

Crystal structure of hydrochlorborite, $\text{Ca}_2[\text{B}_3\text{O}_3(\text{OH})_4 \cdot \text{OB}(\text{OH})_3]\text{Cl} \cdot 7\text{H}_2\text{O}$, a seasonal evaporite mineral

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Abstract

The crystal structure of the rare playa mineral hydrochlorborite from the Salar Carcote, Antofagasta, Chile—the second world occurrence—has been solved by direct and difference Fourier methods and refined to a conventional R of 0.050, including hydrogen positions. Our crystal data agree with those previously reported (monoclinic, $I2/a$, $Z = 8$, $a = 22.783(3)$, $b = 8.745(1)$, $c = 17.066(1)\text{Å}$, $\beta = 96.705(1)^\circ$, $V = 3376.9(3)\text{Å}^3$, $G = 1.852$); however, our formula unit contains one less water molecule than previously assigned, resulting in a calculated density of 1.841 rather than 1.876 g cm^{-3} . The structure has isolated borate polyanions, each composed of two borate tetrahedra and one borate triangle, corner-linked to form a three-membered ring, with a side borate tetrahedron corner-linked to the triangle $[3:(2\text{T} + \Delta) + \text{T}]$; this group is unique among borate polyanions reported to date. The polyanions are cross-linked by hydrogen bonds to water molecules and by $\text{CaO}_2(\text{OH})_3(\text{H}_2\text{O})_3$ polyhedra, four of which share two corners and an edge to form four-membered chains. The most unusual feature of the structure involves the Cl anion, which is not bonded to Ca as expected, but instead is hydrogen-bonded to eight oxygens (three hydroxyls and five water molecules) at distances ranging from 3.182 to 3.395Å. To our knowledge, this is the largest number of hydrogens bonded to Cl reported to date in an inorganic structure. The average $\text{B}^{\text{III}}\text{-O}$, $\text{B}^{\text{IV}}\text{-O}$, $\text{Ca}^{\text{VIII}}\text{-O}$, and $\text{Cl}^{\text{VIII}}\text{-O}$ distances are 1.367, 1.474, 2.478, and 3.296Å, respectively. The good {001} cleavage and tabular morphology parallel to {001} are consistent with the structure, wherein slabs of composition $2\{\text{Ca}_2(\text{H}_2\text{O})_3[\text{B}_3\text{O}_3(\text{OH})_4 \cdot \text{OB}(\text{OH})_3]\}^{1+}$, which are parallel to {001}, are hydrogen-bonded to $[\text{Cl}(\text{H}_2\text{O})_3]^{1-}$ anions. This arrangement is also consistent with the mineral's reported slow solubility in water at 23°C and its observed seasonal nature. The formation of this mineral may result from a reaction between associated ulexite and halite when pH increases. However, its apparent rarity suggests that such a reaction takes place only under unusual circumstances.

Introduction

The playa mineral hydrochlorborite, $3\text{CaO} \cdot \text{CaCl}_2 \cdot 4\text{B}_2\text{O}_3 \cdot 21\text{H}_2\text{O}$, was first reported from China (Ch'ien and Chen, 1965; Ch'ien *et al.*, 1965), although no detailed locality information was given by these authors. In 1966, a second occurrence of this mineral was found in northern Chile. In this locality, hydrochlorborite is associated with ulexite, halite, and clay minerals. This occurrence was described by

Hurlbut *et al.* (1977), who also gave crystallographic, physical, optical and chemical data for the mineral. Among the more interesting observations made by Hurlbut *et al.* were the slow dissolution in water (at 23°C) and the seasonal nature of hydrochlorborite; the mineral apparently occurs in this locality only during the dry season of the year. In order to shed light on its slow rate of dissolution and to determine the structural role of water in this mineral, we under-

took the structure determination and refinement reported below. Our investigation shows that the chemical formula, $3\text{CaO} \cdot \text{CaCl}_2 \cdot 4\text{B}_2\text{O}_3 \cdot 22\text{H}_2\text{O}$, assigned by the studies reported above, has one water molecule too many, the correct formula having only 21 water molecules (Brown and Clark, 1977).

Experimental and computational details

The crystal selected for intensity measurements was provided by R. C. Erd, U. S. Geological Survey, and came from the Salar Carcote, Antofagasta, Chile, the locality described by Hurlbut *et al.* (1977). The specimen was prismatic, having $\{110\}$, $\{\bar{2}11\}$, and $\{001\}$ forms, and dimensions $0.15 \times 0.2 \times 0.2$ mm. The c^* axis of the crystal was oriented parallel to the ϕ -axis of a Picker FACS-I diffractometer, and the orientation was refined by least-squares fit of the angular coordinates of 35 automatically centered reflections in the 2θ range 30° to 40° . The resulting cell parameters [$a = 22.783(4)$, $b = 8.749(1)$, $c = 17.061(3)\text{Å}$, $\beta = 96.696(5)^\circ$, $V = 3377.5\text{Å}^3$] agree well with those reported by Hurlbut *et al.* [$a = 22.783(3)$, $b = 8.745(1)$, $c = 17.066(1)\text{Å}$, $\beta = 96.705(1)^\circ$, $V = 3376.9(3)\text{Å}^3$]; however, Hurlbut's values were used in all further calculations because of their higher precision. Space group $I2/a$, assigned by Hurlbut *et al.* on the basis of systematic absences on precession photographs and morphology, was assumed to be correct.

