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Aristarainite: $Na_2Mg[B_6O_8(OH)_4]_2 \cdot 4H_2O$: a sheet structure with chains of hexaborate polyanions

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Abstract

The rare sodium magnesium borate mineral aristarainite from Salta, Argentina, is monoclinic, space group $P2_1/a$, with $a = 18.886(4)$, $b = 7.521(2)$, $c = 7.815(1)$A, $\beta = 97.72(1)°$, $Z = 2$. The atomic positions, including those of hydrogens, were determined by the symbolic addition method and difference Fourier syntheses, and refined by the method of least squares to an R factor of 0.036 for 1941 reflections, measured on a single crystal automatic diffractometer. The chemical composition has been revised to $Na_2O \cdot MgO \cdot 6B_2O_3 \cdot 8H_2O$, as opposed to $Na_2O \cdot MgO \cdot 6B_2O_3 \cdot 10H_2O$ reported by Hurlbut and Erd (1974).

Aristarainite contains the hexaborate polyanion $[B_6O_9(OH)_4]^{4-}$, consisting of three borate triangles and three borate tetrahedra sharing corners. These polyanions are linked into infinite chains, $[B_6O_8(OH)_4]_n^{2n-}$, parallel to the b axis, by sharing a common oxygen corner between a borate tetrahedron and a borate triangle belonging to two different but adjacent polyanions. Aristarainite provides the first example of such chains. Mg and Na, respectively in octahedral and distorted square-pyramidal coordination, bind these chains into sheets parallel to (001), which in turn are cross-linked by hydrogen bonds. The average bond distances (A) are: Mg–O, 2.094; Na–O, 2.509; B–O tetrahedral, 1.471; triangular, 1.363; O–H, 0.89; H···O, 1.91; and O–H···O, 2.782. The average B–O bond, involving the oxygen bonded to three tetrahedrally coordinated borons, is significantly longer (1.517A) than the average tetrahedral B–O bond. All hydrogens are involved in hydrogen bonding except those belonging to one water molecule bonded solely to Na.

Introduction

Aristarainite, a new hydrated sodium magnesium borate from the Tincalayu borax deposit, Salta, Argentina, was first described by Hurlbut and Erd (1974), who named the mineral after L. F. Aristarain of Argentina for his contributions to borate mineralogy. At Tincalayu, it occurs in a matrix of borax and kernite, in association with halite and other borates, mcallisterite, rivadavaite, ezcurrite, ameghinite, kurnakovite, probertite, ulexite, ginorite, tincalconite, and the borosilicate searlesite.

Two of these borates, mcallisterite and rivadavaite, contain the isolated borate polyanion, $[B_6O_7(OH)_6]^{2-}$, consisting of three borate tetrahedra and three borate triangles sharing corners (Dal Negro *et al.*, 1969; Dal Negro *et al.*, 1973). This polyanion has also been found in aksaite (Dal Negro *et al.*, 1971). These polyanions are polymerized into sheets in the structures of tunellite (Clark, 1964), and strontioginorite (Konnert *et al.*, 1970). Following Christ's fourth rule (Christ, 1960), the isolated hexaborate polyanions can polymerize into chains by splitting out water molecules. Aristarainite provides the first example of such a polymerized chain of hexaborate polyanions.

Chemical composition

The chemical composition of aristarainite was reported by Hurlbut and Erd (1974) as $Na_2O \cdot MgO \cdot 6B_2O_3 \cdot 10H_2O$, with two formula units in the unit cell (space group $P2_1/a$). The structure determination indicates the presence of two independent water molecules and four different hydroxyl groups, resulting in a revised chemical formula, $Na_2O \cdot MgO \cdot 6B_2O_3 \cdot 8H_2O$. The calculated density for this composition (2.005 g cm^{-3}) is slightly less than the measured value (2.027 g cm^{-3}). A three-dimensional difference Fourier synthesis, calculated following the final refinement of the structure, was completely featureless, thus confirming the chemical composition of aristarainite reported here.

Experimental

A prismatic crystal of aristarainite (0.08 × 0.14 × 0.42 mm, elongated parallel to *b*) from Salta, Argentina, was mounted with the *b* axis parallel to the phi axis of the computer-controlled automatic single-crystal X-ray diffractometer (Syntex P$\bar{1}$). The unit-cell dimensions, determined from a least-squares refinement of 15 reflections, with 2θ values between 30° and 40°, measured with Mo$K\alpha$ radiation, are listed in Table 1 and are in agreement with those reported by Hurlbut and Erd (1974). The intensity data were collected by the 2θ–θ scan method on the diffractometer with a scintillation counter and Mo$K\alpha$ radiation, monochromatized by reflection from a graphite "single" crystal. A variable-scan method was used, the minimum scan rate being 1°/min. All reflections with 2θ less than 50° were measured, a total of 1941 reflections, of which 292 were below $3\sigma(I)$, $\sigma(I)$ being the standard deviation of I, as measured from counting statistics. For reflections for which I is less than $0.7\sigma(I)$, I was set equal to $0.7\sigma(I)$, regardless of whether I was positive or negative. The intensity data were corrected for Lorentz and polarization factors. An absorption correction was neglected, since the linear absorption coefficient of aristarainite for Mo$K\alpha$ radiation is small (Table 1).

Determination and refinement of the structure

The structure was determined by the symbolic addition method (Karle and Karle, 1966), using the program MULTAN (Germain and Woolfson, 1968). The origin of the unit cell was fixed by choosing the signs of the following reflections:

h	*k*	*l*	Sign
5	3	0	+
8	0	$\bar{7}$	+
4	5	$\bar{1}$	+

Table 1. Aristarainite: crystal data

Aristarainite, $Na_2Mg[B_6O_8(OH)_4]_2\cdot4H_2O$: Salta, Argentina	
Transparent, colorless prisms	
Monoclinic, $2/m$	Space group: $P2_1/a$
a: 18.8862(42)A	Cell content: $Na_4Mg_2[B_6O_8(OH)_2]_4\cdot8H_2O$
b: 7.5208(15)	D_m: 2.027(5) g cm^{-3} (Hurlbut & Erd, 1974)
c: 7.8152(8)	D_c: 2.005 g cm^{-3}
β: 97.719(14)°	$\mu_{(MoK\alpha)}$: 8.57 cm^{-1}
Cell volume: 1100.0(4)A^3	

In addition, the following reflections were assigned symbols:

h	*k*	*l*
16	0	1
3	1	7
6	1	3

The signs for these three reflections turned out to be all "+". In addition, using the Σ_1 relationship, the sign for the reflection (0,8,0) was found to be "−".

The atomic positions of the magnesium, six boron, and thirteen oxygen atoms were found from the first *E*-map. Successive structure-factor calculations and Fourier and difference Fourier syntheses yielded the positions of the sodium atom, the remaining oxygen atom, O(14) (water molecule), and the hydrogen atoms. Refinement of one of the two hydrogen atom positions, H(8A), attached to O(14) posed some difficulty, since it turned out to be occupied half the time. A difference Fourier map indicated a third possible location, H(8B), for the other half hydrogen. Further refinement was carried out holding the occupancy of each of these two hydrogen atoms at 0.5.

A full matrix least-squares program RFINE (Finger, 1969) was used for the final refinement. The atomic scattering factors of Na, Mg, B, O, and H were taken from Cromer and Mann (1968). Anomalous dispersion factors were taken from Cromer and Liberman (1970). The observed structure factors (F_O's) were weighted using the formula $1/\sigma^2(F_O)$, where $\sigma(F_o)$ is the standard deviation of F_o, estimated from the counting statistics.

