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Ulexite, $NaCaB_5O_6(OH)_6 \cdot 5H_2O$: structure refinement, polyanion configuration, hydrogen bonding, and fiber optics

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Abstract

The crystal structure of ulexite, $NaCaB_5O_6(OH)_6 \cdot 5H_2O$, triclinic, $P\bar{1}$, has been refined to a conventional $R = 0.046$ using least-squares methods, partially block-diagonal, for 4911 reflections collected on a single-crystal diffractometer with graphite-monochromatized Mo radiation. All 16 hydrogen atoms in the asymmetric unit were located, and all form hydrogen bonds. Refined cell constants are: $a = 8.816(3)$, $b = 12.870(7)$, $c = 6.678(1)$ A, $\alpha = 90.36(2)°$, $\beta = 109.05(2)°$, $\gamma = 104.98(4)°$, $V = 688.4(4)$ A^3, $Z = 2$, density (calc) = 1.955 g/cm^3. The structure contains isolated pentaborate-type polyanions composed of three tetrahedra and two triangles, plus chains of Na octahedra and chains of Ca polyhedra, all cross-linked by polyanion bonds to the cations and by a network of hydrogen bonds. Average bond distances (A) are: B–O, tetrahedral 1.475, triangular 1.367; Na–O, 2.421; Ca–O, 2.484; hydrogen bonds, O–H 0.80, H···O 2.08, O···O 2.852. The octahedral and polyhedral chains are parallel to *c*, the elongation direction, and cause the fibrous habit of ulexite crystals that is essential to the optical fiber bundles. The hydrogen bonds range from strong with a minimum O···O distance of 2.595(3) A to very weak and possibly bifurcated with O···O distances of 3.082(4) and 3.194(3) A. The water molecule environments are normal; each contacts at least one Na or Ca on its lone-pair side. Bond strengths calculated using the observed O–H and H···O values agree fairly well with those obtained from an empirical relationship. A good cleavage parallel to $\{\bar{1}20\}$, rather than to {010} as previously suggested, breaks hydrogen and Na–OH(5) bonds only; a reproducible fracture surface is parallel to {001}.

Introduction

According to *Dana's System of Mineralogy* (Palache *et al.*, 1951, p. 345–348), ulexite has been recognized as a valid species since about 1840. Its formula, $Na_2O \cdot 2CaO \cdot 5B_2O_3 \cdot 16H_2O$, assigned by chemist George Ludwig Ulex for whom the mineral was named, has been associated with the mineral almost as long. Ulexite occurs in salt playas and dry saline lakes and has also been found associated with gypsum deposits. Frequently it occurs in bundles of fibers matted together to resemble a cotton ball, and this habit is known as "cottonball ulexite." Less frequently the fibers are oriented in parallel bundles that transmit an optical image with remarkable clarity and resolution. This phenomenon was investigated by Weichel-Moore and Potter (1963), who conclude their paper with the sentence "The discovery and study of ulexite show that it is possible to find in Nature a device almost as good as a man-made [optical] fibre bundle."

The crystallography of ulexite was studied by Murdoch (1940) and reexamined by Clark and Christ (1959), who also gave indexed X-ray diffraction powder data. Clark and Appleman (1964) solved the structure, but published only a brief report because the data were too numerous to be refined economically at that time. Even today the dimensions of the structure refinement are too large to be treated economically by the usual full-matrix least-squares method. In the present work with new data, we have been able to determine all the hydrogen positions and

Table 1. Crystallographic and optical data for ulexite

*Crystallographic data**	*Optical data*
Triclinic, $P\bar{1}$ $Z = 2[NaCaB_5O_6(OH)_6 \cdot 5H_2O]$	Biaxial positive (+)
a = 8.816(3) Å b =12.870(7) c = 6.678(1)	α = 1.491 β = 1.506 } ** γ = 1.529
a:b:c = 0.6850:1:0.5189	2V, calc. = 79°
α = 90.36(2)° β = 109.05(2)° γ = 104.98(4)° V = 688.4(4) $Å^3$	ϕ ρ X 11.5° 81° Y 100° 21.5° } † Z 107° 70°
Constants for Cartesian matrices (Evans, 1948): v_1 = -0.27568 v_2 = 0.96123	Y∧c 21.5°
Density: calc. = 1.955 g cm^{-3} obs., Murdoch (1940), = 1.955(1)	

**Number in parentheses is one standard deviation; for 8.816(3) Å, read 8.816±0.003 Å, etc.*

***W. T. Schaller, U.S. Geological Survey, unpublished data, average of seven determinations.*

†Murdoch (1940) as given by Palache et al. (1951).

refine the structure successfully using partial block-diagonal least-squares methods. We describe here the results of this refinement, interpreting the physical properties of the mineral in terms of its structure.

Experimental data

The ulexite crystal used for the X-ray diffraction experiments was selected from a specimen provided by the late Waldemar T. Schaller, U.S. Geological Survey, who found the beautiful specimen with a cluster of radiating ulexite needles at the Boron Mine, U.S. Borax Corporation, Boron, California. A prismatic crystal (0.12 × 0.20 × 0.28 mm) elongated parallel to c was mounted parallel to the ϕ-axis of the single-crystal, automatic diffractometer for the determination of unit-cell dimensions and collection of intensity data. Mo$K\alpha$ radiation, monochromatized by reflection from a graphite "single" crystal, and a solid-state detection system were used for the measurements. The cell dimensions were refined by the method of least squares, based on 15 reflections with 2θ values between 35° and 45° measured on the diffractometer (Table 1). All reported cell dimensions for ulexite are in reasonable agreement. The intensity data were collected by the 2θ–θ method using a variable scan rate, the minimum being 2°/minute (50 kV, 15mA). All reflections with $2\theta \leqq 65°$ were measured, yielding a total of 4911 reflections; of these, 1246 were below 3σ (I), where σ (I) is the standard deviation of the intensity (I) as calculated from the counting statistics. The intensity data were corrected for Lorentz and polarization factors. No corrections were made for absorption (μ = 29.73 cm^{-1}, Mo$K\alpha$) or extinction effects. At the end of the refinement (see below) no serious discrepancies between strong observed and calculated structure factors with low 2θ values were found, indicating that there were no serious extinction effects.

Hydrogen locations and refinement of the structure

The structure-factor calculation using the positions of non-hydrogen atoms, namely, one calcium, one sodium, five boron, and seventeen oxygen atoms as given by Clark and Appleman (1964) yielded an R factor of 0.18. These atomic positions were refined with anisotropic temperature factors for Na and Ca and isotropic temperature factors for B and O atoms to R = 0.088, using the full-matrix least-squares program RFINE (Finger, 1969). At this stage the positions of sixteen hydrogen atoms were determined from a three-dimensional difference Fourier synthesis on the basis of peak heights and reasonable stereochemistry. The positional and isotropic thermal parameters of the hydrogen atoms were refined next, keeping the positional and thermal parameters of non-hydrogen atoms constant, and the R factor was reduced to 0.07. Unfortunately, due to the large dimensions of the problem, further refinement using anisotropic temperature factors could not be carried out using the full-matrix least-squares program. Hence, subsequent refinement was carried out by the CRYLSQ program incorporated in the X-RAY SYSTEM (Stewart *et al.*, 1972). The positional parameters of all atoms, anisotropic thermal parameters for non-hydrogen atoms, and isotropic thermal parameters for hydrogen atoms (280 parameters for 40 atoms) were divided into 24 blocks. Blocks 1 through 13 contained Na, Ca, and O atoms with anisotropic thermal parameters, whereas each of the blocks 14 through 24 consisted of an oxygen atom and the hydrogen(s) associated with it, *i.e.*, one block each for six (OH) groups and five H_2O molecules.

