

## The Crystal Structure of $\text{Na}_3[\text{B}_3\text{O}_5(\text{OH})_2]$

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The crystal structure of the synthetic compound  $3\text{Na}_2\text{O} \cdot 3\text{B}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$ , space group  $Pnma$ ,  $a = 8.923$  (1),  $b = 7.152$  (1),  $c = 9.548$  (1) Å, was determined from single-crystal diffractometer X-ray data. Direct methods were used to solve the structure which was later refined by least-squares calculations to an  $R$  of 0.029. The structure determination showed that the compound labelled in the literature as '1:1:1' has actually a composition corresponding to  $\text{Na}_2\text{O}-\text{B}_2\text{O}_3-\text{H}_2\text{O}$  molar proportions of 3:3:2. The basic structural unit is the isolated polyion  $[\text{B}_3\text{O}_5(\text{OH})_2]^{3-}$  formed by corner-sharing among one tetrahedron and two triangles. Of the four attached oxygen atoms only the two linked to the tetrahedral boron exist as hydroxyl groups. Na polyhedra form a tight two-dimensional network by the sharing of corners, edges and faces. All oxygen atoms linked to the Na atoms belong at the same time to the B-O polyions and *vice-versa*. A high cohesion in all directions is the result of the perpendicular arrangement between B-O rings and Na-O sheets. The crystal chemical formula of the compound investigated is  $\text{Na}_3[\text{B}_3\text{O}_5(\text{OH})_2]$ .

### Introduction

One of the many phases obtained in the  $\text{Na}_2\text{O}-\text{B}_2\text{O}_3-\text{H}_2\text{O}$  system (Stoppioni, 1974) has an X-ray powder pattern identical with the one assigned by Nies & Hulbert (1967) to the sodium metaborate hemihydrate, that is to the compound with  $\text{Na}_2\text{O}-\text{B}_2\text{O}_3-\text{H}_2\text{O}$  molar proportions 1:1:1. There has been discussion about the region of stability of this phase, while about the chemical composition there was a general agreement on the molar proportions 1:1:1 (Sborgi, 1932; Bouaziz, 1962; Nies & Hulbert, 1967; Kocher, 1970).

However, the structural study, undertaken as a part of a programme on hydrated sodium borates, revealed that this phase has actually the crystal chemical formula  $\text{Na}_3[\text{B}_3\text{O}_5(\text{OH})_2]$  corresponding to the molar proportions 3:3:2. This compound seems also of interest because of the presence of oxygen atoms linked to only one boron; they do not bond to a proton as they do in fully hydrated borates according to Christ's (1960) third rule.

### Experimental

Crystals of the title compound were prepared in a pressure vessel under hydrothermal conditions at 150°C and in the range of  $\text{Na}_2\text{O}:\text{B}_2\text{O}_3$  molar ratios from 0.614 to 3.909. The 3:3:2 phase was always associated with more or less important amounts of sodium metaborate dihydrate (1:1:4), evidently formed while cooling. The crystals, slightly deliquescent, are sometimes well formed with dimensions up to 2 mm and a pseudo-tetragonal habit. The identity between the 3:3:2 phase and the phase labelled '1:1:1' in previous works was confirmed by the close similarity of X-ray powder patterns.

Crystal data are given in Table 1. The agreement be-

tween the specific gravity (determined by flotation in a bromonaphthalene-bromoform mixture) and the calculated density is not completely satisfactory, possibly because of the deliquescence of the crystals. The unit-cell dimensions were determined from 25 high-angle reflexions measured on a single-crystal diffractometer. The space group, determined from the absences, is  $Pnma$  or  $Pna2_1$ ; a statistical test (Karle, Dragonette & Brenner, 1965) indicated the centrosymmetric group as the most likely one.

