

## Hungchaoite, $\text{Mg}(\text{H}_2\text{O})_5\text{B}_4\text{O}_5(\text{OH})_4 \cdot 2\text{H}_2\text{O}$ : a hydrogen-bonded molecular complex

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### Abstract

The hydrated magnesium borate mineral hungchaoite,  $\text{MgO} \cdot 2\text{B}_2\text{O}_3 \cdot 9\text{H}_2\text{O}$ , from Furnace Creek borate area, Death Valley, California, is triclinic, space group  $P\bar{1}$ , with cell dimensions:  $a = 8.807(1)$ ,  $b = 10.657(1)$ ,  $c = 7.897(1)\text{Å}$ ,  $\alpha = 103.39(1)$ ,  $\beta = 108.53(1)$ ,  $\gamma = 97.18(1)^\circ$ , and  $Z = 2$ . The crystal structure has been determined by the symbolic addition method and difference Fourier syntheses, and refined by the method of least squares to an  $R$ -factor of 0.049, based on 4860 reflections measured on an automatic single-crystal X-ray diffractometer. All hydrogens have been located and their positions refined.

The crystal structure consists of a molecular complex,  $[\text{Mg}(\text{H}_2\text{O})_5\text{B}_4\text{O}_5(\text{OH})_4]$ , and two water molecules, hydrogen-bonded into a three-dimensional framework; the molecular complex consists of a  $[\text{Mg}(\text{H}_2\text{O})_5(\text{OH})]$  octahedron and the tetraborate polyanion  $[\text{B}_4\text{O}_5(\text{OH})_4]^{2-}$  ( $4:2\Delta + 2T$ ) sharing a common tetrahedral (OH) corner. The orientation of the Mg-octahedron with respect to the tetraborate polyanion is fixed by means of an intramolecular hydrogen bond between a water molecule bonded to magnesium and an oxygen atom belonging to the tetraborate polyanion. The average Mg-O, B-O(tetrahedral), and B-O(triangular) bond lengths are: 2.084, 1.476, and 1.368Å respectively. All hydrogen atoms are involved in hydrogen bonding. The average O-H, H...O, and O-H...O distances are 0.86, 1.94, and 2.781Å respectively. All the hydrogen bonds are nearly straight (av. O-H...O angle  $171^\circ$ ), except one, which is bent (O-H...O angle  $111^\circ$ ). The two isolated water molecules show a distorted tetrahedral coordination, whereas those bonded to magnesium show a distorted trigonal planar coordination.

### Introduction

The hydrous magnesium borate mineral hungchaoite,  $\text{MgO} \cdot 2\text{B}_2\text{O}_3 \cdot 9\text{H}_2\text{O}$ , was first reported from salt lakes in China (Chu *et al.*, 1964). No reliable crystallographic data other than the X-ray powder pattern were available for this mineral until its discovery in the Furnace Creek area, Inyo County, Death Valley, California (McAllister, 1970). In Death Valley, hungchaoite occurs as an efflorescence on weathered colemanite, in association with two other magnesium borate minerals, inderite and kurnakovite, both with the composition  $\text{Mg}[\text{B}_3\text{O}_3(\text{OH})_5] \cdot 5\text{H}_2\text{O}$ , and with ulexite,  $\text{NaCa}[\text{B}_5\text{O}_6(\text{OH})_6] \cdot 5\text{H}_2\text{O}$ . The occurrence and description of hungchaoite from the Death Valley region will be presented in a forthcoming paper by Erd *et al.* (in preparation).

### Experimental

A colorless transparent hungchaoite crystal ( $0.08 \times 0.20 \times 0.25$  mm) from Death Valley was mounted

on the computer-controlled, single-crystal X-ray diffractometer (Syntex  $P\bar{1}$ ). The cell dimensions were refined by the least-squares method based on 15 reflections with  $2\theta$  values between  $35$  and  $45^\circ$  measured with  $\text{MoK}\alpha$  radiation (Table 1). Intensity data for all reflections with  $2\theta < 65^\circ$  were collected by the  $2\theta$ - $\theta$  scan method, using  $\text{MoK}\alpha$  radiation monochromatized by reflection from a graphite "single" crystal, and a scintillation counter. The variable scan method was used, the minimum scan rate being  $2^\circ/\text{min}$  (50 kV, 15 mA). A total of 4860 reflections were measured, out of which 1373 reflections were less than  $3\sigma(I)$ , where  $\sigma(I)$  is the standard deviation of the intensity, as determined from counting statistics.

These intensities were corrected for Lorentz and polarization factors. Absorption corrections were neglected, because the absorption coefficient of hungchaoite for  $\text{MoK}\alpha$  radiation is very small (Table 1). An  $N(z)$  test based on the measured intensities in-

Table 1. Hungchaoite: crystal data

Hungchaoite, $\text{Mg}(\text{H}_2\text{O})_5\text{B}_4\text{O}_5(\text{OH})_4 \cdot 2\text{H}_2\text{O}$ : Furnace Creek, Inyo County, Death Valley, California	
Colorless transparent prism	
Triclinic, $\bar{1}$	Cell volume: $667.6(2)\text{\AA}^3$
$a$ : 8.807(1) $\text{\AA}$	Space group: $P\bar{1}$
$b$ : 10.657(1)	Cell content: $2[\text{Mg}(\text{H}_2\text{O})_5\text{B}_4\text{O}_5(\text{OH})_4 \cdot 2\text{H}_2\text{O}]$
$c$ : 7.897(1)	$D_m$ : 1.706(5) $\text{g cm}^{-3}$ (R. C. Erd, Priv. Commun.)
$\alpha$ : 103.39(1) $^\circ$	$D_x$ : 1.700 $\text{g cm}^{-3}$
$\beta$ : 108.53(1)	$\mu$ (MoK $\alpha$ ): 7.19 $\text{cm}^{-1}$
$\gamma$ : 97.18(1)	

indicated the presence of a center of symmetry and  $P\bar{1}$  as the correct space group.

#### Determination and refinement of the crystal structure

The crystal structure was determined by the symbolic addition method (Karle and Karle, 1966), using the computer program MULTAN (Germain *et al.*, 1971). E-values of all reflections were calculated. The

signs of the three following reflections with large E-values were chosen to define the origin:

$h$	$k$	$l$	E	Sign
6	7	-11	4.26	+
3	0	-4	3.38	+
8	10	-5	3.30	+

In addition, the following three reflections with large E-values were given symbols:

$h$	$k$	$l$	E	Symbol
2	-5	-4	4.45	<i>e</i>
0	3	-6	3.38	<i>f</i>
0	8	-4	2.84	<i>g</i>

In addition to these six reflections, signs and symbols of 232 additional reflections with E-values  $> 2.0$  were determined. Out of the eight resulting E-maps, one showed the correct structure, which yielded the positions of one magnesium, three boron, and thirteen oxygen atoms.