The atomic scattering factors for Ca, Na, B, and O were taken from Cromer and Waber (1965) and for H from Stewart *et al.* (1965). Anomalous dispersion corrections were applied according to Cromer and Liberman (1970). The observed structure factors (F_o) were weighted by the formula $1/\sigma^2(F_o)$. The final conventional R factor, $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, is 0.045 for all 4911 reflections, 0.041 for the 3665 ob-

Table 2. Atomic coordinates and thermal parameters for ulexite

Atom	Structural role*	Coordinates**			Thermal parameters (Å^2)†							
		x	y	z	$B_{eq.}$	$\bar{U}$	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ca		0.1422(1)	0.0256(1)	0.3042(1)	1.59	0.0202	0.0115(2)	0.0103(2)	0.0125(2)	0.0020(2)	0.0017(2)	-0.0003(1)
Na		0.4774(1)	0.5015(1)	0.2438(2)	4.06	0.0514	0.0316(6)	0.0235(6)	0.0266(5)	0.0100(5)	0.0096(5)	0.0012(4)
B(1)	central T	0.0506(3)	0.2002(2)	0.6685(4)	1.91	0.0242	0.012(1)	0.012(1)	0.015(1)	0.0056(9)	0.0016(9)	0.0009(9)
B(2)	T	0.3464(3)	0.2700(2)	0.8995(4)	1.90	0.0241	0.013(1)	0.013(1)	0.013(1)	0.004(1)	0.0027(9)	0.0007(9)
B(3)	Δ	-0.1891(3)	0.2240(2)	0.7821(4)	2.25	0.0285	0.015(1)	0.015(1)	0.016(1)	0.007(1)	0.004(1)	-0.0009(9)
B(4)	T	0.2344(3)	0.0737(2)	0.7834(4)	1.92	0.0243	0.013(1)	0.011(1)	0.015(1)	0.0050(9)	0.0037(9)	0.0021(9)
B(5)	Δ	-0.1737(3)	0.2697(2)	0.4276(4)	2.10	0.0266	0.015(1)	0.015(1)	0.013(1)	0.006(1)	0.0021(9)	-0.0005(9)
O(1)	T-Δ	0.1985(2)	0.2890(1)	0.7929(3)	2.21	0.0280	0.0123(8)	0.0107(8)	0.0219(9)	0.0043(6)	-0.0005(7)	-0.0012(6)
O(2)	T-T	0.1024(2)	0.1066(1)	0.6208(2)	1.72	0.0218	0.0111(7)	0.0121(7)	0.0118(7)	0.0057(6)	0.0011(6)	-0.0008(6)
O(3)	T-Δ	-0.0289(2)	0.2424(1)	0.4664(3)	2.41	0.0305	0.0138(8)	0.0180(8)	0.0141(8)	0.0087(7)	0.0039(6)	0.0044(6)
O(4)	T-T	-0.0650(2)	0.1677(1)	0.7840(3)	2.36	0.0299	0.0147(8)	0.0152(8)	0.0146(8)	0.0082(7)	0.0064(7)	0.0030(6)
O(5)	T-Δ	0.3701(2)	0.1692(1)	0.9112(3)	1.93	0.0244	0.0123(8)	0.0114(8)	0.0170(8)	0.0036(6)	0.0025(6)	0.0007(6)
O(6)	T-Δ	-0.2591(2)	0.2602(2)	0.5667(3)	3.10	0.0393	0.0160(8)	0.028(1)	0.0122(8)	0.0134(8)	0.0031(7)	0.0011(7)
OH(1)	T	0.2992(2)	0.0085(1)	0.6683(3)	2.80	0.0355	0.0158(9)	0.0195(9)	0.0194(9)	0.0100(7)	0.0050(7)	-0.0008(7)
OH(2)	T	-0.1132(2)	0.3228(1)	0.9369(3)	2.55	0.0323	0.0227(9)	0.0131(8)	0.0152(8)	0.0074(7)	0.0023(7)	-0.0009(7)
OH(3)	T	0.1580(2)	0.0068(1)	0.9265(3)	2.25	0.0285	0.0153(8)	0.0126(8)	0.0175(8)	0.0059(7)	0.0037(7)	0.0028(6)
OH(4)	T	-0.3183(3)	0.1469(2)	0.8361(3)	4.15	0.0525	0.020(1)	0.0163(9)	0.039(1)	0.0046(8)	0.0167(9)	-0.0002(8)
OH(5)	Δ	0.4776(2)	0.3597(1)	0.0025(3)	2.25	0.0284	0.0136(8)	0.0124(8)	0.0211(9)	0.0033(7)	-0.0017(7)	-0.0004(7)
OH(6)	Δ	-0.2383(2)	0.3130(2)	0.2405(3)	4.23	0.0535	0.024(1)	0.035(1)	0.0128(8)	0.0202(9)	0.0052(7)	0.0056(7)
H_2O(1)		0.1462(2)	0.2106(2)	0.2240(3)	3.17	0.0402	0.0205(9)	0.022(1)	0.0196(9)	0.0105(8)	0.0064(8)	0.0031(7)
H_2O(2)		0.4293(3)	0.1021(2)	0.3302(4)	3.44	0.0436	0.018(1)	0.029(1)	0.026(1)	0.0001(9)	0.0007(9)	0.0018(9)
H_2O(3)		0.4707(3)	0.3586(2)	0.4870(4)	3.73	0.0472	0.024(1)	0.022(1)	0.031(1)	0.0079(9)	0.0067(9)	-0.0028(9)
H_2O(4)		0.1925(3)	0.4794(2)	0.1850(4)	3.94	0.0499	0.028(1)	0.022(1)	0.034(1)	0.0040(9)	0.001(1)	-0.000(1)
H_2O(5)		0.2252(3)	0.4765(2)	0.6107(4)	5.07	0.0642	0.040(1)	0.017(1)	0.041(1)	0.008(1)	0.013(1)	0.0054(9)
H(1)	OH(1)	0.397(4)	0.022(3)	0.698(5)	2.0	0.025(9)						
H(2)	OH(2)	-0.134(4)	0.373(3)	0.878(5)	2.4	0.03(1)						
H(3)	OH(3)	0.193(4)	-0.045(3)	0.975(5)	2.3	0.029(9)						
H(4)	OH(4)	-0.379(5)	0.169(3)	0.872(6)	2.7	0.03(1)						
H(5)	OH(5)	0.555(5)	0.342(3)	0.078(6)	3.4	0.04(1)						
H(6)	OH(6)	-0.189(5)	0.313(3)	0.147(6)	3.4	0.04(1)						
H(7)	H_2O(1)	0.086(4)	0.230(3)	0.285(5)	1.9	0.024(9)						
H(8)	H_2O(1)	0.092(7)	0.218(4)	0.088(9)	7.1	0.09(2)						
H(9)	H_2O(2)	0.439(6)	0.127(4)	0.229(8)	5.9	0.07(2)						
H(10)	H_2O(2)	0.513(5)	0.134(3)	0.418(6)	3.3	0.04(1)						
H(11)	H_2O(3)	0.392(5)	0.316(3)	0.421(6)	3.2	0.04(1)						
H(12)	H_2O(3)	0.555(5)	0.335(3)	0.513(6)	3.4	0.04(1)						
H(13)	H_2O(4)	0.120(6)	0.431(4)	0.113(7)	5.1	0.06(1)						
H(14)	H_2O(4)	0.192(5)	0.473(3)	0.294(6)	2.5	0.03(1)						
H(15)	H_2O(5)	0.202(5)	0.422(4)	0.664(6)	3.8	0.05(1)						
H(16)	H_2O(5)	0.191(5)	0.521(4)	0.662(6)	4.0	0.05(1)						

*See Figs. 4, 5. T=tetrahedron, Δ=triangle, T-Δ=linking tetrahedron to triangle, etc. H atoms are associated with the designated OH or H_2O.