A total of 1441 nonzero symmetry independent intensities in the angular range 5° to 40° 2θ were measured using an ω - 2θ scan mode, a scan range of 2.0° plus the α_1 - α_2 dispersion, graphite monochromatized $\text{MoK}\alpha$ radiation, and a solid-state detection system. Two standard reflections, at 0° and 90° χ , were monitored every 30 reflections and showed no significant variation in integrated intensity during the 3 days required for data collection. Of the observed intensities, 188 were less than $3\sigma(I)$, where $\sigma(I)$ is the standard deviation of the intensity (I) as calculated using the formula of Corfield *et al.* (1967) and an instrumental instability constant of 0.04. These data were corrected for Lorentz and polarization factors, the latter assuming a 50 percent ideally mosaic monochromator crystal; no corrections were made for absorption ($\mu = 9.00 \text{ cm}^{-1}$, $\text{MoK}\alpha$) or extinction effects. After refinement was completed, no systematic discrepancies between strong observed and calculated structure factors were found, indicating that there were no serious extinction effects.

The resulting structure factors were converted to normalized structure factors, E , using programs from the University of Rochester Crystallographic Pro-

gram Library. For this calculation and the refinements discussed below, neutral atomic scattering factors were calculated by using the analytical expression and coefficients of Doyle and Turner (1968) and the anomalous dispersion values of Cromer and Liberman (1970); for hydrogen, the SDS coefficients given by Ibers and Hamilton (1974, Table 2.2B) were used. The chemical formula applied at this stage was the one reported by Hurlbut *et al.* (1977). The statistical distribution of $|E|$, E^2 , and $|E^2 - 1|$ confirmed the centrosymmetric space group $I2/a$. The signs of the three largest E -values were fixed as positive, and a set of the 100 largest and 50 ψ_0 E 's was used in the tangent formula program MULTAN (Main *et al.*, 1971) to search for solutions. The solution that had the best figure of merit proved to be the correct one and yielded an E -map having 40 major peaks. The 18 strongest peaks were assigned to the 2 calcium, 1 chlorine, and 16 of the 18 oxygen atoms of the asymmetric unit. Structure-factor calculations based on this assignment gave a conventional residual, R , of 0.260. The positions of the four borons and two remaining oxygens in the asymmetric unit were located by a three-dimensional difference Fourier synthesis and by study of a structure model. Two of the oxygen positions assigned using E -maps were incorrect; however, in retrospect, the E -maps from the correct MULTAN solution were found to show all nonhydrogen atoms of the asymmetric unit, plus several spurious ones.

Seven cycles of full-matrix isotropic refinement were computed using RFINE (Finger and Prince, 1975), resulting in a conventional, unweighted $R = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$ of 0.071. Twelve additional refinement cycles having anisotropic temperature factors reduced the unweighted R to 0.058 ($R = 0.073$, all data); 18 of the 1253 structure factors greater than $3\sigma_F$ were not included in the refinement because $|\Delta F|$ was larger than an arbitrary cutoff value. The average shift/error at this stage of refinement was 0.03. The structure model from the isotropic refinement was used to compute another three-dimensional difference Fourier synthesis, which, together with crystal chemical considerations, provided approximate locations for the 21 hydrogen atoms in the asymmetric unit. Six additional cycles of refinement were carried out in which positional parameters and an isotropic thermal parameter of each hydrogen were allowed to vary, and the positional and anisotropic thermal parameters of the 25 nonhydrogen atoms were fixed at their refined values after cycle 19. The final unweighted R was 0.050 for the 1244 observed data

with F greater than $3\sigma_F$; nine observations were excluded from these cycles because of poor fit. The final unweighted R for all 1441 data was 0.063. A final three-dimensional difference Fourier was featureless, confirming that the chemical formula is indeed $\text{Ca}_4\text{B}_8\text{O}_{16}\text{Cl}_2 \cdot 21\text{H}_2\text{O}$.

The final positional parameters, isotropic temper-

ature factors for all atoms in the asymmetric unit, and anisotropic thermal parameters for all non-hydrogen atoms are listed in Table 1, together with the estimated standard error of each parameter. Observed and calculated structure factors from the final cycle of refinement (cycle 25) are compared in Table 2, and the orientations and dimensions of the thermal

