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The Crystal Structure of Synthetic Sodium Pentaborate Monohydrate

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Synthetic $Na_3[B_5O_8(OH)_2].H_2O$, orthorhombic, space group *Pbca*, $a = 8{\cdot}804$ (3), $b = 18{\cdot}371$ (5), $c = 10{\cdot}924$ (3) Å, $Z = 8$. The structure was solved by direct methods and was refined by least-squares techniques to the final R value of 0·073. The structure is characterized by B–O sheets with the repeat unit $[B_5O_8(OH)_2]^{3-}$.

Introduction

This work is part of a structural study of phases obtained in the sodium hydroxide–boric anhydride–water system under hydrothermal conditions at 150°C (Corazza, Menchetti, Sabelli & Stoppioni, 1977). The title compound, with Na_2O–B_2O_3–H_2O molar proportions of 3:5:4, is quite new among natural and synthetic hydrated sodium borates. Crystals of the title compound (hereafter 3:5:4) are plate-like and are normally arranged in stacks. The single crystals being too thin, a stack of crystals with dimensions 0·22 × 0·03 × 0·05 mm was chosen in order to collect intensity data; as a consequence diffraction peaks were not well defined. Therefore, experimental data are poor in quality, yielding, for instance, some spurious peaks in the difference Fourier map.

Intensities were measured with a Philips PW 1100 computer-controlled diffractometer (Centro di Cristallografia Strutturale del CNR, Pavia, Italy) with Cu $K\alpha$ radiation and the ω–2θ scan technique. Of 893 reflexions scanned within the range $2° < \theta < 50°$, 627 were considered to be significant according to the criterion $|F_o| > 3\sigma(F_o)$. An absorption correction was not applied.

The structure was solved with the *MULTAN* program. All 140 reflexions with $|E| > 1{\cdot}37$ were included in the phase-determining process with eight sets of starting phases. On the first Fourier map, all atoms were recognized with the exception of one B atom, which was identified in a subsequent Fourier synthesis, and the H atoms. The latter were inserted in calculated positions in the final structure factor calculation. Refinement was by full-matrix least-squares techniques using first isotropic (R index reduced from 0·28 to 0·13) and then anisotropic thermal parameters, to a final $R = 0{\cdot}073$ for the 'observed' reflexions and $R = 0{\cdot}117$ for all data. A weight of $1/\sqrt{\sigma}$ was used, with σ derived from counting statistics. Scattering factors for non-hydrogen atoms were those of Cromer & Waber (1965) and for H those of Stewart, Davidson & Simpson (1965). Final atomic coordinates are given in Table 1.*

Discussion

The pentaborate polyanion $[B_5O_8(OH)_2]^{3-}$ (see Fig. 1) is formed by three tetrahedra and two triangles and consists of two similar six-membered alternating B–O

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32729 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 1. *Fractional atomic coordinates* ($\times 10^4$, *for* H $\times 10^2$) *and isotropic thermal parameters* (Å^2)

B's of the non-hydrogen atoms are the equivalent values after Hamilton (1959). The H atoms were assigned $B = 2$ Å^2.