A difference Fourier synthesis calculated subsequently yielded the positions of an additional boron and three oxygen atoms. The three symbols *e*, *f*, and *g* turned out to be +, +, and - respectively. Four

Table 2a. Hungchaoite,  $\text{Mg}(\text{H}_2\text{O})_5\text{B}_4\text{O}_5(\text{OH})_4 \cdot 2\text{H}_2\text{O}$ : positional and thermal parameters of non-hydrogen atoms (standard deviations in parentheses)

Atom	$x$	$y$	$z$	$u_{11}^*$	$u_{22}^*$	$u_{33}^*$	$u_{12}^*$	$u_{13}^*$	$u_{23}^*$
Mg	0.82907(6)	0.22643(5)	0.13238(7)	0.0165(2)	0.0193(3)	0.0181(2)	0.0028(2)	0.0035(2)	0.0067(2)
B(1)	0.1812(2)	0.3017(2)	0.4835(2)	0.0133(7)	0.0151(8)	0.0151(7)	0.0019(5)	0.0035(6)	0.0060(6)
B(2)	0.2242(2)	0.0830(2)	0.5269(2)	0.0200(8)	0.0172(8)	0.0179(8)	0.0053(6)	0.0053(6)	0.0061(7)
B(3)	0.2786(2)	0.2761(2)	0.7926(2)	0.0152(7)	0.0161(8)	0.0137(7)	0.0027(6)	0.0048(6)	0.0048(6)
B(4)	0.4629(2)	0.4094(2)	0.6887(2)	0.0138(7)	0.0171(8)	0.0153(8)	0.0021(6)	0.0053(6)	0.0043(6)
O(1)	0.1915(1)	0.1614(1)	0.4106(1)	0.0207(5)	0.0159(5)	0.0144(5)	0.0045(4)	0.0050(4)	0.0060(4)
O(2)	0.2731(1)	0.1322(1)	0.7163(1)	0.0236(5)	0.0148(5)	0.0149(5)	0.0042(4)	0.0049(4)	0.0055(4)
O(3)	0.4437(1)	0.3536(1)	0.8219(1)	0.0127(5)	0.0231(6)	0.0149(5)	0.0001(4)	0.0025(4)	0.0087(4)
O(4)	0.3412(1)	0.3893(1)	0.5202(1)	0.0138(5)	0.0218(6)	0.0145(5)	0.0016(4)	0.0027(4)	0.0077(4)
O(5)	0.1545(1)	0.3188(1)	0.6596(1)	0.0124(4)	0.0180(5)	0.0152(5)	0.0043(4)	0.0052(4)	0.0064(4)
O(OH1)	0.0509(1)	0.3305(1)	0.3391(1)	0.0151(5)	0.0162(6)	0.0186(5)	0.0014(4)	0.0000(4)	0.0080(4)
O(OH2)	0.2054(2)	0.9517(1)	0.4428(2)	0.0595(9)	0.0163(6)	0.0194(6)	0.0091(6)	0.0082(6)	0.0055(5)
O(OH3)	0.2539(1)	0.2893(1)	0.9977(2)	0.0225(5)	0.0203(6)	0.0136(5)	0.0005(4)	0.0079(4)	0.0040(4)
O(OH4)	0.6132(1)	0.4891(1)	0.7326(2)	0.0163(5)	0.0279(6)	0.0158(5)	0.0056(4)	0.0037(4)	0.0080(5)
O(W1)	0.6108(2)	0.1148(1)	0.9272(2)	0.0183(6)	0.0251(7)	0.0304(7)	0.0054(5)	0.0019(5)	0.0025(6)
O(W2)	0.8876(2)	0.0453(1)	0.1425(2)	0.0198(6)	0.0211(6)	0.0311(7)	0.0028(5)	0.0040(5)	0.0104(5)
O(W3)	0.7246(2)	0.2192(1)	0.3387(2)	0.0204(6)	0.0269(7)	0.0236(6)	0.0029(5)	0.0072(5)	0.0066(5)
O(W4)	0.7415(2)	0.3950(1)	0.1071(2)	0.0274(7)	0.0221(7)	0.0311(7)	0.0093(5)	0.0044(5)	0.0052(6)
O(W5)	0.9268(2)	0.2267(1)	0.9257(2)	0.0237(6)	0.0336(7)	0.0199(6)	0.0012(5)	0.0090(5)	0.0035(6)
O(W6)	0.3975(2)	0.1503(1)	0.2039(2)	0.0226(6)	0.0298(7)	0.0260(7)	0.0080(5)	0.0112(5)	0.0093(6)
O(W7)	0.8919(2)	0.4104(1)	0.6640(2)	0.0252(6)	0.0255(6)	0.0359(7)	0.0105(5)	0.0143(6)	0.0110(6)

\*Anisotropic temperature factor expression:

$$\exp [-2\pi^2(u_{11}^2 a^{*2} + u_{22}^2 b^{*2} + u_{33}^2 c^{*2} + 2u_{12}^* hka^*b^* \cos\gamma^* + 2u_{13}^* hla^*c^* \cos\beta^* + 2u_{23}^* klb^*c^* \cos\alpha^*)]$$

Table 2b. Hungchaoite: positional and thermal parameters of hydrogen atoms (standard deviations in parentheses)

Atom	$x$	$y$	$z$	$u^{\dagger}$
H(1)	0.077(3)	0.413(2)	0.346(3)	0.053(7)
H(2)	0.227(3)	0.907(3)	0.510(4)	0.063(8)
H(3)	0.293(3)	0.366(3)	0.049(3)	0.055(7)
H(4)	0.619(3)	0.520(2)	0.651(3)	0.040(6)
H(5)	0.518(3)	0.127(2)	0.866(3)	0.049(7)
H(6)	0.609(3)	0.028(3)	0.877(4)	0.065(8)
H(7)	0.838(3)	0.987(3)	0.178(4)	0.064(8)
H(8)	0.994(3)	0.059(2)	0.208(4)	0.057(8)
H(9)	0.617(3)	0.211(2)	0.300(3)	0.058(7)
H(10)	0.762(3)	0.291(3)	0.432(4)	0.062(8)
H(11)	0.776(3)	0.475(3)	0.180(4)	0.065(8)
H(12)	0.649(2)	0.390(2)	0.023(3)	0.036(5)
H(13)	0.030(3)	0.250(3)	0.947(4)	0.058(8)
H(14)	0.883(3)	0.169(3)	0.823(4)	0.059(8)
H(15)	0.340(3)	0.156(2)	0.268(3)	0.050(7)
H(16)	0.357(3)	0.192(3)	0.133(4)	0.064(8)
H(17)	0.975(3)	0.379(3)	0.665(4)	0.060(8)
H(18)	0.858(3)	0.403(2)	0.755(3)	0.050(7)

