

HYDROGEN BONDING IN MEYERHOFFERITE: AN X-RAY AND STRUCTURE ENERGY STUDY

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ABSTRACT

The crystal structure of meyerhofferite, $\text{CaB}_3\text{O}_3(\text{OH})_5\cdot\text{H}_2\text{O}$, triclinic, a 6.632(1), b 8.337(1), c 6.4748(6) Å, α 90.81(1), β 101.97(1), γ 86.76(1)°, V 349.66(8) Å³, $Z = 2$, space group $P\bar{1}$, has been refined by full-matrix least-squares methods to an R index of 3.0% and a wR index of 3.8% for 1788 unique observed [$I \geq 2.5\sigma(I)$] reflections measured with $\text{MoK}\alpha$ X-radiation. The H-positions were located on difference-Fourier maps and refined using the "soft" constraints that H–O distances are approximately 0.97 Å. Meyerhofferite is a complex cycloborate with two $\text{B}\phi_4$ tetrahedra (ϕ : unspecified anion) and one $\text{B}\phi_3$ triangle linked by corner-sharing to form rings of $[\text{B}_3\text{O}_3(\text{OH})_5]^{2-}$ composition. The eight-coordinate Ca polyhedra link by edge-sharing to form chains along [001], with enhanced chain rigidity given by the boron–oxygen rings that link by corner-sharing and edge-sharing to two sides of the Ca polyhedral chains. Bonding between the heteropolyhedral chains is through hydrogen bonding only, with six hydrogen bonds along [100], four along [010] and four between elements of the same heteropolyhedral chain per unit cell. Minimum-energy H-positions were calculated with a directionally isotropic H–O potential function. The calculations successfully predict the positions of all hydrogen atoms and the hydrogen-bonding arrangement in the meyerhofferite structure.

Keywords: meyerhofferite, borate, cycloborate, structure refinement, hydrogen bonding, crystal structure, energy minimization.

SOMMAIRE

Nous avons affiné la structure cristalline de la meyerhofferite, $\text{CaB}_3\text{O}_3(\text{OH})_5\cdot\text{H}_2\text{O}$, triclinique, a 6.632(1), b 8.337(1), c 6.4748(6) Å, α 90.81(1)°, β 101.97(1)°, γ 86.76(1)°, V 349.66(8) Å³, $Z = 2$, groupe spatial $P\bar{1}$, par moindres carrés sur matrice entière, jusqu'à un résidu R de 3.0% (et un wR de 3.8%), en utilisant 1788 réflexions uniques observées [$I \geq 2.5\sigma(I)$] et mesurées avec rayonnement $\text{MoK}\alpha$. Les atomes H ont été localisés sur les projections par différence de Fourier, et leurs positions ont été affinées en utilisant comme contrainte approximative que toute distance H–O devrait être 0.97 Å. Il s'agit d'un cycloborate complexe ayant deux tétraèdres $\text{B}\phi_4$ (ϕ : anion non spécifié) et un triangle $\text{B}\phi_3$ liés par les coins pour former des anneaux de composition $[\text{B}_3\text{O}_3(\text{OH})_5]^{2-}$. Les polyèdres entourant le Ca, à coordinence huit, liés par partage d'arêtes, sont agencés en chaînes le long de [001]. Les chaînes sont rendues plus rigides par les anneaux à bore–oxygène, qui sont articulés par partage de coins et d'arêtes avec deux côtés des chaînes de polyèdres Ca. Les liaisons entre les feuillets hétéropolyédriques dépendent uniquement des liaisons hydrogène, dont six le long de [100], quatre le long de [010], et quatre entre éléments de la même chaîne hétéropolyédrique par maille. Nous avons calculé la position des atomes H par minimisation d'énergie avec une fonction potentielle H–O ayant une isotropie directionnelle. Les calculs réussissent à reproduire toutes ces positions et l'agencement des liaisons hydrogène dans la structure de cette espèce.

(Traduit par la Rédaction)

Mots-clés: meyerhofferite, borate, cycloborate, affinement de la structure, liaison hydrogène, structure cristalline, minimisation d'énergie.

INTRODUCTION

Meyerhofferite, $\text{CaB}_3\text{O}_3(\text{OH})_5\cdot\text{H}_2\text{O}$, occurs as an alteration product of inyoite [$\text{CaB}_3\text{O}_3(\text{OH})_5\cdot 5\text{H}_2\text{O}$] in the colemanite deposits of the Mount Blanco district, near Death Valley, California, in the borate deposits at Boron, California, and in the borate deposits of Eskişehir district, Turkey. The crystal structure was solved by Christ & Clark (1960) and refined by Clark *et al.* (1964). Meyerhofferite is a complex cycloborate that contains

heteropolyhedral chains formed by the linkage of $[\text{B}_3\text{O}_3(\text{OH})_5]^{2-}$ rings and $\text{Ca}\phi_8$ (ϕ : unspecified ligand) polyhedra. Bonding between chains occurs *via* hydrogen bonding only.

