

Synthesis and crystal structure of oxonium 2,4,8,10-tetrahydroxy-1,3,5,7,9,11-hexaoxa-2,4,6,8,10-pentaboraspiro[5.5]undecan-6-uide hydrate

L. Dimowa, K. Kossev, H. I. Sbirikova, R. P. Nikolova,
B. L. Shivachev*

*Institute of Mineralogy and Crystallography "Academician Ivan Kostov",
Bulgarian Academy of Sciences,
1113 Sofia, Acad. Georgi Bonchev Str., Building 107, Bulgaria*

Received February, 2013; Revised May, 2013

Oxonium 2,4,8,10-tetrahydroxy-1,3,5,7,9,11-hexaoxa-2,4,6,8,10-pentaboraspiro[5.5]undecan-6-uide hydrate, was synthesized and its structure was investigated by single crystal X-ray diffraction and ^{11}B NMR analyses. The title compound, $\text{B}_5\text{H}_9\text{O}_{12}$, crystallizes in the orthorhombic crystal system, space group *Aba2* with cell parameters $a = 11.3286(5)$ Å, $b = 11.0118(4)$ Å, $c = 9.2314(4)$ Å, $Z = 4$ and $V = 1151.60(8)$ Å³. The crystal structure is stabilized through hydrogen-bonding interactions, involving all possible donors and acceptors.

Key words: boroxine, single crystal, ^{11}B NMR.

INTRODUCTION

Borate materials are very attractive due to their use in various applications, ranging from agriculture, nuclear containment shields, in the production of glasses and ceramics, in chemistry synthesis, wood treatment, optical materials, treatments for cancer etc. Amongst the multitude of borate compounds (crystals, ceramics, glasses) employed in the optical field one should pay special attention to borate crystal phases that exhibit non-linear optical activity (barium borates, β -BBO, cesium borate, cesium lithium borate etc.). Aforementioned crystal phases are nowadays used routinely in laser setups for second- and third- harmonic generation (SHG and THG), phase-matching etc. A large number of inorganic (potassium, cesium), organic (alkylammonium, heterocyclic) or coordination (tris(ethylenediamine-*N,N'*)-cobalt(II)) [1, 2] salts of the unknown in free state pentaboric acid $\text{H}^+[\text{B}_5\text{O}_6(\text{OH})_4]^-$ have been described. They have been obtained mainly within attempts to optimize the optical, thermal and structural properties of

known borate phases. Attempts to introduce organic molecular fragments to enhance the polarization or charge transfer while maintaining the boron surrounding have been also made. Amongst the factors contributing to the large diversity of borate crystal phases are the performed variations of the molar ratio of the reactants, the temperature, the solvent media and the presence of impurities (hampering or initiating the crystallization). Continuing our investigation on boronic acids crystallization and co-crystallization [3–5] here we present the crystal structure of oxonium 2,4,8,10-tetrahydroxy-1,3,5,7,9,11-hexaoxa-2,4,6,8,10-pentaboraspiro[5.5]undecan-6-uide hydrate (**1**), $\text{B}_5\text{H}_9\text{O}_{12}$.

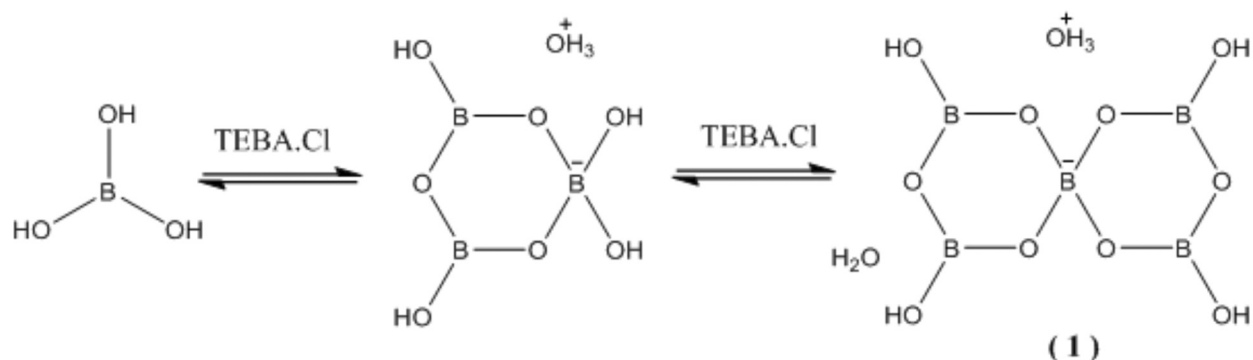
EXPERIMENTAL

Synthesis and characterization

The title compound (**1**) was obtained according to the reaction scheme 1.