$\dagger$ For hydrogen atoms, the isotropic temperature factor,

$$B: 8\pi^2 u$$

cycles of least-squares refinement using isotropic temperature factors, and two cycles using anisotropic temperature factors for all atoms reduced the  $R$ -factor to 0.06. A difference Fourier synthesis calculated at this stage yielded the positions of all (18) hydrogen atoms. Subsequent least-squares refinement was carried out using isotropic temperature factors for hydrogen atoms and anisotropic temperature factors for all non-hydrogen atoms. The scattering factors for Mg, B, O, and H were taken from Cromer and Mann (1968). Anomalous dispersion corrections were made according to Cromer and Liberman (1970).

The final  $R$ -factor for 4860 reflections is 0.049. The atomic positional and thermal parameters are listed in Table 2. Table 3<sup>1</sup> compares observed and calculated structure factors. The bond lengths and angles are listed in Table 4. The average standard deviations in Mg–O, B–O, and O–H bond lengths are 0.002, 0.002, and 0.03Å and in O–Mg–O, O–B–O, and H–O–H angles 0.06, 0.13, and 2.6° respectively.

The Fourier and least-squares refinement programs incorporated in the X-RAY SYSTEM-72 (Steward *et al.*, 1972) were used for the calculations.

### Description of the structure

The crystal structure of hungchaoite consists of a neutral molecular complex,  $[\text{Mg}(\text{H}_2\text{O})_5\text{B}_4\text{O}_5(\text{OH})_4]$ ,

<sup>1</sup> To obtain a copy of this table, order document AM-77-056 from the Business Office, Mineralogical Society of America, 1909 K Street, N.W., Washington, D.C. 20006. Please remit \$1.00 in advance for the microfiche.

formed by a  $[\text{Mg}(\text{H}_2\text{O})_5(\text{OH})]^+$  octahedron and a tetraborate polyanion  $[\text{B}_4\text{O}_5(\text{OH})_4]^{2-}$  sharing a common (OH) corner, and two crystallographically distinct water molecules.

### The tetraborate polyanion

The tetraborate polyanion,  $[\text{B}_4\text{O}_5(\text{OH})_4]$  ( $4: 2\Delta + 2T$ )<sup>2</sup> consists of two  $\text{BO}_3(\text{OH})$  tetrahedra and two  $\text{BO}_2(\text{OH})$  triangles sharing corners (Fig. 1). The highest point-group symmetry this polyanion can have is  $mm2$ , the two-fold axis passing through the oxygen atom O(5), shared by the two borate tetrahedra. This symmetry is only approximated by the tetraborate polyanion in hungchaoite, where the true point-group symmetry is  $I$ . The deviation from the point symmetry  $mm2$  is most pronounced in terms of the terminal O–H directions (Fig. 1).

The average B–O bond distances within the borate triangles and borate tetrahedra are 1.368 and 1.477Å, respectively. Within each borate tetrahedron, the B–O bond involving an oxygen bonded to a triangular boron (av. 1.498Å) is significantly longer than the B–O bond involving an oxygen bonded to a tetrahedral boron (av. 1.456Å). The  $[\text{B}_4\text{O}_5(\text{OH})_4]$  polyanion found in  $\text{K}_2[\text{B}_4\text{O}_5(\text{OH})_4] \cdot 2\text{H}_2\text{O}$  (Marezio *et al.*, 1963) shows a similar trend. This is a reflection of the fact that the triangular B–O bond is more covalent than the tetrahedral B–O bond. The average terminal O–H bond distance is 0.83Å, and the average B–O–H angle

<sup>2</sup> Notation suggested by Christ and Clark (1977) 4: tetraborate;  $\Delta$ : borate triangle;  $T$ : borate tetrahedron.

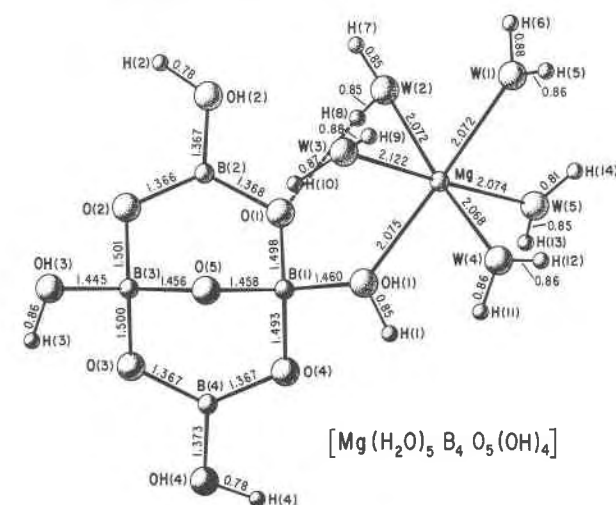


Fig. 1. A view of the neutral molecular complex  $[\text{Mg}(\text{H}_2\text{O})_5\text{B}_4\text{O}_5(\text{OH})_4]$  in hungchaoite, made up of the tetraborate polyanion and the Mg-octahedron sharing a corner. Note the intra-molecular hydrogen bond between H(8) and O(1).