**Number in parentheses is one standard deviation; for 0.1422(1) read 0.1422±0.0001, etc.

†$B_{eq.}=8\pi^2\bar{U}$. Temperature-factor expression, $\exp[-2\pi^2(U_{11}h^2a^{*2}+U_{22}k^2b^{*2}+U_{33}\ell^2c^{*2}+2U_{12}hka^*b^*\cos\gamma^*+2U_{13}h\ell a^*c^*\cos\beta^*+2U_{23}k\ell b^*c^*\cos\alpha^*)]$. Number in parentheses is one standard deviation; for 0.0115(2) read 0.0115±0.0002, etc.

served reflections, and 0.175 for the 1246 reflections with $I < 3\sigma(I)$. The average shift/error at this stage was 0.27.

The final positional and thermal parameters are listed in Table 2. Observed and calculated structure factors are given in Table 3.[1] The bond lengths and angles with standard deviations were calculated using the program BONDLA (Stewart *et al.*, 1972) and are listed in Tables 4–9. The estimated standard deviations in bond lengths and angles include the standard deviations in unit-cell dimension measurements but should be applied conservatively because of the block method that had to be used for the refinement. The average estimated standard deviations in Ca–O, Na–O, and B–O bond lengths are 0.002, 0.003, 0.003 A, respectively, and in O–Ca–O, O–Na–O, and O–B–O bond angles, 0.07°, 0.07°, and 0.20°, respectively. The standard deviations in O–H, H···O bond distances and O–H···O angles are 0.04, 0.04 A, and 4°, respectively.

Discussion of the structure

As described by Clark and Appleman (1964), the structure contains three kinds of groups: isolated

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[1] To receive a copy of Table 3, order document AM-78-063 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.

pentaborate polyanions, Ca-coordination polyhedra, and Na-coordination octahedral chains, all cross-linked by hydrogen bonds. We now note that the Ca-coordination polyhedra also share edges to form chains (Fig. 1). These chains are separate from the Na-coordination octahedral chains (Fig. 2); the pentaborate polyanions sandwich between the two kinds of chains to help link them together (Fig. 3). Both kinds of chains run parallel to *c*, the fiber-axis optical direction. The polyanions (Fig. 4) are the pentaborate type with three tetrahedra and two triangles, $5{:}2\Delta + 3T$, $A = B$ (Christ and Clark, 1977), formula $[B_5O_6(OH)_6]^{3-}$.

Stereochemical configuration of the pentaborate polyanion

The $[B_5O_6(OH)_6]^{3-}$ polyanion found in ulexite is formed by two six-membered boron-oxygen rings joined through a common tetrahedral boron atom (Fig. 4). Each ring consists of the central BO_4-tetrahedron, a $BO_2(OH)_2$-tetrahedron, and a $BO_2(OH)$-triangle sharing corners. The polyanion has the point symmetry 1 and the two $BO_2(OH)_2$ tetrahedra are in *cis*-configuration with respect to the central borate tetrahedron.

The two boron–oxygen rings are nearly perpendicular to each other, the angle between the mean planes being 88.6°. Within each ring the average B–B separation is very similar (2.498 and 2.505 A); however, the separation of 2.545 A between two tetrahedral borons is significantly larger than the separation of 2.480 A between a tetrahedral and a triangular boron (Table 4). Both rings are nearly planar with internal angles averaging 117.9° in ring 1 [O(1)–B(1)–O(2)–B(4)–O(5)–B(2)], and 118.4° in ring 2 [O(3)–B(1)–O(4)–B(3)–O(6)–B(5)]. The maximum deviation of a boron atom from the mean plane in ring 1 is −1.40 A, in ring 2 +0.31 A; hence, ring 2 is more nearly planar than ring 1.

The average tetrahedral and triangular B–O distances are in good agreement with similar values found in other borates. However, within each borate triangle or tetrahedron, there are variations in B–O distances (Table 5) which are significant. Within the borate triangles, the (non-bridging) B–(OH) bond is significantly longer (average 1.383 A) than the bridging B–O bonds (average 1.359 A). Within the three borate tetrahedra the B–O distances (average 1.488 A) involving oxygens further bonded to triangular borons are distinctly longer than those (average 1.459 A) involving oxygens further bonded to tetrahedral boron atoms. This result is a reflection of the fact that the triangular B–O bond has more covalent character than the tetrahedral B–O bond. Within the B(4)-tetrahedron, the B(4)–OH(3) distance, 1.496 A, is significantly longer than the B(4)–OH(1) distance, 1.466 A. This difference is most likely due to the fact that OH(3) is further bonded to two Ca cations whereas OH(1) is further bonded to only one Ca cation. A similar difference in the B–OH distances is observed within the $B(3)O_2(OH)_2$ tetrahedron, where the B(3)–OH(2) distance, 1.492 A, is longer than the B(3)–OH(4), 1.449 A; in this case, OH(2) is the acceptor of two hydrogen bonds, one strong, whereas OH(4) is an acceptor of one weak hydrogen bond plus possibly one other very weak one (Table 8). Neither of these two OH groups is bonded to cations other than boron; therefore, the hydrogen bonds apparently play a significant role in determining their non-bridging B–OH distances. The temperature factors of these two OH groups are the highest of any polyanion atoms in ulexite (Table 2). The average of six O–H distances is 0.80 A and the average B–O–H angle, 115°.

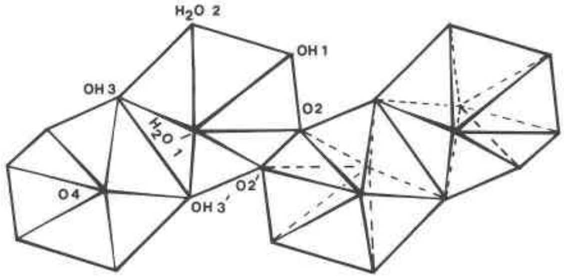

Fig. 1. View of the distorted hexagonal bipyramid of oxygen atoms surrounding Ca and the chain formed by edge-sharing. The view is looking down $+b^*$ with $+a$ approximately vertical, $+c$ horizontal to the right (*cf.* Table 7).

This same polyanion is found in linked form in several other structures, although none of these has

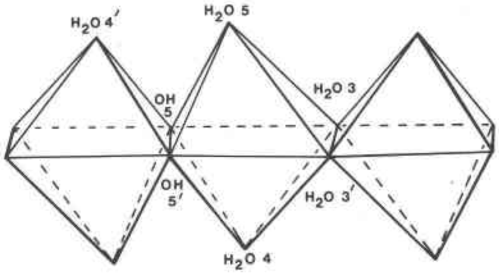

Fig. 2. View of the octahedron of oxygen atoms surrounding Na and the chains formed by edge-sharing. The view is looking down $+b^*$ with $+a$ approximately vertical, $+c$ horizontal to the right (*cf.* Table 6).