Table 1. Atomic coordinates and thermal parameters for hydrochlorborite

Atom	Structural role ¹	Coordinates ²			Equivalent isotropic B (\AA^2)	Thermal parameters $\times 10^4$ ³					
		x	y	z		β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ca(1)		0.03304(8)	0.1717(2)	0.1619(1)	1.14(4)	7.5(4)	31(3)	8.6(7)	-2.0(9)	2.4(4)	1(1)
Ca(2)		0.21377(8)	0.0575(2)	0.2956(1)	1.14(4)	6.8(4)	38(3)	8.1(7)	0.5(8)	2.3(4)	2(1)
B(1)	ring T(1)	0.1592(4)	0.3150(11)	0.1914(6)	0.8(2)	5(2)	31(16)	5(4)	-4(5)	1(2)	6(6)
B(2)	ring T(2)	0.1897(5)	0.4666(12)	0.3166(6)	1.5(2)	9(3)	44(17)	11(5)	-4(6)	3(3)	5(7)
B(3)	ring Δ	0.0884(4)	0.4902(11)	0.2469(6)	0.8(2)	4(3)	0	14(4)	-1(5)	2(3)	7(7)
B(4)	side T(4)	-0.0107(4)	0.5596(12)	0.1714(6)	1.1(2)	5(2)	44(16)	10(4)	1(5)	1(3)	1(7)
Cl		0.1335(1)	0.6356(3)	0.0084(1)	2.09(5)	12.8(6)	68(4)	14.1(9)	5(1)	2.6(6)	2(2)
O(1)	T(1)-T(2)	0.1939(2)	0.3289(6)	0.2693(3)	1.1(1)	8(1)	36(9)	5(2)	2(3)	0(1)	-1(4)
O(2)	T(1)- Δ	0.1007(2)	0.3904(6)	0.1885(3)	0.8(1)	5(1)	40(9)	1(2)	7(3)	-1(1)	-1(3)
O(3)	T(2)- Δ	0.1293(2)	0.5301(7)	0.3076(3)	1.6(1)	5(1)	68(10)	14(2)	7(3)	-3(1)	-14(4)
O(4)	Δ -T(4)	0.0336(2)	0.5556(7)	0.2414(3)	1.6(1)	8(1)	49(9)	13(2)	2(3)	3(1)	-15(4)
OH(1)	T(1)	0.1475(2)	0.1498(6)	0.1803(3)	1.1(1)	10(1)	27(8)	5(2)	-3(3)	3(1)	-9(4)
OH(2)	T(1)	0.1934(2)	0.3764(6)	0.1312(3)	1.4(1)	8(1)	54(9)	8(2)	-1(3)	4(1)	0(4)
OH(3)	T(2)	0.2056(2)	0.4355(7)	0.4012(3)	1.4(1)	11(1)	54(9)	3(2)	1(3)	0(1)	-2(4)
OH(4)	T(2)	0.2318(2)	0.5793(7)	0.2887(3)	1.6(1)	9(1)	58(9)	10(2)	-4(3)	4(1)	-2(4)
OH(5)	T(4)	-0.0575(2)	0.6534(7)	0.1975(3)	1.7(1)	8(1)	71(10)	13(2)	-6(3)	3(1)	13(4)
OH(6)	T(4)	-0.0302(2)	0.4001(7)	0.1507(3)	1.7(1)	8(1)	47(9)	17(2)	-1(3)	1(1)	8(4)
OH(7)	T(4)	0.0110(3)	0.6323(7)	0.1021(3)	1.6(1)	12(1)	51(9)	8(2)	-3(3)	3(1)	6(4)
H ₂ O(1)		0.0547(3)	0.2142(8)	0.0269(3)	2.8(1)	19(2)	103(11)	13(2)	8(4)	7(2)	9(4)
H ₂ O(2)		0.0610(3)	0.9145(7)	0.1354(4)	2.3(1)	14(2)	52(10)	22(3)	-4(3)	2(2)	-9(4)
H ₂ O(3)		0.0561(2)	0.5759(7)	0.4218(3)	2.1(1)	10(1)	98(11)	12(2)	7(3)	4(1)	-3(4)
H ₂ O(4)		0.2379(3)	-0.1601(7)	0.3917(3)	2.0(1)	12(2)	64(10)	13(2)	-1(3)	0(1)	2(4)
H ₂ O(5)		0.1358(3)	0.8585(7)	0.2767(3)	2.1(1)	11(1)	46(10)	23(3)	0(3)	0(2)	6(4)
H ₂ O(6)		0.1637(3)	0.1488(7)	0.4039(3)	2.1(1)	16(1)	62(10)	11(2)	-1(3)	7(2)	2(4)
H ₂ O(7)		0.1745(3)	0.9943(7)	0.0443(3)	2.5(1)	14(2)	101(11)	12(2)	-5(3)	4(2)	-8(4)
H(1)	OH(1)	0.158(5)	0.120(15)	0.147(7)	4(3)						
H(2)	OH(2)	0.159(6)	0.431(16)	0.096(8)	6(3)						
H(3)	OH(3)	0.245(5)	0.451(12)	0.418(6)	1(2)						
H(4)	OH(4)	0.242(4)	0.668(11)	0.328(5)	1(2)						
H(5)	OH(5)	-0.103(7)	0.670(16)	0.153(9)	9(5)						
H(6)	OH(6)	-0.061(6)	0.379(16)	0.102(8)	6(4)						
H(7)	OH(7)	0.050(5)	0.570(13)	0.088(6)	3(2)						
H(8)	H ₂ O(1)	0.064(8)	0.158(16)	0.003(9)	11(7)						
H(9)	H ₂ O(1)	0.038(5)	0.257(14)	-0.003(7)	3(3)						
H(10)	H ₂ O(2)	0.037(6)	0.813(16)	0.117(8)	7(4)						
H(11)	H ₂ O(2)	0.098(6)	0.877(16)	0.160(8)	5(3)						
H(12)	H ₂ O(3)	0.086(4)	0.564(12)	0.385(6)	1(2)						
H(13)	H ₂ O(3)	0.079(6)	0.633(17)	0.456(8)	5(3)						
H(14)	H ₂ O(4)	0.211(6)	-0.173(16)	0.423(8)	5(3)						
H(15)	H ₂ O(4)	0.277(5)	-0.183(13)	0.422(6)	2(2)						
H(16)	H ₂ O(5)	0.142(9)	0.785(16)	0.277(8)	15(7)						
H(17)	H ₂ O(5)	0.093(6)	0.845(16)	0.294(8)	8(4)						
H(18)	H ₂ O(6)	0.157(5)	0.111(15)	0.440(8)	3(2)						
H(19)	H ₂ O(6)	0.174(6)	0.241(18)	0.409(8)	4(3)						
H(20)	H ₂ O(7)	0.185(6)	1.048(16)	0.004(8)	8(4)						
H(21)	H ₂ O(7)	0.158(8)	0.907(16)	0.046(8)	14(6)						

¹See Fig. 1. T = tetrahedron, Δ = triangle, T-T = linking one tetrahedron to another, etc. H atoms are associated with the OH or H₂O as noted.

²Number in parentheses is one standard deviation; for 0.03304(8), read 0.03304 \pm 0.00008, for 0.3150(11), read 0.3150 \pm 0.0011, etc.

³Thermal parameters in the expression, $\exp \left\{ \sum_{i=1}^3 \sum_{j=1}^3 \left[\frac{h_i h_j}{n_i n_j} \beta_{ij} \right] \right\}$. The thermal ellipsoid of B(3) was nonpositive definite, so β_{22} was arbitrarily set at 0.