Table 4. Hungchaoite,  $Mg(H_2O)_5B_4O_5(OH)_4 \cdot 2H_2O$ : interatomic distances (Å) and angles ( $^\circ$ ) (standard deviations in parentheses)

<i>The Mg - Octahedron</i>				<i>Hydrogen Bonds</i>			
Mg - OH(1)	2.075(1)	OH(1) - Mg - O(W2)	92.81(5)	<i>Hydroxyl, OH(1)</i>			
Mg - O(W1)	2.072(1)	OH(1) - Mg - O(W3)	90.00(5)	H(1) - OH(1)	0.86(3)	OH(1) - H(1) - O(W7)	172(2)
Mg - O(W2)	2.072(2)	OH(1) - Mg - O(W4)	93.68(5)	H(1) - O(W7)	1.89(3)	B(1) - OH(1) - H(1)	108(1)
Mg - O(W3)	2.122(2)	OH(1) - Mg - O(W5)	91.53(5)	OH(1) - O(W7)	2.752(3)	Mg - OH(1) - H(1)	115(1)
Mg - O(W4)	2.068(2)	O(W1) - Mg - O(W2)	84.64(5)	<i>Hydroxyl, OH(2)</i>			
Mg - O(W5)	2.074(2)	O(W2) - Mg - O(W3)	89.93(6)	H(2) - OH(2)	0.78(3)	OH(2) - H(2) - O(W3)	175(3)
Mean 2.081		O(W1) - Mg - O(W4)	88.87(5)	H(2) - O(W3)	2.00(3)	B(2) - OH(2) - H(2)	116(2)
OH(1) - O(W2)	3.003(2)	O(W1) - Mg - O(W5)	88.48(6)	OH(2) - O(W3)	2.781(2)		
OH(1) - O(W3)	2.968(2)	O(W2) - Mg - O(W3)	89.04(6)	<i>Hydroxyl, OH(3)</i>			
OH(1) - O(W4)	3.021(2)	O(W3) - Mg - O(W4)	88.63(7)	H(3) - OH(3)	0.86(2)	OH(3) - H(3) - OH(4)	166(2)
OH(1) - O(W5)	2.972(2)	O(W4) - Mg - O(W5)	92.58(7)	H(3) - OH(4)	1.89(2)	B(3) - OH(3) - H(3)	116(2)
O(W1) - O(W2)	2.790(2)	O(W5) - Mg - O(W2)	89.57(7)	OH(3) - OH(4)	2.742(2)		
O(W1) - O(W3)	2.964(2)	Mean 89.98		<i>Hydroxyl, OH(4)</i>			
O(W1) - O(W4)	2.899(2)			H(4) - OH(4)	0.80(3)	OH(4) - H(4) - O(4)	172(2)
O(W1) - O(W5)	2.892(2)			H(4) - O(4)	1.93	B(4) - OH(4) - H(4)	113(1)
O(W2) - O(W3)	2.940(2)			OH(4) - O(4)	2.721(2)		
O(W3) - O(W4)	2.927(2)			<i>Water molecule, W(1)</i>			
O(W4) - O(W5)	2.994(2)			O(W1) - H(5)	0.85(2)	H(5) - O(W1) - H(6)	105(2)
O(W5) - O(W2)	2.920(2)			O(W1) - H(6)	0.92(3)	O(W1) - H(5) - O(2)	172(2)
Mean 2.941				H(5) - O(2)	2.12(2)	O(W1) - H(6) - O(W6)	175(3)
<i>The B(1)-Tetrahedron</i>				H(6) - O(W6)	1.84(3)	Mg - O(W1) - H(5)	138(2)
B(1) - O(1)	1.498(2)	O(1) - B(1) - O(5)	109.19(14)	O(W1) - O(2)	2.964(2)	Mg - O(W1) - H(6)	116(5)
B(1) - O(5)	1.458(2)	O(1) - B(1) - O(4)	108.45(13)	O(W1) - O(W6)	2.756(2)		
B(1) - O(4)	1.493(2)	O(1) - B(1) - OH(1)	107.47(10)	<i>Water molecule, W(2)</i>			
B(1) - OH(1)	1.459(2)	O(5) - B(1) - O(4)	108.14(10)	O(W2) - H(7)	0.86(3)	H(7) - O(W2) - H(8)	106(3)
Mean 1.477		O(5) - B(1) - OH(1)	113.65(13)	O(W2) - H(8)	0.89(2)	O(W2) - H(7) - O(2)	174(2)
O(1) - O(5)	2.409(2)	O(4) - B(1) - OH(1)	109.84(14)	H(7) - O(2)	1.99(3)	O(W2) - H(8) - O(1)	151(2)
O(1) - O(4)	2.426(2)	Mean 109.46		H(8) - O(1)	1.93(2)	Mg - O(W2) - H(7)	125(2)
O(1) - OH(1)	2.384(2)			O(W2) - O(2)	2.853(2)	Mg - O(W2) - H(8)	109(2)
O(5) - O(4)	2.389(2)			O(W2) - O(1)	2.745(2)		
O(5) - OH(1)	2.441(2)			<i>Water molecule, W(3)</i>			
O(4) - OH(1)	2.415(1)			O(W3) - H(9)	0.88(3)	H(9) - O(W3) - H(10)	104(2)
Mean 2.411				O(W3) - H(10)	0.87(3)	O(W3) - H(9) - O(W6)	165(2)
<i>The B(3) - Tetrahedron</i>				H(9) - O(W6)	1.81(2)	O(W3) - H(10) - O(W7)	161(3)
B(3) - O(2)	1.501(2)	O(2) - B(3) - OH(3)	105.78(14)	H(10) - O(W7)	1.87(2)	Mg - O(W3) - H(9)	115(2)
B(3) - OH(3)	1.445(2)	O(2) - B(3) - O(3)	108.44(13)	O(W3) - O(W6)	2.670(2)	Mg - O(W3) - H(10)	112(2)
B(3) - O(3)	1.499(2)	O(2) - B(3) - O(5)	110.18(10)	O(W3) O O(W7)	2.709(2)		
B(3) - O(5)	1.457(2)	OH(3) - B(3) - O(3)	111.07(10)	<i>Water molecule, W(4)</i>			
Mean 1.476		OH(3) - B(3) - O(5)	113.01(14)	O(W4) - H(11)	0.87(2)	H(11) - O(W4) - H(12)	108(2)
O(2) - OH(3)	2.349(2)	O(3) - B(3) - O(5)	108.26(14)	O(W4) - H(12)	0.86(2)	O(W4) - H(11) - O(5)	175(3)
O(2) - O(3)	2.434(2)	Mean 109.46		H(11) - O(5)	2.16(2)	O(W4) - H(12) - O(3)	172(2)
O(2) - O(5)	2.425(2)			H(12) - O(3)	1.91(2)	Mg - O(W4) - H(11)	131(2)
OH(3) - O(3)	2.428(2)			O(W4) - O(5)	3.026(2)	Mg - O(W4) - H(12)	120(1)
OH(3) - O(5)	2.420(2)			O(W4) - O(3)	2.766(2)		
O(3) - O(5)	2.395(2)			<i>Water molecule, W(5)</i>			
Mean 2.409				O(W5) - H(13)	0.86(3)	H(13) - O(W5) - H(14)	109(3)
<i>The B(2) - Triangle</i>				O(W5) - H(14)	0.83(2)	O(W5) - H(13) - OH(3)	174(3)
B(2) - O(1)	1.368(2)	O(1) - B(2) - OH(2)	116.12(14)	H(13) - OH(3)	1.91(3)	O(W5) - H(14) - OH(2)	171(3)
B(2) - OH(2)	1.366(2)	O(1) - B(2) - O(2)	122.31(14)	H(14) - OH(2)	2.03(2)	Mg - O(W5) - H(13)	124(2)
B(2) - O(2)	1.367(2)	OH(2) - B(2) - O(2)	131.56(17)	O(W5) - OH(3)	2.769(2)	Mg - O(W5) - H(14)	119(2)
Mean 1.367		Mean 120.00		O(W5) - OH(2)	2.858(2)		
O(1) - OH(2)	2.320(2)			<i>Water molecule, W(6)</i>			
O(1) - O(2)	2.396(2)			O(W6) - H(15)	0.82(3)	H(15) - O(W6) - H(16)	101(3)
O(2) - OH(2)	2.385(2)			O(W6) - H(16)	0.82(3)	O(W6) - H(15) - O(1)	176(3)
Mean 2.367				H(15) - O(1)	1.98(3)	O(W6) - H(16) - OH(3)	178(3)
<i>The B(4) - Triangle</i>				H(16) - OH(3)	1.93(3)		
B(4) - O(3)	1.366(2)	O(3) - B(4) - OH(4)	116.27(12)	O(W6) - O(1)	2.798(2)		
B(4) - OH(4)	1.373(2)	O(3) - B(4) - O(4)	123.07(13)	O(W6) - OH(3)	2.745(2)		
B(4) - O(4)	1.367(2)	OH(4) - B(4) - O(4)	120.66(17)	<i>Water molecule, W(7)</i>			
Mean 1.369		Mean 120.00		O(W7) - H(17)	0.84(3)	H(17) - O(W7) - H(18)	114(3)
O(3) - OH(4)	2.326(2)			O(W7) - H(18)	0.88(3)	O(W7) - H(17) - O(5)	176(3)
O(3) - O(4)	2.403(2)			H(17) - O(5)	1.78(3)	O(W7) - H(18) - OH(4)	112(2)
OH(4) - O(4)	2.381(1)			H(18) - OH(4)	2.41(3)		
Mean 2.370				O(W7) - O(5)	2.627(2)		
<i>B - B Separation</i>		<i>B - O - B Angles</i>		O(W7) - OH(4)	2.858(2)		
B(1) - B(2)	2.491(3)	B(1) - O(5) - B(3)	111.55(12)				
B(1) - B(3)	2.409(3)	B(1) - O(1) - B(2)	120.62(13)				
B(1) - B(4)	2.443(2)	B(1) - O(4) - B(4)	117.33(14)				
B(2) - B(3)	2.446(2)	B(2) - O(2) - B(3)	117.02(13)				
B(3) - B(4)	2.478(3)	B(3) - O(3) - B(4)	119.59(11)				