Considerable effort has recently been focused on finding a suitable potential energy function for H-bonding in mineral structures (*e.g.*, Abbott 1991, Abbott *et al.* 1989). In a recent study of hydrogen bonding in colemanite, Burns & Hawthorne (1993) noted that a realistic description of hydrogen bonding could be obtained through constrained least-squares refinement

using X-ray data. Comparison of the refined H-positions with minimum-energy positions obtained using an O-H interaction potential function of the form given by Abbott *et al.* (1989) was found to indicate that the structure-energy calculations failed to predict the locations of two of the five hydrogen atoms. Here we report a study of H-bonding in meyerhofferite, and compare refined H-positions with positions obtained from structure-energy calculations.

EXPERIMENTAL

Meyerhofferite from Mount Blanco, Death Valley, California, was obtained from the R.B. Ferguson Mineralogy Museum at the University of Manitoba. A cleavage fragment was mounted on a Nicolet R3m automated four-circle diffractometer. Twenty-five reflections were centered using graphite-monochromated MoK α X-radiation. The unit-cell dimensions (Table 1) were derived by least-squares techniques from the setting angles of twenty-five automatically aligned reflections. A total of 2225 reflections were measured over the range ($3^\circ \leq 2\theta \leq 60^\circ$) with index ranges $-9 \leq h \leq 9$, $-11 \leq k \leq 11$, $0 \leq l \leq 9$. Two standard reflections were measured every fifty reflections; no significant changes in their net intensities occurred during data collection. An empirical absorption correction based on 396 psican reflections was applied, reducing R (azimuthal) from 1.7% to 1.4%. The data were corrected for Lorentz, polarization and background effects; of the 2225 reflections measured, there were 1788 unique observed [$I \geq 2.5\sigma(I)$] reflections.

STRUCTURE REFINEMENTS

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 given as percentages.

TABLE 1. MISCELLANEOUS INFORMATION FOR MEYERHOFFERITE

Space group	$P\bar{1}$	Crystal size (mm)	0.16 \times 0.20 x.10
a (Å)	6.632(1)	Total Ref.	2225
b (Å)	8.337(1)		
c (Å)	6.4748(6)	[$I \geq 2.5\sigma(I)$]	1788
α (°)	90.81(1)		
β (°)	101.97(1)	Final R	3.0%
γ (°)	86.76(1)	Final wR	3.8%
V (Å ³)	349.66(8)		
F(000)	228		
Unit-cell contents	2[CaB ₃ O ₃ (OH) ₃ ·H ₂ O]		
$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			

TABLE 2. ATOMIC POSITIONAL PARAMETERS AND EQUIVALENT ISOTROPIC DISPLACEMENT PARAMETERS (Å² $\times 10^4$) FOR MEYERHOFFERITE

	x	y	z	U _{equiv.}
Ca	0.01073(4)	0.37602(3)	0.24440(4)	106(1)
B(1)	0.3168(2)	0.7974(2)	0.4855(2)	112(3)
B(2)	0.2879(2)	0.6323(2)	0.1654(2)	96(3)
B(3)	0.0393(2)	0.2652(2)	0.6992(2)	94(3)
O(1)	0.4042(1)	0.7358(1)	0.3274(1)	137(3)
OH(2)	0.4224(1)	0.8874(1)	0.6483(2)	155(3)
O(3)	0.1150(1)	0.7776(1)	0.4925(1)	125(2)
OH(4)	0.3363(2)	0.4617(1)	0.2059(2)	149(2)
O(5)	0.0617(1)	0.6519(1)	0.1481(1)	99(2)
OH(6)	0.1694(1)	0.3799(1)	0.6186(1)	119(2)
OH(7)	0.1521(2)	0.1071(1)	0.2112(2)	161(3)
OH(8)	0.1540(2)	0.1223(1)	0.7989(2)	152(2)
OH(9)	0.3315(1)	0.6711(1)	0.9564(1)	129(2)
H(1)	0.565(2)	0.901(3)	0.642(4)	200
H(2)	0.453(3)	0.429(3)	0.148(4)	200
H(3)	0.313(2)	0.352(3)	0.642(4)	200
H(4)	0.253(3)	0.065(3)	0.733(4)	200
H(5)	0.373(4)	0.779(2)	0.951(4)	200
H(6)	0.052(3)	0.032(3)	0.227(4)	200
H(7)	0.164(4)	0.104(3)	0.066(2)	200

* fixed during refinement

TABLE 3. ANISOTROPIC DISPLACEMENT PARAMETERS (Å² $\times 10^4$) FOR MEYERHOFFERITE

	U ₁₁	U ₂₂	U ₃₃	U ₂₃	U ₁₃	U ₁₂
Ca	118(1)	113(1)	91(1)	3(1)	27(1)	-13(1)
B(1)	114(6)	121(5)	100(5)	-11(4)	16(4)	-24(4)
B(2)	81(5)	119(5)	96(5)	-3(4)	35(4)	-2(4)
B(3)	84(5)	109(5)	93(5)	-2(4)	30(4)	-3(4)
O(1)	95(4)	183(2)	135(4)	-49(3)	30(3)	-28(3)
OH(2)	117(4)	191(4)	159(4)	-50(3)	25(3)	-51(3)
O(3)	97(4)	186(4)	98(4)	-30(3)	29(3)	-43(3)
OH(4)	126(4)	124(4)	214(5)	21(3)	82(3)	28(3)
O(5)	73(4)	129(4)	96(4)	-20(3)	25(3)	3(3)
OH(6)	88(4)	151(4)	127(4)	8(3)	37(3)	-28(3)
OH(7)	174(4)	153(4)	157(4)	-5(3)	36(3)	-5(3)
OH(8)	168(4)	145(4)	151(4)	24(3)	69(3)	61(3)
OH(9)	124(4)	160(4)	117(4)	5(3)	33(3)	-15(3)