Table 4. Bond distances and angles in the borate polyanion of hydrochlorborite

Atoms ¹	Distance ² (Å)	Atoms ¹	Distance ² (Å)	Atoms ¹	Distance ² (Å)	Atoms ¹	Distance ² (Å)
B(1)-O(1)	1.470(11)	O(1)-O(2)	2.453(7)	B(4)-O(4)	1.471(11)	O(4)-OH(5)	2.289(8)
-O(2)	1.483(11)	O(1)-OH(1)	2.346(7)	-OH(5)	1.455(11)	O(4)-OH(6)	2.414(8)
-OH(1)	1.477(11)	O(1)-OH(2)	2.393(7)	-OH(6)	1.494(12)	O(4)-OH(7)	2.466(8)
-OH(2)	1.464(11)	O(2)-OH(1)	2.370(7)	-OH(7)	1.478(11)	OH(5)-OH(6)	2.459(8)
		O(2)-OH(2)	2.433(7)			OH(5)-OH(7)	2.389(8)
		OH(1)-OH(2)	2.436(7)			OH(6)-OH(7)	2.423(8)
average	1.474	average	2.405	average	1.474	average	2.407
B(2)-O(1)	1.459(12)	O(1)-O(3)	2.431(7)	B(3)-O(2)	1.378(11)	O(2)-O(3)	2.396(7)
-O(3)	1.476(12)	O(1)-OH(3)	2.421(7)	-O(3)	1.356(11)	O(2)-O(4)	2.358(7)
-OH(3)	1.471(11)	O(1)-OH(4)	2.364(8)	-O(4)	1.366(11)	O(3)-O(4)	2.346(7)
-OH(4)	1.491(12)	O(3)-OH(3)	2.368(7)	average	1.367	average	2.367
		O(3)-OH(4)	2.432(7)	B(1)-B(2)	2.541(14)		
		OH(3)-OH(4)	2.427(8)	B(1)-B(3)	2.490(14)		
average	1.474	average	2.407	B(2)-B(3)	2.480(14)		
average of 12	1.474	average of 18	2.406	B(4)-B(3)	2.539(14)		
				average	2.512		

Central atom	Other atoms	Angle (°)	Central atom	Other atoms	Angle (°)
B(1)	O(1), O(2)	112.4(7)	B(4)	O(4), OH(5)	102.9(7)
	O(1), OH(1)	105.5(7)		O(4), OH(6)	109.1(7)
	O(1), OH(2)	109.3(7)		O(4), OH(7)	113.4(7)
	O(2), OH(1)	106.4(7)		OH(5), OH(6)	113.0(7)
	O(2), OH(2)	111.3(7)		OH(5), OH(7)	109.1(7)
	OH(1), OH(2)	111.8(7)		OH(6), OH(7)	109.3(7)
	average	109.4		average	109.5
B(2)	O(1), O(3)	111.8(7)	B(3)	O(2), O(3)	122.4(8)
	O(1), OH(3)	111.5(7)		O(2), O(4)	118.5(8)
	O(1), OH(4)	106.5(7)		O(3), O(4)	119.0(8)
	O(3), OH(3)	106.9(7)		Σ	359.9
	O(3), OH(4)	110.1(7)			
	OH(3), OH(4)	110.0(7)			
	average	109.5			
O(1)	B(1), B(2)	120.4(7)	O(3)	B(2), B(3)	122.2(7)
O(2)	B(1), B(3)	121.0(6)	O(4)	B(3), B(4)	127.0(7)

¹All atoms at x, y, z (Table 1)

²Number in parentheses is one standard deviation; for 1.470(11), read 1.470±0.011 Å, etc.

vibration ellipsoids for calcium, chlorine, and oxygens, calculated using L. W. Finger's unpublished ERROR program, are given in Table 3¹.

The distances, angles, and associated standard errors for the borate polyanion and Ca polyhedra re-

ported in Tables 4 and 5 were calculated using ERROR and the refined boron, calcium, and oxygen positions and variance-covariance matrix from refinement cycle 25. Several additional cycles of refinement were carried out during which the positional and anisotropic thermal parameters of all cations were fixed at their refined values and the positional and thermal parameters of chlorine, oxygens, and hydrogens were allowed to vary. The resulting positional parameters and variance-covariance matrix were used to com-

¹To receive copies of Tables 2 and 3, order Document AM-78-087 from the Business Office, Mineralogical Society of America, 1909 K Street, NW, Washington, DC 20006. Please remit \$1.00 in advance for the microfiche.