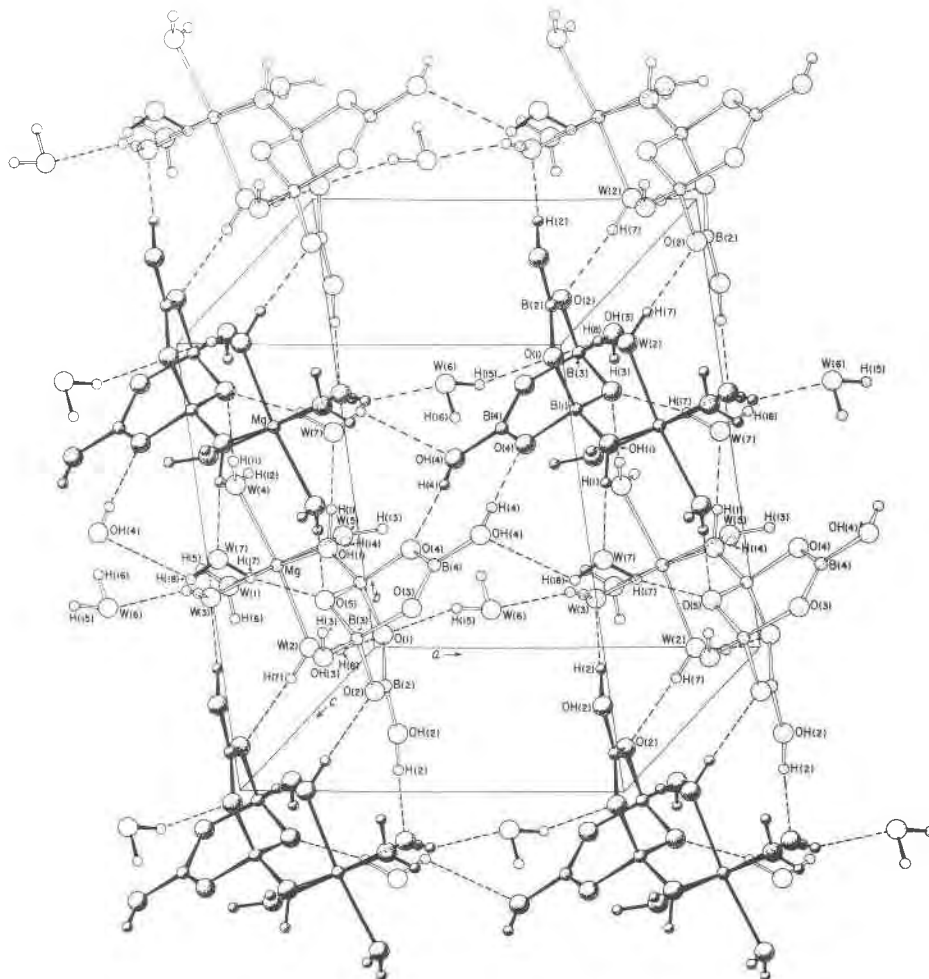


Fig. 2. A view of the hungchaoite structure showing the three-dimensional network of hydrogen bonds between the  $[\text{Mg}(\text{H}_2\text{O})_5\text{B}_4\text{O}_5(\text{OH})_4]$  molecular complexes and two isolated water molecules, W(6) and W(7).

is  $113^\circ$ . The dihedral angle between B(1)B(2)B(3) and B(1)B(3)B(4) planes is  $87.8^\circ$ .