The final *R*-factor is 0.036 for all 1941 reflections. Final atomic positional and thermal parameters are listed in Table 2, and a list of observed and calculated structure factors appears in Table 3.[1]

Least-squares planes of the hexaborate polyanion have been fitted following Schomaker *et al.* (1959), and the results are listed in Table 4. The bond lengths and angles, as well as thermal ellipsoids and their standard deviations, were calculated using the program ERROR (Finger, 1972, private communication) and are listed in Tables 5 and 6 respectively. The average standard deviation in Na–O, Mg–O, and B–O bond lengths are 0.001, 0.001, and 0.002A, and in O–Na–O, O–Mg–O, and O–B–O angles 0.04, 0.05, and 0.1° respectively.

[1] To obtain a copy of this table, order document Am-77-052 from the Business Office, Mineralogical Society of America, 1909 K Street, N.W., Washington, D. C. 20560. Please remit $1.00 in advance for the microfiche.

Table 2. Aristarainite: atomic positional and thermal parameters* (standard deviation in parentheses)

Atom	x	y	z	$B_{eq.}^{+}$	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Mg	0.00000	0.0000	0.0000	1.07(2)	70(2)	554(15)	410(13)	45(5)	17(4)	9(11)
Na	0.15952(4)	0.3596(1)	0.2899	3.40(2)	157(3)	2380(23)	1059(15)	-167(6)	-1(5)	-302(15)
B1	0.43470(10)	0.3460(3)	0.3264(2)	1.00(3)	66(5)	528(35)	350(30)	6(11)	-10(10)	-27(27)
B2	0.38760(9)	0.1974(3)	0.0335(2)	0.99(3)	65(5)	470(35)	421(29)	0(11)	28(10)	-61(27)
B3	0.30083(10)	0.4000(3)	0.1834(2)	1.00(3)	62(5)	544(35)	377(30)	22(11)	13(10)	-41(26)
B4	0.47496(11)	0.0483(3)	0.2533(3)	1.43(4)	117(6)	659(38)	523(34)	67(12)	92(11)	65(29)
B5	0.25658(10)	0.1548(3)	0.9888(2)	1.06(3)	78(5)	429(33)	448(30)	-9(11)	9(10)	64(27)
B6	0.33928(11)	0.4416(3)	0.4961(3)	1.40(3)	102(6)	684(36)	515(34)	39(12)	37(11)	-20(29)
O1	0.47237(6)	0.1790(2)	0.3709(1)	1.46(2)	114(4)	685(23)	475(19)	91(8)	-34(7)	-5(18)
O2(OH)	0.48064(6)	0.4734(2)	0.2541(1)	1.40(2)	94(3)	852(24)	385(20)	-110(7)	-1(7)	-28(17)
O3	0.37300(5)	0.3084(1)	0.1864(1)	0.94(2)	60(3)	486(21)	354(18)	15(7)	-1(6)	-30(17)
O4	0.40957(6)	0.4121(2)	0.4814(1)	1.28(2)	83(3)	773(23)	376(19)	2(7)	14(6)	-92(17)
O5	0.43580(6)	0.0515(2)	0.0943(1)	1.30(2)	105(4)	556(22)	475(21)	69(7)	14(7)	-31(17)
O6(OH)	0.42279(6)	0.3154(2)	0.9188(1)	1.08(2)	75(3)	528(21)	423(19)	-25(7)	42(6)	-60(17)
O7	0.32265(6)	0.1240(2)	0.9421(1)	1.30(2)	66(3)	723(23)	552(20)	-53(7)	31(7)	-208(17)
O8	0.24590(6)	0.2806(2)	0.1069(1)	1.31(2)	61(3)	639(23)	680(21)	-31(7)	33(7)	-177(18)
O9	0.19713(6)	0.0630(2)	0.9168(2)	1.37(2)	57(3)	617(23)	783(22)	-21(7)	9(7)	-208(18)
O10	0.28768(6)	0.4373(2)	0.3579(1)	1.54(2)	80(3)	1054(25)	453(20)	80(7)	19(7)	-114(19)
O11(OH)	0.48078(8)	0.0953(2)	0.7071(2)	2.89(3)	340(6)	1275(30)	404(21)	480(11)	38(9)	107(21)
O12	0.31871(7)	0.4800(2)	0.6537(2)	2.63(3)	137(4)	2170(36)	438(23)	226(10)	34(8)	-154(23)
O13(H_2O)	0.08086(6)	0.2036(2)	0.0388(1)	1.54(2)	87(3)	671(23)	790(22)	8(7)	41(7)	61(19)
O14(H_2O)	0.16514(11)	0.3779(3)	0.5931(3)	6.20(5)	392(8)	3457(59)	2377(46)	174(18)	383(15)	26(43)
H1	0.489(1)	0.491(3)	0.667(3)	0.8(5)						
H2	0.438(1)	0.238(3)	0.842(3)	1.2(5)						
H3	0.476(1)	0.118(3)	0.599(3)	1.4(5)						
H4	0.348(1)	0.444(3)	0.741(3)	1.4(5)						
H5	0.073(1)	0.309(3)	0.983(3)	1.0(5)						
H6	0.119(2)	0.161(4)	-0.007(3)	2.4(6)						
H7	0.166(2)	0.502(5)	0.562(4)	3.2(8)						
H8A††	0.184(4)	0.367(10)	0.715(10)	5.0(1.9)						
H8B††	0.117(4)	0.289(9)	0.585(7)	3.6(1.4)						

*$\beta_{ij} \times 10^5$; form of the anisotropic temperature factor, $\exp\{\sum_{i=1}^{3}\sum_{j=1}^{3} h_i h_j \beta_{ij}\}$

†Equivalent isotropic temperature factors ($\AA^2$), calculated from the anisotropic temperature factors except for hydrogens

††Occupancy factor 0.5

Description of the structure

The crystal structure of aristarainite consists of $[B_6O_9(OH)_4]^{4-}$ hexaborate polyanions linked into chains, $[Mg(OH)_4(H_2O)_2]$ octahedra, and $[NaO_3(H_2O)_2]$ polyhedra.

The $[Mg(OH)_4(H_2O)_2]$ octahedron

The $[Mg(OH)_4(H_2O)_2]$ octahedron with point symmetry $\bar{1}$ is a tetragonal bipyramid, with the four (OH) groups forming a square plane and the two H_2O molecules completing the octahedron. The average Mg–O distance is 2.094A. The longest Mg–O bond (2.155A) involves the water molecule O(13). The configuration is shown in Figure 1. The O–H distances vary from 0.83 to 0.91A and the Mg–O–H angles from 106 to 119°.

The $[NaO_3(H_2O)_2]$ polyhedron

The Na-polyhedron is a highly distorted square pyramid, with three oxygen atoms O(7), O(8), O(10) and a water molecule, O(13) forming the base and a water molecule O(14) forming the apex.[2] Two centrosymmetrically related Na-square pyramids share O(13) corners with the Mg-octahedron, thereby forming isolated trimers (Fig. 2). The average Na–O distance is 2.509A. The water molecule, O(14), is solely bonded to Na. The chemical analysis of aristarainite (Hurlbut and Erd, 1974) indicates a small amount of K replacing Na, which is understandable in view of the unusually large average Na–O distance.

The hexaborate $[B_6O_9(OH)_4]^{4-}$ polyanion

The basic structural unit of aristarainite is the hexaborate polyanion, $[B_6O_9(OH)_4]^{4-}$ (Fig. 3), consisting of a BO_4 tetrahedron, two $BO_3(OH)$ tetrahedra, two

[2] Two further (OH) ions, O(12), and O(11), at distances of 2.910 and 3.191A respectively, may be considered bonded to Na. However, in view of the closest Na–B approach [Na–B(3) 2.916A], these long Na–O bonds do not appear to be significant.