Table 5. Bond distances and angles for the Ca polyhedra in hydrochlorborite

Ca atom	Oxygen atom ¹	Distance ² (Å)	Polyhedral edges		Comment ¹	O-Ca-O angle ³ (°)	Polyhedral edges		O-Ca-O angle ³ (°)
			Oxygen atoms	Distance ² (Å)			Oxygen atoms	Distance ² (Å)	
1	H ₂ O(2): x, y-1, z	2.395(6)	O(2)-OH(1)	* 2.370(7)	Edge of T(1)	* 55.8	O(4)-O(2)	4.496(7)	126.1
	OH(5): \bar{x} , y- $\frac{1}{2}$, $\frac{1}{2}$ -z	2.405(6)	OH(1)-H ₂ O(2)	* 2.891(8)		* 70.6	-OH(1)	4.558(7)	123.5
	H ₂ O(1)	2.440(6)	H ₂ O(2)-H ₂ O(3)	* 3.074(9)		* 78.0	-H ₂ O(2)	* 3.413(8)	* 86.6
	OH(6)	2.457(6)	H ₂ O(3)-OH(6)	* 3.122(8)		* 78.3	-H ₂ O(3)	* 3.067(7)	* 74.5
	O(2)	2.465(5)	OH(6)-O(2)	* 2.977(7)		* 74.4	-OH(6)	* 3.537(8)	* 89.2
	H ₂ O(3): \bar{x} , $\frac{1}{2}$ +y, $\frac{1}{2}$ -z	2.487(6)	average of 5	2.887		71.4	average of 5	3.814	100.0
	O(4): \bar{x} , y- $\frac{1}{2}$, $\frac{1}{2}$ -z	2.579(6)	OH(5)-O(2)	* 3.081(7)		* 78.5	H ₂ O(1)-O(2)	* 3.225(8)	* 82.2
	OH(1)	2.597(6)	-OH(1)	* 3.091(7)		* 76.2	-OH(1)	* 3.217(8)	* 79.3
	average of 8	2.478	-H ₂ O(2)	3.544(8)		95.2	-H ₂ O(2)*	3.202(9)	* 83.0
			-H ₂ O(3)	4.416(8)		129.0	-H ₂ O(3)*	3.019(8)	* 75.6
2	OH(4): $\frac{1}{2}$ -x, $\frac{1}{2}$ -y, $\frac{1}{2}$ -z	2.336(6)	average of 5	3.579		96.0	average of 5	3.220	81.8
	OH(2): $\frac{1}{2}$ -x, $\frac{1}{2}$ -y, $\frac{1}{2}$ -z	2.398(6)	OH(5)-O(4)	* 2.289(3)	Edge of T(4) ¹	* 54.6	average of *16	3.063	76.6
	H ₂ O(6)	2.419(6)	OH(5)-H ₂ O(1)	4.727(8)		154.6			
	O(1)	2.448(6)	O(4)-H ₂ O(1)	4.844(8)		149.7			
	OH(1)	2.471(5)	O(1)-OH(1)	2.346(7)	Edge of T(1)	57.0	H ₂ O(6)-O(1)	2.932(8)	74.1
	H ₂ O(5): x, y-1, z	2.480(6)	OH(1)-H ₂ O(5)	3.060(8)		76.4	-OH(1)	3.791(7)	101.6
	H ₂ O(4)	2.530(6)	H ₂ O(5)-H ₂ O(4)	2.867(8)		69.8	-H ₂ O(5)	3.352(8)	86.4
	O(1) ¹ : $\frac{1}{2}$ -x, $\frac{1}{2}$ -y, $\frac{1}{2}$ -z	2.681(5)	H ₂ O(4)-OH(2)	2.983(8)		74.4	-H ₂ O(4)	3.206(8)	80.7
			OH(2)-O(1) ¹	2.393(7)	Edge of T(1) ¹	55.9	-OH(2)	3.385(5)	89.3
			average of 6	3.045(10)	Edge shared with Ca(2) ¹ polyhedron	72.7	-O(1) ¹	4.642(8)	131.0
Ca-Ca distances	average of 8	2.470	average of 6	2.782		67.7	average of 6	3.551	93.8
	Ca(1)-Ca(2)	4.579(2)	OH(4)-O(1)	4.121(8)		119.0	average of 18	3.212	83.1
	Ca(2)-Ca(2) ¹	4.133(3)	-OH(1)	3.394(8)		89.8			
	$\frac{1}{2}$ -x, $\frac{1}{2}$ -y, $\frac{1}{2}$ -z		-H ₂ O(5)	3.380(8)		89.1			
	Ca-O-Ca angles ³		-H ₂ O(4)	3.309(8)		85.6			
	Ca(1)-OH(1)-Ca(2)	129.2°	-OH(2)	3.255(8)		86.9			
	Ca(2)-O(1)-Ca(2) ¹	107.3°	-O(1) ¹	2.364(8)	Edge of T(2) ¹	55.7			
			average of 6	3.304		87.7			
			OH(4)-H ₂ O(6)	4.721(8)		166.3			

¹All atoms at x, y, z (Table 1) unless trans-
formed as noted. See Figs. 1, 3 for coordination.
T(1) refers to tetrahedron B(1), T(1)¹, and T(2)¹;
to tetrahedra B(1) and B(2) located at $\frac{1}{2}$ -x, $\frac{1}{2}$ -y,
 $\frac{1}{2}$ -z, and T(4)¹ to tetrahedron B(4) located at
-x, y- $\frac{1}{2}$, $\frac{1}{2}$ -z.

²Number in parentheses is one standard deviation;
for 2.395(6), read 2.395 ± 0.006Å, etc.

³One standard deviation for all angles is ±0.2°.

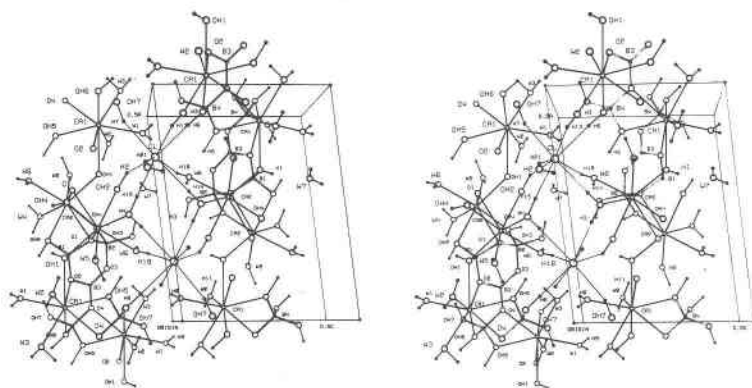


Fig. 1. Stereoscopic-pair view (+*b* towards reader) of selected portions of the hydrochlorborite structure with spheres of arbitrary size for atoms, showing the Cl-H bonding, some Ca-O polyhedral chains, and the borate polyanions. The O...H bonds are not drawn, but most can be noted with reference to Table 6. Drawing from ORTEP (Johnson, 1965).

pute the H-O, H-Cl, H...O, H...Cl, and Cl...O distances and associated errors reported in Table 6. Because the errors associated with the H positions and these bond lengths are relatively large, the reported H positions and distances involving H should be considered as approximate. The large errors are due in part to the fact that our intensity data extend only to $40^\circ 2\theta$ and the number of parameters to be refined is large compared with the number of data available.