#### The $[\text{Mg}(\text{H}_2\text{O})_5(\text{OH})]$ octahedron

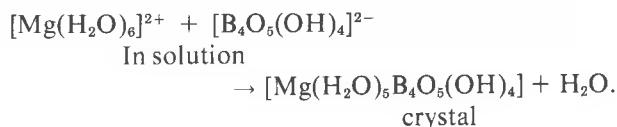
The magnesium atom is surrounded by five water molecules and a hydroxyl ion at the corners of a nearly regular octahedron, with point symmetry  $1$ . However, one of the Mg–O distances [Mg–W(3), 2.122Å] is significantly larger than the others, which average 2.072Å. The reason for this deviation from regular octahedral symmetry is not clear.

Within the ligand water molecules and the (OH) ion, the O–H distances average 0.86Å, H–O–H angles  $106^\circ$ . The Mg–O–H angles are highly variable and average  $121^\circ$ .

#### The $[\text{Mg}(\text{H}_2\text{O})_5\text{B}_4\text{O}_5(\text{OH})_4]$ molecular complex

The tetraborate polyanion  $[\text{B}_4\text{O}_5(\text{OH})_4]^{2-}$  shares a common (OH) corner with the  $[\text{Mg}(\text{H}_2\text{O})_5(\text{OH})]^+$

octahedron, thereby forming a molecular complex  $[\text{Mg}(\text{H}_2\text{O})_5\text{B}_4\text{O}_5(\text{OH})_4]$  with zero charge. The configuration of this molecular complex is fixed through an intra-molecular hydrogen bond between H(8) belonging to a water molecule, W(2) bonded to Mg, and a corner oxygen atom O(1) of the tetraborate polyanion (Fig. 1). Such a molecular complex can be formed at low temperatures by the following reaction of the tetraborate polyanion and a hydrated magnesium ion, presumably existing in the solution:



A similar molecular complex,  $[\text{Mn}(\text{H}_2\text{O})_5\text{B}_4\text{O}_5(\text{OH})_4]$ , occurs in the structure of  $\text{MnB}_4\text{O}_7 \cdot 9\text{H}_2\text{O}$  (Berzinya *et al.*, 1975).

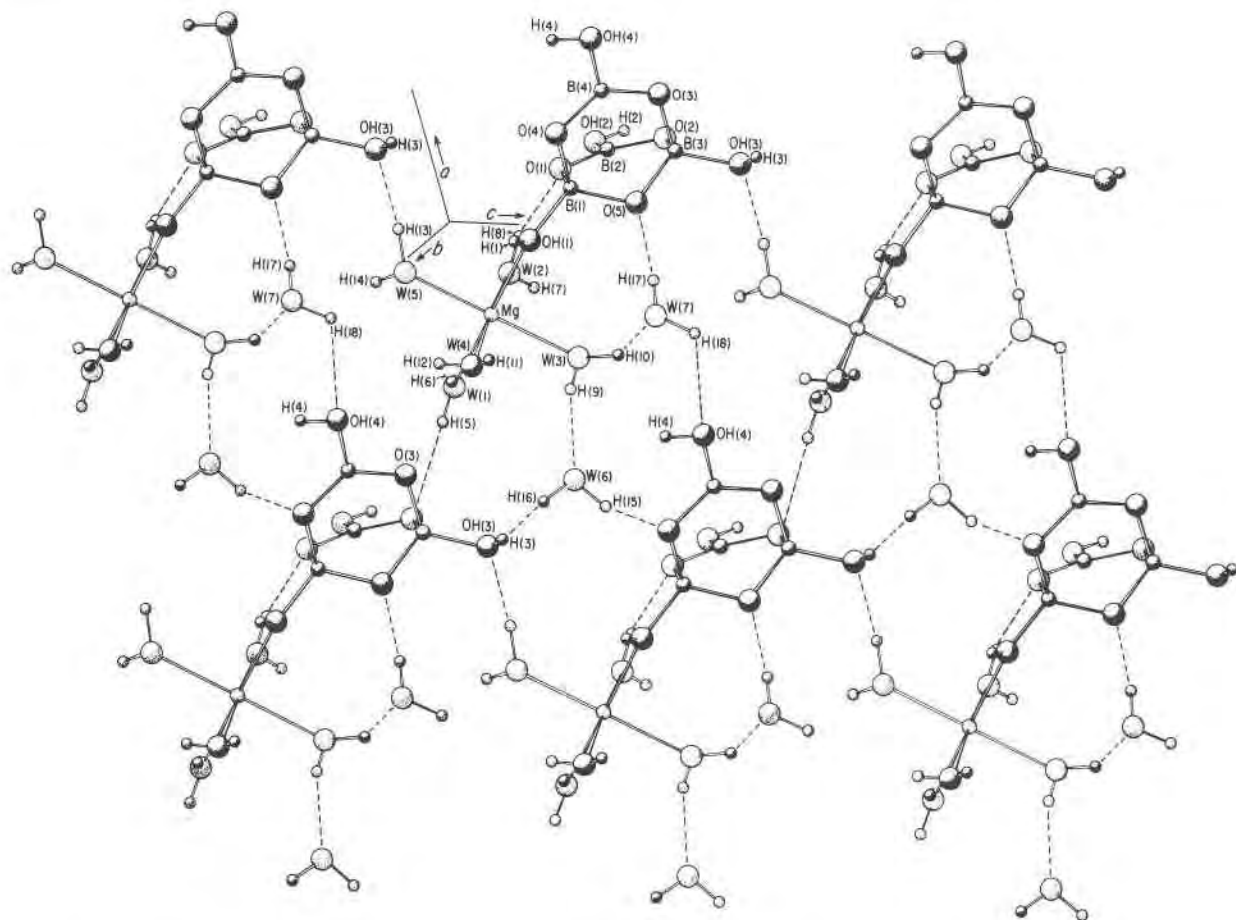


Fig. 3. A partial view of the hungchaoite structure showing the hydrogen-bonded chains of the isolated water molecules, W(6) and W(7), parallel to *c*- and *a*-axes respectively.

### Hydrogen bonds

The hydrogen bonding plays a very important rôle in the structure of hungchaoite. All 18 hydrogen atoms are involved in a three-dimensional network of hydrogen bonds and account for the existence of hungchaoite as a solid phase (Figs. 2 and 3). Some of the inter-molecular hydrogen bonds between two centrosymmetrically-related molecular complexes are reminiscent of such hydrogen bonds in organic molecules [e.g., OH(4)–H(4) . . . O(4); OH(2)–H(2) . . . W(3); W(2)–H(7) . . . O(2) and so on in Fig. 2].