Refinement of the structure was done in the space group $P\bar{1}$, with the structural parameters given by Christ & Clark (1960) as the starting model. Refinement of the positional parameters and isotropic displacement parameters converged to an R index of 4.9%. Conversion to an anisotropic displacement model, together with the refinement of all parameters, improved convergence to an R index of 3.5%. A three-dimensional difference-Fourier map was calculated at this stage of the refinement, and the positions of all seven hydrogen atoms were located. Attempts to refine all positional parameters at this stage resulted in some improbable positions for the hydrogen atoms, as indicated by anomalously short O-H distances. Anomalously short O-H bond-distances are a common problem where hydrogen positions are refined using X-ray data, and the same problem occurred when refining the structure of colemanite (Burns & Hawthorne 1993). The soft constraint that each O-H bond distance

TABLE 4. SELECTED BOND-DISTANCES (Å), ANGLES (°) AND POLYHEDRAL EDGE-LENGTHS (Å) FOR MEYERHOFFERITE

				Ca polyhedron			
B(1)-O(1)	1.359(2)	Ca-OH(4)	2.374(1)	OH(4)-O(5)	2.319(1)	OH(4)-Ca-O(5)	57.4(0)
B(1)-OH(2)	1.376(2)	Ca-O(5)	2.451(1)	OH(4)-OH(6)	3.193(2)	OH(4)-Ca-OH(6)	83.2(0)
B(1)-O(3)	<u>1.368(2)</u>	Ca-OH(6)	2.433(1)	OH(4)-OW(7)	3.265(2)	OH(4)-Ca-OW(7)	86.2(0)
<B(1)-O>	1.368	Ca-OW(7)	2.405(1)	OH(4)-O(5)b	3.291(2)	OH(4)-Ca-O(5)b	85.0(0)
B(2)-O(1)	1.468(2)	Ca-O(3)a	2.451(1)	O(5)-O(5)b	3.196(2)	O(5)-Ca-O(5)b	80.4(0)
B(2)-OH(4)	1.455(2)	Ca-O(5)b	2.497(1)	O(5)-OH(6)a	2.391(2)	O(5)-Ca-OH(6)a	57.2(0)
B(2)-O(5)	1.481(2)	Ca-OH(6)a	2.544(1)	OH(6)-OW(7)	3.446(2)	OH(6)-Ca-OW(7)	90.8(0)
B(2)-OH(9)c	<u>1.485(2)</u>	Ca-OH(9)a	<u>2.420(1)</u>	OH(6)-O(3)a	2.342(1)	OH(6)-Ca-O(3)a	57.3(0)
<B(2)-O>	1.472	<Ca-O>	2.447	OH(6)-OH(6)a	3.093(2)	OH(6)-Ca-OH(6)a	76.8(0)
B(3)-OH(6)	1.492(2)			OW(7)-O(3)a	2.985(2)	OW(7)-Ca-O(3)a	75.8(0)
B(3)-OH(8)	1.459(2)			OW(7)-O(5)b	3.147(2)	OW(7)-Ca-O(5)a	79.8(0)
B(3)-O(3)a	1.489(2)			OW(7)-OH(9)a	3.581(2)	OW(7)-Ca-OH(9)a	95.8(0)
B(3)-O(5)a	<u>1.451(2)</u>			O(3)a-OH(6)a	3.407(2)	O(3)a-Ca-OH(6)a	86.0(0)
<B(3)-O>	1.473			O(3)a-OH(9)a	3.165(2)	O(3)a-Ca-OH(9)a	81.0(0)
				O(5)b-OH(9)a	2.393(1)	O(5)b-Ca-OH(9)a	58.2(0)
				OH(6)a-OH(9)a	<u>3.317(2)</u>	OH(6)a-Ca-OH(9)a	<u>83.8(0)</u>
				<O-O>	3.033	<O-Ca-O>	77.2
Hydrogen bonding							
B(1) triangle				OH(2)-H(1)	0.95(2)	H(1)...OW(7)d	1.93(1)
O(1)-OH(2)	2.401(2)	O(1)-B(1)-OH(2)	122.8(1)	OH(4)-H(2)	0.95(2)	H(2)...OH(9)d	1.86(2)
O(1)-O(3)	2.390(2)	O(1)-B(1)-O(3)	122.4(1)	OH(6)-H(3)	0.95(1)	H(3)...O(1)d	1.94(1)
OH(2)-O(3)	<u>2.312(1)</u>	OH(2)-B(1)-O(3)	<u>114.8(1)</u>	OH(8)-H(4)	0.96(2)	H(4)...OH(2)e	1.95(2)
<O-O>	2.368	<O-B(1)-O>	120.0	OH(9)-H(5)	0.96(2)	H(5)...OH(2)	2.26(3)
B(2) tetrahedron				OW(7)-H(6)	0.96(2)	H(6)...OH(8)f	1.91(2)
O(1)-OH(4)	2.442(2)	O(1)-B(2)-OH(4)	113.3(1)	OW(7)-H(7)	0.96(1)	H(7)...OH(8)c	1.72(1)
O(1)-O(5)	2.462(1)	O(1)-B(2)-O(5)	113.2(1)	H(6)-H(7)	1.55(4)	H(6)-OW(7)-H(7)	102(2)
O(1)-OH(9)c	2.410(1)	O(1)-B(2)-OH(9)c	109.4(1)				
OH(4)-O(5)	2.319(1)	OH(4)-B(2)-O(5)	104.4(1)	OH(2)-OW(7)d	2.782(2)	OH(2)-H(1)-OW(7)d	151(1)
OH(4)-OH(9)c	2.389(2)	OH(4)-B(2)-OH(9)c	108.7(1)	OH(4)-OH(9)d	2.799(2)	OH(4)-H(2)-OH(9)d	170(2)
O(5)-OH(9)c	<u>2.393(2)</u>	O(5)-B(2)-OH(9)c	<u>107.6(1)</u>	OH(6)-O(1)d	2.888(2)	OH(6)-H(3)-O(1)d	172(2)
<O-O>	2.402	<O-B(2)-O>	109.4	OH(8)-OH(2)e	2.869(2)	OH(8)-H(4)-OH(2)e	160(2)
				OH(9)-OH(2)	2.884(2)	OH(9)-H(5)-OH(2)	122(2)
B(3) tetrahedron				OW(7)-OH(8)f	2.858(2)	OW(7)-H(6)-OH(8)f	169(2)
OH(6)-OH(8)	2.475(2)	OH(6)-B(3)-OH(8)	114.0(1)	OW(7)-OH(8)c	2.677(2)	OW(7)-H(7)-OH(8)c	171(2)
OH(6)-O(3)a	2.342(1)	OH(6)-B(3)-O(3)a	103.6(1)				
OH(6)-O(5)a	2.391(2)	OH(6)-B(3)-O(5)a	108.7(1)				
OH(8)-O(3)a	2.433(1)	OH(8)-B(3)-O(3)a	111.2(1)				
OH(8)-O(5)a	2.363(1)	OH(8)-B(3)-O(5)a	108.6(1)				
O(3)a-O(5)a	<u>2.417(1)</u>	O(3)a-B(3)-O(5)a	<u>110.6(1)</u>				
<O-O>	2.403	<O-B(3)-O>	109.4				