Table 4. Aristarainite: ring angles, planes, and deviations from ring planes

Ring	Ring atoms	B-O-B angles (°)	
1	B(1)-O(3)-B(2)-O(5)-B(4)-O(1)	B(1)-O(3)-B(2)	118.0(1)
		B(2)-O(5)-B(4)	123.3(1)
		B(4)-O(1)-B(1)	121.6(1)
2	B(2)-O(3)-B(3)-O(8)-B(5)-O(7)	B(2)-O(3)-B(3)	119.7(1)
		B(3)-O(8)-B(5)	123.6(1)
		B(5)-O(7)-B(2)	123.3(1)
3	B(3)-O(3)-B(1)-O(4)-B(6)-O(10)	B(3)-O(3)-B(1)	121.8(1)
		B(1)-O(4)-B(6)	123.9(1)
		B(6)-O(10)-B(3)	124.1(1)

Parameters of planes defined by ring oxygens*

Ring	A	B	C	D	Angle (°) between ring planes	
1	13.00944	4.54929	-3.81706	5.54414	1 ^ 2	141.5
2	1.71999	5.91848	-4.82170	1.56835	2 ^ 3	161.5
3	4.39169	6.82850	-2.94417	3.19559	3 ^ 1	148.1
Parameters of planes defined by three tetrahedral borons, B(1), B(2), B(3)						
4	6.83866	5.98688	-4.13592	3.69365	1 ^ 4	157.6
					2 ^ 4	162.8
					3 ^ 4	167.4

Deviation from ring-planes defined by three oxygens

Atom	Ring 1 Deviation (Å)	Atom	Ring 2 Deviation (Å)	Atom	Ring 3 Deviation (Å)
B(1)	+0.439	B(2)	+0.105	B(1)	+0.115
B(2)	+0.268	B(3)	+0.432	B(3)	+0.317
B(4)	-0.113	B(5)	-0.157	B(6)	-0.151
O(11)	-0.341	O(9)	-0.455		-0.443

Deviation from ring-planes defined by three tetrahedral borons

Atom	Deviation (Å)
O(3)	-0.067

*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 planes from the origin in Å units.

$BO_2(OH)$ triangles, and a BO_3 triangle. The three borate tetrahedra share a common oxygen atom O(3). Although the hexaborate polyanion found in aristarainite approximates C_{3v} symmetry, the oxygen atoms O(2) and the terminal hydrogen atoms do not conform to this symmetry. The equations for the best-fit least-squares planes for the three B–O rings defined by three oxygens, O(3), O(1), O(5); O(3), O(7), O(9); and O(3), O(10), O(4) are listed in Table 4. In each case, the triangularly-coordinated boron and the terminal oxygen atoms attached to it are considerably below these planes. The angles between these planes are 141.5°, 161.5°, and 148.1°. The triply-coordinated oxygen atom O(3) deviates very slightly (0.067A) from the least-squares plane defined by the three tetrahedral boron atoms.

The average tetrahedral B–O distances within B(1)-, B(2)-, and B(3)-tetrahedra are 1.470, 1.475, and 1.467A, respectively. However, within these tetrahedra the bond distances between the boron and the triply-coordinated oxygen atom O(3) (1.514, 1.514, and 1.524A) are significantly larger, in agreement with the prediction based on bond strengths made by Zachariasen (1963) for the B–O distance of an oxygen linked to three borons. The average B–O distance in the three boron–oxygen triangles is 1.363 ± 002A; the terminal (nbr) B–O distance (av. 1.375A) is slightly larger than the bridging B–O distances (av. 1.358A). The average B–B separation within the polyanion is 2.521A. However, the separation between the tetrahedral borons (av. 2.625A) is much larger than the tetrahedral–triangular B–B separations (av. 2.472A).

The stereochemical features of the hexaborate polyanion contained in aristarainite are closely com-

Table 5. Aristarainite: interatomic distances (A) and angles (°) (standard deviations in parentheses)

Mg - Octahedron

Mg - O(2)(OH)	2.077(1)(x2)	O(2) - Mg - O(6)	91.23(4)(x2)
Mg - O(6)(OH)	2.051(1)(x2)	O(2) - Mg - O(6')	88.77(4)(x2)
Mg - O(13)(w)	2.155(1)(x2)	O(2) - Mg - O(13)	90.54(5)(x2)
Mean	2.094	O(2) - Mg - O(13')	89.46(5)(x2)
		O(6) - Mg - O(13)	91.35(4)(x2)
O(2) - O(6)	2.950(2)(x2)	O(6) - Mg - O(13')	88.65(4)(x2)
O(2) - O(6')	2.887(2)(x2)	Mean	90.00
O(2) - O(13)	3.007(2)(x2)		
O(6) - O(13)	3.010(2)(x2)		
O(2') - O(13)	2.979(2)(x2)		
O(6') - O(13)	1.940(2)(x2)		
Mean	2.962		

Na - Polyhedron

Na - O(7)	2.742(1)	O(7) - Na - O(8)	68.26(4)
Na - O(8)	2.385(1)	O(7) - Na - O(10)	76.57(4)
Na - O(10)	2.477(1)	O(7) - Na - O(13)	86.35(4)
Na - O(13)(w)	2.579(1)	O(7) - Na - O(14)	128.93(8)
Na - O(14)(w)	2.362(1)	O(8) - Na - O(10)	57.32(4)
Mean	2.509	O(8) - Na - O(13)	78.52(4)
O(7) - O(8)	2.891(2)	O(8) - Na - O(14)	132.38(7)
O(7) - O(10)	3.241(2)	O(10) - Na - O(13)	135.81(5)
O(7) - O(13)	3.643(2)	O(10) - Na - O(14)	81.95(6)
O(7) - O(14)	4.056(3)	O(13) - Na - O(14)	137.18(7)
O(8) - O(10)	2.333(2)	Mean	98.43
O(8) - O(13)	3.145(3)		
O(8) - O(14)	4.342(3)		
O(10) - O(13)	4.731(3)		
O(10) - O(14)	3.174(3)		
O(13) - O(14)	4.228(3)		
Mean	3.578		

B(1) - Tetrahedron

B(1) - O(1)	1.462(2)	O(1) - B(1) - O(2)	111.2(1)
B(1) - O(2)(OH)	1.457(2)	O(1) - B(1) - O(3)	108.3(1)
B(1) - O(3)	1.514(2)	O(1) - B(1) - O(4)	107.5(1)
B(1) - O(4)	1.447(2)	O(2) - B(1) - O(3)	106.4(1)
Mean	1.470	O(2) - B(1) - O(4)	112.2(1)
O(1) - O(2)	2.408(2)	O(3) - B(1) - O(4)	111.2(1)
O(1) - O(3)	2.413(2)	Mean	109.47
O(1) - O(4)	2.345(2)		
O(2) - O(3)	2.380(2)		
O(2) - O(4)	2.411(2)		
O(3) - O(4)	2.444(1)		
Mean	2.400		

B(2) - Tetrahedron

B(2) - O(3)	1.513(2)	O(3) - B(2) - O(5)	109.2(1)
B(2) - O(5)	1.463(2)	O(3) - B(2) - O(6)	106.9(1)
B(2) - O(6)(OH)	1.481(2)	O(3) - B(2) - O(7)	111.6(1)
B(2) - O(7)	1.444(2)	O(5) - B(2) - O(6)	109.6(1)
Mean	1.475	O(5) - B(2) - O(7)	108.9(1)
O(3) - O(5)	2.426(2)	O(6) - B(2) - O(7)	110.5(1)
O(3) - O(6)	2.401(1)	Mean	109.45
O(3) - O(7)	2.446(2)		
O(5) - O(6)	2.406(2)		
O(5) - O(7)	2.366(2)		
O(6) - O(7)	2.403(2)		
Mean	2.408		

