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A New Borate Polyanion in the Structure of $Na_8[B_{12}O_{20}(OH)_4]$

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Abstract

$2Na_2O.3B_2O_3.H_2O$ is a new phase synthesized at 523 K under hydrothermal conditions. Crystal data are: a = 8·709 (3), b = 11·917 (5), c = 9·468 (3) Å, β = 96·02 (2)°, space group $P2_1/c$ and Z = 4. The atomic positions, including those of the H atoms, were determined by direct methods and difference Fourier syntheses, and refined by least-squares calculations to an R of 0·030 for 2077 reflexions measured on a computer-controlled automatic diffractometer. The basic structural unit is the isolated polyanion $[B_{12}O_{20}(OH)_4]^{8-}$ with point symmetry $\bar{1}$. The polyanion, which is new in the crystal chemistry of borates, is built up by the linkage of three tetrahedra and three triangles, doubled by the symmetry centre. It can be described as a loop of six six-membered B—O rings. Of the three independent oxygens linked to only one triangular boron, only two exist as hydroxyl groups. Na—O polyhedra form a tight network by sharing corners, edges and faces. All O atoms linked to Na atoms belong at the same time to the B—O polyanions. The structural formula is $Na_8[B_{12}O_{20}(OH)_4]$.

Introduction

Some time ago in this laboratory the sodium hydroxide–boric anhydride–water system was studied at 423 K and under hydrothermal conditions (Corazza, Menchetti, Sabelli & Stoppioni, 1977). Structural studies of the compounds corresponding to the $Na_2O:B_2O_3:H_2O$ molar proportions 3 : 3 : 2 (Corazza, Menchetti & Sabelli, 1975*a*), 2 : 5 : 5 (Corazza, Menchetti & Sabelli, 1975*b*), 3 : 5 : 4 (Menchetti & Sabelli, 1977), 1 : 2 : 1 (Menchetti & Sabelli, 1978*b*) and 1 : 5 : 4 (Menchetti & Sabelli, 1978*a*) were performed.

Recently we have extended our study of the system to the 523 K isotherm. One of the phases obtained shows an X-ray powder pattern which does not agree with any of the known sodium borate patterns; it is therefore a new phase. The present paper reports the structural study of this compound which has the structural formula $Na_8[B_{12}O_{20}(OH)_4]$ corresponding to the $Na_2O:B_2O_3:H_2O$ molar proportions 2 : 3 : 1 (hereafter 2 : 3 : 1).

According to the structural results, 2 : 3 : 1 can be placed, in the crystal-chemical classification of Tennyson (1963), among the soroborates with a new kind of borate polyanion. However, in the scheme of crystal-chemical classification proposed by Christ & Clark (1977) the present compound should be regarded as a dodecaborate 12: $6\Delta + 6T$.

Experimental

Crystals of the compound 2 : 3 : 1 were obtained from a mixture of B_2O_3 and NaOH held in a hydrothermal environment at 523 ± 5 K in a pressure vessel for 48 h. The 2 : 3 : 1 phase was associated with another unidentified compound, which was highly deliquescent and soluble in cold water, from which 2 : 3 : 1 was easily separated since it is insoluble. The crystals were rather large and had well defined crystal forms.

Crystal data are given in Table 1. Lattice constants were determined from 25 high-angle reflexions measured on a single-crystal diffractometer. The diffraction symmetry observed is $2/m$ and the systematic absences are $h0l$, $l = 2n + 1$ and $0k0$, $k = 2n + 1$. These results uniquely characterize the space group $P2_1/c$.

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 ω-scan technique. A total of 2869 reflexions in the range $2° < \theta < 30°$ were measured; only 2077 reflexions were judged to be actually observed according to the criterion $I \geq 5\sigma(I)$.

Intensities were corrected for Lorentz–polarization effects; absorption was considered negligible because of the low linear absorption coefficient (Table 1) and the small size of the crystal.

