

# Synthesis and Crystal Structure of a New Modification of Sodium Tetrahydroxyborate $\text{NaB}(\text{OH})_4$

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**Abstract**—A new polymorphic modification of sodium tetrahydroxyborate  $\text{NaB}(\text{OH})_4$  is synthesized and its crystal structure is determined. The compound crystallizes in symmetry space group  $P2_12_12_1$  with the unit cell parameters  $a = 5.323(5)$  Å,  $b = 9.496(5)$  Å, and  $c = 6.596(5)$  Å. The discrepancy factor for 511 symmetrically nonequivalent reflections is  $R = 0.0188$ . Layers that are formed by boron tetrahedra, aligned parallel to the (010) planes, and alternate with layers of sodium cations can be distinguished in the structure.

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## INTRODUCTION

As is known, the structure of borates is more complex than the structure of silicates [1, 2]. In this respect, the determination of the structures of new borates has attracted the particular interest explained by their various applications in high-tech processes.

In this work, sodium tetrahydroxyborate was synthesized within the framework of basic research associated with the development of water-soluble compositions for preparing microspheres as microcontainers for a gaseous fuel used in laser fusion [3].

## SAMPLE PREPARATION

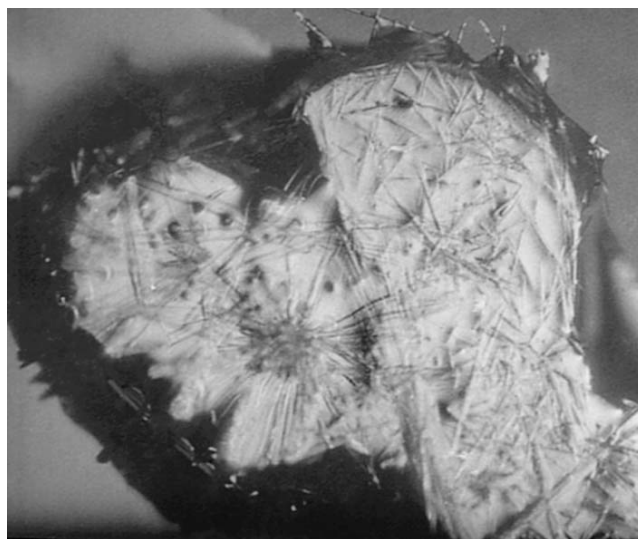
A solution was prepared using boric acid and sodium hydroxide, because it is these hydroxides rather than carbonates that enter into the composition of batches for preparing microspheres. It was shown using IR spectroscopy that the boric acid used (special-purity grade) was actually a mixture of metaboric and orthoboric acids and amorphous boron oxide [4].

Separately prepared aqueous solutions of “boric acid” and sodium hydroxide were mixed by adding an alkaline solution with a dosing device to the boric acid solution (pH 5) until pH 12 was attained. The calculated borate ratio  $N_B$  of the prepared solution was, on average (for solutions with different initial concentrations of

reagents),  $N_B = \frac{C_{\text{B}_2\text{O}_3}}{C_{\text{Na}_2\text{O}}} = 1.5$ . Solutions were left to stand

in air at room temperature, so that crystallization occurred as water evaporated. Crystals grew in the form

of radially arranged needles (Fig. 1); in this case, the formation of planar aggregates was initiated on the surface of the solution, which indicates that the density of crystals was lower than the density of the solution. The length of individual needles in aggregates was as large as a millimeter. The preliminary X-ray powder diffraction analysis showed that we prepared a new crystalline compound. It is known that, in the case of synthesis of borate crystals from aqueous solutions, the borate ratio in the crystal is primarily governed by the alkalinity of the medium and the nature of the cation rather than by



**Fig. 1.** External view of needle-shaped crystals of  $\text{NaB}(\text{OH})_4$ . The diameter of the spherulite in the lower part of the micrograph is about 2 mm.

