

1 σ . Zum Vergleich: in dem genannten SbCl_6^- -Salz besitzt das S_2N^+ -Kation (kristallographische) Zentrosymmetrie und beläuft sich der S–N-Abstand auf 1,464 (3) Å. In beiden Verbindungen führen die S-Atome allerdings relativ starke thermische Schwingungen aus. Eine Abstandskorrektur entsprechend dem 'riding model' (Busing & Levy, 1964) führt zu den folgenden Abständen: 1,494 und 1,517 Å für S(1)–N bzw. S(2)–N in $\text{NS}_2^+ \cdot \text{AlCl}_4$ und 1,502 Å für S–N in $\text{NS}_2^+ \cdot \text{SbCl}_6^-$. Wie bei anderen kristallinen Verbindungen, die aus N_mS_n^+ -Kationen und Chlorometallat-anionen aufgebaut sind, ist die Packung der Ionen offenbar durch enge $\text{S} \cdots \text{Cl}$ -Kontakte bestimmt. Die kürzesten $\text{S} \cdots \text{Cl}$ -Kontakte sind 3,26 (1) und 3,36 (1) Å. Der kürzeste $\text{N} \cdots \text{Cl}$ -Abstand ist 3,37 (1) Å. Zum Vergleich: Die van der Waals-Abstände $\text{S} \cdots \text{Cl}$ und $\text{N} \cdots \text{Cl}$ liegen bei 3,6 bzw. 3,4 Å (Bondi, 1964). Zwischen NS_2^+ -Kationen treten keine Kontakte < 5 Å auf. Faggiani *et al.* haben bereits darauf hingewiesen, dass die naheliegende Formulierung $\text{S}=\text{N}=\text{S}$ für das S_2N^+ -Kation wahrscheinlich eine zu einfache Darstellung der Bindungsverhältnisse ist und dass die S–N-Bindungen möglicherweise Dreifachbindungscharakter aufweisen. Der (korri-

gierte) S–N-Abstand im Thionitrosyl-Kation NS^+ (Clegg, Glemser, Harms, Hartmann, Mews, Noltemeyer & Sheldrick, 1981) ist mit 1,42 (1) Å noch deutlich kürzer als der S–N-Abstand im NS_2^+ -Kation.

Wir danken dem Fonds der chemischen Industrie für die Unterstützung der vorliegenden Untersuchung.

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Acta Cryst. (1982). **B38**, 1282–1285

Structure of Hydrated Sodium Borate $\text{Na}_2[\text{BO}_2(\text{OH})]$

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(Received 20 November 1981; accepted 8 December 1981)

Abstract. $\text{Na}_2[\text{BO}_2(\text{OH})]$, $M_r = 105.8$, orthorhombic, *Pnma*, $a = 8.627$ (2), $b = 3.512$ (1), $c = 9.863$ (2) Å, $V = 298.8$ (1) Å³, $Z = 4$, $D_x = 2.351$ Mg m⁻³, $\mu(\text{Mo } K\alpha) = 0.477$ mm⁻¹, $F(000) = 208$. $\text{Na}_2[\text{BO}_2(\text{OH})]$ was synthesized under hydrothermal conditions at 523 K. The structure was solved by direct methods and refined to a final $R = 0.028$ for 531 independent reflections with $I > 5\sigma(I)$. The structure consists of dense sheets of edge-sharing Na–O polyhedra. These sheets, parallel to (001), are linked together by isolated $\text{BO}_2(\text{OH})$ triangles and by H bonds. The title compound can be classified among the nesoborates.

Introduction. The structure determination of the compound $2\text{Na}_2\text{O} \cdot \text{B}_2\text{O}_3 \cdot \text{H}_2\text{O}$ (hereafter named 2:1:1) was undertaken as part of a systematic investigation of hydrated sodium borates. This phase, synthesized under hydrothermal conditions at 523 K, is of

particular interest being one of the few compounds known in the Na-rich portion of the $\text{Na}_2\text{O}–\text{B}_2\text{O}_3–\text{H}_2\text{O}$ system. The phase has already been described by Sborgi (1932) during his study on isotherms of the above system, and was later confirmed by Kocher & Lahlou (1969) who also reported an X-ray powder pattern. A reference to this phase can also be found in a previous work, performed in this laboratory (Corazza, Menchetti, Sabelli & Stoppioni, 1977), concerning the X-ray study of products obtained by hydrothermal synthesis at 423 K in the same ternary system.