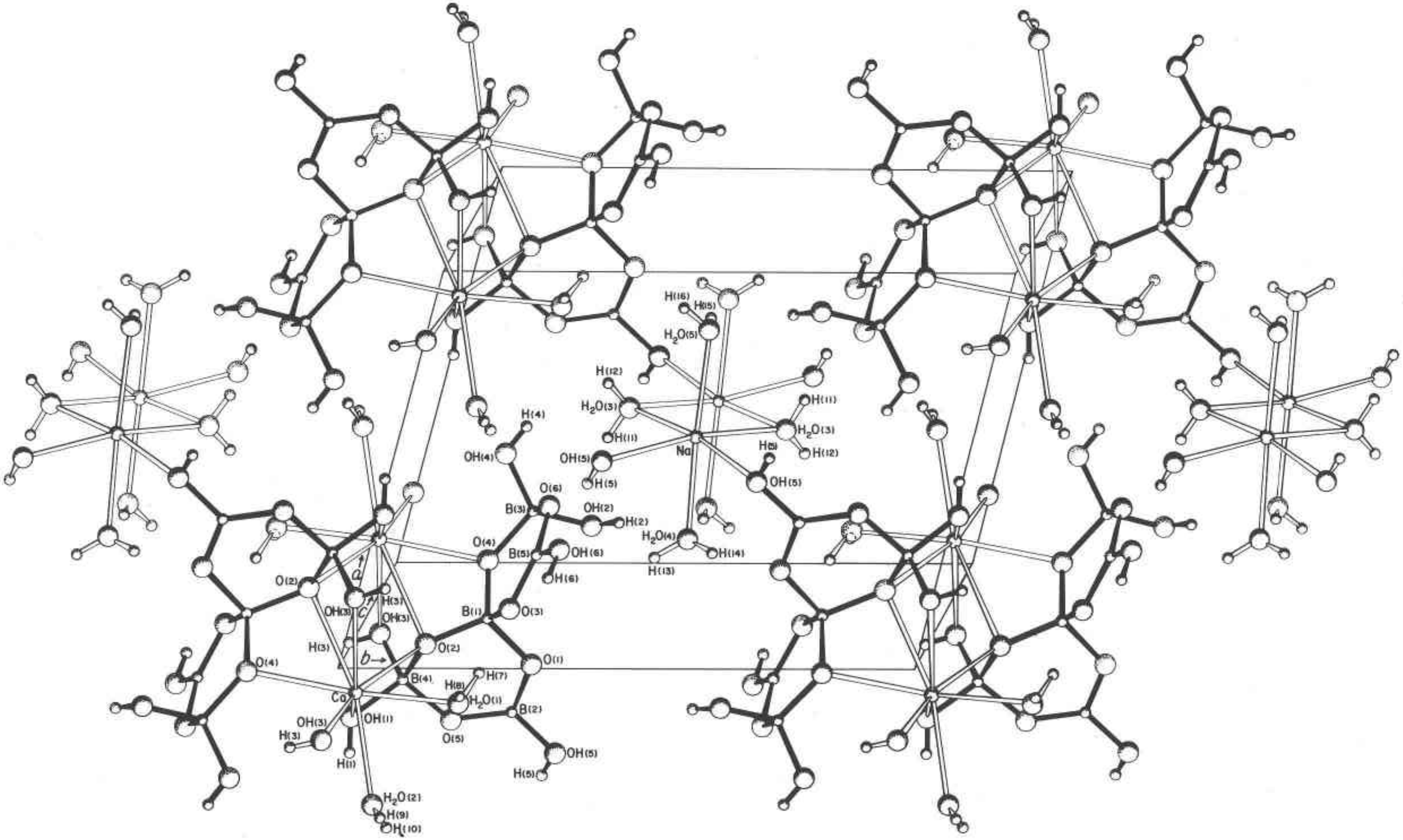

Fig. 3. A view of the ulexite structure showing the linking of the pentaborate polyanions to the Ca-polyhedral and Na-octahedral chains; only selected atoms are shown. Adapted from Ortep drawings (Johnson, 1965).

been refined by modern methods. Simple chains composed of this polyanion, linked *via* an oxygen atom common to a triangle of one polyanion and a tetrahedron of the next (Christ, 1960), are found in the structure of probertite, $NaCaB_5O_7(OH)_4 \cdot 3H_2O$ (Kurbanov *et al.*, 1963). Similar chains, modified by attachment of a side triangle, are found in the structure of kaliborite, $HKMg_2[B_5O_7(OH)_3 \cdot OB(OH)_2]_2 \cdot 4H_2O$ (Corazza and Sabelli, 1966; Christ and Clark, 1977). The same polyanions, further linked into sheets (Christ, 1960), are found in the structure of heidornite, $Na_2Ca_3Cl[B_5O_8(OH)_2][SO_4]_2$ (Burzlaff, 1967). The anhydrous analog of the ulexite pentaborate-type polyanion, $[B_5O_{12}]^{9-}$, (5:2Δ + 3*T*), is found in garrelsite, $NaBa_3Si_2B_7O_{16}(OH)_4$ (Ghose *et al.*, 1976). Other kinds of pentaborate-type polyanions are discussed by Christ and Clark (1977).

The polyhedral chains

These chains dominate the structure and are undoubtedly responsible for the fibrous habit of ulexite. Na is octahedrally coordinated by four water molecules and two hydroxyl ions, the latter from two different polyanions. As Figure 2 shows, the octahedra share edges OH(5)–OH(5)′ and $H_2O(3)$–$H_2O(3)'$ to form chains parallel to *c*. The four edge-sharing atoms are arranged around the central part of the octahedron, water molecules $H_2O(4)$ and $H_2O(5)$ forming the vertices. As might be expected, the temperature factors for these vertex atoms are high (Table 2). The distances and angles for the octahedron (Table 6) are somewhat distorted from those of a regular octahedron. The relationship in a regular octahedron, edge distance = $\sqrt{2}$ (center-vertex distance), gives 3.424 A using the average Na–O distance, slightly longer than the observed average of 3.415 A.

Ca is coordinated by three oxygen atoms and three hydroxyl ions from three different polyanions, plus two water molecules. The latter are not those coordinating Na; the two polyhedral chains are separate in the structure (Fig. 3). Figure 1 shows that the Ca polyhedron can be described as a distorted hexagonal bipyramid, atoms OH(3)–$H_2O(2)$–OH(1)–O(2)–O(2)′–OH(3)′ constituting the central part, and O(4)′, $H_2O(1)$ forming the vertices. Edges OH(3)–OH(3)′ and O(2)–O(2)′ are shared to produce the polyhedral chains parallel to *c*. Three edges of tetrahedra in the polyanions are also edges of the Ca polyhedron; these are noted in Table 7 where all the distances and angles are listed.

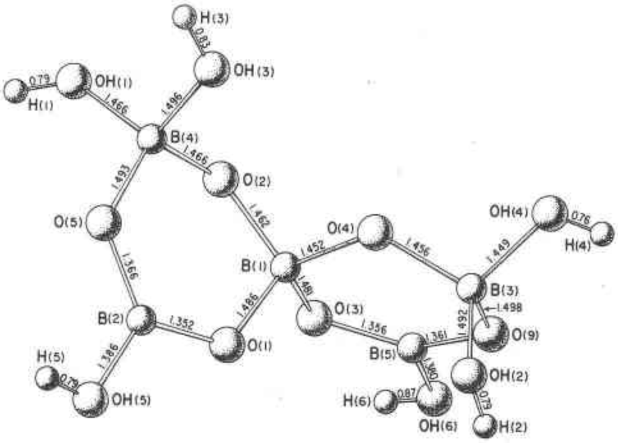

Fig. 4. The borate polyanion $[B_5O_6(OH)_6]^{3-}$ and its bond distances.

Although the average Na–O and Ca–O bond distances are not too different in value, 2.421 A and 2.484 A, respectively, the quite different spatial arrangements around the two cations are striking (Figs. 1–3) and clearly demonstrate their structural distinction. The Na–Na approaches are substantially closer than those for Ca–Ca, 3.4 A compared with 4.0 A, undoubtedly due to the difference in cation charge. The Na temperature factor is considerably higher than that of the Ca (Table 2), probably because it is lighter, less highly charged, and has a lower coordination.