B(3) - Tetrahedron

B(3) - O(3)	1.524(2)	O(3) - B(3) - O(8)	108.5(1)
B(3) - O(8)	1.440(2)	O(3) - B(3) - O(9')	107.5(1)
B(3) - O(9')	1.457(2)	O(3) - B(3) - O(10)	109.8(1)
B(3) - O(10)	1.446(2)	O(8) - B(3) - O(9')	111.8(1)
Mean	1.467	O(8) - B(3) - O(10)	107.9(1)
O(3) - O(8)	2.406(1)	O(9') - B(3) - O(10)	111.3(1)
O(3) - O(9')	2.405(1)	Mean	109.47
O(3) - O(10)	2.432(2)		
O(8) - O(9')	2.399(2)		
O(8) - O(10)	2.333(2)		
O(9') - O(10)	2.398(2)		
Mean	2.396		

B(4) - Triangle

B(4) - O(1)	1.351(2)	O(1) - B(4) - O(5)	123.0(2)
B(4) - O(5)	1.358(2)	O(1) - B(4) - O(11)	119.7(2)
B(4) - O(11)(OH)	1.375(2)	O(5) - B(4) - O(11)	117.4(2)
Mean	1.361	Mean	120.0
O(1) - O(5)	2.381(2)		
O(1) - O(11)	2.357(2)		
O(5) - O(11)	2.335(2)		
Mean	2.358		

B(5) - Triangle

B(5) - O(7)	1.366(2)	O(7) - B(5) - O(8)	121.7(2)
B(5) - O(8)	1.356(2)	O(7) - B(5) - O(9)	122.1(2)
B(5) - O(9)	1.373(2)	O(8) - B(5) - O(9)	116.3(2)
Mean	1.365	Mean	120.0
O(7) - O(8)	2.376(2)		
O(7) - O(9)	2.397(2)		
O(8) - O(9)	2.317(2)		
Mean	2.363		

B(6) - Triangle

B(6) - O(4)	1.366(2)	O(4) - B(6) - O(10)	122.2(2)
B(6) - O(10)	1.354(2)	O(4) - B(6) - O(12)	120.4(2)
B(6) - O(12)(OH)	1.371(2)	O(10) - B(6) - O(12)	117.5(2)
Mean	1.364	Mean	120.0
O(4) - O(10)	2.381(2)		
O(4) - O(12)	2.374(2)		
O(10) - O(12)	2.329(2)		
Mean	2.361		

Av. tetrahedral B-O distance	1.471
Av. triangular B-O distance	1.363

Hydrogen Bonds

(OH) Group (1)

H(1) - O(2)	0.83(3)	O(2) - H(1)...O(4)	176(2)
H(1) - O(4)	2.03(3)	Mg - O(2) - H(1)	119(2)
O(2) - O(4)	2.857(2)	B(1) - O(2) - H(1)	108(3)

(OH) Group (2)

H(2) - O(6)	0.91(2)	O(6) - H(2)...O(11)	171(2)
H(2) - O(11)	1.78(2)	Mg - O(6) - H(2)	112(2)
O(6) - O(11)	2.676(2)	B(2) - O(6) - H(2)	102(3)

(OH) Group (3)

H(3) - O(11)	0.86(3)	O(11) - H(3)...O(1)	174(2)
H(3) - O(1)	1.83(3)	B(4) - O(11) - H(3)	111(3)
O(11) - O(1)	2.686(2)		

(OH) Group (4)

H(4) - O(12)	0.86(3)	O(12) - H(4)...O(6)	169(2)
H(4) - O(6)	2.08(3)	B(6) - O(12) - H(4)	114(3)
O(12) - O(6)	2.932(2)	Na - O(12) - H(4)	97(3)

Water Molecule (1)

H(5) - O(13)	0.91(3)	H(5) - O(13) - H(6)	102(2)
H(6) - O(13)	0.91(3)	O(13) - H(5)...O(5)	169(2)
H(5) - H(6)	1.41(4)	O(13) - H(6)...O(9)	175(2)
H(5) - O(5)	1.92(3)	Mg - O(13) - H(5)	119(2)
O(13) - O(5)	2.818(2)	Mg - O(13) - H(6)	106(2)
H(6) - O(9)	1.81(3)		
O(13) - O(9)	2.723(2)		

Water Molecule (2)

H(7) - O(14)	0.96(3)	H(7) - O(14) - H(8A)	108(5)
H(8A) - O(14)	0.98(8)	H(7) - O(14) - H(8B)	127(5)
H(8B) - O(14)	1.13(7)	H(8A) - O(14) - H(8B)	101(7)
H(7) - H(8A)	1.57(8)	Na - O(14) - H(7)	79(2)
H(7) - H(8B)	1.87(7)	Na - O(14) - H(8A)	159(5)
H(8A) - H(8B)	1.63(9)	Na - O(14) - H(8B)	89(4)

B-B Distances

tetrahedral-tetrahedral		tetrahedral-triangular	
B(1) - B(2)	2.595(3)	B(1) - B(4)	2.456(3)
B(1) - B(3)	2.655(3)	B(1) - B(6)	2.483(3)
B(2) - B(3)	2.626(3)	B(2) - B(4)	2.483(3)
Mean	2.625	B(2) - B(5)	2.473(3)
		B(3) - B(5)	2.464(3)
		B(3) - B(6)	2.474(3)
		Mean	2.472

Table 6. Aristarainite: thermal ellipsoids (standard deviations in parentheses)

Atom	Axis	rms amplitude (Å)	Angle (°) with respect to +a	+b	+c
Mg	r1	0.102	33(11)	58(11)	89(9)
	r2	0.112	92(8)	97(5)	168(5)
	r3	0.133	122(5)	35(5)	99(4)
Na	r1	0.147	149(3)	71(2)	59(3)
	r2	0.188	122(2)	91(1)	141(2)
	r3	0.269	77(1)	15(1)	99(1)
B1	r1	0.095	130(16)	89(9)	32(16)
	r2	0.116	133(34)	114(18)	121(30)
	r3	0.125	109(20)	30(13)	109(18)
B2	r1	0.105	56(59)	64(31)	52(38)
	r2	0.109	32(102)	116(67)	113(70)
	r3	0.122	89(13)	40(17)	129(17)
B3	r1	0.102	165(45)	105(45)	82(61)
	r2	0.106	99(57)	108(22)	155(29)
	r3	0.129	108(9)	27(9)	107(9)
B4	r1	0.112	56(17)	78(14)	44(17)
	r2	0.126	109(17)	145(16)	60(11)
	r3	0.161	139(10)	53(10)	69(8)
B5	r1	0.105	91(17)	35(18)	124(16)
	r2	0.114	30(48)	112(38)	117(46)
	r3	0.127	56(19)	66(14)	50(14)
B6	r1	0.122	62(32)	68(27)	43(26)
	r2	0.129	48(51)	60(41)	130(49)
	r3	0.148	127(13)	38(13)	95(8)
O1	r1	0.105	129(9)	118(8)	45(9)
	r2	0.128	108(6)	131(6)	131(3)
	r3	0.168	136(4)	56(4)	109(4)
O2	r1	0.100	128(11)	67(9)	41(10)
	r2	0.118	125(11)	68(8)	131(10)
	r3	0.171	58(3)	34(3)	85(2)
O3	r1	0.097	141(21)	92(10)	43(21)
	r2	0.107	124(21)	119(10)	127(17)
	r3	0.122	113(9)	36(8)	112(9)
O4	r1	0.104	95(7)	77(3)	14(3)
	r2	0.122	19(7)	85(4)	79(6)
	r3	0.151	94(4)	15(3)	104(3)
O5	r1	0.110	55(15)	38(15)	81(12)
	r2	0.119	80(10)	91(11)	177(13)
	r3	0.152	139(5)	56(5)	104(4)
O6	r1	0.107	57(38)	84(20)	41(37)
	r2	0.111	46(47)	132(41)	111(30)
	r3	0.131	62(9)	36(7)	115(8)
O7	r1	0.100	148(13)	61(10)	72(9)
	r2	0.116	121(10)	110(4)	135(9)
	r3	0.160	80(2)	34(3)	123(3)
O8	r1	0.101	163(5)	73(6)	88(4)
	r2	0.121	108(7)	133(5)	128(4)
	r3	0.158	93(2)	129(4)	40(4)
O9	r1	0.098	161(6)	72(5)	80(3)
	r2	0.121	113(6)	140(5)	117(3)
	r3	0.167	84(2)	120(3)	33(3)
O10	r1	0.109	43(40)	71(20)	61(37)
	r2	0.116	58(24)	90(9)	156(24)
	r3	0.181	106(2)	24(2)	102(2)
O11	r1	0.102	113(10)	128(12)	43(11)
	r2	0.119	114(10)	123(12)	132(10)
	r3	0.292	144(9)	55(9)	94(1)
O12	r1	0.110	73(5)	80(2)	27(4)
	r2	0.137	20(5)	71(4)	105(5)
	r3	0.262	110(2)	23(2)	97(1)
O13	r1	0.124	166(4)	96(8)	95(5)
	r2	0.137	84(9)	159(6)	71(6)
	r3	0.157	89(3)	72(6)	20(6)
O14	r1	0.218	46(4)	81(1)	53(4)
	r2	0.289	58(6)	62(3)	141(5)
	r3	0.324	113(4)	25(3)	79(3)