Table 1. *Crystal data*

Asymmetric unit $Na_4[B_6O_{10}(OH)_2]$

FW 350·8	Space group $P2_1/c$
a = 8·709 (3) Å	V = 977·2 Å^3
b = 11·917 (5)	Z = 4
c = 9·468 (3)	D_x = 2·38 Mg m^{-3}
β = 96·02 (2)°	μ(Mo $K\alpha$) = 0·347 mm^{-1}
	$F(000)$ = 688

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Structure analysis and refinement

The structure was solved by direct methods using *MULTAN* (Main, Woolfson, Lessinger, Germain & Declercq, 1974). The 240 largest normalized structure amplitudes were selected as input for the phase determination. The structural model obtained from F_o maps computed with the set of signs with the highest combined figure of merit gave clear positions for all atoms but three of the O atoms and the H atoms. The R index was at this stage 0·30. In the next electron-density map, the missing O atoms were located and two cycles of isotropic full-matrix least-squares refinement led to $R = 10{\cdot}4$; a weight $W = 1/\sigma^2(F_o)$, with σ derived from counting statistics, was given to all observed reflexions. Two more least-squares cycles with the introduction of anisotropic thermal parameters were carried out. A difference Fourier synthesis at this stage gave indications for the positioning of the H atoms. With all positional and thermal parameters (isotropic for H atoms) varied at the same time as well as the scale factor, the last cycle achieved convergence at $R = 0{\cdot}030$ for the observed reflexions and $R = 0{\cdot}049$ including 'less thans'. Two reflexions (202, $40\bar{2}$) were considered to be affected by secondary extinction and therefore excluded from least-squares calculations. Scattering-factor curves for non-hydrogen atoms were taken from *International Tables for X-ray Crystallography* (1974) and for H from Stewart, Davidson & Simpson (1965).

Positional parameters, with their standard deviations, and equivalent isotropic thermal parameters are given in Table 2.*

Discussion

The basic unit of the present structure is the isolated polyanion $[B_{12}O_{20}(OH)_4]^{8-}$ with point symmetry $\bar{1}$. It consists of six BO_4 tetrahedra, four $BO_2(OH)$ triangles and two BO_3 triangles; because of the symmetry centre, only three triangles and three tetrahedra are crystallographically independent. The six BO_4 tetrahedra are linked to each other by corner sharing, forming a twelve-membered B—O ring, as shown in Fig. 1.

Each tetrahedron also shares two corners with triangles located on the external side of the twelve-membered ring. The polyanion may be described as a loop of six six-membered rings each composed of two tetrahedra and one triangle; each ring shares two tetrahedra with as many adjacent rings. According to the third modified rule of Christ & Clark (1977), there are only three O atoms in 2 : 3 : 1 available for protonation, each of which is linked to only one triangular boron. Since only two protons are available, proton assignment was made according to the analysis of the related B—O distances. Experimental confirmation was obtained by means of a difference Fourier synthesis, where H atom positions were clearly observable.

Table 2. *Fractional atomic coordinates and equivalent isotropic thermal parameters*