Table 1. Crystal data

$\text{Na}_3[\text{B}_3\text{O}_5(\text{OH})_2]$	$V = 609.3 \text{ \AA}^3$
F.W. 215.4	$Z = 4$
Space group: $Pnma$	$D_m = 2.2 \text{ g cm}^{-3}$
Unit-cell dimensions	$D_s = 2.349 \text{ g cm}^{-3}$
$a = 8.923$ (1) Å	$\mu(\text{Mo } K\alpha) = 4.2 \text{ cm}^{-1}$
$b = 7.152$ (1)	$F(000) = 424$
$c = 9.548$ (1)	

Intensities were measured with a Philips PW 1100 four-circle computer-controlled diffractometer (Centro di Cristallografia Strutturale del CNR, Pavia, Italy), with Mo  $K\alpha$  radiation and the  $\omega-2\theta$  scan technique. 955 reflexions within the range  $3^\circ < \theta < 30^\circ$  were inspected with scan speed  $0.07^\circ \text{ s}^{-1}$  and scan range  $1.4^\circ$ . The background was measured on both sides of the peak; for lower intensities scans were repeated up to three times. Reflexions for which  $(I_{\text{peak}} - 2I_{\text{back}}) \leq I_{\text{back}}$  were considered as unobserved. The set actually used in the structure analysis consisted of 829 non-zero reflexions.

Intensities were corrected for Lorentz-polarization effects; absorption was considered negligible because of the low linear absorption coefficient and the small size of the crystal (nearly equidimensional with a 'radius' of 0.16 mm).

Structure analysis and refinement

The structure factors were converted into normalized structure amplitudes. The 234 largest *E*'s (*E* ≥ 1.0)

were selected as input to the *MULTAN* program (Germain, Main & Woolfson, 1971) which was used in its fully automatic mode. The structural model obtained from *F<sub>o</sub>* maps computed with the set of signs with the

Table 2. Fractional atomic coordinates, anisotropic thermal parameters (× 10<sup>5</sup>) and equivalent isotropic thermal parameters

The estimated standard deviations are given in parentheses. The temperature factors refer to the expression:  $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{23}kl + 2\beta_{13}hl)]$ .

	<i>x</i>	<i>y</i>	<i>z</i>	$\beta_{11}$	$\beta_{22}$	$\beta_{33}$	$\beta_{12}$	$\beta_{13}$	$\beta_{23}$	<i>B<sub>eq</sub></i>
Na(1)	0.27174 (7)	0.50189 (9)	0.30250 (7)	338 (8)	575 (12)	381 (7)	-36 (8)	-5 (6)	-51 (8)	1.2
Na(2)	0.53606 (11)	0.75	0.33138 (10)	355 (11)	597 (18)	433 (11)	0	62 (9)	0	1.3
B(1)	0.51456 (28)	0.25	0.21562 (25)	220 (27)	502 (44)	171 (23)	0	-17 (21)	0	0.8
B(2)	0.59687 (28)	0.25	-0.04128 (27)	270 (27)	355 (41)	265 (24)	0	10 (21)	0	0.9
B(3)	0.32457 (27)	0.25	0.01941 (26)	263 (27)	353 (41)	243 (25)	0	2 (21)	0	0.8
OH(1)	0.53287 (13)	0.41888 (16)	0.30500 (11)	346 (13)	496 (20)	266 (11)	23 (14)	-64 (10)	-31 (13)	1.0
O(2)	0.36184 (17)	0.25	0.15959 (16)	206 (17)	739 (31)	198 (16)	0	-16 (14)	0	1.0
O(3)	0.62712 (17)	0.25	0.10239 (16)	222 (17)	765 (31)	205 (15)	0	22 (14)	0	1.0
O(4)	0.70061 (18)	0.25	-0.13946 (17)	349 (19)	751 (32)	280 (17)	0	87 (15)	0	1.2
O(5)	0.44165 (17)	0.25	-0.07923 (16)	266 (19)	1247 (37)	191 (17)	0	10 (14)	0	1.4
O(6)	0.18312 (16)	0.25	-0.02559 (16)	236 (18)	772 (31)	236 (17)	0	-29 (14)	0	1.1
H	0.578 (2)	0.392 (3)	0.374 (2)							2.0 (5)

Table 3. Observed and calculated structure factors

An asterisk marks unobserved reflexions.