	x	y	z	B_{eq}
Na(1)	4317 (4)	5669 (2)	3967 (3)	1·76
Na(2)	4171 (4)	7409 (2)	4260 (3)	1·48
Na(3)	1194 (4)	4590 (2)	4002 (4)	2·72
O(1)	2622 (6)	6534 (3)	1740 (5)	0·61
O(2)	129 (6)	6731 (3)	2537 (6)	0·54
O(3)	2126 (6)	7633 (3)	2935 (5)	0·97
O(4)	2246 (6)	6468 (3)	3924 (5)	0·56
O(5)	−385 (6)	6447 (3)	4651 (5)	0·63
O(6)	1558 (6)	6971 (3)	5889 (6)	0·95
O(7)	1430 (6)	5651 (3)	5541 (5)	0·66
O(8)	2669 (7)	6169 (2)	7362 (5)	1·39
O(9)	1963 (7)	4943 (2)	7359 (5)	1·37
O(10)	3992 (6)	5303 (3)	6096 (6)	1·44
O(11)	5811 (7)	6509 (4)	5229 (5)	1·70
B(1)	1783 (13)	6846 (6)	2849 (10)	1·05
B(2)	−848 (14)	6586 (6)	3467 (11)	1·03
B(3)	1254 (12)	6370 (6)	4979 (10)	1·05
B(4)	2125 (13)	6839 (6)	7015 (11)	1·18
B(5)	2492 (7)	5544 (7)	6548 (7)	1·06
H(1)	21	45	72	
H(2)	48	56	67	
H(3)	64	65	46	
H(4)	62	68	58	

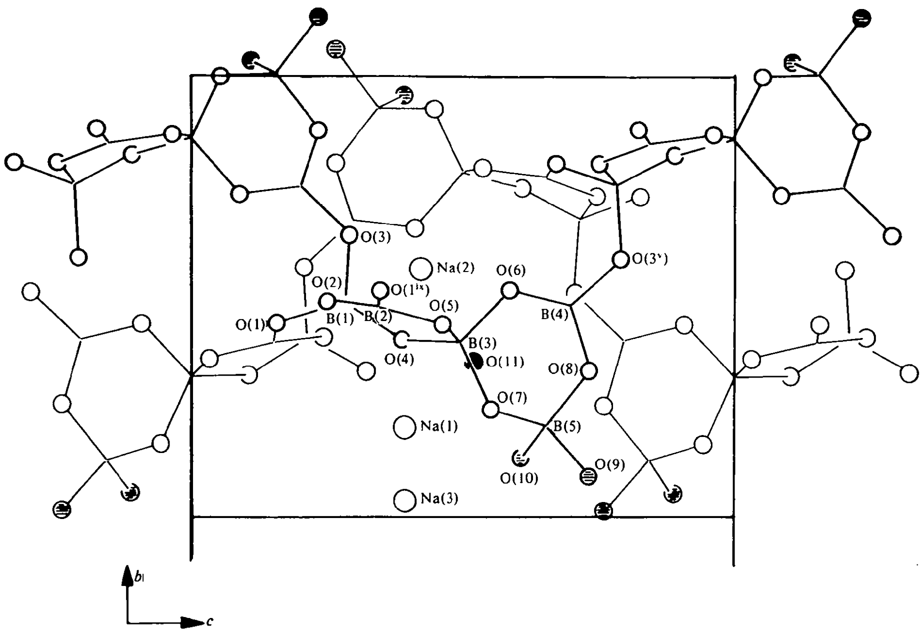

Fig. 1. Part of a B–O sheet running in the *ac* plane. Shaded and full circles represent hydroxyls and the water molecule respectively.

rings in approximately perpendicular planes. These polyanions are interlinked by a two-dimensional polymerization to form B–O sheets lying parallel to the *ac* plane. The $[B_5O_6(OH)_6]^{3-}$ polyanion with the same configuration but not polymerized was found in the structure of ulexite (Clark & Appleman, 1964). In probertite (Kurbanov, Rumanova & Belov, 1963) the same polyanion was found polymerized in B–O chains with the repeat unit $[B_5O_7(OH)_4]^{3-}$. In the mineral heidornite, Burzlaff (1967) found the $[B_5O_8(OH)_2]^{3-}$ group building a two-dimensional network; the pentaborate polyanion is exactly the same as that found in 3:5:4, but polymerization takes place in a different way. In heidornite the central B of the polyanion lies on a twofold axis so that the two hydroxyl groups are symmetrically related by this axis; in 3:5:4, on the other hand, there is no internal symmetry of the pentaborate group and the two independent hydroxyls, *i.e.* the two free corners of the polyanion, belong to the same peripheral tetrahedron. In garrelsite (Ghose, Che'ng & Ulbrich, 1976), which is a silicoborate mineral, the $[B_5O_{12}]^{9-}$ polyanion was found to build up a two-dimensional network together with silicoborate chains. This pentaborate group can be considered as the anhydrous analogue of the polyanion found in ulexite.