parable with those of similar polyanions found in tunellite (Clark, 1964), strontioginorite (Konnert *et al.*, 1970), mcallisterite (Dal Negro *et al.*, 1969), and aksaite (Dal Negro *et al.*, 1971). The average angle between the fitted least-squares ring planes within the hexaborate polyanion in aristarainite (150°) is very close to those found in tunellite (151°) and strontioginorite (150 and 155°), where the polyanions are polymerized into sheets. On the other hand, within the monomeric hexaborate polyanions in aksaite and mcallisterite, this average inter-ring angle is much larger (160 and 162° respectively). The value of the inter-ring angle apparently decreases as a result of the polymerization.

The $[B_6O_8(OH)_4]_n^{2n-}$ chains

The $[B_6O_9(OH)_4]^{4-}$ polyanions form infinite chains running parallel to the *b* axis by sharing an oxygen corner [O(9)] of a triangular borate group [B(5)] of one polyanion with a tetrahedral borate group [B(3)] of another polyanion (Fig. 1).

Sheet structure

Each of the two centrosymmetrically-related hexaborate polyanions occurring on either side of the magnesium atom share apices of B(1)- and B(2)-tetrahedra, *i.e.* O(2) and O(6), with corners of the Mg-octahedron (Fig. 1). Infinite chains, parallel to the *a* axis, are formed in this way. Such chains are cross-linked by Na atoms, which share on one side the O(13) corner of the Mg-octahedron and on the other the O(8)–O(10) edge of the B(3)-tetrahedron and O(7), a corner common between the B(5)-triangle and the B(2)-tetrahedron. Linking of two sets of cross-chains by Na atoms results in a sheet structure parallel to the (001) plane (Figs. 1 and 4). Such sheets are cross-linked through hydrogen bonds. The sheet structure explains the excellent {001} cleavage of this mineral, which breaks only hydrogen bonds. The other good cleavage, {100}, breaks Mg–O bonds.

Hydrogen bonds

The O–H distances range from 0.83 to 1.13A. All the hydrogens except those belonging to the water molecule O(14) are involved in hydrogen bonding. The O–H···O distances range from 2.676 to 2.932A, whereas the O–H···O angles range from 169 to 175°. Of the six hydrogens involved in hydrogen bonding, H(2), H(5), and H(6) form weak bonds within the sheet, linking the Mg-octahedron and the Na-polyhedron with adjacent borate polyanions (Fig. 1). The other three hydrogen atoms H(1), H(3), and H(4), cross-link composite Na–Mg–borate sheets (Fig. 4).

The situation with the water molecule, O(14) is anomalous, since it is not involved in any hydrogen bonding. Furthermore, one of the two hydrogens is split into two "half-hydrogens." Two of the H–O–H angles are normal (101 and 109°), whereas the third one (127°) is unusually large.

Anisotropic thermal vibrations

Within the hexaborate polyanion, the anisotropy of the thermal vibration is most pronounced for the two terminal oxygen atoms O(11) and O(12), and least pronounced for the triply-coordinated oxygen atom O(3) (Table 5 and Fig. 5). The vibrations of the boron atoms are mildly anisotropic; on the average the triangular borons are slightly more anisotropic than the tetrahedral borons. Whereas vibration of the magnesium atom is slightly anisotropic, that of the sodium atom is very strongly anisotropic, which is consistent with each of their bonding environments. Strong anisotropic thermal vibration is also shown by one of the two water molecules O(14), which is bonded only to Na, as opposed to O(13), which is bonded to both Mg and Na (Fig. 6).

Comparison with other magnesium borates containing the hexaborate polyanion

As mentioned earlier, the isolated hexaborate $[B_6O_7(OH)_6]^{2-}$ polyanion has been found in mcallisterite (Dal Negro *et al.*, 1969), aksaite (Dal Negro *et al.*, 1971), and rivadavaite (Dal Negro *et al.*, 1973). In mcallisterite, the hexaborate polyanion shares three corners of tetrahedral borate groups with the Mg-octahedron and occurs as isolated polyanion-octahedron complexes (Fig. 1 in Dal Negro *et al.*, 1969). In aksaite, on the other hand, the apices of three borate-tetrahedra are shared by the Mg-octahedron on one side and a corner of a borate-triangle on the other, thereby forming infinite chains (Fig. 2 in Dal Negro *et al.*, 1971). In aristarainite, two centrosymmetrically-related hexaborate polyanions share two tetrahedral corners each on either side of the Mg-octahedron (Fig. 1), forming infinite chains parallel to the *a* axis. In rivadavaite, two centrosym-

Table 7. Nature of the polyanions contained in the borate minerals of the Tincalayu deposit, Salta, Argentina