The two isolated water molecules W(6) and W(7) occur within the voids left by the packing of the molecular complexes, and form linear hydrogen-bonded chains parallel to the *c*- and *a*-axes respectively (Fig. 3). These two isolated water molecules are also the acceptors of two hydrogen bonds each (Fig. 4), and show a tetrahedral coordination around the oxygen atom. In contrast, the five water molecules

which serve as ligands to Mg show approximately trigonal planar coordination (Fig. 4).

All the hydrogen bonds except one are straight, with H . . . O distances varying from 1.81 to 2.16 Å (av. 1.97 Å) and O–H . . . O angles varying from 151 to 178° (av. 171°). The exception is the bent bond W(7)–H(18) . . . OH(4), where the H . . . O distance is 2.41 Å and O–H . . . O angle is 111°. Figure 4 indicates that the environment around W(7) is such that one of the two hydrogen bonds involving the nearest hydrogens has to be a bent bond.

### Antisotropic thermal vibration

The thermal vibration ellipsoids of the  $[\text{Mg}(\text{H}_2\text{O})_5\text{B}_4\text{O}_5(\text{OH})_4]$  molecular complex are shown in Figure 5 (see also Table 2). The thermal vibrations of the boron atoms are nearly isotropic, the triangular borons being slightly more anisotropic than the tetrahedral borons. Within the tetraborate polyanion, the bridging oxygen atoms are slightly anisotropic, the

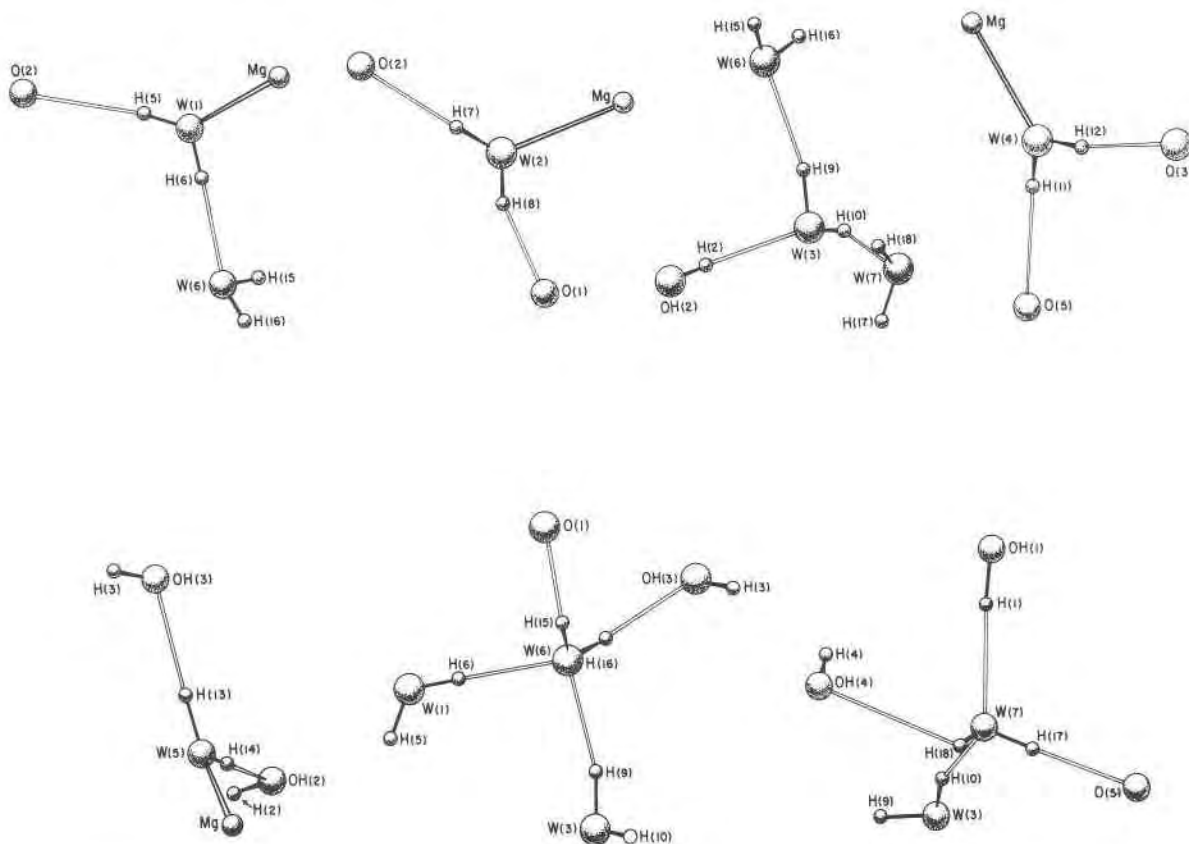


Fig. 4. Coordination of the water molecules in hungchaoite. Note that the water molecules [W(1) through W(5)] bonded to Mg show trigonal planar coordination, whereas the isolated water molecules W(6) and W(7) show tetrahedral coordination.

maximum vibration direction being normal to the B–O–B plane. The non-bridging terminal (OH) groups are strongly anisotropic, the maximum vibration direction being normal to the B–O bond. The OH (1) group, which is bridging B(1) and Mg, is nearly isotropic. The thermal vibration of the Mg atom is nearly isotropic, whereas those of the five ligand water molecules are strongly anisotropic, the maximum vibration direction being normal to the Mg–O bond. The two isolated water molecules show fairly strong anisotropic thermal vibrations, comparable in magnitude to those of the ligand water molecules.

## Discussion

### Comparison with other tetraborate structures

A synthetic monoclinic phase of  $\text{Mg}[\text{B}_4\text{O}_4(\text{OH})_6] \cdot 6\text{H}_2\text{O}$ , isochemical with hungchaoite, reportedly contains a tetraborate polyanion, consisting of two tetrahedra and one triangle modified by an additional borate triangle sharing a tetrahedral corner, accord-

ing to a structure determination by Abdullaev and Mamedov (1969). Although this polyanion is crystalchemically plausible, our interatomic distance calculation, based on the unit-cell dimensions, space group, and atomic positions given by Abdullaev and Mamedov, revealed a number of impossibly short ( $<2\text{\AA}$ ) oxygen–oxygen contacts, throwing considerable doubt on the validity of this structure.