From a general consideration of the above-quoted structures it can be noted that the pentaborate polyanion exists both in right-handed and left-handed enantiomorphous forms.

The B–O sheets in 3:5:4 are linked to each other by the three independent Na polyhedra. Na(1) and Na(2) have a sixfold irregular coordination while Na(3) exhibits a fivefold coordination. No doubts are supposed to exist about these coordination numbers; in fact, the Na–O bond distances do not show a large

Table 2. Na–O *and* B–O *bond distances,* O–O *edges of boron coordination polyhedra,* B–B *distances and hydrogen bridges* (Å)

Na(1)–O(10^{i})	2·327 (6)	B(3) tetrahedron	
Na(1)–O(4)	2·341 (6)	O(4)–O(5)	2·449 (7)
Na(1)–O(9^{vii})	2·373 (6)	O(4)–O(6)	2·418 (8)
Na(1)–O(10)	2·442 (7)	O(4)–O(7)	2·430 (7)
Na(1)–O(11)	2·454 (7)	O(5)–O(6)	2·385 (8)
Na(1)–O(2^{viii})	2·650 (6)	O(5)–O(7)	2·374 (7)
Mean	2·431	O(6)–O(7)	2·458 (7)
Na(2)–O(3)	2·349 (6)		
Na(2)–O(6^{iii})	2·395 (6)	B(5) tetrahedron	
Na(2)–O(11)	2·438 (7)	O(7)–O(8)	2·464 (7)
Na(2)–O(5^{iii})	2·448 (7)	O(7)–O(9)	2·423 (7)
Na(2)–O(4)	2·449 (6)	O(7)–O(10)	2·422 (8)
Na(2)–O(2^{viii})	2·477 (7)	O(8)–O(9)	2·335 (7)
Mean	2·426	O(8)–O(10)	2·409 (8)
		O(9)–O(10)	2·354 (8)
Na(3)–O(7^{ii})	2·405 (6)		
Na(3)–O(8^{vii})	2·482 (7)	B(1)–O(1)	1·531 (12)
Na(3)–O(5^{ii})	2·512 (7)	B(1)–O(2)	1·510 (12)
Na(3)–O(9^{vii})	2·569 (7)	B(1)–O(3)	1·481 (12)
Na(3)–O(7)	2·584 (6)	B(1)–O(4)	1·425 (12)
Mean	2·510		
		B(2)–O(1^{ix})	1·369 (14)
B(1) tetrahedron		B(2)–O(2)	1·359 (13)
O(1)–O(2)	2·389 (7)	B(2)–O(5)	1·383 (13)
O(1)–O(3)	2·444 (7)		
O(1)–O(4)	2·416 (7)	B(3)–O(4)	1·459 (12)
O(2)–O(3)	2·455 (7)	B(3)–O(5)	1·494 (12)
O(2)–O(4)	2·452 (8)	B(3)–O(6)	1·510 (13)
O(3)–O(4)	2·400 (7)	B(3)–O(7)	1·466 (13)

Table 2 (*cont.*)

B(4)–O(6)	1·351 (13)
B(4)–O(8)	1·374 (12)
B(4)–O(3^{v})	1·398 (12)
B(5)–O(7)	1·459 (9)
B(5)–O(8)	1·461 (12)
B(5)–O(9)	1·491 (12)
B(5)–O(10)	1·478 (9)
B(2) triangle	
O(1^{ix})–O(2)	2·374 (8)
O(1^{ix})–O(5)	2·329 (8)
O(2)–O(5)	2·414 (8)