Boric acid (165 mg, 2.67 mmol) and triethylbenzylammonium chloride (TEBA.Cl) (600 mg, 2.64 mmol), were dissolved in 50 ml distilled water. Colorless (transparent) crystals of **1**, suitable for single crystal X-ray diffraction analyses have been obtained after slow evaporation of water at room temperature.

* To whom all correspondence should be sent:
E-mail: blshivachev@gmail.com



Scheme 1. Reaction scheme and chemical diagram of the title compound (1)

X-ray – single crystal analyses

A crystal of the title compound having approximate dimension $0.22 \times 0.20 \times 0.16$ mm³ was placed on a glass fiber and mounted on an Agilent, SuperNovaDual four-circle diffractometer equipped with Atlas CCD detector and using mirror-mono-

chromatized MoK α ($\lambda = 0.7107$ Å) radiation from micro-focus source. Diffraction data were collected at room temperature by the ω -scan technique. The determination of cell parameters, data integration, scaling and absorption correction were carried out using the CrysAlisPro program package [6]. The structure was solved by direct methods using

Table 1. Crystal data and most important structure refinement indicators for **1**

B ₅ H ₉ O ₁₂ (PBA)	$D_x = 1.581$ Mg m ⁻³
$M_r = 255.11$	Melting point: 314 K
Orthorhombic, <i>Aba2</i>	Mo <i>K</i> α radiation, $\lambda = 0.7107$ Å
$a = 11.3286$ (5) Å	Cell parameters from 3322 reflections
$b = 11.0118$ (4) Å	$\theta = 2.9$ – 32.7°
$c = 9.2314$ (4) Å	$\mu = 0.16$ mm ⁻¹
$V = 1151.60$ (8) Å ³	$T = 290$ K
$Z = 4$	Prism, colorless
$F(000) = 564$	$0.22 \times 0.20 \times 0.16$ mm
Supernova Dual, Atlas CCD diffractometer	1704 independent reflections
Radiation source: Mova (Mo) X-ray Source	1671 reflections with $I > 2\sigma(I)$
mirror	$R_{\text{int}} = 0.025$
Detector resolution: 10.3974 pixels mm ⁻¹	$\theta_{\text{max}} = 32.7^\circ$, $\theta_{\text{min}} = 2.9^\circ$
ω scans	$h = -14 \rightarrow 16$
Absorption correction: multi-scan	$k = -15 \rightarrow 15$
<i>CrysAlis PRO</i> , Oxford Diffraction Ltd., Version 1.171.34.40	$l = -13 \rightarrow 12$
$T_{\text{min}} = 0.837$, $T_{\text{max}} = 1.000$	Primary atom site location: structure-invariant direct methods
4244 measured reflections	Hydrogen site location: from difference Fourier map and inferred from neighboring sites
Refinement on F^2	H-atom parameters constrained
Least-squares matrix: full	$w = 1/[\sigma^2(F_o^2) + (0.1086P)^2 + 0.2796P]$
$R[F^2 > 2\sigma(F^2)] = 0.050$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.150$	$(\Delta/\sigma)_{\text{max}} < 0.001$
$S = 1.10$	Secondary atom site location: difference Fourier map
1702 reflections	$\Delta\rho_{\text{max}} = 0.32$ e Å ⁻³
85 parameters	$\Delta\rho_{\text{min}} = -0.30$ e Å ⁻³
1 restraint	Extinction correction: none

ShelXS [7] and refined by full-matrix least-square procedures on F^2 with ShelXL-97 [7]. The boroxin and oxonium (Ow2) hydrogen atoms were located from difference Fourier map and refined as riding on their parent atoms, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{O})$. Ow1 hydrogen atoms were placed on calculated position fulfilling hydrogen bonding criteria with acceptor atoms and refined as riding on their parent atoms, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{O})$.

NMR

The ^{11}B NMR data were obtained on a Bruker AMX 500MHz at 300K. The data were referenced to

a H_3BO_3 solution D_2O (35 ppm). ^{11}B NMR (THF-D_8 , 160.4 MHz): $\delta = -4.8$ (O_4B^-), 16.9 (BO_3).

RESULTS AND DISCUSSION

The chemical diagram of the studied compound (**1**) is illustrated in Scheme 1 and experimental conditions are summarized in Table 1. Selected bond distances and bond angles are listed in Table 2. Hydrogen bonding geometry is presented in Table 3. A diagram of the molecular structure with 50% probability and the atom numbering scheme is shown in Fig. 1. The data for publication were prepared with

Table 2. Selected geometrical parameters for **1** (\AA , $^\circ$)