<i>hkl</i>	<i>F<sub>o</sub></i>	<i>F<sub>c</sub></i>	<i>hkl</i>	<i>F<sub>o</sub></i>	<i>F<sub>c</sub></i>	<i>hkl</i>	<i>F<sub>o</sub></i>	<i>F<sub>c</sub></i>	<i>hkl</i>	<i>F<sub>o</sub></i>	<i>F<sub>c</sub></i>	<i>hkl</i>	<i>F<sub>o</sub></i>	<i>F<sub>c</sub></i>
2 0 0	140	142	2 0 0	140	142	2 0 0	140	142	2 0 0	140	142	2 0 0	140	142
4 0 0	412	425	4 0 0	412	425	4 0 0	412	425	4 0 0	412	425	4 0 0	412	425
6 0 0	117	118	6 0 0	117	118	6 0 0	117	118	6 0 0	117	118	6 0 0	117	118
8 0 0	118	119	8 0 0	118	119	8 0 0	118	119	8 0 0	118	119	8 0 0	118	119
10 0 0	215	216	10 0 0	215	216	10 0 0	215	216	10 0 0	215	216	10 0 0	215	216
12 0 0	319	320	12 0 0	319	320	12 0 0	319	320	12 0 0	319	320	12 0 0	319	320
14 0 0	201	202	14 0 0	201	202	14 0 0	201	202	14 0 0	201	202	14 0 0	201	202
16 0 0	415	416	16 0 0	415	416	16 0 0	415	416	16 0 0	415	416	16 0 0	415	416
18 0 0	313	314	18 0 0	313	314	18 0 0	313	314	18 0 0	313	314	18 0 0	313	314
20 0 0	417	418	20 0 0	417	418	20 0 0	417	418	20 0 0	417	418	20 0 0	417	418
22 0 0	519	520	22 0 0	519	520	22 0 0	519	520	22 0 0	519	520	22 0 0	519	520
24 0 0	621	622	24 0 0	621	622	24 0 0	621	622	24 0 0	621	622	24 0 0	621	622
26 0 0	723	724	26 0 0	723	724	26 0 0	723	724	26 0 0	723	724	26 0 0	723	724
28 0 0	825	826	28 0 0	825	826	28 0 0	825	826	28 0 0	825	826	28 0 0	825	826
30 0 0	927	928	30 0 0	927	928	30 0 0	927	928	30 0 0	927	928	30 0 0	927	928
32 0 0	1029	1030	32 0 0	1029	1030	32 0 0	1029	1030	32 0 0	1029	1030	32 0 0	1029	1030
34 0 0	1131	1132	34 0 0	1131	1132	34 0 0	1131	1132	34 0 0	1131	1132	34 0 0	1131	1132
36 0 0	1233	1234	36 0 0	1233	1234	36 0 0	1233	1234	36 0 0	1233	1234	36 0 0	1233	1234
38 0 0	1335	1336	38 0 0	1335	1336	38 0 0	1335	1336	38 0 0	1335	1336	38 0 0	1335	1336
40 0 0	1437	1438	40 0 0	1437	1438	40 0 0	1437	1438	40 0 0	1437	1438	40 0 0	1437	1438
42 0 0	1539	1540	42 0 0	1539	1540	42 0 0	1539	1540	42 0 0	1539	1540	42 0 0	1539	1540
44 0 0	1641	1642	44 0 0	1641	1642	44 0 0	1641	1642	44 0 0	1641	1642	44 0 0	1641	1642
46 0 0	1743	1744	46 0 0	1743	1744	46 0 0	1743	1744	46 0 0	1743	1744	46 0 0	1743	1744
48 0 0	1845	1846	48 0 0	1845	1846	48 0 0	1845	1846	48 0 0	1845	1846	48 0 0	1845	1846
50 0 0	1947	1948	50 0 0	1947	1948	50 0 0	1947	1948	50 0 0	1947	1948	50 0 0	1947	1948
52 0 0	2049	2050	52 0 0	2049	2050	52 0 0	2049	2050	52 0 0	2049	2050	52 0 0	2049	2050
54 0 0	2151	2152	54 0 0	2151	2152	54 0 0	2151	2152	54 0 0	2151	2152	54 0 0	2151	2152
56 0 0	2253	2254	56 0 0	2253	2254	56 0 0	2253	2254	56 0 0	2253	2254	56 0 0	2253	2254
58 0 0	2355	2356	58 0 0	2355	2356	58 0 0	2355	2356	58 0 0	2355	2356	58 0 0	2355	2356
60 0 0	2457	2458	60 0 0	2457	2458	60 0 0	2457	2458	60 0 0	2457	2458	60 0 0	2457	2458