<sup>†</sup> Deceased.

the borate ratio in the mother solution. In our case for sodium borate in the medium with pH 12, we should expect the crystallization of the compound with the borate ratio  $N_B = 1$ , in which for one molecule of basic oxide there is one molecule of boron oxide, which was actually confirmed by the structural analysis.

During long-term storage in air, the crystals of the new compound lost the transparency, most likely, due to the formation of carbonates (or hydrocarbonates) on their surface. However, we failed to identify the resulting product of the reaction of the crystals with air by X-ray diffraction analysis.

### EXPERIMENTAL TECHNIQUE

A colorless single crystal irregular in shape ( $0.35 \times 0.17 \times 0.50$  mm in size in the tetragonal prism approximation), which was chosen for the X-ray diffraction analysis, represented a fragment of one of the described needles. The preliminary study revealed that the crystal belongs to the orthorhombic crystal system with the parameters of the primitive unit cell  $a = 5.323(5)$  Å,  $b = 9.496(5)$  Å, and  $c = 6.596(5)$  Å. The integrated intensities of X-ray reflections were measured on an automated three-circle diffractometer operating in the perpendicular beam scheme with layer-by-layer recording of reflections (MoK $\alpha$  radiation, graphite monochromator,  $\omega$ - $2\theta$  scan mode). By rotating the crystal around the  $c$  axis, we measured the intensities of 531 reflections, among which the intensities  $I(hkl)$  of 511 reflections were used in further calculations. The integrated intensities were estimated and the background was taken into account with the use of the profile analysis algorithm [5]. The stability of the crystal and the intensity of the primary beam during the experiment were controlled by periodically measuring the intensity of the reference reflection. The measured intensities were corrected for the drift of the reference, the Lorentz effect, and polarization. Absorption was not included because of its insignificance. The presence of extinctions unambiguously indicated symmetry space group  $P2_12_12_1$ .

The starting structural model was determined by the direct method. The model was refined by the least-squares method in the full-matrix approximation with the SHELXL-97 program package [6]. The positions of the hydrogen atoms were determined from the difference Fourier syntheses of the electron density, alternating with the refinement of the model by the least-squares method. The temperature factors of the non-hydrogen atoms were refined in the anisotropic approximation, and the temperature factors of the H atoms were refined in the isotropic approximation. The main experimental data are presented in Table 1. The final values of the coordinates and the equivalent isotropic thermal parameters of the atoms in the structure of NaB(OH) $_4$  are given in Table 2. The selected interatomic distances, the bond angles, and the hydrogen bond lengths are listed in Table 3. The projection of the structure along the shortest

**Table 1.** Main experimental data and refinement parameters for the structure of NaX(S)

Empirical formula	H $_4$ BNaO $_4$
Molecular weight $M$	101.83
Temperature $T$ , K	293(2)
Wavelength, Å	0.71073
Crystal system	Orthorhombic
Symmetry space group	$P2_12_12_1$
Unit cell parameters, Å	$a = 5.323(5)$ , $b = 9.496(5)$ , $c = 6.596(5)$
$V$ , Å $^3$	333.38(9)
$Z$	4
Density (calcd), g/cm $^3$	2.029
Absorption coefficient, cm $^{-1}$	3.06
$F(000)$	208
Crystal sizes, mm	$0.35 \times 0.17 \times 0.50$
$2\theta_{\max}$ , deg	60
Index ranges	$-7 \leq h \leq 7$ , $-11 \leq k \leq 12$ , $-9 \leq l \leq 9$
Number of reflections measured $I(hkl)$	531
Number of symmetrically nonequivalent reflections with $I(hkl) \geq 2\sigma(I(hkl))$	511
Number of parameters refined	72
$S$	1.006
$R1$	0.0188
$wR2$	0.0467
Maximum and minimum peaks in the difference Fourier synthesis, e Å $^{-3}$	0.165 and $-0.155$