The isolated  $[\text{B}_4\text{O}_5(\text{OH})_4]^-$  polyanion was first found in borax,  $\text{Na}_2\text{B}_4\text{O}_7 \cdot 8\text{H}_2\text{O}$  (Morimoto, 1956). In borax the tetraborate polyanions are hydrogen-bonded to edge-sharing Na-octahedral chains. In tinalconite,  $\text{Na}_2[\text{B}_4\text{O}_5(\text{OH})_4] \cdot 3\text{H}_2\text{O}$ , the tetraborate polyanions (with point symmetry 2) occur in the cavities of a framework of Na-polyhedra (Giacovazzo *et al.*, 1973). In  $\text{K}_2[\text{B}_4\text{O}_5(\text{OH})_4] \cdot 2\text{H}_2\text{O}$ , columns of K-polyhedra are linked by isolated tetraborate polyanions and water molecules (Marezio *et al.*, 1963). In the structure of  $\text{Rb}_2\text{SrB}_5\text{O}_{14} \cdot 12\text{H}_2\text{O}$ , two crystallographically-distinct hydrated tetraborate polyanions occur within eight-membered rings of Rb-polyhedra and Sr-octahedra (Ivchenko *et al.*, 1975). A partially-

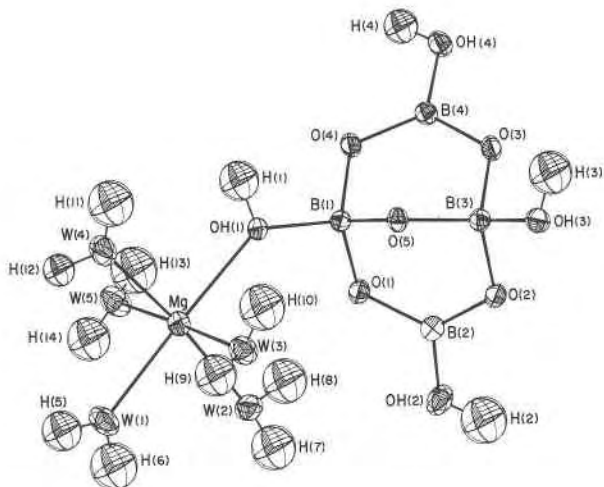


Fig. 5. The  $[\text{Mg}(\text{H}_2\text{O})_3\text{B}_4\text{O}_5(\text{OH})_4]$  complex in hungchaoite, showing the ellipsoids of thermal vibration.

hydrated isolated tetraborate polyanion,  $[\text{B}_4\text{O}_7(\text{OH})_2]^{4-}$  with point symmetry  $m$  occurs in roweite,  $\text{CaMn}_2(\text{OH})_4[\text{B}_4\text{O}_7(\text{OH})_2]_2$  (Moore and Araki, 1974).

Kernite,  $\text{Na}_2\text{B}_4\text{O}_6(\text{OH})_2 \cdot 3\text{H}_2\text{O}$ , contains borate chains (Giese, 1966; Cialdi *et al.*, 1967; Cooper *et al.*, 1973) formed by the polymerization of tetraborate polyanions:



(Christ and Garrels, 1959).

Anhydrous tetraborate polyanions,  $[\text{B}_4\text{O}_7]^{2-}$ , form two separate interpenetrating three-dimensional networks by sharing corners of borate triangles with corners of borate tetrahedra in  $\text{Li}_2\text{B}_4\text{O}_7$  (Krogh-Moe, 1968) and isostructural borates,  $\text{MgB}_4\text{O}_7$  (Bartl and Schuckmann, 1966),  $\text{CdB}_4\text{O}_7$  (Ihara and Krogh-Moe, 1971),  $\text{ZnB}_4\text{O}_7$  (Martinez-Ripoll *et al.*, 1971), and  $\text{MnB}_4\text{O}_7$  (Abrahams *et al.*, 1974).

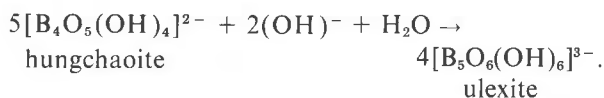
#### Molecular complexes involving borate polyanions

Molecular complexes of zero charge involving a borate polyanion and a hydrated metal cation, such as the one found in hungchaoite and in  $\text{MnB}_4\text{O}_7 \cdot 9\text{H}_2\text{O}$ , are relatively rare. A neutral molecular complex  $[\text{Mg}(\text{H}_2\text{O})_4\text{B}_3\text{O}_3(\text{OH})_5]$ , formed by a  $[\text{Mg}(\text{OH})_2(\text{H}_2\text{O})_4]$  octahedron sharing two tetrahedral (OH) corners of a triborate polyanion,  $[\text{B}_3\text{O}_3(\text{OH})_5]^{2-}$ , occurs in the structure of inderite (Corazza, 1976). Another magnesium borate, meallisterite,  $\text{Mg}_2[\text{B}_6\text{O}_7(\text{OH})_6]_2 \cdot 9\text{H}_2\text{O}$ , contains the molecular complex  $[\text{Mg}(\text{H}_2\text{O})_3\text{B}_6\text{O}_7(\text{OH})_6]$ , formed by a  $[\text{Mg}(\text{H}_2\text{O})_3(\text{OH})_3]^-$  octahedron sharing three tetrahe-

dral (OH) corners of a hexaborate polyanion,  $[\text{B}_6\text{O}_7(\text{OH})_6]^{2-}$  ( $6:3\Delta+3T$ ) (Dal Negro *et al.*, 1969).

#### Paragenesis of hungchaoite at Death Valley, California

At Death Valley, hungchaoite occurs in association with inderite, kurnakovite, and ulexite. The crystal structures of inderite and hungchaoite indicate that these two minerals have crystallized from aqueous solutions at relatively low temperatures. The crystal structure of kurnakovite consists of  $[\text{B}_3\text{O}_3(\text{OH})_5]^{2-}$  groups sharing (OH) corners with  $[\text{Mg}(\text{OH})_2(\text{H}_2\text{O})_4]$  octahedra, forming chains (Corazza, 1974). Ulexite contains the pentaborate polyanion  $[\text{B}_5\text{O}_6(\text{OH})_6]^{3-}$  sharing (OH) corners with edge-sharing chains of Ca-polyhedra and Na-octahedra (Clark and Appleman, 1964; Ghose *et al.*, 1977). In aqueous borate solutions in the pH range encountered under natural conditions, triborate, tetraborate, and pentaborate polyanions are present (Ingri, 1963), and one kind of polyanion can be readily derived from another. Following Christ *et al.* (1967), the transformation of hungchaoite to ulexite can be written in terms of the polyanions as:



So increasing pH will favor the formation of ulexite. The phase relations of the borate minerals will also depend on the type of cations present and their concentration in the aqueous solution.

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