Structural description

As shown by the stereographic-pair view in Figure 1, the structure of hydrochlorborite consists of isolated borate polyanions which are linked to each other by Ca polyhedra and hydrogen bonding to

form slabs stacked sandwich-like along *c*. These slabs are held to each other by hydrogen bonding to Cl anions. The Cl anions do not coordinate Ca, as was expected, but instead are held in the structure by eight hydrogen bonds to oxygens. The Ca polyhedra are linked together in groups of four through the sharing of two corners and an edge to form short chains approximately parallel to *a*; these groups do not link to form infinite chains parallel to *b* as previously suggested in the preliminary report of this work (Brown and Clark, 1977).

The borate polyanion

Each polyanion is formed by corner-sharing among two borate tetrahedra and a triangle, producing a triborate ring. This triborate polyanion type is the most frequently reported in borate structures studied to date and has been given the notation $3:(2T + \Delta)$ by Christ and Clark (1977). However, in hydrochlorborite, this basic unit is modified by attachment of a tetrahedron to the non-ring oxygen of the borate triangle (Fig. 2), and the notation becomes $3:(2T + \Delta) + T$. This is the first such modification to the $3:(2T + \Delta)$ polyanion reported to date².

The only other modified triborate group known at this time is the $3:(3T) + T$ polyanion in the structure of uralborite, $\text{Ca}_2[\text{B}_3\text{O}_3(\text{OH})_5 \cdot \text{OB}(\text{OH})_3]$ (Shashkin *et al.*, 1970; Simonov *et al.*, 1977; Christ and Clark, 1977). Ten other borate structures having the isolated, unmodified $3:(2T + \Delta)$ polyanion have been discussed by Christ and Clark (1977).

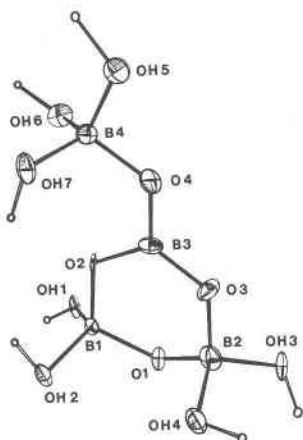


Fig. 2. View along *b* of one $[\text{B}_3\text{O}_3(\text{OH})_4 \cdot \text{OB}(\text{OH})_3]^{9-}$ polyanion in hydrochlorborite, *c* approximately horizontal, thermal ellipsoids of 50 percent probability except for unlabelled hydrogen atoms (spheres of arbitrary size). Drawing from ORTEP (Johnson, 1965).

² Modification by attachment of a triangle, $3:(2T + \Delta) + \Delta$, was reported in the structure of a synthetic magnesium borate $\text{MgB}_4\text{O}_7 \cdot 9\text{H}_2\text{O}$ (Abdullaev and Mamedov, 1969), but the structure is probably wrong (Wan and Ghose, 1977).

In hydrochlorborite, B(3) is trigonally coordinated by oxygen anions which lie approximately in a plane with B(3) at an average distance of 1.367Å. This average B^{III}-O distance is considerably shorter than the average B^{IV}-O distance of 1.474Å for the three borate tetrahedra. The shorter B^{III}-O bonds are presumably related to the stabilization of the $1a_2'$ and $3e'$ molecular orbitals of [BO₃]³⁻, which are composed of boron 2*p* and oxygen 2*p* atomic orbitals, relative to the 3*t*₂ molecular orbital of [BO₄]⁵⁻ (Vaughan and Tossell, 1973). The B(1)^{IV}-O(2)-B(3)^{III}-O(3)-B(2)^{IV}-O(1) ring is essentially planar except for puckering of the B(1)-O(1)-B(2) linkage. The angle from the ring to the attached tetrahedron, B(4)^{IV}-O(4)-B(3)^{III}, is 127.0°, somewhat larger than the average B-O-B angle of 121.2° within the ring. The experimental location of protons in this hydrated borate is in complete agreement with the rules of Christ and Clark (1977). Those oxygens attached to only one boron add a proton to form hydroxyl ion, and all oxygens not associated with the borate polyanion are doubly protonated, forming water molecules. As might be expected, the equivalent isotropic temperature factors for oxygen and hydroxyl ions are significantly lower than those for the water molecules (Table 1).

The calcium polyhedra

The two crystallographically distinct Ca cations, Ca(1) and Ca(2), are each coordinated by two oxygens, three hydroxyls, and three water molecules at distances ranging from 2.336 to 2.681Å (Table 5), the grand mean Ca^{VIII}-O distance being 2.474Å. Each polyhedron shares two O-O edges with borate tetrahedra, averaging 2.350Å in length relative to the unshared edges, which average 3.236Å. As expected, the O-Ca-O angles opposite shared edges are narrower than those opposite unshared edges; the cation-cation repulsions across shared edges result in significant distortions of the polyhedra. Two Ca(2) poly-

hedra share an O-O edge, 3.045Å, and each shares a corner with a Ca(1) polyhedron so that a four-membered chain is formed, oriented approximately parallel to *a* (Fig. 3). These chains are joined to others through borate polyanions to form ribbons parallel to *a*. Adjacent ribbons are joined together through hydrogen bonding to form slabs that are oriented parallel to {001}.