	x	*y*	*z*	*B* (Å^2)
Na(1)	0·58976 (10)	0·15659 (7)	0·43046 (8)	1·40
Na(2)	0·08793 (9)	0·38199 (7)	0·44288 (9)	1·23
Na(3)	0·43318 (9)	0·36553 (6)	0·56695 (8)	1·09
Na(4)	0·97425 (9)	0·14796 (8)	0·46194 (8)	1·24
O(1)	0·7771 (1)	0·5832 (1)	0·7713 (1)	0·80
O(2)	0·5332 (1)	0·4852 (1)	0·7500 (1)	0·64
O(3)	0·7697 (2)	0·3826 (1)	0·7648 (1)	0·75
O(4)	0·6944 (2)	0·4924 (1)	0·5542 (1)	0·77
OH(5)	0·9775 (2)	0·2602 (1)	0·7488 (1)	0·95
O(6)	0·8308 (2)	0·3166 (1)	0·5369 (1)	0·84
O(7)	0·6046 (1)	0·3560 (1)	0·3734 (1)	0·66
O(8)	0·8447 (1)	0·4615 (1)	0·3640 (1)	0·73
OH(9)	0·9340 (2)	0·4814 (1)	0·1362 (1)	0·87
O(10)	0·6785 (2)	0·4286 (1)	0·1506 (1)	0·78
O(11)	0·4455 (2)	0·3262 (1)	0·1517 (1)	0·83
O(12)	0·1946 (2)	0·2561 (1)	0·0823 (1)	1·01
B(1)	0·6872 (2)	0·4862 (2)	0·7066 (2)	0·57
B(2)	0·8553 (2)	0·3197 (2)	0·6811 (2)	0·69
B(3)	0·7358 (2)	0·4069 (2)	0·4567 (2)	0·61
B(4)	0·8165 (2)	0·4562 (2)	0·2196 (2)	0·64
B(5)	0·5472 (2)	0·4076 (2)	0·2363 (2)	0·63
B(6)	0·2866 (2)	0·3321 (2)	0·1514 (2)	0·67
H(1)	1·061 (4)	0·256 (2)	0·687 (3)	1·70
H(2)	1·038 (3)	0·475 (2)	0·182 (3)	1·75

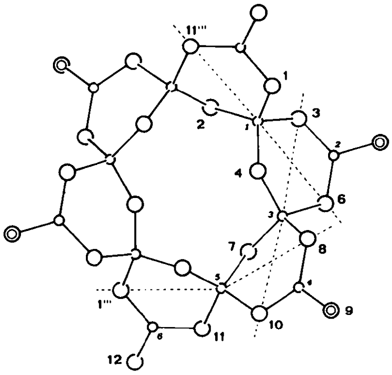

Fig. 1. The a cos 20°–c cos 20° projection of the B—O polyanion. Double circles represent hydroxyls. Dotted lines join each tetrahedral boron with the two oxygens at the opposite ring corners; the lack of alignment between $O(1^{\prime\prime\prime})$, B(5) and O(8) is evident.

The arrangement of B—O polyanions in the structure is shown in Fig. 2.

Recently Christ & Clark (1977) proposed a scheme of crystal-chemical classification of hydrated borates and a set of modified and extended rules governing their

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34467 (18 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

formation. The structures of hydrated borates can be readily classified when the fundamental building blocks (FBB), from which borate polyanions are constructed, are identified. The FBB is defined on the basis of the number *n* of B atoms characteristic of the block. In a shorthand notation triangles and tetrahedra are denoted Δ and *T* respectively. According to this scheme the polyanion found in the present structure can be described as $12: 6\Delta + 6T$; this is a new maximum in the crystal-chemical classification of known borate structures where the highest value of *n* observed previously was 9, for the mineral preobrazhenskite (Rumanova, Razmanova & Belov, 1972). The 12-polyanion may be considered as the cyclization of the 9-polyanion into a ring with all 'outer' B atoms in triangular coordination.

On the other hand it is easy to observe that there is an interesting analogy in the B—O arrangement between the present phase and the mineral kernite, $Na_2[B_4O_6(OH)_2].3H_2O$. The latter compound (Giese, 1966; Cialdi, Corazza & Sabelli, 1967) has B—O chains with a repeat unit $[B_4O_6(OH)_2]^{2-}$ formed by the linkage of two triangles and two tetrahedra; kernite chains are mainly formed by *n* six-membered rings like those in 2:3:1. If we cyclize three successive repeat units of kernite (that is six six-membered rings), rather than linking them to form chains, the polyanion of 2:3:1 results. A difference lies in the fact that in kernite all the O atoms linked to only one triangular B atom are protonated, while in 2:3:1 only two out of the three analogous O atoms are protonated. In conclusion, from this point of view, kernite resembles 2:3:1 (FBB with $n = 12$) more than it does borax, although kernite and borax are classified together among the tetraborates.