Table 4. Ring angles, planes, and deviations from ring planes for the borate polyanion in ulexite

Ring	*Ring atoms*	*B-O-B angles*	
1	B(1)-O(2)-B(4)- O(5)-B(2)-O(1)	B(1)-O(2)-B(4) B(4)-O(5)-B(2) B(2)-O(1)-B(1)	120.1(2)° 120.2(2)° 121.5(2)°
2	B(1)-O(3)-B(5)- O(6)-B(3)-O(4)	B(1)-O(3)-B(5) B(5)-O(6)-B(3) B(3)-O(4)-B(1)	121.9(2)° 120.3(2)° 122.7(2)°

Parameters of planes* defined by ring oxygens

	A	B	C	D
1	-4.10514	8.81817	-3.52214	-1.66667
2	1.79183	9.48293	2.43122	3.38038

Angle between ring planes, 88.58°

Deviation from ring-planes defined by three oxygens

Ring 1		Ring 2	
Atom	Deviation (Å)	Atom	Deviation (Å)
B(1)	+0.870	B(1)	+0.234
B(2)	-0.542	B(3)	+0.306
B(4)	-1.405	B(5)	-0.094
OH(1)	-1.841	OH(4)	-0.525
OH(5)	-0.653	OH(6)	-0.254

*The equations of the planes in direct space are of the form Ax + By + Cz = D, where x, y, z are the atomic coordinates in Å units and D is the distance of the plane from the origin in Å units.

Table 5. Bond distances and angles in the borate polyanion $[B_5O_6(OH)_6]^{3-}$ of ulexite

Atoms	Distance* (Å)	Oxygens of O-B-O angle	Angle(°)*	Oxygens of O-B-O angle	Angle(°)*	Atoms	Distance* (Å)
Tetrahedra							
B(1)-O(1)	1.486(3)	O(1), O(2)	110.3(2)	O(2), O(4)	109.0(2)	B(1)-B(3)	2.552(5)
-O(2)	1.462(4)	O(1), O(3)	106.4(2)	O(3), O(4)	110.8(2)	-B(4)	2.537(4)
-O(3)	1.481(3)	O(1), O(4)	111.2(2)			-B(2)	2.476(4)
-O(4)	1.452(4)	O(2), O(3)	109.1(2)			-B(5)	2.481(4)
Average	1.470					B(3)-B(5)	2.481(4)
						B(4)-B(2)	2.480(4)
B(3)-O(4)	1.456(4)	O(4), O(6)	110.6(2)	O(6),OH(4)	110.8(2)	Average	2.501
-O(6)	1.498(3)	O(4),OH(2)	111.0(2)	OH(2),OH(4)	111.6(2)		
-OH(2)	1.492(3)	O(4),OH(4)	105.9(2)				
-OH(4)	1.449(4)	O(6),OH(2)	107.0(2)				
Average	1.474						
B(4)-O(2)	1.466(3)	O(2), O(5)	111.6(2)	O(5),OH(3)	109.8(2)		
-O(5)	1.493(3)	O(2),OH(1)	106.1(2)	OH(1),OH(3)	110.4(2)		
-OH(1)	1.466(1)	O(2),OH(3)	108.3(2)				
-OH(3)	1.496(3)	O(5),OH(1)	110.7(2)				
Average	1.480						
Triangles							
B(2)-O(1)	1.352(3)	O(1), O(5)	123.5(2)	O(3), O(6)	123.8(2)	B(5)-O(3)	1.356(4)
-O(5)	1.366(4)	O(1),OH(5)	116.4(2)	O(3),OH(6)	119.3(3)	-O(6)	1.361(4)
-OH(5)	1.386(3)	O(5),OH(5)	120.0(2)	O(6),OH(6)	116.9(3)	-OH(6)	1.380(3)
Average	1.368	Σ	359.9	Σ	360.0	Average	1.366

Number in parentheses is one standard deviation; for 1.486(3) read 1.486±0.003, etc.

Hydrogen bonds

As expected in this kind of structure, all the hydrogen atoms form bonds to oxygen atoms and there is even one possibly bifurcated bond. All the oxygen atoms except O(2) participate in the hydrogen bonding. Most of these bonds are illustrated in Figure 5, and the relevant values are listed in order of increasing O···O distance in Table 8. Following Brown (1976), the hydrogen bonds can be divided into two classes: four strong, 2.595–2.711 A and either 12 or 13 weak, greater than 2.73 A. Of the weak bonds, those greater than 3.0 A should probably be classified as very weak. H(1) makes two contacts that suggest a bifurcated bond. In both contacts the H···O distance is greater than the 2.4 A proposed by Baur (1972) as an upper limit, but in view of the associated errors in our study we include both in the Table. Charge balance considerations (see *Bond strengths*) suggest that OH(4), being slightly charge-deficient, is a more likely recipient than $H_2O(2)$, which is fully satisfied by other bonds. However, the OH(1)···OH(4) distance, 3.194(3) A, is actually longer than the OH(1)···$H_2O(2)$ distance, 3.082(4) A, and both are pushing the limits that have been suggested as cut-off values for hydrogen bonds (*e.g.* Brown, 1976, suggests 3.1 A). Thus a final decision about the H(1) bonding cannot be made unambiguously on the basis of available data. The values in Table 8 show that the extreme values of distances, both short and long, and maximum bending are all associated with hydroxyl ions, although the average values for all hydroxyl ions do not differ significantly from the average values for the water molecules except for O···O (ave.), 2.883 A hydroxyls,[2] 2.833 A H_2O. The strong bonds are important in linking polyanions to one another and to the cation chains. One of the strong bonds, OH(5)···OH(6), links triangle hydroxyls of polyanions adjacent along *a*, and another links triangle hydroxyl OH(6) to tetrahedral hydroxyl OH(2) of a polyanion adjacent along *c*. The other two strong bonds link water molecules $H_2O(1)$ from the Ca polyhedron and $H_2O(5)$ from the Na octahedron to ring oxygen atoms of the same polyanion.

The hydrogen atoms are all located about 0.8 A from their associated oxygen atoms, the average O–H being 0.80 A as previously noted. Correcting for rid-

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[2] Using OH(1)···OH(4); with OH(1)···$H_2O(2)$ the average is 2.865 A.

ing motion (Busing and Levy, 1964) does not change the average value. Despite the high estimated standard deviations for individual values, this average of 16 determinations should be a reasonably good one for X-ray work. It is 0.16–0.18 A shorter than the O–H values determined from neutron diffraction studies uncorrected for thermal motion (Baur, 1972, Table 2). The H···O bond varies from an average 1.85 A for the four strong bonds to 2.12 A for 11 weak bonds (excluding the two longest ones). Neutron studies give H···O approximately 1.88 A for water molecules (Ferraris and Franchini-Angela, 1972).