Chlorine coordination and hydrogen bonding

The Cl anion is hydrogen-bonded to eight oxygens, five associated with water molecules and three with hydroxyls, all at distances ranging from 3.182 to 3.395Å, the average Cl^{VIII}-O distance being 3.296Å (Table 6). The eight H...Cl distances average 2.43Å, a value that agrees reasonably well with two H...Cl distances of 2.41 and 2.49Å reported in the structure of hilgardite (Ghose and Wan, 1978). The occurrence of six hydrogen bonds to chlorine has been reported in several structures, but, to our knowledge, hydrochlorborite is the first inorganic structure in which as many as eight H...Cl bonds occur. Its average O...Cl distance is somewhat longer than the average of 3.194Å reported for six O...Cl in MgCl₂·12H₂O (Sasvari and Jeffrey, 1966) where that chlorine does not coordinate to Mg but is hydrogen-bonded only.

The Cl(OH)₃(H₂O)₅ polyhedra in hydrochlorborite occur as isolated pairs, sharing an edge, H₂O(4)-H₂O(4)', the long axis of the dimer being oriented along *a* (Fig. 1). These dimers connect the slabs of borate polyanions and Ca-polyhedral chains discussed earlier, literally holding the structure together through Cl...H-O linkages.

Each proton in hydrochlorborite is bonded to only one other anion, either chlorine or oxygen, in addition to its own associated hydroxyl- or water-oxygen atom. Of the 13 hydrogen bonds to water oxygens (Table 6), 2 can be considered strong, O...O < 2.7Å, and 11 weak, O...O > 2.7Å. Of the latter, only one must be considered very weak, *i.e.* > 3.0Å.

The seven water molecules can be classified following the scheme devised by Chidambaram *et al.* (1964) and modified by Ferraris and Franchini-Angela (1972), which is based on the coordination of lone-pair orbitals on the water oxygens. H₂O(1), H₂O(2), and H₂O(5) each have one Ca cation oriented approximately along the bisectrix of the lone-pair orbitals on the water oxygen, and hence are classified as 1D. H₂O(3), H₂O(4), and H₂O(6) each bond to one Ca cation and accept one hydrogen bond, both lying along the lone-pair orbitals, and so are classified as 2H water molecules. The seventh water molecule,

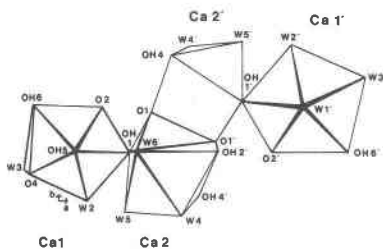


Fig. 3. An isolated four-membered chain of calcium polyhedra sharing corners and an edge in hydrochlorborite, viewed along *c*. Adapted from a drawing of ORTEP (Johnson, 1965).

Table 6. Hydrogen bonds in hydrochlorborite

Donor oxygen atom	Hydrogen atom of donor	Acceptor atom ¹	Distance ² (Å)			Angle ² (°)
			O···O	O-H	H···O	O-H···O
H ₂ O(6)	H(19)	OH(3)	2.685(9)	0.85(15)	1.85(15)	168(13)
H ₂ O(7)	H(20)	OH(3): $x, \frac{3}{2}-y, \frac{1}{2}-z$	2.693(8)	0.88(13)	1.88(13)	152(13)
	average	2 strong bonds	2.689	0.86	1.86	160
H ₂ O(3)	H(12)	O(3)	2.740(8)	1.00(10)	1.75(11)	170(8)
H ₂ O(2)	H(10)	OH(7)	2.749(8)	1.07(13)	1.70(13)	168(13)
OH(5)	H(5)	H ₂ O(6): $\bar{x}, \frac{1}{2}+y, \frac{1}{2}-z$	2.805(8)	1.21(13)	1.61(13)	166(13)
OH(1)	H(1)	H ₂ O(7): $x, y-1, z$	2.819(8)	0.69(12)	2.14(13)	167(13)
H ₂ O(2)	H(11)	H ₂ O(5)	2.829(8)	0.96(13)	2.07(13)	134(11)
OH(3)	H(3)	H ₂ O(7): $\frac{1}{2}-x, \frac{3}{2}-y, \frac{1}{2}-z$	2.847(8)	0.92(10)	1.93(10)	174(10)
H ₂ O(5)	H(17)	OH(6): $\bar{x}, y+\frac{1}{2}, \frac{1}{2}-z$	2.856(8)	1.06(13)	1.87(13)	153(13)
H ₂ O(1)	H(9)	OH(7): $\bar{x}, 1-y, \bar{z}$	2.849(8)	0.72(12)	2.14(12)	174(12)
OH(4)	H(4)	H ₂ O(4): $x, y+1, z$	2.871(8)	1.03(10)	1.87(10)	163(7)
H ₂ O(5)	H(16)	O(3)	2.927(8)	0.66(13)	2.32(13)	155(13)
	average	10 bonds	2.829	0.93	1.94	162
H ₂ O(1)	H(8)	H ₂ O(3): $x, \frac{1}{2}-y, \bar{x}-\frac{1}{2}$	3.109(9)	0.69(13)	2.46(13)	157(13)
	average	all 13 bonds	2.829	0.90	1.97	162
			O···Cl	O-H	H···Cl	O-H···Cl
H ₂ O(6)	H(18)	Cl: $x, \frac{1}{2}-y, \frac{1}{2}+z$	3.182(6)	0.74(13)	2.53(14)	148(13)
H ₂ O(4)	H(14)	Cl: $x, \frac{1}{2}-y, \frac{1}{2}+z$	3.220(6)	0.88(14)	2.43(14)	165(12)
OH(2)	H(2)	Cl	3.274(6)	1.05(14)	2.36(14)	145(10)
H ₂ O(4)	H(15)	Cl: $\frac{1}{2}-x, \frac{1}{2}-y, \frac{1}{2}-z$	3.283(6)	1.00(11)	2.27(11)	158(9)
H ₂ O(3)	H(13)	Cl: $x, \frac{3}{2}-y, \frac{1}{2}+z$	3.325(7)	0.90(15)	2.48(15)	157(12)
H ₂ O(7)	H(21)	Cl	3.310(7)	0.85(15)	2.50(15)	158(13)
OH(7)	H(7)	Cl	3.376(6)	1.10(11)	2.52(11)	134(8)
OH(6)	H(6)	Cl: $\bar{x}, 1-y, \bar{z}$	3.395(6)	1.04(15)	2.36(15)	173(13)
	average	8 bonds	3.296	0.94	2.43	155
next nearest neighbor, H ₂ O(2)		Cl	3.769(6)			