62 0 0	2559	2560	62 0 0	2559	2560	62 0 0	2559	2560	62 0 0	2559	2560	62 0 0	2559	2560
64 0 0	2661	2662	64 0 0	2661	2662	64 0 0	2661	2662	64 0 0	2661	2662	64 0 0	2661	2662
66 0 0	2763	2764	66 0 0	2763	2764	66 0 0	2763	2764	66 0 0	2763	2764	66 0 0	2763	2764
68 0 0	2865	2866	68 0 0	2865	2866	68 0 0	2865	2866	68 0 0	2865	2866	68 0 0	2865	2866
70 0 0	2967	2968	70 0 0	2967	2968	70 0 0	2967	2968	70 0 0	2967	2968	70 0 0	2967	2968
72 0 0	3069	3070	72 0 0	3069	3070	72 0 0	3069	3070	72 0 0	3069	3070	72 0 0	3069	3070
74 0 0	3171	3172	74 0 0	3171	3172	74 0 0	3171	3172	74 0 0	3171	3172	74 0 0	3171	3172
76 0 0	3273	3274	76 0 0	3273	3274	76 0 0	3273	3274	76 0 0	3273	3274	76 0 0	3273	3274
78 0 0	3375	3376	78 0 0	3375	3376	78 0 0	3375	3376	78 0 0	3375	3376	78 0 0	3375	3376
80 0 0	3477	3478	80 0 0	3477	3478	80 0 0	3477	3478	80 0 0	3477	3478	80 0 0	3477	3478
82 0 0	3579	3580	82 0 0	3579	3580	82 0 0	3579	3580	82 0 0	3579	3580	82 0 0	3579	3580
84 0 0	3681	3682	84 0 0	3681	3682	84 0 0	3681	3682	84 0 0	3681	3682	84 0 0	3681	3682
86 0 0	3783	3784	86 0 0	3783	3784	86 0 0	3783	3784	86 0 0	3783	3784	86 0 0	3783	3784
88 0 0	3885	3886	88 0 0	3885	3886	88 0 0	3885	3886	88 0 0	3885	3886	88 0 0	3885	3886
90 0 0	3987	3988	90 0 0	3987	3988	90 0 0	3987	3988	90 0 0	3987	3988	90 0 0	3987	3988
92 0 0	4089	4090	92 0 0	4089	4090	92 0 0	4089	4090	92 0 0	4089	4090	92 0 0	4089	4090
94 0 0	4191	4192	94 0 0	4191	4192	94 0 0	4191	4192	94 0 0	4191	4192	94 0 0	4191	4192
96 0 0	4293	4294	96 0 0	4293	4294	96 0 0	4293	4294	96 0 0	4293	4294	96 0 0	4293	4294
98 0 0	4395	4396	98 0 0	4395	4396	98 0 0	4395	4396	98 0 0	4395	4396	98 0 0	4395	4396
100 0 0	4497	4498	100 0 0	4497	4498	100 0 0	4497	4498	100 0 0	4497	4498	100 0 0	4497	4498
102 0 0	4599	4600	102 0 0	4599	4600	102 0 0	4599	4600	102 0 0	4599	4600	102 0 0	4599	4600
104 0 0	4701	4702	104 0 0	4701	4702	104 0 0	4701	4702	104 0 0	4701	4702	104 0 0	4701	4702
106 0 0	4803	4804	106 0 0	4803	4804	106 0 0	4803	4804	106 0 0	4803	4804	106 0 0	4803	4804
108 0 0	4905	4906	108 0 0	4905	4906	108 0 0	4905	4906	108 0 0	4905	4906	108 0 0	4905	4906
110 0 0	5007	5008	110 0 0	5007	5008	110 0 0	5007	5008	110 0 0	5007	5008	110 0 0	5007	5008
112 0 0	5109	5110	112 0 0	5109	5110	112 0 0	5109	5110	112 0 0	5109	5110	112 0 0	5109	5110
114 0 0	5211	5212	114 0 0	5211	5212	114 0 0	5211	5212	114 0 0	5211	5212	114 0 0	5211	5212
116 0 0	5313	5314	116 0 0	5313	5314	116 0 0	5313	5314	116 0 0	5313	5314	116 0 0	5313	5314
118 0 0	5415	5416	118 0 0	5415	5416	118 0 0	5415	5416	118 0 0	5415	5416	118 0 0	5415	5416
120 0 0	5517	5518	120 0 0	5517	5518	120 0 0	5517	551						