Crystals of the compound 2:1:1 were obtained from a mixture of NaOH and B_2O_3 held in a pressure vessel for 48 h. The compound was identified by means of the X-ray powder pattern; it was very similar to that given by Kocher & Lahlou (1969) and quoted in the JCPDS File (Card 23-658). Just-prepared crystals are often transparent and well formed, with dimensions up to

several mm. They are prismatic, elongated along [010], slightly flattened on {001} and terminated by the {010} pinacoid. Unfortunately, these crystals are highly deliquescent and quickly deteriorate. For the X-ray data collection a crystal of approximate size 0.8 × 0.2 × 0.1 mm, coated with vaseline oil, was sealed in a Lindemann-glass capillary tube.

Lattice constants were determined from 25 high-angle reflections measured on a single-crystal diffractometer. The diffraction symmetry is *mmm* and the systematic absences are consistent with the space group *Pnma* or the corresponding noncentrosymmetric *Pn2₁a*. On the basis of the structural refinement the centrosymmetric group is correct.

Intensity data were collected on a Philips four-circle computer-controlled diffractometer (Istituto di Mineralogia dell'Università di Perugia) with Mo *K* α radiation and the ω -2 θ scan technique. Of 734 reflections scanned within the range 3° < θ < 35°, only 531 were judged to be actually observed according to the criterion $I > 5\sigma(I)$. Intensities were corrected for

Lorentz-polarization effects. Because of the low absorption coefficient and the small size of the crystal, no absorption correction was applied.

The structure was solved with the *MULTAN* program (Main, Woolfson, Lessinger, Germain & Declercq, 1974). All 140 reflections with $E \geq 1.26$ were included in the phase-determining process with eight sets of starting phases. On the first F_0 Fourier map all atoms were located with the exception of the H atom, which was positioned by means of a ΔF Fourier synthesis. All atoms lie on the symmetry planes at $y = \frac{1}{4}$ and $\frac{3}{4}$. The refinement was carried out by full-matrix least squares using first isotropic and then anisotropic thermal parameters to give a final $R = 0.028$ for the observed reflections and 0.046 for all data. A weight $w = 1/\sigma^2(F_0)$ with σ derived from counting statistics was given to all observed reflections. Scattering-factor curves for all atoms were taken from *International Tables for X-ray Crystallography* (1974). Three reflections (210, 020 and 004) were considered to be affected by secondary extinction and therefore excluded from least-squares calculations. Positional parameters and equivalent isotropic thermal parameters are given in Table 1.* Interatomic distances and angles are given in Table 2.

Table 1. Fractional atomic coordinates and equivalent isotropic thermal parameters

	<i>x</i>	<i>y</i>	<i>z</i>	B_{eq} (Å ²)
Na(1)	0.42775 (9)	0.75	0.10348 (8)	1.02
Na(2)	0.32810 (10)	0.75	0.44690 (9)	1.45
O(1)	0.1277 (2)	0.25	0.3780 (1)	1.03
O(2)	0.2689 (2)	0.25	0.1678 (1)	1.03
OH	-0.0048 (2)	0.25	0.1633 (1)	1.25
B	0.1365 (3)	0.25	0.2409 (2)	0.77
H	0.408 (4)	0.25	0.273 (3)	3.00

Table 2. Selected interatomic distances (Å) and angles (°)