The average H–O–H angle of the water molecules is 105° (Table 9) compared with 108° (Ferraris and Franchini-Angela, 1972) and 109° (Baur, 1972, Table 2) reported from neutron studies. Following the classification scheme proposed by Chidambaram *et al.* (1964) as revised by Ferraris and Franchini-Angela (1972), all the water molecules can be assigned to Class 2, *i.e.* contacting two cations on the negative side, with the possible exception of $H_2O(2)$, where the

Table 6. Bond distances and angles for the Na octahedron in ulexite

*Atoms**	*Distance†* (Å)	*Octahedral edges* *Oxygen atoms*	*Distance†* (Å)
Na-$H_2O(4)$	2.351(3)	OH(5)-OH(5)', shared edge	3.532(3)
-$H_2O(3)'$, 1-x,1-y,1-z	2.383(3)	$H_2O(3)$-$H_2O(3)'$, shared edge	3.536(3)
-$H_2O(5)'$, 1-x,1-y,1-z	2.418(3)	$H_2O(3)$-OH(5)	3.256(3)
-OH(5)	2.428(3)	$H_2O(3)'$-OH(5)'	3.423(3)
-$H_2O(3)$	2.464(3)	Average	3.437
-OH(5)', 1-x,1-y,$\bar{z}$	2.480(2)	$H_2O(5)'$-OH(5)	3.262(3)
Average	2.421	$H_2O(5)'$-$H_2O(3)'$	3.243(4)
		$H_2O(5)'$-$H_2O(3)$	3.214(4)
Na-Na', 1-x,1-y,1-z	3.315(2)	$H_2O(5)'$-OH(5)'	3.469(3)
		Average	3.297
-Na", 1-x,1-y,$\bar{z}$	3.408(2)		
		$H_2O(4)$-$H_2O(3)'$	3.234(3)
		$H_2O(4)$-$H_2O(3)$	3.360(4)
Angles		$H_2O(4)$-OH(5)'	3.689(3)
		$H_2O(4)$-OH(5)	3.762(3)
Na'-Na-Na"	166.67(6)°		
Na-OH(5)-Na"	87.95(8)°	Average	3.511
Na-$H_2O(3)$-Na'	86.27(9)°		
		Average of 12	3.415
		$H_2O(4)$-$H_2O(5)$	4.738

O-Na-O angles

Oxygen atoms	*Angle†* (°)	*Oxygen atoms*	*Angle†* (°)
OH(5),OH(5)'	92.05(8)	$H_2O(4)$,$H_2O(3)'$	86.2(1)
$H_2O(3)$,$H_2O(3)'$	93.73(9)	$H_2O(4)$,$H_2O(3)$	88.4(1)
$H_2O(3)$,OH(5)	83.44(9)	$H_2O(4)$,OH(5)'	99.55(9)
$H_2O(3)'$,OH(5)'	89.45(9)	$H_2O(4)$,OH(5)	103.85(9)
Average	89.67	Average	94.50
$H_2O(5)'$,OH(5)	84.59(9)	Average of 12	89.90
$H_2O(5)'$,$H_2O(3)'$	85.0(1)		
$H_2O(5)'$,$H_2O(3)$	82.34(9)	$H_2O(4)$,$H_2O(5)$	166.8(1)
$H_2O(5)'$,OH(5)'	90.19(9)		
Average	85.53		

**Atomic coordinates as in Table 1 unless transformed from the Table 1 values as noted.*

†*Number in parentheses is one standard deviation; for 2.351(3) read 2.351±0.003, etc.*

Table 7. Bond distances and angles for the Ca polyhedron in ulexite

*Atoms**	*Distance†* (Å)	*Polyhedral edges* *Oxygen atoms*	*Distance†* (Å)
Ca-$H_2O(2)$	2.414(2)	O(2)-OH(1), edge, B(4) T	2.342(3)
-OH(1)	2.417(2)		
-O(4)', $\bar{x}$,$\bar{y}$,1-z	2.418(2)	OH(3)'-O(2)', edge, B(4)' T	2.401(3)
-$H_2O(1)$	2.438(2)	OH(3)-$H_2O(2)$	2.954(3)
-OH(3)', $\bar{x}$,$\bar{y}$,1-z	2.513(2)	OH(1)-$H_2O(2)$	2.979(4)
		O(2)-O(2)', shared edge	2.979(3)
-O(2)	2.515(2)		
-O(2)', $\bar{x}$,$\bar{y}$,1-z	2.572(2)	OH(3)-OH(3)', shared edge	3.208(3)
-OH(3), x,y,1-z	2.584(2)	Average	2.810
Average	2.484	$H_2O(1)$-$H_2O(2)$	3.057(4)
		$H_2O(1)$-O(2)	3.067(3)
Ca-Ca', $\bar{x}$,$\bar{y}$,1-z	4.124	$H_2O(1)$-OH(3)'	3.218(3)
		$H_2O(1)$-OH(3)	3.324(3)
-Ca", $\bar{x}$,$\bar{y}$,$\bar{z}$	3.961	$H_2O(1)$-OH(1)	4.085
		$H_2O(1)$-O(2)'	4.411
		Average	3.527
Angles			
		O(4)'-O(2)', edge, B(1)' T	2.372(3)
Ca'-Ca-Ca"	111.36°		
Ca-OH(3)-Ca"	102.00°	O(4)'-OH(3)	3.097(3)
Ca-O(2)-Ca'	108.32°	O(4)'-OH(3)'	3.157(3)
		O(4)'-OH(1)	3.457(3)
		O(4)'-$H_2O(2)$	3.944
		O(4)'-O(2)	4.310
		Average	3.390
		Average of 18	3.242
		O(4)'-$H_2O(1)$	4.733

O-Ca-O angles

Oxygen atoms	*Angle†* (°)	*Oxygen atoms*	*Angle†* (°)
O(2),OH(1)	56.65(7)	O(4)',O(2)'	56.66(7)
OH(3)',O(2)'	56.33(6)	O(4)',OH(3)	76.44(6)
OH(3),$H_2O(2)$	72.37(7)	O(4)',OH(3)'	79.62(6)
OH(1),$H_2O(2)$	76.13(8)	O(4)',OH(1)	91.30(6)
O(2),O(2)'	71.68(6)	O(4)',$H_2O(2)$	109.44(8)
OH(3),OH(3)'	78.00(6)	O(4)',O(2)	121.80(6)
Average	68.53	Average	89.21
$H_2O(1)$,$H_2O(2)$	78.10(8)	Average of 18	83.49
$H_2O(1)$,O(2)	76.49(8)		
$H_2O(1)$,OH(3)'	81.08(6)	O(4)',$H_2O(1)$	154.12(6)
$H_2O(1)$,OH(3)	82.82(7)		
$H_2O(1)$,OH(1)	114.57(6)		
$H_2O(1)$,OH(2)'	123.35(8)		
Average	92.74		

**Atomic coordinates as in Table 1 unless transformed from the Table 1 values as noted.*

†*Number in parentheses is one standard deviation; for 2.414(2) read 2.414±0.002, etc.*

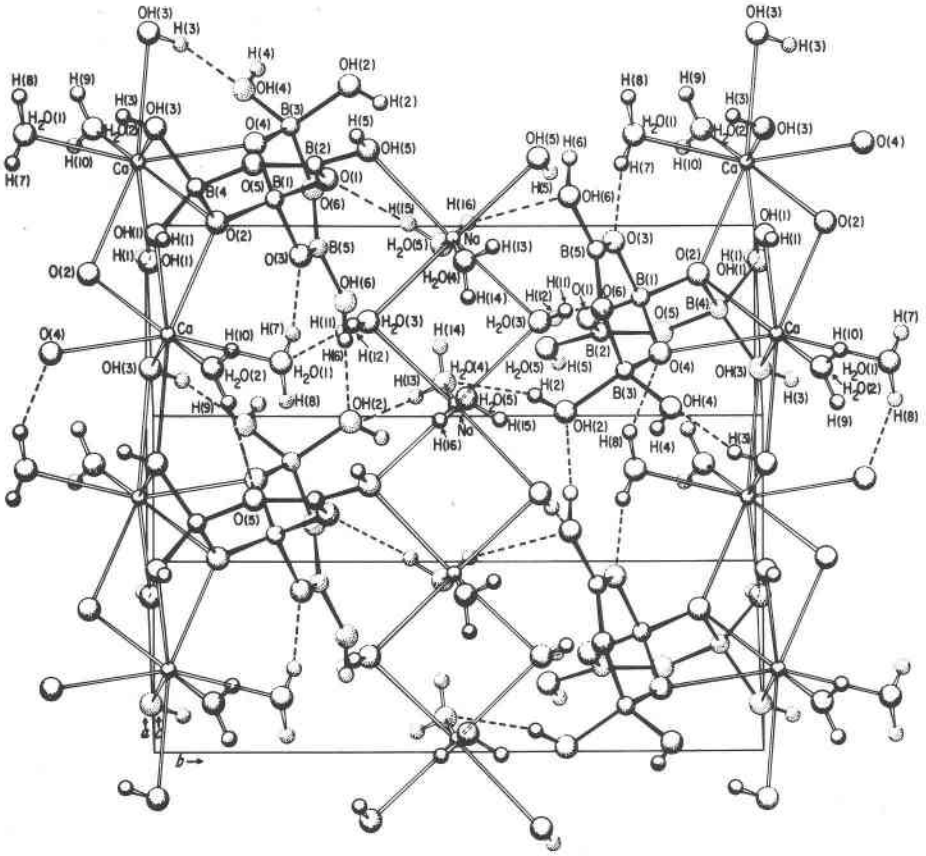

Fig. 5. A view of the ulexite structure nearly along the a^*-axis, showing some of the hydrogen bonds and selected atoms. Adapted from ORTEP drawings (Johnson, 1965).

