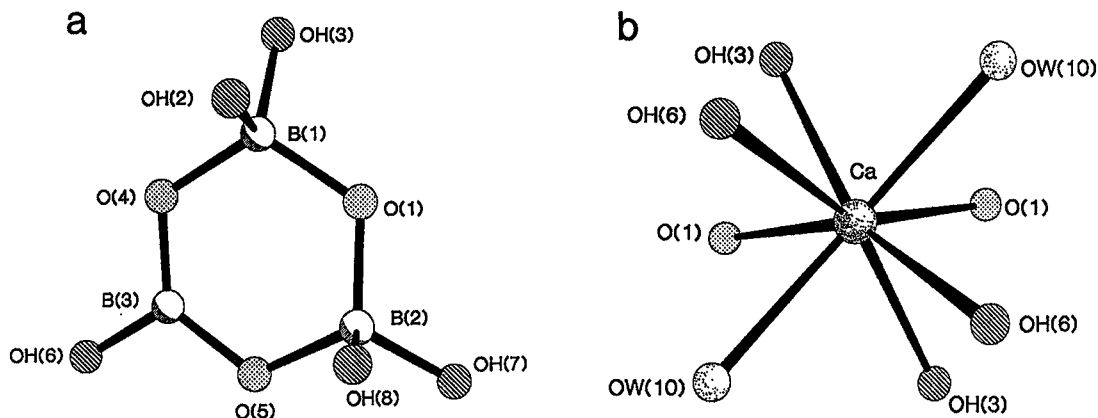

FIG. 1. Elements of the inderborite structure: (a) the $[B_3O_3(OH)_5]^{2-}$ ring; (b) the $Ca\phi_8$ square antiprism.
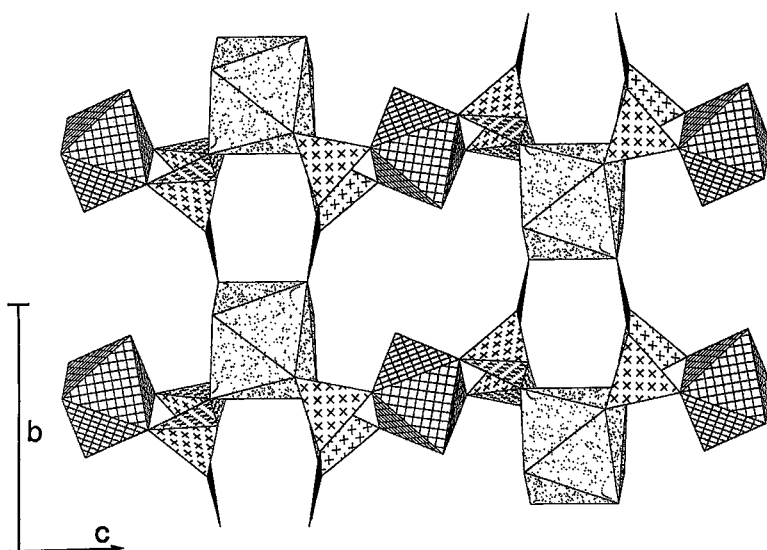
FIG. 2. The heteropolyhedral sheets in inderborite. The $Ca\phi_8$ polyhedra are shaded with a random-dot pattern, $Mg\phi_6$ octahedra are cross-hatched, borate tetrahedra are shaded with crosses, and the borate triangles are solid.