**Table 2.** Coordinates and isotropic thermal parameters of atoms ( $U$ ) in the structure of NaB(OH) $_4$

Atom	$x(dx)$	$y(dy)$	$z(dz)$	$U_{\text{iso}}(\text{Å}^2)$
Na	0.7140(1)	$-0.0199(1)$	0.9668(1)	22(1)
O1	0.8622(2)	0.3791(1)	0.9407(1)	19(1)
O2	0.8749(2)	0.3819(1)	0.5745(1)	19(1)
O3	0.4950(2)	0.3121(1)	0.7439(2)	18(1)
O4	0.8556(2)	0.1613(1)	0.7583(1)	17(1)
B	0.7724(2)	0.3106(1)	0.7556(2)	13(1)
H1	0.778(4)	0.448(2)	0.966(3)	39(5)
H2	0.893(4)	0.330(2)	0.492(3)	29(5)
H3	0.442(5)	0.268(2)	0.841(3)	51(6)
H4	1.002(5)	0.158(3)	0.786(3)	56(7)

**Table 3.** Selected interatomic distances (Å), bond angles (deg), and hydrogen bond lengths (Å)

Bond	<i>d</i>	Angle	$\omega$
Na–O4	2.3280(10)	O4–Na–O4 <sup>i</sup>	161.25(4)
Na–O4 <sup>i</sup>	2.344(10)	O4–Na–O1 <sup>ii</sup>	89.5(4)
Na–O1 <sup>ii</sup>	2.3800(10)	O4 <sup>i</sup> –Na–O1 <sup>ii</sup>	89.27(4)
Na–O3 <sup>iii</sup>	2.3909(11)	O4–Na–O3 <sup>iii</sup>	107.49(4)
Na–O2 <sup>iv</sup>	2.3942(11)	O4 <sup>i</sup> –Na–O3 <sup>iii</sup>	91.17(4)
O1–B	1.4644(15)	O1 <sup>ii</sup> –Na–O3 <sup>iii</sup>	99.07(4)
O2–B	1.4775(15)	O4–Na–O2 <sup>iv</sup>	85.69(4)
O3–B	1.4784(16)	O4 <sup>i</sup> –Na–O2 <sup>iv</sup>	90.82(4)
O4–B	1.4847(15)	O1 <sup>ii</sup> –Na–O2 <sup>iv</sup>	65.23(4)
		O3 <sup>iii</sup> –Na–O2 <sup>iv</sup>	95.69(4)
		O1–B–O2	110.47(10)
		O1–B–O3	111.40(11)
		O2–B–O3	108.81(10)
		O1–B–O4	108.50(10)
		O2–B–O4	109.70(9)
		O3–B–O4	107.92(9)

## Hydrogen bond lengths

O–H...O	O–H	H...O	O...O	O–H–O
O1–H1...O2	0.81(2)	1.95(2)	2.742(2)	167
O2–H2...O3	0.74(2)	2.13(2)	2.865(2)	173
O3–H3...O1	0.81(2)	2.05(2)	2.850(2)	167
O4–H4...O1	0.80(3)	2.66(3)	3.37	150

Symmetry codes: (i)  $-x + 3/2, -y, z + 1/2$ ; (ii)  $x - 1/2, -y + 1/2, -z + 2$ ; (iii)  $-x + 1, y - 1/2, -z + 3/2$ ; (iv)  $-x + 2, y - 1/2, -z + 3/2$ .

*a* axis is depicted in Fig. 2. The coordination of the Na atom is shown in Fig. 3.

## RESULTS

The compound under investigation contains all boron atoms in the fourfold coordination. The independent part of the unit cell contains one Na<sup>+</sup> ion and one tetrahydroxyborate ion B(OH)<sub>4</sub><sup>-</sup>. The B–O bond lengths in the tetrahedron vary in a narrow range 1.464(2)–1.485(2) Å, and the O–B–O bond angles 107.9(1)°–111.4(1)° are close to the tetrahedral angles. Their relation by the three mutually perpendicular non-

intersecting screw axes 2<sub>1</sub> aligned parallel to the crystallographic axes leads to the formation of a sufficiently simple three-dimensional structure depicted in Fig. 2a, in which the boron tetrahedra are linked together only by hydrogen bonds.