MINERAL	STRUCTURAL FORMULA	POLYANION	DESCRIPTION*	DEGREES OF POLYMERIZATION	REFERENCES
Borax	$Na_2[B_4O_5(OH)_4]\cdot 8H_2O$	$[B_4O_5(OH)_4]^{2-}$	4:2Δ+2T	Monomers	Morimoto (1956) Giese (1968)
Tincalconite	$Na_2[B_4O_5(OH)_4]\cdot 3H_2O$	$[B_4O_5(OH)_4]^{2-}$	4:2Δ+2T	Monomers	Giacovazzo *et al.* (1973)
Kernite	$Na_2[B_4O_6(OH)_2]\cdot 3H_2O$	$[B_4O_6(OH)_2]^{2-}$	4:2Δ+2T	Chains	Giese (1966); Cialdi *et al.* (1967); Cooper *et al.* (1973)
Ameghinite	$Na[B_3O_3(OH)_4]$	$[B_3O_3(OH)_4]^{-}$	3:2Δ+1T	Monomers	Dal Negro *et al.* (1975)
Ezcurrite	$Na_2[B_5O_7(OH)_3]\cdot 2H_2O$	$[B_5O_7(OH)_3]^{2-}$	5:3Δ+2T	Chains	Cannillo *et al.* (1973)
Ulexite	$NaCa[B_5O_6(OH)_6]\cdot 5H_2O$	$[B_5O_6(OH)_6]^{3-}$	5:2Δ+3T	Monomers	Clark & Appleman (1964); Ghose *et al.* (in preparation)
Probertite	$NaCa[B_5O_7(OH)_4]\cdot 3H_2O$	$[B_5O_7(OH)_4]^{3-}$	5:2Δ+3T	Chains	Rumanova *et al.* (1966)
Rivadavaite	$Na_6Mg[B_6O_7(OH)_6]_4\cdot 10H_2O$	$[B_6O_7(OH)_6]^{2-}$	6:3Δ+3T	Two distinct monomers	Dal Negro *et al.* (1973)
Aristarainite	$Na_2Mg[B_6O_8(OH)_4]_2\cdot 4H_2O$	$[B_6O_9(OH)_4]^{2-}$	6:3Δ+3T	Chains	This paper
Mcallisterite	$Mg_2[B_6O_7(OH)_6]_2\cdot 9H_2O$	$[B_6O_7(OH)_6]^{2-}$	6:3Δ+3T	Monomers	Dal Negro *et al.* (1969)
Kurnakovite	$Mg[B_3O_3(OH)_5]\cdot 5H_2O$	$[B_3O_3(OH)_5]^{2-}$	3:1Δ+2T	Monomers	Yeh (1965); Razmanova *et al.* (1969); Corazza(1974)
Ginorite†	$Ca_2[B_{14}O_{20}(OH)_6]\cdot 5H_2O$	$[B_{14}O_{20}(OH)_6]^{4-}$	6:3Δ+3T 6:[3Δ+3T]+2Δ	Sheets	Konnert *et al.* (1970)

* Δ: Borate triangle; T: Borate tetrahedron (see Christ and Clark, 1977).

† Konnert *et al.* (1970) determined the structure of strontioginorite, persumably isostructural with ginorite.

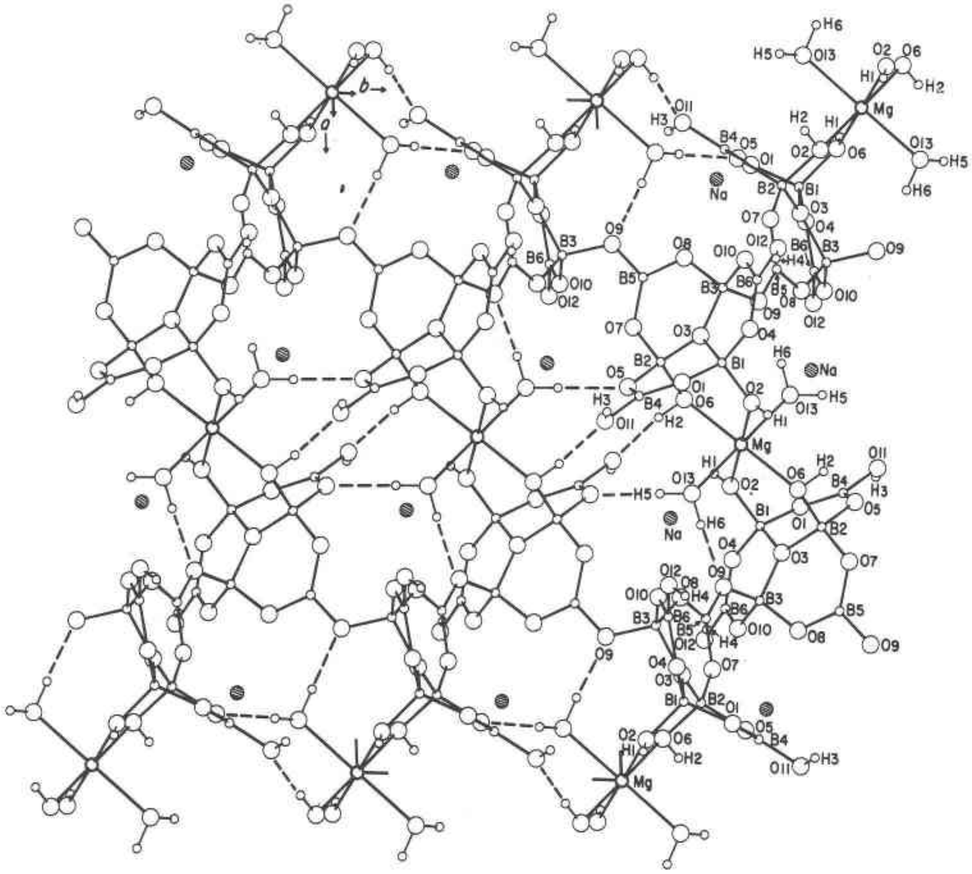

Fig. 1. A view of the crystal structure of aristarainite down the c axis, showing the octahedral Mg-coordination and the chains of hexaborate polyanions parallel to the b axis. Na-coordination not shown.

metrically-related polyanions (one of two sets) sandwich a Mg-octahedron and occur as an isolated polyanion-octahedron complex.

In mcallisterite, the Mg-octahedron consists of three (OH) groups and three H_2O molecules, whereas in aksaite, rivadavaite, and aristarainite the Mg-octahedron consists of four (OH) groups and two H_2O molecules. However, in aksaite the H_2O molecules are in *cis*-configuration, whereas in rivadavaite and aristarainite they are in *trans*-configuration within the Mg-octahedron.

Polymerization of the $[B_6O_7(OH)_6]^{2-}$ polyanions

The isolated hexaborate polyanions can polymerize into chains, as in aristarainite, by the following reaction:

$$n[B_6O_7(OH)_6]^{2-} \rightarrow [B_6O_8(OH)_4]_n^{2n-} + nH_2O.$$

These chains can polymerize further into sheets as found in tunellite by the following reaction:

$$n[B_6O_8(OH)_4]^{2-} \rightarrow [B_6O_9(OH)_2]_n^{2n-} + nH_2O.$$

It is conceivable that such sheets can polymerize further into three-dimensional framework structures by the reaction:

$$n[B_6O_9(OH)_2]^{2-} \rightarrow [B_6O_{10}]_n^{2n-} + nH_2O.$$

Examples of such three-dimensional framework structures are so far unknown.

Borate polyanions and the paragenesis of borate minerals at Salta, Argentina

The Tincalayu borate deposit at Salar del Hombre Muerto, Salta, Argentina, consists mainly of borax and kernite. A number of sodium-magnesium borates and pure magnesium borates, some of which are unique to this deposit, occur as nodules within the borax-kernite matrix (Hurlbut and Erd, 1974). Pure calcium borate minerals such as colemanite are remarkably absent. The borate minerals in this deposit and the polyanions contained in them are listed in

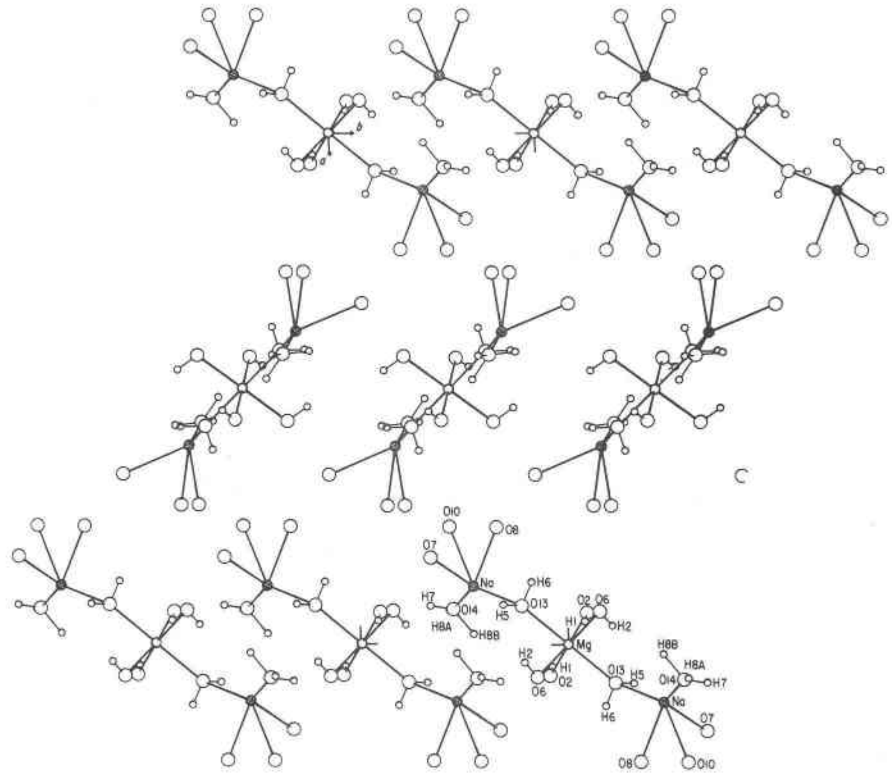

Fig. 2. Mg- and Na-coordination polyhedra in aristarainite viewed along the *c* axis.