presence of an accepted hydrogen bond is ambiguous as previously discussed. $H_2O(3)$ is coordinated to two Na cations and thus is Class 2, Type A, with two lone pairs directed toward two monovalent metal ions. Water molcules $H_2O(4)$ and $H_2O(5)$ are Class 2, Type G, one lone pair being directed toward a monovalent metal ion and the other toward a proton. $H_2O(1)$ is Class 2, Type H, with one lone pair directed toward a divalent metal cation and the other toward a proton. If $H_2O(2)$ accepts the long bifurcated hydrogen bond, it is also Class 2, Type H. If it does not accept this bond, it is classified a Class 1′, Type J, with a divalent metal ion along a lone-pair orbital, in view of the angles involved (Table 9), which are not appropriate for the metal ion being located along the bisectrix of the lone-pair orbitals.

Bond strengths

As these values were compiled, it became evident that the strengths assigned to hydrogen bonds were crucial to the sums. In Table 10 we present two sets of results. One of these uses the empirical values given by Zachariasen (1963) for hydrogen bonds in borate structures, and the good results show that these remain today quite satisfactory for this kind of structure. The other set of values is from direct calculation of strengths using our X-ray values for O–H and H···O in the general equation presented by Brown and Shannon (1973), $s = s_0(R/R_0)^{-N}$, with s_0 chosen as 0.825 (strength of an average O–H bond), R_0 = 0.80 A (average O–H distance in ulexite), and N = 1.6 (empirical constant). It is encouraging to note that the sums obtained using this direct calculation are in general satisfactory and thus it may, after all, be possible to obtain hydrogen-bond strengths directly from good X-ray results. We tried applying values obtained from the curve for valence *vs.* H···O distances given by Brown (1976, Fig. 3), but whatever the reason, those values do not produce sums as satisfactory as the ones obtained from Zachariasen (1963). Finally, with respect to the possible bifurcated hydrogen bond involving H(1), the bond

Table 8. Hydrogen bonds in ulexite

Donor oxygen atom*	Hydrogen atom* of donor	Acceptor oxygen atom*	Distance (Å) O...O	O-H	H...O	Angle(°)† O-H...O
OH(6)	6	OH(2) $x,y,z-1$	2.595(3)	0.87(5)	1.73(5)	170(4)
$H_2O(1)$	7	O(3)	2.668(3)	0.85(4)	1.84(4)	163(4)
$H_2O(5)$	15	O(1)	2.700(3)	0.79(4)	1.92(4)	166(5)
OH(5)	5	OH(6) $x+1,y,z$	2.711(3)	0.79(4)	1.92(4)	171(4)
$H_2O(4)$	14	$H_2O(5)$	2.763(4)	0.73(4)	2.04(4)	171(4)
$H_2O(5)$	16	OH(6)′, $\bar{x},1-y,1-z$	2.840(4)	0.83(5)	2.13(5)	145(4)
$H_2O(2)$	9	O(5) $x,y,z-1$	2.856(3)	0.77(6)	2.12(5)	159(5)
OH(2)	2	$H_2O(4)'$ $\bar{x},1-y,1-z$	2.864(4)	0.79(4)	2.10(4)	162(4)
$H_2O(1)$	8	O(4) $x,y,z-1$	2.877(3)	0.89(5)	2.04(5)	155(5)
$H_2O(3)$	12	O(6) $x+1,y,z$	2.881(4)	0.84(5)	2.04(5)	173(3)
$H_2O(4)$	13	OH(2), $x,y,z-1$	2.882(3)	0.78(4)	2.11(4)	166(6)
$H_2O(2)$	10	O(6) $x+1,y,z$	2.901(3)	0.78(3)	2.16(3)	159(4)
OH(3)	3	OH(4)′, $\bar{x},y,2-z$	2.906(3)	0.83(4)	2.09(4)	166(3)
$H_2O(3)$	11	$H_2O(1)$	2.959(3)	0.76(3)	2.20(3)	172(5)
OH(4)	4	O(5), $x-1,y,z$	3.031(3)	0.76(5)	2.31(4)	130(2)
OH(1)	1	? $H_2O(2)'$, $1-x,\bar{y},1-z$	3.082(4)	0.79(4)	2.52(4)	129(3)
		? OH(4) $1+x,y,z$	3.194(3)	0.79(4)	2.48(3)	152(3)

*Atomic coordinates as in Table 2 unless transformed as noted.
†Number in parentheses is one standard deviation; for 2.595(3) read 2.595±0.003, etc.

Table 9. Angles around the water molecules in ulexite

Water oxygen, classification*	Hydrogen atom	Contacting atoms* C2	C3	Angles(°) H-H_2O-H	H-H_2O-C2, H-H_2O-C3	C2-H_2O-C3
1 Class 2, Type H	7 8	Ca	H(11)	100(5)	107(2) 99(2) 115(3) 125(3)	107(1)
2 Class 2, Type H ?†	9 10	Ca	?H(1)′†	102(5)	113(2) ?91(5) 137(4) ?83(4)	? 120(1)
3 Class 2, Type A	11 12	Na	Na′	111(4)	101(3) 132(4) 112(3) 109(2)	86.3(1)
4 Class 2, Type G	13 14	Na	H(2)′	106(5)	125(4) 110(4) 100(3) 103(4)	110(1)
5 Class 2, Type G	15 16	Na	H(14)	106(5)	94(3) 121(3) 116(2) 118(3)	100(1)

*Classification and notation from Ferraris and Franchini-Angela (1972).
†See text; H(1) may not be forming a hydrogen bond. If it is not, $H_2O(2)$ is Class 1′, Type J. A ? indicates ambiguous designations.