Na(1)—O(1) ^{viii}	2.275 (2)	Na(2)—O(2) ^{vi}	2.334 (2)
Na(1)—O(2)	2.316 (1)	Na(2)—OH ^{iv}	2.519 (1)
Na(1)—O(2) ⁱ	2.316 (1)	Na(2)—OH ^v	2.519 (1)
Na(1)—O(1) ^{iv}	2.468 (1)	Na(2)—O(1)	2.556 (1)
Na(1)—O(1) ^v	2.468 (1)	Na(2)—O(1) ^j	2.556 (1)
		Na(2)—OH ^{vii}	2.623 (2)
Na(1)—Na(1) ⁱⁱ	2.967 (1)	B—O(2)	1.351 (3)
Na(1)—Na(1) ⁱⁱⁱ	2.967 (1)	B—O(1)	1.354 (3)
Na(1)—Na(2) ^{viii}	3.216 (1)	B—OH	1.439 (3)
Na(1)—Na(2) ^{ix}	3.216 (1)	O(2)—O(1)	2.405 (2)
OH—O(2) ^{vi}	2.566 (2)	O(2)—OH	2.362 (2)
OH—H ^{vi}	0.98 (2)	O(1)—OH	2.406 (2)
H...O(2)	1.59 (2)	O(2)—B—O(1)	125.5 (2)
OH—H ^{vi} ...O(2) ^{vi}	178 (2)	O(2)—B—OH	115.6 (2)
		O(1)—B—OH	118.9 (2)

Symmetry code

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

Discussion. The present structure is built up by Na—O sheets linked together by isolated and partially hydrated B—O triangles and by H bonds. As already pointed out, all atoms lie in special positions on the mirror planes at $y = \frac{1}{4}$ and $\frac{3}{4}$.

There is only one independent B atom, which is bound by two O atoms and a hydroxyl. The O—O edges of the triangle range from 2.362 to 2.406 Å, and the O—B—O angles from 115.6 to 125.5°, the largest value belonging to the angle opposite to the longest B—OH distance. Within the standard deviations the B—O(1) and B—O(2) distances are identical (1.354 and 1.351 Å) while B—OH is noticeably longer (1.439 Å). The mean B—O distance of 1.381 Å is very similar to the mean values found in other borates, e.g. 1.382 Å in NaBO₂ (Marezio, Plettinger & Zachariassen, 1963) and 1.378 Å in Na₃[B₃O₅(OH)₂] (Corazza, Menchetti & Sabelli, 1975). On the other hand, in many borates shorter B—O mean distances have been found: 1.361 Å in B(OH)₃ (Zachariassen, 1954), 1.366 Å in Na[B₅O₆(OH)₄] (Menchetti & Sabelli, 1978), 1.367 Å in the mineral hambergite, Be₂[BO₃(OH)] (Zachariassen, Plettinger & Marezio, 1963), etc. According to Marezio *et al.* (1963) there is a relation between the mean B—O bond length and the fluctuations of the individual bond

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36596 (6 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

distances: the mean interatomic distance increases with increasing fluctuations of individual bond distances from the mean. This correlation is verified in the present structure, but it is not always true [see, for instance, pinakiolite and warwickite (Moore & Araki, 1974), and Na_3BO_3 (König & Hoppe, 1977)]. In particular, pinakiolite shows a mean value of 1.379 Å while the individual B–O distances range from 1.376 to 1.381 Å only.

According to the crystal-chemical classification of borates by Christ & Clark (1977), the present structure contains FBB 1:Δ. Isolated triangles have been found in many structures: in $\text{B}(\text{OH})_3$ (Zachariasen, 1954), AlBO_3 (Vegas, Cano & García-Blanco, 1977), Na_3BO_3 (König & Hoppe, 1977), and in the minerals pinakiolite and warwickite (Moore & Araki, 1974), jimboite (Sadanaga, Nishimura & Watanabe, 1965), hambergite (Zachariasen *et al.*, 1963), and others. However, as pointed out by Christ & Clark, 1:Δ isolated groups have been found in anhydrous or in fully hydrated forms. In this light, 2:1:1 seems to be the first known example of a structure containing isolated, partially hydrated, triangular groups.

The O(1), O(2) and OH atoms are also irregularly coordinated by the two independent Na atoms. Na(1) is linked to five O atoms, with Na–O distances ranging from 2.275 to 2.468 Å (mean value 2.369 Å). Within the limit of 3.0 Å, Na(1) has two more symmetric neighbours (namely OH) but the related distance (2.952 Å) is remarkably longer than the mean value. If these two last anions are omitted, the coordination polyhedron resembles an irregular square pyramid. Na(2) is linked to six anions (three O atoms and three hydroxyls) with distances ranging from 2.334 to 2.623 Å (mean value 2.518 Å). The coordination polyhedron resembles an irregular trigonal prism.