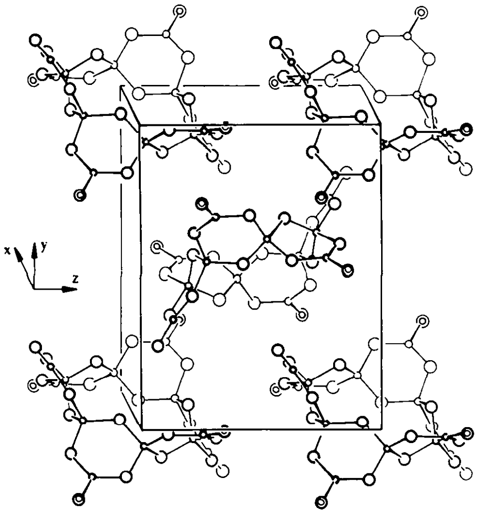

Fig. 2. Arrangement of B—O polyanions in the structure. The unit cell is outlined.

Tables 3 and 4 report interatomic distances and angles. The average tetrahedral B—O distances within the B(1), B(3) and B(5) tetrahedra are 1·473, 1·479 and 1·481 Å respectively, with an overall mean value of 1·477 Å. However, within each tetrahedron, the two bond distances between the B and the O atoms also belonging to triangles are significantly longer than the two others. The average B—O distances in triangles are 1·369, 1·367 and 1·372 Å respectively for B(2), B(4) and B(6) with a mean value of 1·369 Å. There are no O atoms bridging two triangular B atoms; however, noticeable differences in individual B—O distances are present. For instance the B—OH bonds B(2)—OH(5) and B(4)—OH(9) are slightly longer than the mean values. An interesting feature of the borate polyanion is shown by the O(12) atom, which is linked to only one three-coordinated B atom, which, because of a deficiency of water, does not bond to a proton. The B(6)—O(12) distance, 1·334 Å, is well below the average B—O triangular bond length, so that the electrostatic imbalance of O(12) is removed by the strengthening of the B—O bond. This feature is similar to that found in $Na_3[B_3O_5(OH)_2]$ (Corazza, Menchetti & Sabelli, 1975*a*) where the two O atoms linked to only one triangular boron show B—O distances of 1·318 and 1·333 Å respectively.

Some of the individual O—B—O angles in triangles as well as in tetrahedra differ significantly from the corresponding ideal values. In B(2) and B(4) triangles, angles opposite the hydroxyls are nearly 124°, whilst in the third triangle the angle opposite the terminal O(12) atom is nearly 119°. Tetrahedral O—B—O angles range from 104·8 to 114·9°; the smallest in each tetrahedron is that which involves two O atoms which also belong to triangles.

Displacements of atoms from the planes of ring O atoms and dihedral angles in the polyanion are reported in Table 5. The planes are defined by O(3), O(4) and O(6); O(7), O(8) and O(10); and O(1^{iii}), O(2^{iii}) and O(11) respectively. In each case the terminal O atoms attached to triangles deviate considerably from the ring planes; also the triangle–ring angles, which range from 15·5 to 24·8°, are larger than the values generally found in other sodium borate structures. Rings 1 and 2 are almost perpendicular (89·9°) while the angle between rings 2 and 3 deviates significantly from 90°, being only 75·1°.

However, as already observed, the O—B_{tet}—O angles in the B(1), B(3) and B(5) tetrahedra show similar general behaviour, while the pairs of O—B_{tet}—O planes between contacting rings are almost perpendicular to one another; *e.g.* the dihedral angle between the planes defined by O(7), B(5), O(10) and O(11), B(5), O(2^{iii}) is 89·5°. The features which seem to differentiate B(5) from B(1) and B(3) are the noticeable displacement of this atom from the planes of rings 2 and 3 and the lack of alignment between B(5) and the two O atoms, O(8)

Table 3. Na—O, B—O *bond lengths*, O—O *edges of boron coordination polyhedra*, Na—Na *and* B—B *distances, and distances in the hydroxyl groups*

The standard deviations for Na—O are 0·006 Å, for B—O 0·007 Å, for Na—Na 0·006 Å, for O—O and B—B 0·007 Å, and for O—H and H···O 0·03 Å.