Table 7. As mentioned earlier, the hexaborate polyanion occurs as monomers in mcallisterite and rivadavaite, as chains in aristarainite, and as sheets in ginorite. In ginorite, in addition, a small diborate side-chain is attached to one of the two crystallographically-distinct hexaborate polyanions. The pentaborate polyanion, consisting of three tetrahedra and two triangles, occurs as monomers in ulexite and as chains in probertite. Likewise, the tetraborate polyanion, consisting of two tetrahedra and two triangles, occurs as monomers in borax and tincalconite and as chains in kernite. Ezcurrite contains chains of a different type of pentaborate polyanion, consisting of two tetrahedra and three triangles. Ameghinite contains monomers of a triborate polyanion consisting of one tetrahedron and two triangles, whereas kurnakovite contains a monomeric triborate polyanion consisting of two tetrahedra and one triangle. In summary, the borate deposit at Salta contains six different types of polyanions, either as monomers or polymers.

The borate deposit at Salta, Argentina, was originally a playa deposit. It was subsequently folded and uplifted (Hurlbut and Erd, 1974). These orogenic movements may have resulted in the dehydration and low-grade metamorphism of the primary borates. Some of the minerals containing borate polymers, such as aristarainite, may have resulted from the metamorphism of primary minerals such as rivadavaite, which contains two types of monomeric

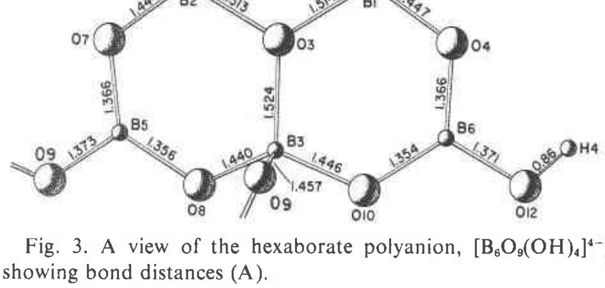

Fig. 3. A view of the hexaborate polyanion, $[B_6O_9(OH)_4]^{4-}$, showing bond distances (Å).

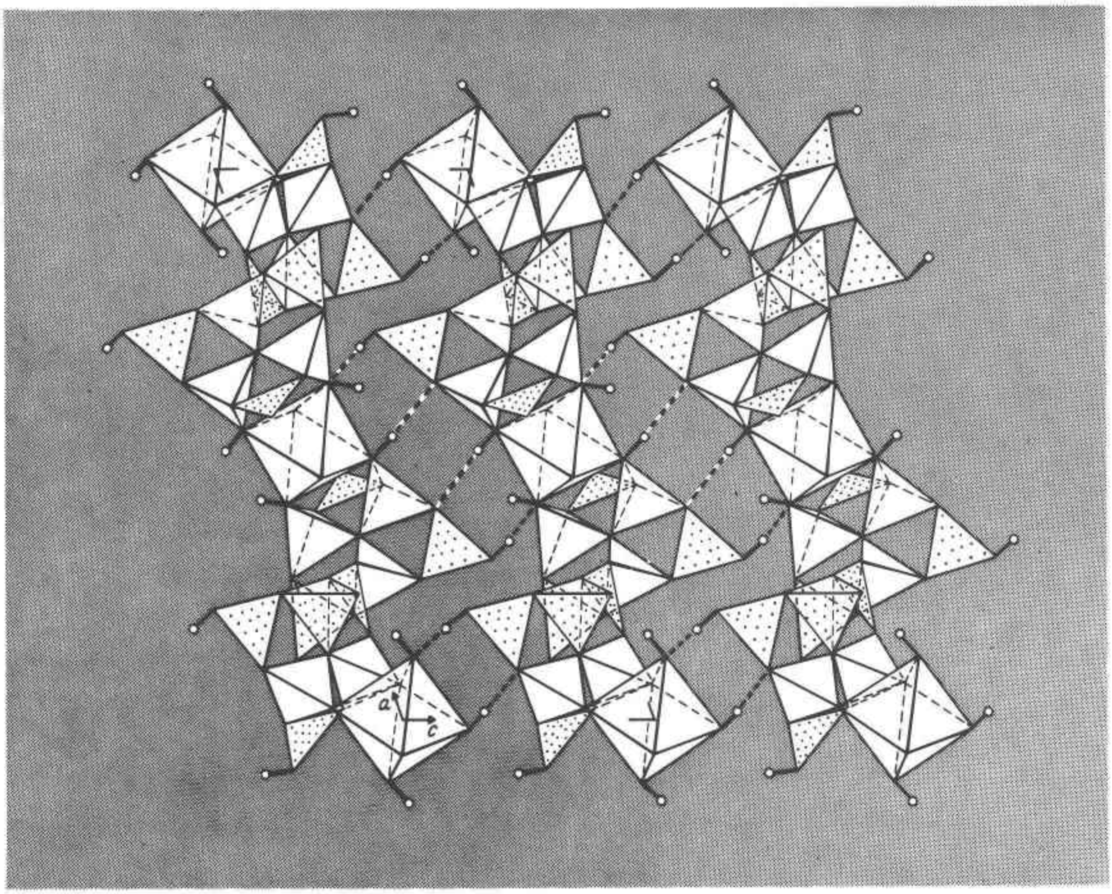

Fig. 4. Aristarainite: the sheet structure made up of hexaborate polyanions and Mg-octahedra (Na-polyhedra not shown), viewed down the *b* axis. The sheets are cross-linked by hydrogen bonds (shown in broken lines).

hexaborate polyanions. This situation is comparable to the formation of kernite from borax at the Kramer deposit, Boron, California (Christ and Garrels, 1959). A knowledge of the phase relations of these minerals both in the solid state and in aqueous solution as a function of the concentration of Na, Ca, Mg would be necessary to unravel the phase relations of the borate minerals in this deposit. The crystal-chemical groundwork for such an understanding has now been completed with the determination of the structure of aristarainite.

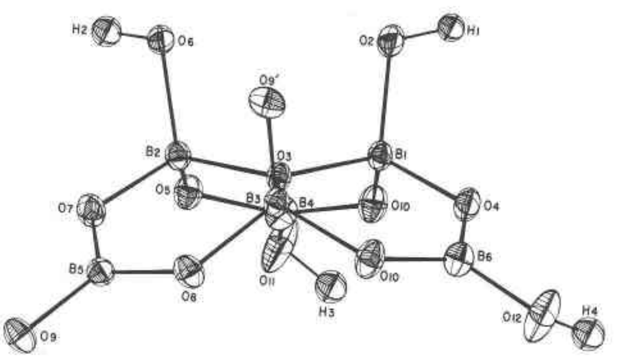

Fig. 5. A view of the hexaborate polyanion in aristarainite, showing ellipsoids of thermal vibration.