Table 10. Bond strengths (*s*) for the oxygen atoms in ulexite

Oxygen atom	(1)* s′ Na, Ca, B	(2)* s′ attached H*		Donor H	(2)* s′ accepted H-bonds		Donor H	Total s
O(1)	1.76			15	0.25 0.20			2.01 1.96
O(2)	1.98			none				1.98
O(3)	1.76			7	0.26 0.22			2.02 1.98
O(4)	1.85			8	0.17 0.18			2.02 2.03
O(5)	1.71			4	0.12 0.15	0.17 0.17	9	2.00 2.03
O(6)	1.72			10	0.16 0.17	0.17 0.18	12	2.05 2.07
OH(1)	1.04	0.90 0.84		none				1.94 1.88
OH(2)	0.71	0.83 0.84		6	0.31 0.24	0.17 0.17	13	2.02 1.96
OH(3)	1.13	0.84 0.78		none				1.97 1.91
OH(4)	0.80	0.88 0.90		3	0.16 0.18	0.08 0.13	1†	1.92 2.01
OH(5)	1.28	0.76 0.84		none				2.04 2.12
OH(6)	0.97	0.69 0.72		5	0.24 0.20	0.19 0.17	16	2.09 2.06
$H_2O(1)$	0.27	0.74 0.75	0.83 0.70	11	0.14 0.16			1.98 1.88
$H_2O(2)$	0.28	0.83 0.88	0.84 0.86	none†				1.95 2.02
$H_2O(3)$	0.35	0.86 0.90	0.83 0.76	none				2.04 2.01
$H_2O(4)$	0.20	0.83 0.86	0.78 0.96	2	0.17 0.18			1.98 2.20
$H_2O(5)$	0.18	0.75 0.84	0.81 0.78	14	0.22 0.18			1.96 1.98

*Bond strengths (valence units) obtained as follows. (1) $s' = \Sigma s(Na) + \Sigma s(Ca) + \Sigma s(B)$ using average from Brown and Shannon (1973, Table 1 for Na, Ca, Table 2 for B), and Donnay and Allmann (1970). (2) s′, attached H and accepted H-bonds, upper values from Zachariasen [1963, Table 9 using O...O and assuming $s(O\text{-}H) = 1-s(O...O)$], lower values using the equation $s = s_0\,(R/R_0)^{-N}$ of Brown and Shannon (1973) with constants $s_0 = 0.825$, $R_0 = 0.80$ Å, $N = 1.6$.
†Assuming OH(1)...OH(4) is a hydrogen bond and OH(1)...$H_2O(2)$ is not (see text).

strengths clearly indicate that best balance is obtained when H(1)···OH(4) is considered a hydrogen bond and $H_2O(2)$ is assigned no charge from this source, as has been done in Table 10. Nevertheless, this is only one piece of evidence and cannot be considered sufficient to resolve the question.

Cleavage, twinning, and fiber optics

Murdoch (1940) reported two good cleavages for ulexite, one "very perfect" parallel to {010} and another "not quite so good" parallel to {$1\bar{1}0$}. He also reported a poor cleavage parallel to {110} and an easy cross-fracture nearly perpendicular to the elongation direction. Examination of the structure (Figs. 3, 5) shows that the reported cleavages do not seem reasonable, because they require breaking both Ca–O and Na–O bonds. Therefore, we have reexamined the cleavage of some single crystals and find that a good cleavage along the elongation is in fact parallel to

$\{\bar{1}20\}$. This is much more reasonable in terms of the structure, as only hydrogen bonds and Na–OH(5) bonds are broken between structural units. We did not find other cleavages but do confirm a fracture surface parallel to {001}.

Murdoch (1940) found twinning "rare in separate crystals, but rather common in the aggregate" and he gave {010} and {100} as well-determined twin planes. Consideration of the structure suggests that such twinning could develop when mistakes in the chain stacking occur as crystals come together during growth.

The excellent light transmission by some ulexite crystals was explained by Weichel-Moore and Potter (1964) in terms of fiber optics. They designate as core the crystals aligned along the fiber direction c with index γ approximately 1.529, and they show that cladding results from random orientations of crystals about the fiber direction, producing a core-to-cladding index difference ranging from 0 to a maximum of $\gamma - \alpha = 0.038$ (Table 1). Their Figure 2 is a photomicrograph of a ulexite fiber bundle taken between crossed polarizers at a magnification of fifty. In our Figure 6 we show two views of the natural surface of a similar ulexite fiber bundle taken at much higher magnifications with the scanning electron microscope. Clearly the crystals are indeed randomly oriented about the fiber axis (a point that is confirmed by X-ray diffraction precession photographs). However, the crystals are not packed solidly, because spaces about 0.5 micrometer in size surround them. If one end of such a bundle is placed in a colored liquid, the color can be observed travelling capillary-fashion, apparently along these spaces (R. C. Erd, U.S.G.S., personal communication). Presumably the spaces do not affect the light transmission. We do not know whether the individuals within the spaces are actually single crystals. To our knowledge, no experiments have been made to determine whether ulexite fibers might be artificially arranged to eliminate the random cross-sectional array and maximize the core-to-cladding index difference. A curious feature shown in Figure 6 is the presence of light and dark bands across some individuals. The dark bands might be due to the presence of minute inclusions of clay particles, but it is not clear why these should congregate into bands.

We have not investigated another curious observation about ulexite single crystals. Murdoch (1940) and R. C. Erd, U.S.G.S. (personal communication) note that some clear single crystals of ulexite remain clear as long as they are stored with others but, when isolated, appear to alter. Is there a loss of water, an

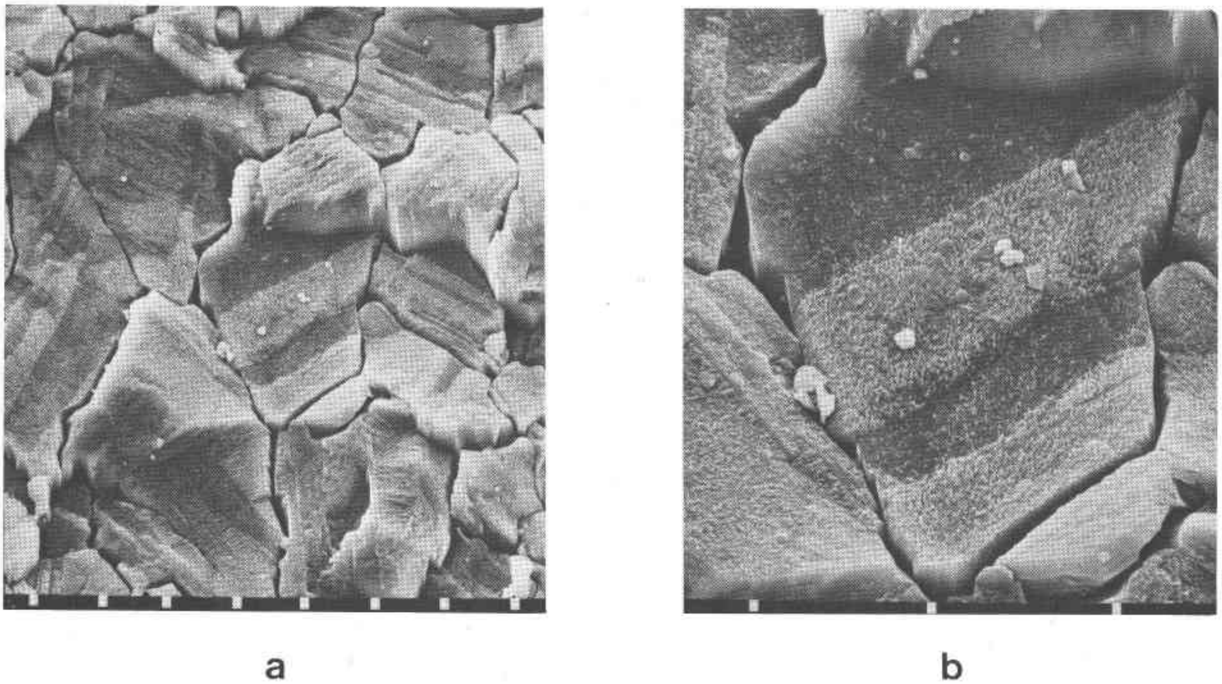

Fig. 6. Two views of the same part of a natural surface on a ulexite fiber bundle, taken with a Cambridge 180 scanning electron microscope by R. L. Oscarson, U.S. Geological Survey. Distance between scale marks is 3 micrometers: (a) magnification 990× (b) magnification 2590×.

actual alteration to probertite, or decomposition? Finally, what characteristics of their formation produced the excellent long clear crystals found at Boron, California? The locality is apparently unique in this regard.

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