Na(1)—O(10^{vi})	2·373 Å	Na(3)—O(4^{iii})	2·269 Å	B(2)—O(3)	1·367 Å	B(5)—O(7)	1·475 Å
Na(1)—O(3^{vii})	2·377	Na(3)—O(2)	2·341	B(2)—OH(5)	1·379	B(5)—O(10)	1·491
Na(1)—O(2^{vii})	2·417	Na(3)—O(11^{vi})	2·420	B(2)—O(6)	1·361	B(5)—O(11)	1·489
Na(1)—O(7)	2·444	Na(3)—O(7)	2·485	Mean	1·369	B(5)—O(2^{iii})	1·467
Na(1)—O(11^{vi})	2·561	Na(3)—O(12^{vi})	2·550			Mean	1·481
Mean	2·434	Na(3)—O(4)	2·745	O(3)—OH(5)	2·340		
		Mean	2·468	O(3)—O(6)	2·408	O(7)—O(10)	2·428
Na(2)—O(12^{vi})	2·248			OH(5)—O(6)	2·360	O(7)—O(11)	2·417
Na(2)—O(8^{i})	2·369	Na(4)—OH(5^{vii})	2·298	Mean	2·369	O(7)—O(2^{iii})	2·468
Na(2)—O(4^{iii})	2·413	Na(4)—OH(9^{vi})	2·311			O(10)—O(11)	2·368
Na(2)—O(1^{iii})	2·483	Na(4)—OH(9^{iv})	2·366	B(3)—O(4)	1·446	O(10)—O(2^{iii})	2·388
Na(2)—OH(5^{viii})	2·608	Na(4)—O(12^{v})	2·415	B(3)—O(6)	1·512	O(11)—O(2^{iii})	2·432
Na(2)—O(6^{i})	2·614	Na(4)—O(3^{vii})	2·468	B(3)—O(7)	1·451	Mean	2·417
Na(2)—O(8^{iii})	2·635	Na(4)—O(6)	2·508	B(3)—O(8)	1·506		
Mean	2·481	Mean	2·394	Mean	1·479	B(6)—O(11)	1·385
						B(6)—O(12)	1·334
Na(1)—Na(3)	3·178 Å			O(4)—O(6)	2·423	B(6)—O(1^{iii})	1·396
Na(2)—Na(3)	3·117			O(4)—O(7)	2·430	Mean	1·372
Na(2)—Na(4^{i})	2·971			O(4)—O(8)	2·363		
				O(6)—O(7)	2·420	O(11)—O(12)	2·367
B(1)—O(1)	1·491	B(4)—O(8)	1·365	O(6)—O(8)	2·391	O(11)—O(1^{iii})	2·398
B(1)—O(2)	1·443	B(4)—OH(9)	1·389	O(7)—O(8)	2·449	O(12)—O(1^{iii})	2·363
B(1)—O(3)	1·504	B(4)—O(10)	1·348	Mean	2·413	Mean	2·376
B(1)—O(4)	1·453	Mean	1·367				
Mean	1·473			Hydroxyls		B(1)—B(2)	2·492
		O(8)—OH(9)	2·380	OH(5)—O(12^{v})	2·593	B(1)—B(3)	2·623
O(1)—O(2)	2·413	O(8)—O(10)	2·391	OH(5)—H(1)	0·98	B(1)—B(5^{iii})	2·508
O(1)—O(3)	2·392	OH(9)—O(10)	2·331	H(1)···O(12^{v})	1·61	B(1)—B(6^{iii})	2·546
O(1)—O(4)	2·367	Mean	2·367	OH(9)—O(1^{ii})	2·688	B(2)—B(3)	2·493
O(2)—O(3)	2·387			OH(9)—H(2)	0·96	B(3)—B(4)	2·492
O(2)—O(4)	2·441			H(2)···O(1^{ii})	1·77	B(3)—B(5)	2·516
O(3)—O(4)	2·418					B(4)—B(5)	2·437
Mean	2·403					B(5)—B(6)	2·495
						Mean	2·511