B(4) triangle	
O(6)–O(8)	2·393 (8)
O(6)–O(3^{v})	2·407 (8)
O(8)–O(3^{v})	2·338 (7)
B(1)–B(2)	2·46 (2)
B(1)–B(3)	2·53 (2)
B(2)–B(3)	2·51 (2)
B(3)–B(4)	2·51 (2)
B(3)–B(5)	2·54 (1)
B(4)–B(5)	2·45 (2)
Hydrogen bridges	
O(9)–O(1^{vi})	2·82
O(11)–O(1^{viii})	2·68
O(11)–O(3^{iii})	2·80

Symmetry code

None	x,	y,	z
(i)	$1-x$,	$1-y$,	$1-z$
(ii)	$-x$,	$1-y$,	$1-z$
(iii)	$\frac{1}{2}+x$,	$\frac{3}{2}-y$,	$1-z$
(iv)	$-\frac{1}{2}+x$,	$\frac{3}{2}-y$,	$1-z$
(v)	x,	$\frac{3}{2}-y$,	$\frac{1}{2}+z$
(vi)	$\frac{1}{2}-x$,	$1-y$,	$\frac{1}{2}+z$
(vii)	$\frac{1}{2}-x$,	$1-y$,	$-\frac{1}{2}+z$
(viii)	$\frac{1}{2}+x$,	y,	$\frac{1}{2}-z$
(ix)	$-\frac{1}{2}+x$,	y,	$\frac{1}{2}-z$

spread of values (2·33–2·65 Å), the nearest 'unbonded' O atom being 3·02 Å from Na. In Fig. 2 only connexions between the three independent Na polyhedra are shown, namely a face between Na(2) and Na(1) and a corner between Na(1) and Na(3); in addition, further connexions take place between each polyhedron and those with which it is symmetrically related.

Distances and angles are shown in Tables 2 and 3; all fall within the usual ranges. It can be noted that three hydrogen bridges are reported while there are four H atoms: two belonging to the hydroxyls O(9) and O(10) and two to the water molecule O(11). The three H bridges are O(9)–O(1), O(11)–O(1) and O(11)–O(3), while suitable distances from the hydroxyl O(10) were not found. H(1), H(3) and H(4) were placed at one-third of the related O–O distances; the missing hydrogen, H(2), was located taking into account the tetrahedral arrangement of bonds around O(10). In fact, direct detection of the H atoms was not possible because of the large number of spurious peaks on the ΔF map owing to the poor quality of the experi-

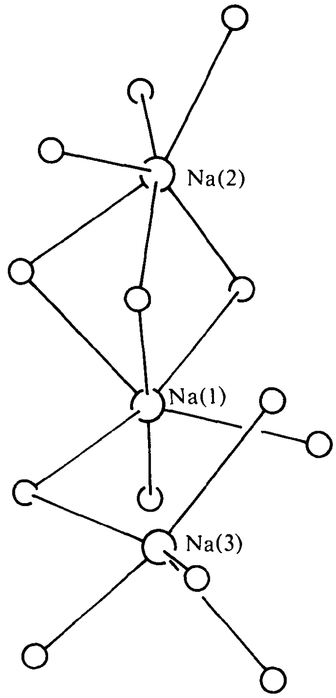

Fig. 2. The connexion of the three independent Na polyhedra.

Table 3. *Bond angles,* B–O–B *angles and the water angle* (°)

O(1)–B(1)–O(2)	103·5 (7)
O(1)–B(1)–O(3)	108·5 (7)
O(1)–B(1)–O(4)	109·6 (7)
O(2)–B(1)–O(3)	110·3 (7)
O(2)–B(1)–O(4)	113·2 (8)
O(3)–B(1)–O(4)	111·3 (7)
O(1^{ix})–B(2)–O(2)	120·8 (9)
O(1^{ix})–B(2)–O(5)	115·6 (9)
O(2)–B(2)–O(5)	123·5 (9)
O(4)–B(3)–O(5)	112·1 (8)
O(4)–B(3)–O(6)	109·0 (8)
O(4)–B(3)–O(7)	112·3 (8)
O(5)–B(3)–O(6)	105·1 (7)
O(5)–B(3)–O(7)	106·7 (8)
O(6)–B(3)–O(7)	111·3 (7)