best figures of merit gave an  $R$  of 0.316. Scattering factor curves for non-hydrogen atoms were those of Cromer & Waber (1965) and for hydrogen those of Stewart, Davidson & Simpson (1965).

Two full-matrix least-squares cycles, with isotropic thermal parameters, led to  $R=0.064$ . A weight  $1/\sigma$ , with  $\sigma$  derived from counting statistics, was given to all observed reflexions. At this stage an  $F_o$  map clearly revealed a maximum ( $\sim 0.65 \text{ e } \text{Å}^{-3}$ ) attributable to the H atom. A further cycle of refinement with anisotropic thermal parameters for all atoms but hydrogen reduced  $R$  to 0.030. In the next difference synthesis residual

peaks of no more than  $\pm 0.15 \text{ e } \text{Å}^{-3}$  were found. After the second and last anisotropic cycle the final  $R$  was 0.029 for the observed reflexions and 0.038 including 'less thans'. Seven reflexions (020, 040, 002, 401, 022, 304, 124) were considered to be affected by secondary extinction and therefore excluded from least-squares calculations.

Positional and thermal parameters, with their standard deviations, are given in Table 2. A list of observed and calculated structure factor amplitudes is shown in Table 3.

### Description of the structure and discussion

The basic unit of the present structure is the isolated  $[\text{B}_3\text{O}_5(\text{OH})_2]^{3-}$  polyion. It consists of a six-membered ring with two of the boron atoms threefold coordinated by oxygen atoms and the third boron fourfold coordinated by two oxygens and two hydroxyl groups. All boron and oxygen atoms (with the exception of the two OH(1) groups) lie on the mirror plane at  $y=\frac{1}{2}$ . As a consequence ring and triangles are perfectly planar. The mutual disposition of rings is shown in Fig. 1.