Symmetry code: None x,y,z; (i) $-1+x, y, z$; (ii) $2-x, 1-y, 1-z$; (iii) $1-x, 1-y, 1-z$; (iv) $2-x, -\frac{1}{2}+y, \frac{1}{2}-z$; (v) $1+x, \frac{1}{2}-y, \frac{1}{2}+z$; (vi) $x, \frac{1}{2}-y, \frac{1}{2}+z$; (vii) $x, \frac{1}{2}-y, -\frac{1}{2}+z$; (viii) $-1+x, \frac{1}{2}-y, -\frac{1}{2}+z$.

Table 4. *Bond angles* (°)

The standard deviations are 0·2° for all angles.

O(1)—B(1)—O(2)	110·6	O(7)—B(5)—O(10)	109·9
O(1)—B(1)—O(3)	106·0	O(7)—B(5)—O(11)	109·3
O(1)—B(1)—O(4)	107·0	O(7)—B(5)—O(2^{iii})	113·9
O(2)—B(1)—O(3)	108·2	O(10)—B(5)—O(11)	105·2
O(2)—B(1)—O(4)	114·9	O(10)—B(5)—O(2^{iii})	107·6
O(3)—B(1)—O(4)	109·7	O(11)—B(5)—O(2^{iii})	110·6
O(3)—B(2)—OH(5)	117·0	O(11)—B(6)—O(12)	121·0
O(3)—B(2)—O(6)	124·0	O(11)—B(6)—O(1^{iii})	119·2
OH(5)—B(2)—O(6)	119·0	O(12)—B(6)—O(1^{iii})	119·8
O(4)—B(3)—O(6)	109·9		
O(4)—B(3)—O(7)	114·0	B(1)—O(3)—B(2)	120·4
O(4)—B(3)—O(8)	106·3	B(2)—O(6)—B(3)	120·3
O(6)—B(3)—O(7)	109·5	B(3)—O(4)—B(1)	129·6
O(6)—B(3)—O(8)	104·8	B(3)—O(7)—B(5)	118·6
O(7)—B(3)—O(8)	111·8	B(5)—O(10)—B(4)	118·2
		B(4)—O(8)—B(3)	120·4
O(8)—B(4)—OH(9)	119·6	B(5)—O(11)—B(6)	120·3
O(8)—B(4)—O(10)	123·6	B(6)—O(1^{iii})—B(1^{iii})	123·8
OH(9)—B(4)—O(10)	116·8	B(5)—O(2^{iii})—B(1^{iii})	118·9
OH(5)—H(1)—O(12^{v})	178		
OH(9)—H(2)—O(1^{ii})	159		

and O(1^{iii}), lying on the ring corners opposite B(5); indeed the O(8)—B(5)—O(1^{iii}) angle is 151·2° while the corresponding values for B(1) and B(3) are 173·0 and 175·9° respectively.

The four independent Na atoms are irregularly coordinated by O atoms which also belong to the borate polyanion. Both Na(4) and Na(3) are linked to six O atoms, but only the former has a coordination polyhedron resembling an irregular octahedron. Na(1) and Na(2) have five and seven neighbours respectively (see Fig. 3*b*). The Na—O distances range from 2·248 to 2·745 Å with an overall mean value of 2·447 Å; the nearest 'non-bonded' O atoms are 2·935 and 3·025 Å from Na(1) and Na(4) respectively. On the whole these values are in agreement with those found in the literature where irregular coordination polyhedra about Na atoms are often described. The Na polyhedra are connected to each other in a complicated way, by sharing corners, edges and faces. For example, Na(2) shares the O(12)—O(4) edge with Na(3), the O(8)—O(8) edge