a = -x, 1-y, 1-z; b = -x, 1-y, -z; c = x, y, z-1;
d = 1-x, 1-y, 1-z; e = x, y-1, z; f = -x, -y, 1-z

should be ~0.97Å was imposed by adding the constraints as additional weighted observations in the least-squares matrix. Refinement of all parameters, together with the

inclusion of a refinable weighting scheme of structure factors and an isotropic extinction correction, led to convergence to a final R index of 3.0% and a wR index

TABLE 5. BOND-VALENCE* ANALYSIS FOR MEYERHOFFERITE

	Ca	B(1)	B(2)	B(3)	H(1)	H(2)	H(3)	H(4)	H(5)	H(6)	H(7)	Σ
O(1)		1.019	0.757				0.17					1.946
OH(2)		0.973			0.82			0.17	0.12			2.083
O(3)	0.258	0.995		0.717								1.970
OH(4)	0.312		0.786			0.82						1.918
O(5)	0.258		0.733	0.795								2.017
	0.231											
OH(6)	0.270			0.771			0.82					2.067
	0.206											
OW(7)	0.289				0.17					0.80	0.80	2.059
OH(8)				0.782				0.80		0.18	0.22	1.982
OH(9)	0.279		0.725			0.19			0.80			1.994
Σ	2.103	2.987	3.001	3.065	0.99	1.01	0.99	0.97	0.92	0.98	1.02	

* bond-valence parameters from Brown (1981), bond-valences in v.u.

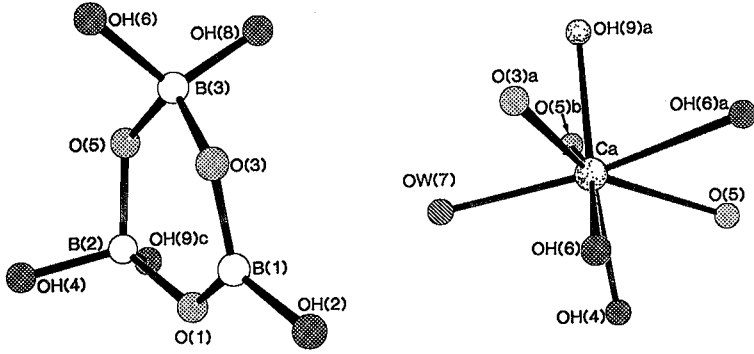


FIG. 1. The $[\text{B}_3\text{O}_3(\text{OH})_5]^{2-}$ rings and $\text{Ca}\phi_8$ polyhedra in meyerhofferite.