The only asymmetric H bond present in this structure occurs between OH(1) and O(6), thus connecting adjacent rings lying on the same mirror plane. In this

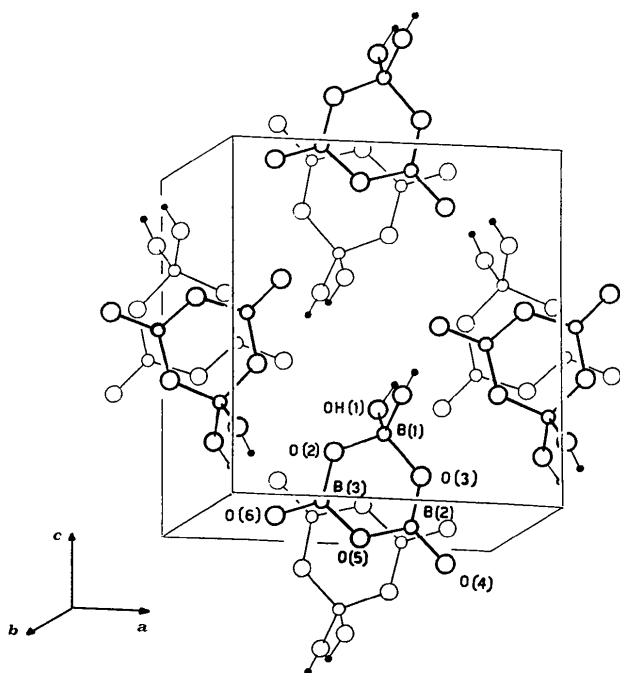


Fig. 1. The arrangement of boron-oxygen polyions in the structure.

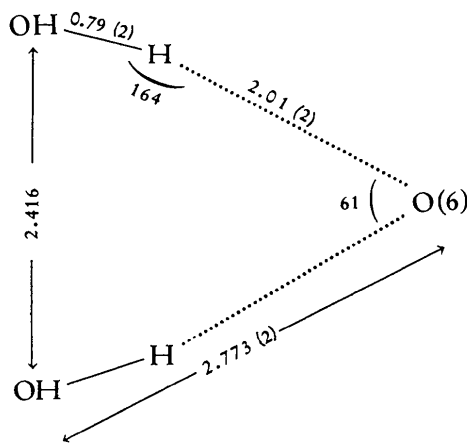


Fig. 2. Distances (Å) and angles ( $^\circ$ ) involving hydrogen bonding.

Table 4. Na-O, B-O bond distances, B-B distances and O-O edges of boron coordination polyhedra

Na(1)-OH(1)	2.405 (1) Å	B(1)-OH(1)	1.488 (2) $\times 2$ Å
-OH(1 <sup>vii</sup> )	2.439 (1)	-O(2)	1.464 (3)
-O(2)	2.399 (1)	-O(3)	1.476 (3)
-O(3 <sup>i</sup> )	2.395 (1)	Mean	1.479
-O(4 <sup>ii</sup> )	2.373 (1)	B(2)-O(3)	1.398 (3)
-O(5 <sup>iii</sup> )	2.837 (1)	-O(4)	1.318 (3)
-O(6 <sup>iiii</sup> )	2.451 (1)	-O(5)	1.432 (3)
Mean	2.471	Mean	1.383
Na(2)-OH(1)	2.382 (1) $\times 2$	B(3)-O(2)	1.379 (3)
-O(4 <sup>ii</sup> )	2.796 (2)	-O(5)	1.407 (3)
-O(4 <sup>iv</sup> )	2.366 (2)	-O(6)	1.333 (3)
-O(5 <sup>ii</sup> )	2.416 (2)	Mean	1.373
-O(6 <sup>iii</sup> )	2.385 (2)	B(1)-B(2)	2.560 (4)
Mean	2.455	B(1)-B(3)	2.527 (3)
B(1) tetrahedron		B(2)-B(3)	2.498 (4)
OH(1)-OH(1 <sup>v</sup> )	2.416 (2)	B(3) triangle	
OH(1)-O(2)	2.391 (2) $\times 2$	O(2)-O(5)	2.389 (2)
OH(1)-O(3)	2.431 (2) $\times 2$	O(2)-O(6)	2.381 (2)
O(2)-O(3)	2.429 (2)	O(5)-O(6)	2.363 (2)
Mean	2.415	Mean	2.378
B(2) triangle			
O(3)-O(4)	2.400 (2)		
O(3)-O(5)	2.397 (2)		
O(4)-O(5)	2.381 (2)		
Mean	2.393		
Symmetry code			
None	$x, y, z$	(iv)	$\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} + z$
(i)	$-\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} - z$	(v)	$x, \frac{1}{2} - y, z$
(ii)	$1 - x, 1 - y, -z$	(vi)	$x, \frac{3}{2} - y, z$
(iii)	$\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} + z$	(vii)	$-\frac{1}{2} + x, y, \frac{1}{2} - z$