Table 5. *Displacements of other atoms* ($\sigma \simeq 0{\cdot}01$ Å) *from the planes of ring oxygens, and dihedral angles* ($\sigma \simeq 0{\cdot}2°$) *in the polyanion*

	Ring 1	Ring 2	Ring 3
Ring oxygen atoms	O(3), O(4), O(6)	O(7), O(8), O(10)	$\mathrm{O(1^{iii})}$, $\mathrm{O(2^{iii})}$, O(11)
Associated atoms	B(1) −0·04 Å	B(3) 0·09 Å	B(5) 0·46 Å
	B(2) 0·25	B(4) −0·20	B(6) −0·20
	B(3) −0·22	B(5) 0·52	$\mathrm{B(1^{iii})}$ 0·21
	OH(5) 0·85	OH(9) −0·61	O(12) −0·54
Angle between rings	1–2 89·9°	2–3 75·1°	1–3 87·8°
Oxygen atoms of triangle	O(3), OH(5), O(6)	O(8), OH(9), O(10)	$\mathrm{O(1^{iii})}$, O(11), O(12)
Boron of triangle	B(2) −0·02 Å	B(4) −0·01 Å	B(6) −0·01 Å
Triangle–ring angle	24·8°	17·5°	15·5°

with a symmetrical Na(2) and the face defined by OH(5), O(6), O(12) with Na(4), as shown in Figs. 3(*b*) and 4. This last connexion is rather unusual, but has been observed previously, *e.g.* in the mineral lecontite (Corazza, Sabelli & Giuseppetti, 1967). The Na(2)–$\mathrm{Na(4^{i})}$ separation is very short, 2·971 Å, compared with values reported in the literature for Na polyhedra sharing one face: for example 3·215 Å in $\mathrm{Na_3[B_5O_8(OH)_2].H_2O}$ (Menchetti & Sabelli, 1977) and 3·15 Å in the mineral lecontite (Corazza *et al.*, 1967). Two other short Na–Na distances are Na(1)–Na(3) 3·178 and Na(2)–Na(3) 3·117 Å.

The Na–O polyhedra build up dense sheets parallel to (001). In the unit cell there are two Na–O sheets, at $z = 0$ and $z = \frac{1}{2}$. However, this structure does not show a general stratiform arrangement. In fact the Na–O layers are linked together directly through the O(2) atom, and indirectly by means of the borate polyanions which lie approximately in the (010) plane (see Fig. 3). This three-dimensional network is reflected in