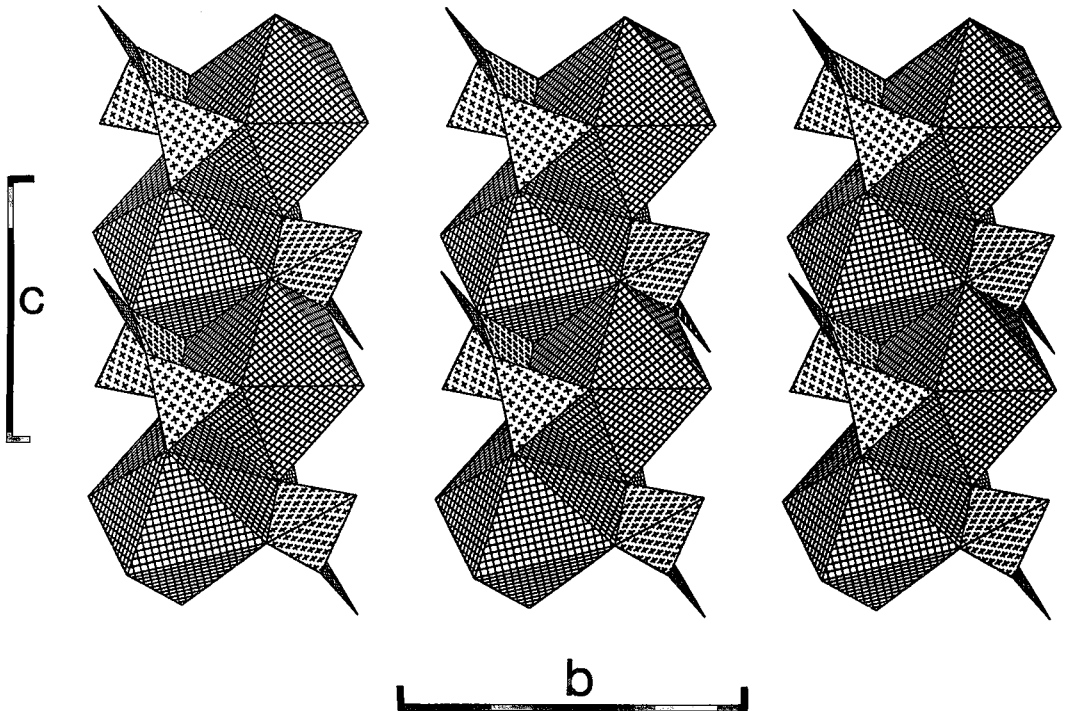


FIG. 2. The heteropolyhedral chains in meyerhofferite. Calcium polyhedra are cross-hatched, and boron tetrahedra and triangles are shaded with crosses.

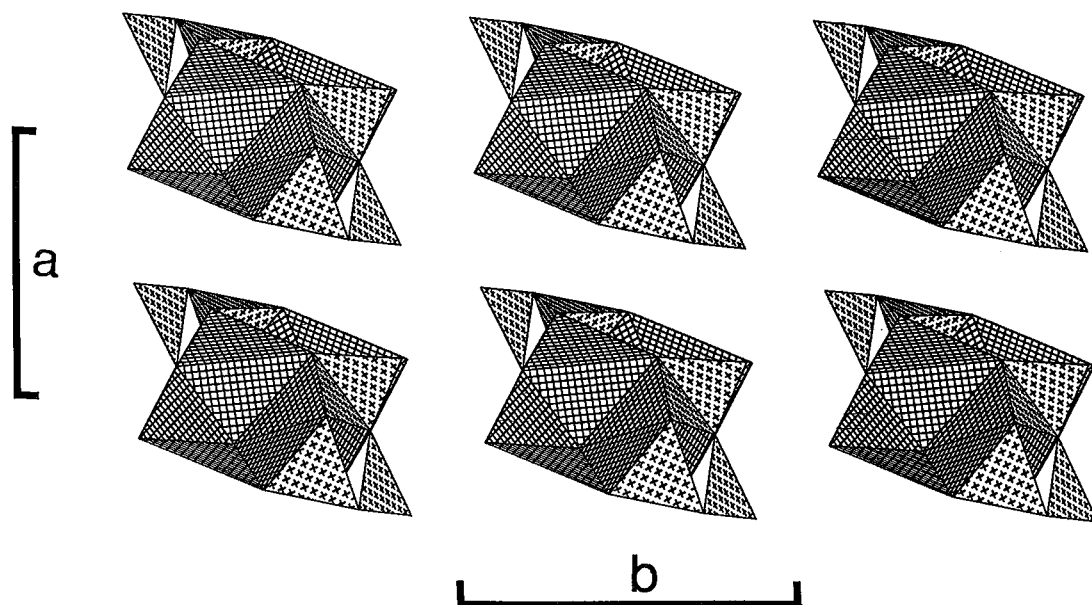


FIG. 3. The meyerhofferite structure projected onto (001). Shading as in Figure 2.

of 3.8%. Final positional parameters and equivalent isotropic displacement factors are given in Table 2, anisotropic displacement factors in Table 3, selected bond-distances, angles and polyhedral edge-lengths 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, Ottawa, Ontario K1A 0S2.