a single calcium polyhedron (Fig. 2), forming infinite rods of composition $[CaMgB_6O_8(OH)_8(H_2O)_4]$ parallel to the c axis. These heteropolyhedral rods are joined through the boron triangles that share a single ligand with the calcium polyhedra of adjacent rods (Fig. 2). The resulting complex heteropolyhedral sheets are parallel to (100) (Fig. 3). There is a lone H_2O position *between* the sheets, and along with the other hydrogen bonds, this H_2O group provides intersheet bonding. The sheets are connected only through hydrogen bonds; thus inderborite has a {100} cleavage.
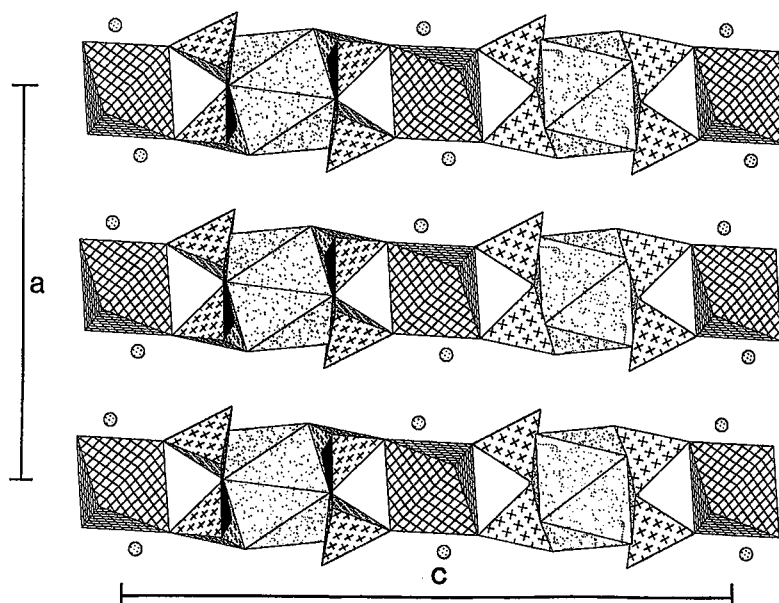
FIG. 3. The inderborite structure projected onto (010). Shading as in Figure 2; intersheet H_2O groups appear as dotted circles.
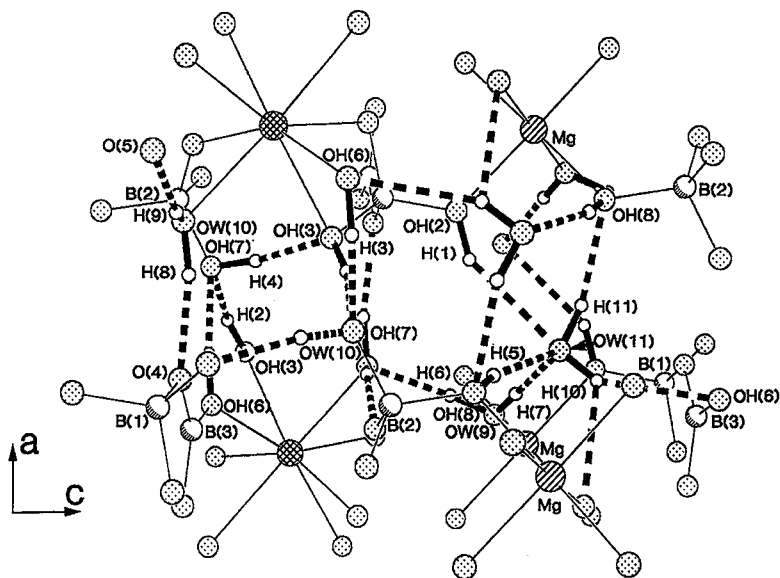
FIG. 4. Hydrogen bonding in inderborite. *D–H* and H...*A* bonds are given as heavy full and broken lines, respectively. Calcium atoms are cross-hatched, magnesium atoms are shaded with parallel lines, boron atoms are open circles with shading in the lower left corners, oxygen atoms are shaded with a regular-dot pattern, and hydrogen atoms are small open circles.