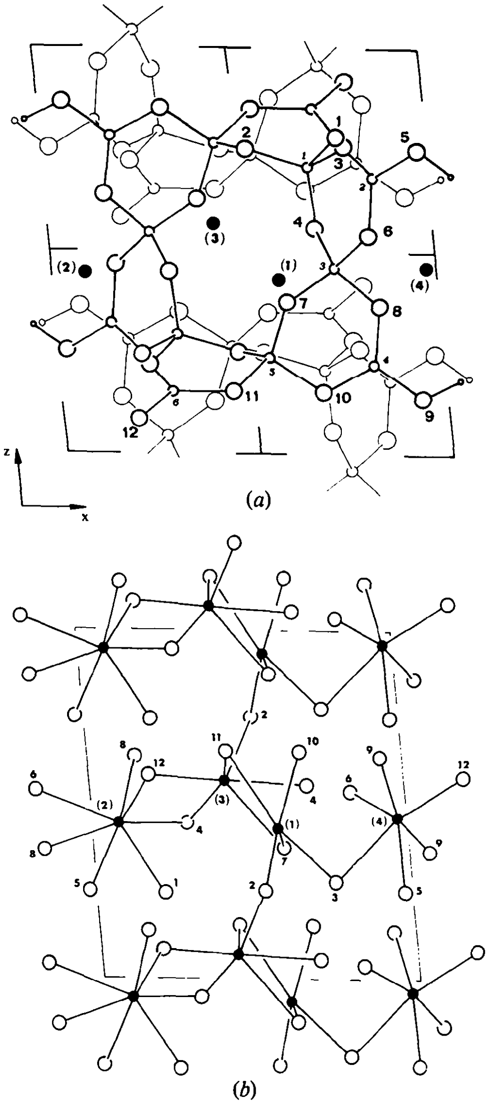

Fig. 3. (*a*) The *ac* projection of the unit cell showing nomenclature of B atoms (small circles), O atoms (large circles) and Na atoms (filled circles). (*b*) The same projection showing the Na–O bond system; the numbering of the O atoms, as in Fig. 4, does not indicate the key symmetry.

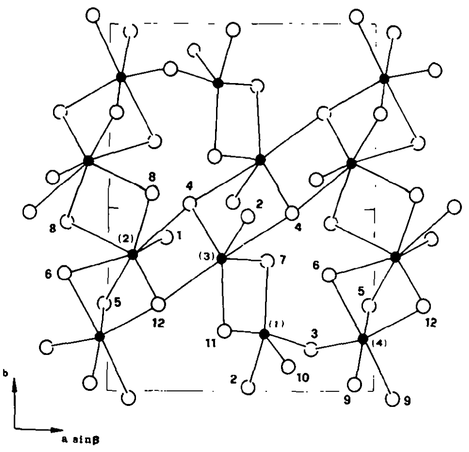

Fig. 4. The framework of Na–O polyhedra viewed along the *c* axis.

Table 6. *Electrostatic valence balance*

Values were computed using the bond distances of Table 3 and bond strengths proposed by Brown & Shannon (1973).

	Na(1)	Na(2)	Na(3)	Na(4)	B(1)	B(2)	B(3)	B(4)	B(5)	B(6)	H(1)	H(2)	Sums
O(1)		0·13			0·71					0·93		0·22	1·99
O(2)	0·20		0·21		0·81				0·77				1·99
O(3)	0·23			0·14	0·69	1·00							2·06
O(4)		0·16	0·25 0·09		0·79		0·82						2·11
OH(5)		0·10		0·21		0·97					0·74		2·02
O(6)		0·10		0·13		1·03	0·68						1·94
O(7)	0·19		0·15				0·80		0·76				1·90
O(8)		0·17 0·10					0·70	1·01					1·98
OH(9)				0·20 0·16				0·93				0·78	2·07
O(10)	0·23							1·06	0·73				2·02
O(11)	0·15		0·17						0·74	0·96			2·02
O(12)		0·24	0·13	0·16						1·11	0·26		1·90

the calculated density of 2·38 Mg m^{-3}. In the structurally known hydrated sodium borates, the calculated densities range from 1·713 (borax) to 2·339 Mg m^{-3} (phase 3:3:2); therefore, in accord with its compact packing, the compound 2:3:1 has the highest value.

As previously described, the two independent H atoms, located from a difference Fourier synthesis, are involved in hydrogen bonding. Donor–acceptor distances (see Table 3) are rather short, 2·593 and 2·688 Å respectively, while O—H lengths, 0·98 and 0·96 Å, agree with the values generally found in X-ray crystal structure determinations. One of the two bonds is almost linear, the O—H···O angle being 178°. These hydrogen bonds provide connexions between adjacent B—O polyanions.

An electrostatic valence balance was computed as suggested by Brown & Shannon (1973). Table 6 reports the contributions of different atoms and the bond-strength sums (v.u.). The balance is satisfactory for all O atoms (maximum deviation 5·5%), thus confirming the general bond system. Three O atoms do not exhibit fourfold coordination: O(10) has three-coordination, while O(4) and O(12) have five neighbours, one of which, however, does make a weak contribution.

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