O(6)–B(4)–O(8)	122·8 (8)
O(6)–B(4)–O(3^{v})	122·2 (8)
O(8)–B(4)–O(3^{v})	114·9 (8)
O(7)–B(5)–O(8)	115·1 (8)
O(7)–B(5)–O(9)	110·5 (6)
O(7)–B(5)–O(10)	111·1 (6)
O(8)–B(5)–O(9)	104·6 (5)
O(8)–B(5)–O(10)	110·1 (6)
C(9)–B(5)–O(10)	104·9 (8)
B–O–B angles	
B(1)–O(2)–B(2)	117·9 (8)
B(2)–O(5)–B(3)	121·9 (8)
B(3)–O(4)–B(1)	122·8 (7)
B(3)–O(7)–B(5)	120·4 (7)
B(5)–O(8)–B(4)	119·8 (7)
B(4)–O(6)–B(3)	122·4 (7)

Water angle

O(1^{viii})–O(11)–O(3^{iii})	108·7 (7)

Table 4. *The electrostatic valence balance*

	Na(1)	Na(2)	Na(3)	B(1)	B(2)	B(3)	B(4)	B(5)	H_d	H_a	Sums
O(1)				0·66	1·00					0·41	2·07
O(2)	0·10	0·15		0·70	1·03						1·98
O(3)		0·20		0·76			0·93			0·20	2·09
O(4)	0·20	0·15		0·88		0·80					2·03
O(5)		0·16	0·20		0·97	0·72					2·05
O(6)		0·18				0·70	1·07				1·95
O(7)			0·42			0·78		0·78			1·98
O(8)			0·21				1·00	0·77			1·98
O(9)	0·18		0·17					0·71	0·82		1·88
O(10)	0·37							0·74	1·00		2·11
O(11)	0·15	0·16							1·57		1·88

mental data. The electrostatic valence balance reported in Table 4 was computed according to the method of Brown & Shannon (1973); as can be seen, the contribution of H(2) was wholly assigned to the hydrogen donor O(10).

In addition to some local programs, the following for the CII 10070 computer were used: *MULTAN* (Germain, Main & Woolfson, 1971), *ORFLS* (Busing, Martin & Levy, 1962), and *BONDLA* (from the XRAY system, 1972).

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Refinement of the Crystal Structure of Di-μ-fluoro-hexafluorohexaaquadizirconium(IV), $Zr_2F_8(H_2O)_6$

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Crystals of $ZrF_4.3H_2O$ are triclinic, space group $P\bar{1}$ with $a = 5.948$, $b = 6.964$, $c = 7.572$ Å, $\alpha = 90.55$, $\beta = 105.06$, $\gamma = 118.72°$, $Z = 2$. The structure was refined to $R = 0.034$. In the crystal F-bridged binuclear units $Zr_2F_8(H_2O)_6$ exist, each Zr atom being in dodecahedral eight coordination. The Zr—F bonds range from 1·996 (4) to 2·214 (3) Å. Zr—O(W) distances are 2·263 (6), 2·264 (5) and 2·323 (5) Å. The packing is dominated by six crystallographically independent hydrogen bonds O—H···F and O—H···O acting between three water molecules and four F atoms.

Introduction

The existence of a mono- and a trihydrate of zirconium tetrafluoride was reported by Chauvenet (1920). They have been identified from X-ray powder diffraction patterns and chemical studies (D'Eye, Burden & Harper, 1956). The ZrF_4/H_2O system has been reinvestigated by Waters (1960). Cell parameters of