DISCUSSION

Description of the structure

The fundamental structural unit in meyerhofferite is a boron–oxygen ring of composition $[B_3O_3(OH)_5]^{2-}$ (Fig. 1). The boron–oxygen ring contains the three symmetrically distinct boron positions. The B(1) position is triangularly coordinated by two oxygen atoms and a hydroxyl group, with a $\langle B(1)-\phi \rangle$ distance of 1.368 Å, a value within the range typically observed for $^{13}B-O$ triangles. The other two boron positions are each tetrahedrally coordinated by two oxygen atoms and two hydroxyl groups, with $\langle B(2)-\phi \rangle$ and $\langle B(3)-\phi \rangle$ distances of 1.472 and 1.473 Å, respectively.

The one Ca site is coordinated by three oxygen atoms, four hydroxyl groups and an H_2O group (Fig. 1). Individual $Ca\phi_8$ polyhedra link by edge-sharing to form zig-zag chains running parallel to [001] (Fig. 2). The rigidity of the Ca polyhedral chain is enhanced by attachment of boron–oxygen rings on two sides of the chain (Fig. 2). Each boron–oxygen ring attaches to three

$Ca\phi_8$ polyhedra, each of which are adjacent in the same chain. Both $B(2)\phi_4$ and $B(3)\phi_4$ tetrahedra are located such that each tetrahedron shares edges with two different Ca polyhedra. The $B(1)\phi_3$ triangle attaches to a $Ca\phi_8$ polyhedron *via* corner-sharing (Fig. 2). The packing of the chains is shown in Figure 3. Each chain is translationally equivalent, and their separations define the *a* and *b* cell dimensions. Linkage between the heteropolyhedral chains is through hydrogen bonding only, explaining the perfect {010} and secondary {100} cleavages observed in meyerhofferite.

Hydrogen bonding in meyerhofferite

As the linkage between the heteropolyhedral chains occurs entirely through hydrogen bonding, the hydrogen-bonding scheme is of fundamental importance in the description of the structure. The hydrogen-bonding arrangement obtained through constrained least-squares refinement using X-ray data is realistic in terms of bond distances and angles (Table 4), as well as the bond-valence requirements of both the anion and hydrogen positions (Table 5).

The strongest hydrogen bonding between the heteropolyhedral chains is in the [100] direction, with six hydrogen bonds directed along [100] per unit cell (Fig. 4). The $OH(2)-H(1)...OW(7)$, $OH(4)-H(2)...OH(9)$ and $OH(6)-H(3)...O(1)$ bonds link the chains along [100]. In each case, relatively short $H...O$ bond-distances (1.86 – 1.94 Å) indicate strong hydrogen bonds, explaining why the {100} cleavage is imperfect.