Conclusions

(1) The crystal structure of aristarainite contains hexaborate polyanions, consisting of three tetrahedra sharing a common oxygen corner and three triangles, linked into chains by sharing an oxygen corner common between a borate tetrahedron and a borate triangle belonging to two different but adjacent polyanions. The polymerization reaction can be written as:

$$n[B_6O_7(OH)_6]^{2-} \rightarrow [B_6O_8(OH)_4]_n^{2n-} + nH_2O.$$

(2) The chains of hexaborate polyanions are bonded into sheets through Mg and Na in octahedral and distorted square-pyramidal coordination respectively, and through hydrogen bonds. Such sheets are cross-linked solely through hydrogen bonds.

(3) The tetrahedral B–O bond involving the triply-

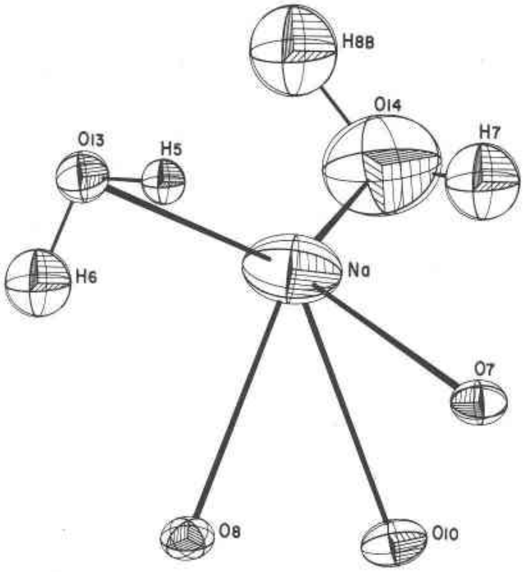

Fig. 6. A view of the Na-polyhedron in aristarainite, showing ellipsoids of thermal vibration.

coordinated oxygen (1.517A) is significantly longer than the average tetrahedral B–O bond (1.471A) consistent with bond strength requirements. The average terminal (nbr) triangular B–O bond (1.375A) is significantly longer than the average triangular B–O bond (1.363A).

(4) The average angle in between least-square planes through three different hexagonal B–O rings in the hexaborate polyanion found in aristarainite is significantly smaller than those in monomeric hexaborate polyanions found in mcallisterite and aksaite. Apparently this angle decreases with polymerization.

Acknowledgments

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References

Cannillo, E., A. Dal Negro and L. Ungaretti (1973) The crystal structure of ezcurrite. *Am. Mineral., 50,* 110–115.

Christ, C. L. (1960) Crystal chemistry and systematic classification of hydrated borate minerals. *Am. Mineral., 45,* 334–340.

—— and R. M. Garrels (1959) Relations among sodium borate hydrates at the Kramer deposit, Boron, California. *Am. J. Sci., 257,* 516–528.

—— and J. R. Clark (1977) A crystal chemical classification of borate structures with special emphasis on hydrated borates. *Phys. Chem. Minerals, 1.,* in press.

Cialdi, G. E. Corazza and C. Sabelli (1967) La struttura cristallina della kernite, $Na_2B_4O_6(OH)_2 \cdot 3H_2O$. *Accad. Naz. Lincei, 42,* 236–251.

Clark, J. R. (1964) The crystal structure of tunellite, $SrB_6O_9(OH)_2 \cdot 3H_2O$. *Am. Mineral., 49,* 1549–1568.

—— and D. E. Appleman (1964) Pentaborate polyanion in the crystal structure of ulexite, $NaCaB_5O_6(OH)_6 \cdot 5H_2O$. *Science, 145,* 1295–1296.

Cooper, W. F., F. K. Larsen, P. Coppens and R. F. Giese (1973) Electron population analysis of accurate diffraction data. V. Structure and one-center charge refinement of the light-atom mineral kernite, $Na_2B_4O_6(OH)_2 \cdot 3H_2O$. *Am. Mineral., 58,* 21–31.

Corazza, E. (1974) The crystal structure of kurnakovite: a refinement. *Acta Crystallogr., B30,* 2194–2199.

Cromer, D. T. and J. B. Mann (1968) X-ray scattering factors computed from numerical Hartree-Fock wave function. *Acta Crystallogr., A24,* 321–324.

—— and D. Liberman (1970) Relativistic calculation of anomalous scattering factors for x-rays. *J. Chem. Phys., 53,* 1891–1898.

Dal Negro, A., C. Sabelli and L. Ungaretti (1969) The crystal structure of mcallisterite, $Mg_2[B_6O_7(OH)_6]_2 \cdot 9H_2O$. *Accad. Naz. Lincei, 47,* 353–364.

——, L. Ungaretti and C. Sabelli (1971) The crystal structure of aksaite. *Am. Mineral., 56,* 1553–1564.

——, —— and —— (1973) Crystal structure of rivadavaite. *Naturwissenschaften, 60,* 350.

——, J. M. Martin Pozas and L. Ungaretti (1975) The crystal structure of ameghinite. *Am. Mineral.,* 879–883.

Finger, L. W. (1969) Determinations of cation distributions by least-squares refinement of X-ray data. *Carnegie Inst. Wash. Year Book, 67,* 216–217.

Germain, G. and M. M. Woolfson (1968) On the application of phase relationships to complex structures. *Acta Crystallogr., B24,* 91–96.

Giacovazzo, C., S. Menchetti and F. Scordari (1973) The crystal structure of tincalconite. *Am. Mineral., 58,* 523–530.

Giese, R. F. (1966) Crystal structure of kernite, $Na_2B_4O_6(OH)_2 \cdot 3H_2O$. *Science, 154,* 1453–1454.

—— (1968) A refinement of the crystal structure of borax, $Na_2B_4O_5(OH)_4 \cdot 8H_2O$. *Can. Mineral., 9,* 573.

Hurlbut, C. S., Jr. and R. C. Erd (1974) Aristarainite, $Na_2O \cdot MgO \cdot 6B_2O_3 \cdot 10H_2O$, a new mineral from Salta, Argentina. *Am. Mineral., 59,* 647–651.

Karle, J. and I. L. Karle (1966) The symbolic addition procedure for phase determination for centrosymmetric and non-centrosymmetric crystals. *Acta Crystallogr., 21,* 849–859.

Konnert, J. A., J. R. Clark and C. L. Christ (1970) Studies of borate minerals XIV. Crystal structure of strontioginorite, $(Sr,Ca)_2B_{14}O_{20}(OH)_6 \cdot 5H_2O$. *Am. Mineral., 55,* 1911–1931.

Morimoto, N. (1956) The crystal structure of borax. *Mineral. Journal Japan, 2,* 1–18.

Razmanova, Z. P., I. M. Rumanova and N. V. Belov (1969) Crystal structure of kurnakovite [in Russian]. *Dokl. Akad. Nauk SSSR, 189,* 1003–1006.

Rumanova, I. M., Kh. M. Kurbanov and N. V. Belov (1966) Crystal structure of probertite, $CaNa[B_5O_7(OH)_4] \cdot 3H_2O$. *Soviet Phys. Crystallogr. 10,* 513–522.

Schomaker, V., J. Waser, R. E. Marsh and G. Bergman (1959) To fit a plane or a line to a set of points by least squares. *Acta Crystallogr., 12,* 600–604.

Yeh, Da-nean (1965) The structure of kurnakovite. *Scientia Sinica, XIV,* 1086–1089.

Zachariasen, W. H. (1963) The crystal structure of monoclinic metaboric acid. *Acta Crystallogr., 16,* 385–389.

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