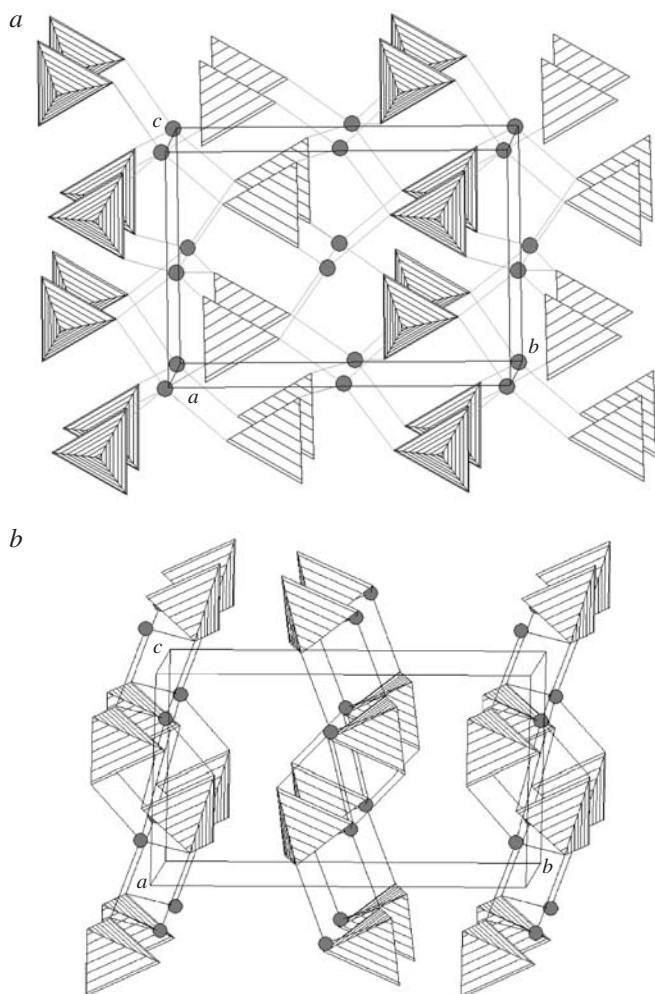
In the structure, it is possible to distinguish layers that are formed by boron tetrahedra and aligned parallel to the (010) plane. It can be seen that all tetrahedra inside the layer are oriented in one direction and all tetrahedra in the adjacent layers are oriented in opposite directions. The layers are located at a distance of 2.24 Å from each other. The hydrogen bonds are formed between the boron tetrahedra both inside the layers and between them. As can be seen from Fig. 2a, sodium atoms are located in the space between the layers. Each atom is coordinated by five oxygen atoms at distances of 2.328(1)–2.394(1) Å, and the coordination polyhedron is well described by a tetragonal pyramid (Fig. 3). The maximum displacement of the oxygen atoms from the basal plane is equal to 0.04 Å, the sodium atom is displaced from it by 0.3 Å, and the vertex occupied by O2 atom is displaced by 2.7 Å.

Three of four hydrogen bonds formed in the structure are sufficiently strong, as can be judged from their lengths lying in the range 2.74–2.87 Å. At the same time, the distance between the O4 and O1 atoms is equal to 3.37 Å, which reflects a very weak interaction between these atoms, most likely, due to the steric reasons.