Table 6. *The electrostatic valence balance*

All atoms but Na(1), OH(1) and H lie in special positions. Therefore values reported in the row and in the columns corresponding to OH(1), Na(1) and H are to be doubled.

Atom	B $\square$	B $\Delta$	Na(1)	Na(2)	H <sup>-</sup>	...H	Sums
O(2)	0.78	0.98	0.16				2.08
O(3)	0.76	0.95	0.16				2.03
O(4)		1.19	0.17	0.20			1.81
				0.08			
O(5)		0.86	0.06	0.17			2.05
		0.90					
O(6)		1.12	0.14	0.19		0.20	1.99
OH(1)	0.73		0.16	0.18	0.80		2.02
			0.15				

angles are 1.378 and 2.385 Å. The connexions between B–O polyions are provided by H bonds and Na–O bonds.

In this structure there are two independent Na atoms: Na(1), which lies in a general position, is sevenfold coordinated by five oxygens and two hydroxyl groups; Na(2), on the mirror plane, links two hydroxyl groups and four oxygen atoms. All atoms linked by Na(1) and Na(2) belong to the B–O polyion; this is due to the insufficient presence of water, already mentioned. The individual Na–O distances (see Table 4) form a rather homogeneous set with two exceptions: Na(1)–O(5<sup>iii</sup>) and Na(2)–O(4<sup>ii</sup>). These distances are 2.837 and 2.796 Å, while the average value for both polyhedra is 2.464 Å. The polyhedra around Na(1) and Na(2) resemble rather distorted octahedra, the first having a seventh corner which centres a face.

As depicted in Fig. 3, these polyhedra form their own tight two-dimensional network which is built up in the following way: Na(2) polyhedra form chains parallel to **a** by corner sharing, while Na(1) polyhedra form chains in the **b** direction by the sharing of an edge and a face alternately. Adjacent Na(1) chains are joined together in the **a** direction by corner-sharing to form sheets in the **ab** plane. The consequence of the alternation of Na(2) zigzag chains through Na(1) sheets is that each Na(2) polyhedron shares four faces with as many surrounding Na(1) polyhedra; each Na(1) polyhedron shares three adjacent faces with two Na(2)'s and one Na(1), respectively.

In the unit cell there are two of the above described Na–O sheets lying at a mean *z* of  $\frac{1}{4}$  and  $\frac{3}{4}$ ; they are related to each other by the symmetry centre. However, on the whole this structure does not show a general stratiform arrangement. The mutual disposition of Na polyhedra actually causes dense layers in the structure. On the other hand the water insufficiency forces all oxygen atoms to be coordinated at the same time by boron atoms in such a way that an orientation perpendicular to the Na sheets results for hexagonal B–O rings; hence there is high cohesion in all directions.

An electrostatic valence balance is shown in Table 6, computed according to the method of Brown & Shannon (1973) and with the data from their Table 1. For the H bonds the curve by the same authors, quoted in Donnay & Donnay (1973), was employed. From Table 6 it can be seen that the balance is completely satisfactory for all oxygen atoms, except for O(4). This is one of the two oxygens linked to only one triangular boron, while the other, O(6), seems instead to be well balanced owing to the contribution of the two H bonds.

In addition to some local programs, the following programs for the CII 10070 computer were used: *MULTAN*; the *ORFLS* least-squares program by Busing, Martin & Levy; the *BONDLA* bond distances and angles program, from the X-RAY System, 1972; the *ORTEP* plotting program of Johnson.

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