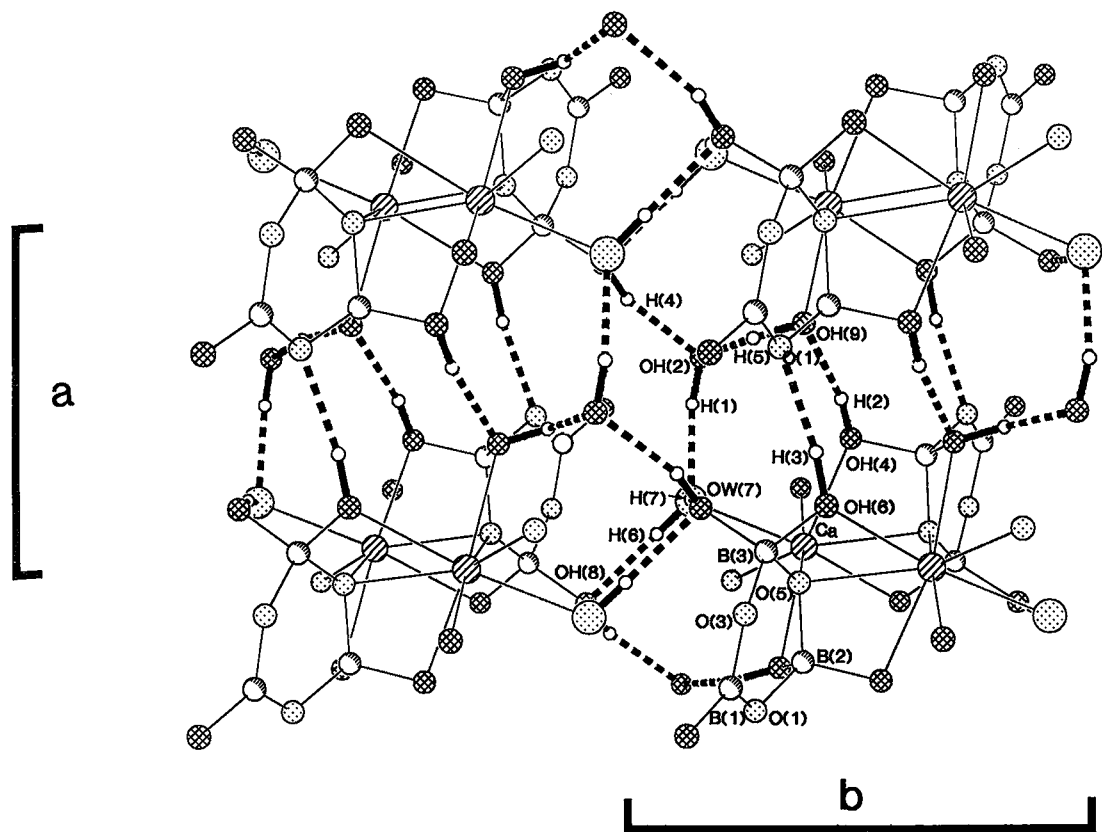


FIG. 4. The meyerhofferite structure projected onto (001). ϕ -H and H... ϕ bonds are given as heavy full and broken lines, respectively. Calcium atoms are shaded with straight lines, boron atoms are open circles with shading in the lower left corners, simple oxygen atoms are shaded with a regular dot pattern, OH⁻ oxygen atoms are cross-hatched, H₂O oxygen atoms are shown as large circles shaded with a regular dot pattern, and H atoms are small open circles.

Considerable hydrogen bonding also is directed along [010] between adjacent heteropolyhedral chains (Figs. 4, 5), with four hydrogen bonds occurring along [010] per unit cell. The OH(8)–H(4)...OH(2) and OW(7)–H(6)...OH(8) bonds directed along [010] are quite strong bonds, as indicated by relatively short H... ϕ bond-distances (1.91 – 1.95 Å). However, there are two fewer hydrogen bonds per unit cell along [010] than along [100], explaining why the {010} cleavage is excellent, whereas the {100} cleavage is not as good.

The OH(9)–H(5)...OH(2) and OW(7)–H(7)...OH(8) bonds are directed along [001]. Each bond involves two ϕ belonging to the same polyhedral chain (Fig. 5). The OH(9)–H(5)...OH(2) bond is quite weak, whereas the OW(7)–H(7)...OH(8) bond is relatively strong, as indicated by the H... ϕ bond-distances (Table 4). The H₂O group [OW(7)] is bonded to Ca (one bond), is a hydrogen-bond donor for H(6) and H(7), and is a

hydrogen-bond acceptor for H(1). Thus the oxygen of the H₂O group is tetrahedrally coordinated, with two strong bonds and two weak bonds, as is commonly the case in hydrated minerals.

Minimum-energy H-positions

Minimum energy H-positions were calculated using the program WMIN (Busing 1981). The B³⁺, O²⁻ and Ca²⁺ ions were held fixed during energy minimization, whereas the minimum-energy positions for all H⁺ ions were obtained simultaneously by six cycles of steepest-descent minimization followed by six cycles of minimization by Newton's method (Busing 1981). The starting positions for the hydrogen atoms were those obtained from the constrained X-ray refinement of the structure. The H–O and H...O interactions were modeled using the

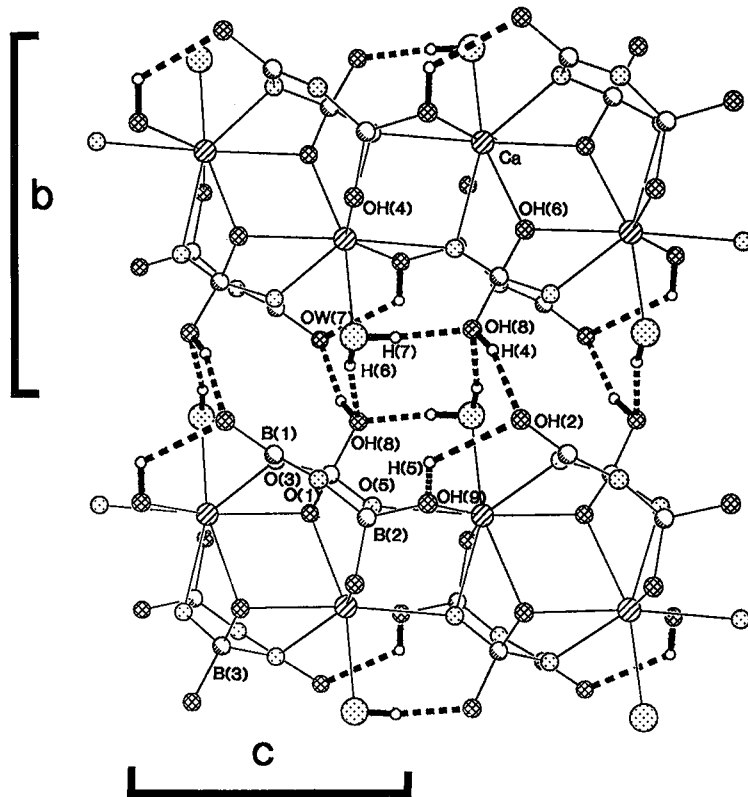


FIG. 5. The meyerhofferite structure projected onto (100). Legend as in Figure 4.