The Na polyhedra are connected to each other, by edge sharing, to form dense sheets parallel to the *ab* plane. In the unit cell there are two Na–O sheets lying

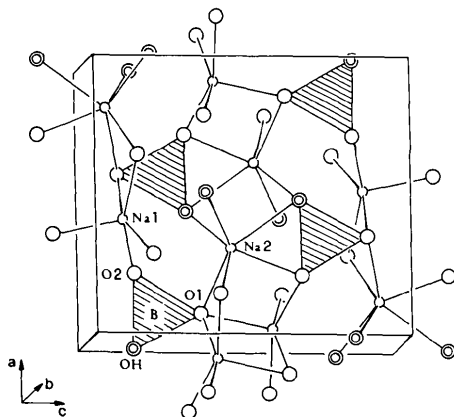


Fig. 1. A view of the $\text{Na}_2[\text{BO}_2(\text{OH})]$ structure. The unit cell is outlined.

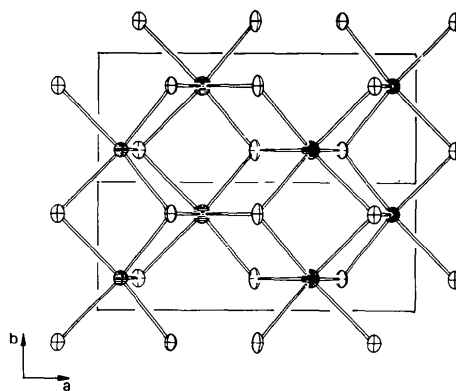


Fig. 2. A sheet of Na–O polyhedra through two unit cells. Na atoms are shaded. Thermal ellipsoids are scaled at the 60% probability level (Johnson, 1965).

at $z = 0$ and $\frac{1}{2}$ (Fig. 1). In Fig. 2 a single sheet (z values in the range $\frac{1}{4}$ – $\frac{3}{4}$) is depicted. In this sheet each Na appears nearly on the centre of a wavy six-membered ring of Na atoms: $4\text{Na}(1) + 2\text{Na}(2)$ around Na(1), and $4\text{Na}(2) + 2\text{Na}(1)$ around Na(2). If the two adjacent symmetry-related sheets are also taken into account, the arrangement of the Na atoms resembles hexagonal closest packing. Na–Na distances show a wide range of values. In Table 2 are reported the four distances shorter than 3.3 Å; the Na(1)–Na(1)ⁱⁱ separation and its symmetry-related counterpart are very short (2.967 Å). This value is close to that (2.971 Å) found in the structure of $\text{Na}_8[\text{B}_{12}\text{O}_{20}(\text{OH})_4]$ (Menchetti & Sabelli, 1979) for an Na–Na separation between two polyhedra sharing one face.

Connections between adjacent Na–O sheets are provided in the *c* direction by borate triangles, which lie on the *ac* plane; indeed, each B links two anions belonging to one sheet and a third anion belonging to an adjacent sheet. This is clearly shown in Fig. 1. Further connections between sheets are provided by the H bond which occurs between OH and O(2) (in the unit cell there are four equivalent bonds). Owing to the short donor–acceptor distance (2.566 Å) the bond should be considered rather strong.

Table 3. *Electrostatic valence balance*

	Na(1)	Na(2)	B	H	Sums
O(1)	0.24	0.15	1.07		1.93
	0.16	0.15			
	0.16				
O(2)	0.22	0.25	1.08	0.27	2.04
	0.22				
OH		0.16	0.85	0.73	2.03
		0.16			
		0.13			

An electrostatic valence balance was computed as suggested by Brown & Shannon (1973). For the H bonds the curve quoted in Donnay & Donnay (1973) was employed. Table 3 reports the contributions of different atoms and the bond-strength sums (v.u.). The balance is satisfactory for all O atoms (maximum deviation 3.5%), thus confirming the general bond system.

The authors wish to thank Professor P. F. Zanazzi, Università di Perugia, for collecting the data.

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