¹Atoms at x, y, z (Table 1) unless transformed as noted.

²Number in parentheses is one standard deviation for 2.685(9), read 2.685 ± 0.009 Å; for 1.85(15), read 1.85 ± 0.15 Å, etc.

H₂O(7), has two hydrogen acceptor atoms forming bonds along the lone-pair orbitals and so is of Class 2E.

The relative importance of hydrogen bonding in this structure is illustrated by the contribution of hydrogen to the bond strength summations for the oxygen atoms (Table 7). Because large errors are

associated with the hydrogen positions, as discussed earlier, the bond strengths involving hydrogen have been obtained using the O···O distances and the associated bond strengths proposed by Zachariasen (1963), recently shown to be the best available method for evaluating hydrogen bonding in borate structures (Ghose *et al.*, 1978). However, to our

Table 7. Bond strengths (s) in hydrochlorborite

Anion	Σs (valence units)				
	B-O	Ca-O	O-H	O...O	Σ
O(1)	1.54	0.44	—	—	1.98
O(2)	1.71	0.25	—	—	1.96
O(3)	1.77	—	—	0.38	2.15
O(4)	1.76	0.22	—	—	1.98
OH(1)	0.74	0.46	0.80	—	2.00
OH(2)	0.77	0.27	0.88	—	1.92
OH(3)	0.76	—	0.81	0.51	2.08
OH(4)	0.72	0.30	0.82	—	1.84
OH(5)	0.79	0.28	0.80	—	1.87
OH(6)	0.71	0.26	0.88	0.18	2.03
OH(7)	0.74	—	0.88	0.43	2.05
H ₂ O(1)	—	0.26	1.73	—	1.99
H ₂ O(2)	—	0.28	1.56	—	1.84
H ₂ O(3)	—	0.25	1.65	0.09	1.99
H ₂ O(4)	—	0.23	1.75	0.17	2.15
H ₂ O(5)	—	0.25	1.66	0.19	2.10
H ₂ O(6)	—	0.27	1.62	0.20	2.09
H ₂ O(7)	—	—	1.62	0.38	2.00
Cl	—	—	—	—	1.00

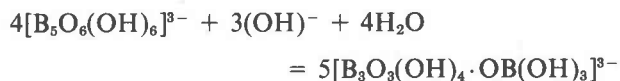
Bond strengths obtained as follows:
 (1) B-O, Ca-O—Donnay and Allmann (1970); Brown and Shannon (1973)
 (2) O...O—Zachariassen (1963, Table 9, assuming s for O-H = 1 - s for O...O)
 (3) O...Cl, assuming s = 0.125 for each of 8 O...Cl and associated O-H s = 0.875

knowledge, no Cl...O bond strength-bond length relationship has been proposed. Therefore, we have assumed that a reasonable Cl...H strength is approximately 0.125 valence units in the present case, although obviously this value should vary somewhat with distance. Using this value and assuming the balance, 0.875 v.u., for the associated H-O bond strength, summations ranging from 1.84 to 2.15 are obtained for the oxygen atoms (Table 7). Considering the assumptions involved, these values seem satisfactory and do confirm the importance of hydrogen bonds in this structure and their correct assignment as acceptor and donor.

Relationship of crystal structure to cleavage, morphology, solubility, and paragenesis of hydrochlorborite

The good {001} cleavage, tabular morphology parallel to {001}, slow dissolution in water at 23°C, and the reported seasonal nature of this evaporite mineral can be rationalized in terms of the crystal structure which consists of slabs of composition $2\{Ca_2(H_2O)_3[B_3O_3(OH)_4 \cdot OB(OH)_3]\}^{1+}$, oriented parallel to {001} and bonded through hydrogen to $[Cl(H_2O)_5]^{1-}$ anions. Water apparently breaks these hydrogen bonds and conceivably those holding together the ribbons of borate polyanions and four-membered Ca polyhedral chains parallel to *a*. Hurl-

but *et al.* (1977) suggested that when the water table in the Salar Carcote intersects the clay layer containing crystals of hydrochlorborite, these crystals dissolve. A mechanism for the reformation of hydrochlorborite as the water table drops could involve the simple type of polyanion equilibrium suggested by Christ *et al.* (1967) to explain transformations with changing pH and activity of H₂O among hydrated Na, Ca, and Mg borate minerals. The association of hydrochlorborite with ulexite, NaCa[B₅O₆(OH)₆]·5H₂O, and halite permits the following hypothesis. If we assume that total boron in the system remains constant but that the activities of Na⁺, Ca²⁺, H⁺, Cl⁻, and H₂O can be varied independently, following the suggestions by Christ *et al.*, the transformation between ulexite and hydrochlorborite may be expressed in terms of the polyanions as



This reaction suggests that increasing pH in the presence of halite and water favors the formation of hydrochlorborite from ulexite. However, the apparent rarity of this mineral also suggests that other unaccounted-for factors may prevent or invalidate this simple reaction.

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