(directionally isotropic) potential of Abbott *et al.* (1989), where the energy W_{ij} for the ion pair $i-j$ is given as

$$W_{ij} = W_{C,ij} + W_{R,ij} \quad (1)$$

where $W_{C,ij}$ is the Coulombic electrostatic energy and $W_{R,ij}$ is the short-range repulsive energy. The Coulombic energy is given by:

$$W_{C,ij} = q_i q_j / r_{ij} \quad (2)$$

where q_i and q_j are the formal charges of ions i and j , and r_{ij} is the internuclear separation. The Born short-range repulsion energy (Born & Huang 1954) is given by:

$$W_{R,ij} = \lambda_{ij} \exp(-r_{ij} / \rho_{ij}) \quad (3)$$

where λ_{ij} and ρ_{ij} are pair-specific parameters. Throughout their work, Abbott *et al.* (1989) used $\rho_{ij} = 0.25 \text{ \AA}$ for H-O and H...O interactions. They found that the value of λ_{ij} is structurally dependent; 30000 kJ/mol worked well for trioctahedral micas and tremolite, whereas

24250 kJ/mol worked best for H-O pairs belonging to the "brucite" sheet of chlorite.

In our recent study of hydrogen bonding in colemanite (Burns & Hawthorne 1993), we obtained the best agreement between minimum-energy H-positions and X-ray structure refinement for $\rho = 0.25 \text{ \AA}$ and $\lambda_{ij} = 26500 \text{ kJ/mol}$. Applied to meyerhofferite, this set of parameters resulted in calculated H-positions that are in good agreement with the X-ray-refined H-positions (Table 6), such that calculated and observed hydrogen-bonding schemes are the same. This is in contrast to the results obtained for colemanite, where the minimum-energy calculations incorrectly predicted the positions of two of the five hydrogen atoms (Burns & Hawthorne 1993).

In the case of colemanite, we suggested that the directionally isotropic O-H potential failed to give the correct H-positions in the case where there was more than one potential acceptor ion located near the hydrogen position. In these cases, the potential function gave a minimum-energy position that best satisfied all possible H...O interactions, rather than the correct bond(s). In meyerhofferite, all potential donor-acceptor distances are involved in a hydrogen bond, so that this problem

TABLE 6. MINIMUM-ENERGY H-POSITIONS COMPARED TO X-RAY REFINEMENT H-POSITIONS

	X-ray	Minimum* Energy		X-ray'	Min. Energy
H(1)	x	0.563(2)	0.518	OH(2)-H(1)	0.95(2) 1.03
	y	0.901(3)	0.906	H(1)...OH(7)d	1.93(1) 1.76
	z	0.642(4)	0.670	OH(2)-H(1)-OH(7)d	151(1) 168
H(2)	x	0.453(3)	0.429	OH(4)-H(2)	0.95(2) 0.94
	y	0.429(3)	0.401	H(2)...OH(9)d	1.86(2) 1.89
	z	0.148(4)	0.139	OH(4)-H(2)-OH(9)d	170(2) 162
H(3)	x	0.313(2)	0.314	OH(6)-H(3)	0.95(1) 0.95
	y	0.392(3)	0.376	H(3)...O(1)d	1.94(1) 2.01
	z	0.642(4)	0.621	OH(6)-H(3)-O(1)d	172(2) 153
H(4)	x	0.253(3)	0.265	OH(8)-H(4)	0.96(2) 0.98
	y	0.065(3)	0.053	H(4)...OH(2)e	1.95(2) 1.91
	z	0.733(4)	0.761	OH(4)-H(4)-OH(2)e	160(2) 165
H(5)	x	0.373(4)	0.358	OH(9)-H(5)	0.96(2) 0.93
	y	0.779(2)	0.761	H(5)...OH(2)	2.26(3) 2.00
	z	0.951(4)	0.884	OH(9)-H(5)-OH(2)	122(2) 158
H(6)	x	0.052(3)	0.061	OW(7)-H(6)	0.96(2) 0.93
	y	0.032(3)	0.062	H(6)...OH(8)f	1.91(2) 2.14
	z	0.227(4)	0.283	OW(7)-H(6)-OH(8)f	169(2) 133
H(7)	x	0.164(4)	0.152	OW(7)-H(7)	0.96(1) 1.06
	y	0.104(3)	0.117	H(7)...OH(8)e	1.72(1) 1.62
	z	0.066(2)	0.049	OW(7)-H(7)-OH(8)e	171(2) 177
				H(6)-H(7)	1.55(4) 1.82
				H(6)-OW(7)-H(7)	102(2) 132

* bond-distances in Å and angles in °
 † $\rho = 0.25 \text{ \AA}$, $\lambda_{ij} = 26500 \text{ kJ/mol}$

does not arise: either there is only one possible acceptor, or the other possible acceptor(s) is a donor(s), with the position in question acting as the acceptor. The H-H Coulombic repulsion included in the structure-energy calculations prevents any two hydrogen atoms from being located between a ϕ - ϕ pair that is close enough together to act as a donor-acceptor pair.

The O-H potential given by Abbott *et al.* (1989) was derived specifically for use with hydroxyl positions only. Here, the potential we used ($\rho = 0.25 \text{ \AA}$ and $\lambda_{ij} = 26500 \text{ kJ/mol}$) predicts bonding involving an H_2O group [OW(7)], and the resulting hydrogen positions are in good agreement with those obtained from X-ray data (Table 6). This suggests that the potential we used may give good results for the determination of hydrogen positions of H_2O groups where there is no ambiguity as to the hydrogen-bonding interactions.

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