## RESULTS AND DISCUSSION

Earlier, the structure of another modification of this compound was determined in [7]. This modification, despite the close resemblance of the parameters ( $a = 5.886(3)$  Å,  $b = 10.566(6)$  Å,  $c = 6.143(3)$  Å,  $\beta = 111.6^\circ$ ) to the parameters determined in our work, crystallizes in the monoclinic crystal system with symmetry space group  $P2_1/a$ . A comparison of this structure and the structure investigated in our work shows that they are built up of the same borate ions. As can be seen from Fig. 2, each layer of borate ions in the structure investigated in our work is formed by the unidirectional tetrahedra (Fig. 2a), whereas, in the previously determined structure (Fig. 2b), tetrahedra inside the layer are differently directed and are related in pairs by the centers of inversion. Therefore, the anionic parts of two structures are topologically different. The arrangements of the sodium ions also differ substantially.

In the monoclinic modification, these atoms are situated not between the layers but inside each (010) layer, which, most likely, leads to its monoclinic distortion and the necessity of alternating the oppositely oriented tetrahedra in these layers in contrast to the structure with the unidirectional tetrahedra investigated in our work. The coordination polyhedron of the sodium atom is a tetragonal pyramid formed by five O atoms,

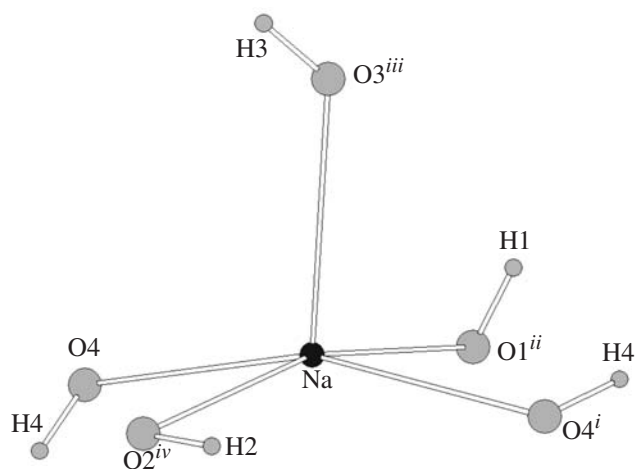


**Fig. 2.** Crystal structures of the modifications of  $\text{NaB(OH)}_4$ : (a) new orthorhombic modification and (b) monoclinic modification according to the data taken from [7]. The  $\text{BO}_4$  groups are depicted by hatched tetrahedra, and the Na ions are shown by circles of an arbitrary radius. Dotted lines indicate the coordination of sodium atoms.

which are located at distances of 2.328(1)–2.394(1) Å. The next nearest O atom is located at a distance of 3.126(1) Å. The deviation of the O atoms forming the base from the plane is less than 0.042 Å, the Na atom deviates from the plane by 0.34 Å, and the apical O atom deviates from this plane by 2.7 Å.

## CONCLUSIONS

Crystallization of borates from aqueous solutions involves considerable difficulties due to the variability of the form of the groups formed by borate ions in the solutions. Nonetheless, by knowing the borate ratio and the acidity of medium, it is possible with a greater or smaller confidence to predict the borate ratio in the crystals and the ratio between the threefold- and fourfold-coordinated boron atoms in them. However, the



**Fig. 3.** Coordination of the Na atom in the structure of  $\text{NaB(OH)}_4$ .

reason for the formation of one compound from the solutions of different modifications is obviously associated with the specific structuring of borate ions in the solutions and the appearance of a certain intermediate-range order. The factors responsible for this structuring are not understood. Therefore, it is necessary to accumulate information on the crystallization of the polymorphic modifications of compounds and their structural features.

In this case, a comparison of the structures of two modifications of the  $\text{NaB(OH)}_4$  compound, which are built up of the same borate anions, makes it possible to assume that the specific character of each structure is determined by the first and second coordination spheres of the sodium ion. The difference between the environments of the sodium ions should exist already in the solution. Most likely, the use of the orthorhombic form of the reagent with the composition corresponding to the formula  $\text{H}_3\text{BO}_3$  but with the phase composition different from the metaboric acid in the synthesis of the  $\text{NaB(OH)}_4$  compound led to the crystallization of the new  $\text{NaB(OH)}_4$  modification from the same parent solution.

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