Hydrogen bonding

The hydrogen-atom positions obtained *via* constrained least-squares refinement of the X-ray data are reasonable both in terms of donor *D–H* and acceptor *H*...*A* bond lengths and angles (Table 4) and the bond-valence requirements of both the donor and acceptor anions (Table 5). The hydrogen-bonding scheme is very complex in inderborite, with the hydrogen bonds playing three structural roles (Fig. 4): (1) they link anions *within* the same heteropolyhedral sheet, (2) they bridge *between* adjacent heteropolyhedral sheets, and (3) the interstitial H_2O group is hydrogen-bonded to the heteropolyhedral sheets on either side.

Hydrogen bonding within structural units: The OH(7)–H(4)...OH(3), OW(9)–H(6)...OW(10) and OW(10)–H(9)...O(5) bonds bridge between anions of the same heteropolyhedral sheet (Fig. 4), and the acceptor distances of 1.91(2), 1.85(2) and 1.83(2) Å, respectively, indicate relatively strong hydrogen bonds. The OH(7)–H(4)...OH(3) bond links anions of two adjacent borate FBBs, the OW(9)–H(6)...OW(10) bond links anions belonging to the $Mg\phi_6$ octahedron and the $Ca\phi_8$ polyhedron, and the OW(10)–H(9)...O(5) bond links anions of the $Ca\phi_8$ polyhedron and the borate FBB.

Hydrogen bonding between structural units: The OH(3)–H(2)...OH(7), OH(6)–H(3)...OH(7) and OW(10)–H(8)...O(4) bonds link anions of adjacent heteropolyhedral sheets (Fig. 4), providing significant intersheet linkage. The OH(3)–H(2)...OH(7), OH(6)–H(3)...OH(7) and OW(10)–H(8)...O(4) bonds have acceptor distances of 1.94(3), 1.71(1) and 1.86(1) Å, respectively, indicating that these are relatively strong hydrogen bonds. The donor anions for the OH(3)–H(2)...OH(7) and OH(6)–H(3)...OH(7) bonds belong to the same borate FBB, and these anions are shared with adjacent $Ca\phi_8$ polyhedra. These two hydrogen bonds link to the OH(7) anion, which is part of the borate FBB in an adjacent sheet. The donor anion for the OW(10)–H(8)...O(4) bond is part of the $Ca\phi_8$ polyhedron, and the bond links to the borate FBB in an adjacent sheet. The acceptor anion is O(4), the bridging oxygen between the B(1) tetrahedron and the B(3) triangle, and the two B atoms contribute 1.763 v.u. toward the bond-valence requirements of O(4); the additional bond-valence is provided by the hydrogen bond.

Interstitial H_2O: The OW(11) position is sandwiched between the heteropolyhedral sheets (Fig. 3), and is held in place solely by hydrogen bonding (Fig. 4). The OW(11) group acts as the acceptor for three hydrogen

bonds from adjacent structural units. The OH(8)–H(5)...OW(11) and OW(9)–H(7)...OW(11) bonds link the OW(11) anion to the nearer of the two heteropolyhedral sheets; the acceptor distances are 2.00(3) and 1.88(3) Å, respectively, indicating that the hydrogen bonds are relatively strong. The OW(11) anion also accepts a single hydrogen bond from the heteropolyhedral sheet that is farther from the anion (Fig. 4); the OH(2)–H(1)...OW(11) bond has an acceptor distance of 2.42(3) Å, indicating that the hydrogen bond is quite weak. In addition, the H(10) and H(11) positions each provide ~0.8 v.u. toward the bond-valence requirements of the OW(11) oxygen atom.

The OW(11) oxygen atom also acts as the donor for two hydrogen bonds to adjacent structural units. The OW(11)–H(11)...OH(8) bond links to the farthest sheet, and it is of intermediate strength, as indicated by the acceptor distance of 2.15(2) Å. The H(10) position weakly bonds to the nearest heteropolyhedral sheet, but there are two possible acceptor anions. The OW(11)–H(10)...OW(9) and OW(11)–H(10)...OH(6) configurations have acceptor distance of 2.45(3) Å and 2.42(2) Å, respectively, and both bonds involve a reasonable OW(11)–H(10)...φ bond angle (Table 4).

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