Bond distance			
B1 — O2	1.372 (2)	B2 — O1 ⁱ	1.4659 (19)
B3 — O5	1.353 (2)	B2 — O3	1.475 (2)
B1 — O3	1.3557 (19)	B2 — O3 ⁱ	1.475 (2)
B1 — O4	1.353 (2)	B3 — O1	1.351 (2)
B2 — O1	1.4660 (19)	B3 — O2	1.379 (2)
Bond angle			
O3 — B1 — O2	121.74 (13)	O3 ⁱ — B2 — O3	108.1 (2)
O4 — B1 — O2	118.38 (14)	O1 — B3 — O2	121.77 (14)
O4 — B1 — O3	119.88 (14)	O1 — B3 — O5	124.23 (14)
O1 ⁱ — B2 — O1	108.7 (2)	O5 — B3 — O2	113.98 (15)
O1 — B2 — O3	111.39 (6)	B3 — O1 — B2	123.16 (11)
O1 ⁱ — B2 — O3	108.62 (8)	B1 — O2 — B3	119.01 (13)
O1 ⁱ — B2 — O3 ⁱ	111.39 (6)	B1 — O3 — B2	122.91 (11)
O1 — B2 — O3 ⁱ	108.62 (8)		
Torsion angle			
O1 ⁱ — B2 — O1 — B3	120.73 (19)	O3 ⁱ — B2 — O1 — B3	-117.91 (17)
O1 ⁱ — B2 — O3 — B1	-120.07 (14)	O3 — B2 — O1 — B3	1.1 (3)
O1 — B2 — O3 — B1	-0.4 (2)	O3 ⁱ — B2 — O3 — B1	118.91 (16)
O1 — B3 — O2 — B1	0.3 (3)	O4 — B1 — O2 — B3	179.93 (19)
O2 — B1 — O3 — B2	-0.3 (3)	O4 — B1 — O3 — B2	-179.86 (17)
O2 — B3 — O1 — B2	-1.1 (3)	O5 — B3 — O1 — B2	-179.6 (2)
O3 — B1 — O2 — B3	0.4 (3)	O5 — B3 — O2 — B1	178.95 (19)

Symmetry code: (i) $-x+1, -y+1, z$

Table 3. Hydrogen bond for **1** (\AA , $^\circ$)

D—H...A	D—H	d(H...A)	d(D...A)	$\angle(\text{DHA})$
OW2—HW2B...O1	0.954	1.912	2.857(5)	170.2
O4—H4...OW2 ⁱ	0.949	1.741	2.687(4)	174.5
O5—H5...O4 ⁱⁱ	0.820	1.907	2.664(4)	152.9
OW1—HW1A...O5 ⁱⁱⁱ	1.152	1.844	2.962(5)	161.9
OW1—HW1B...O2 ^{iv}	1.068	1.888	2.935(5)	166.1
OW1—HW1B...O5 ^{iv}	1.068	2.332	2.962(5)	116.2
OW2—HW2A...O3 ^v	0.783	2.116	2.881(4)	164.9
OW2—HW2C...OW1 ^{vi}	0.748	2.342	2.992(5)	146.0

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

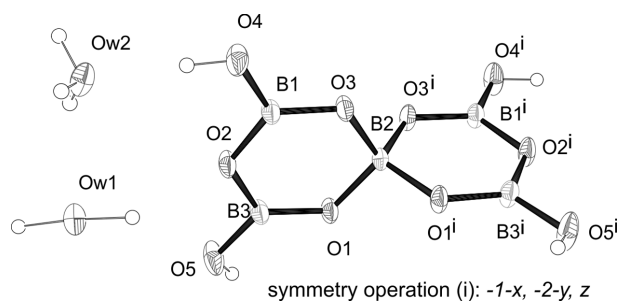


Fig. 1. View of molecule with an atom-numbering scheme. Displacement ellipsoids for the non-H atoms are drawn at the 50% probability level. The H atoms are presented with spheres with arbitrary radii

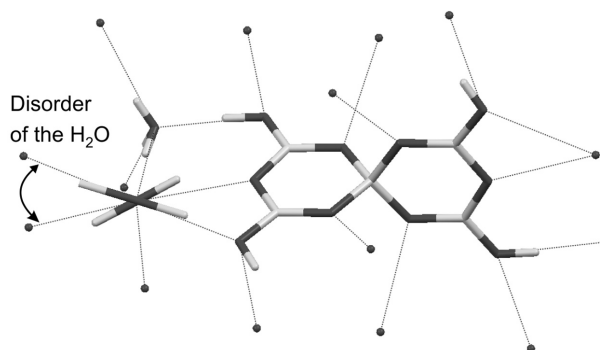


Fig. 2. The PBA, water, and oxonium ion hydrogen bonding interactions (see Table 3) are shown as dotted lines

WinGX [8], ORTEP [9], and Mercury [10] program packages. The location of the disordered H atoms of the solvent water (Ow1) has been performed using DHA program. [11]

The title compound crystallizes in the noncentrosymmetric space group *Aba2* (No 41) and thus

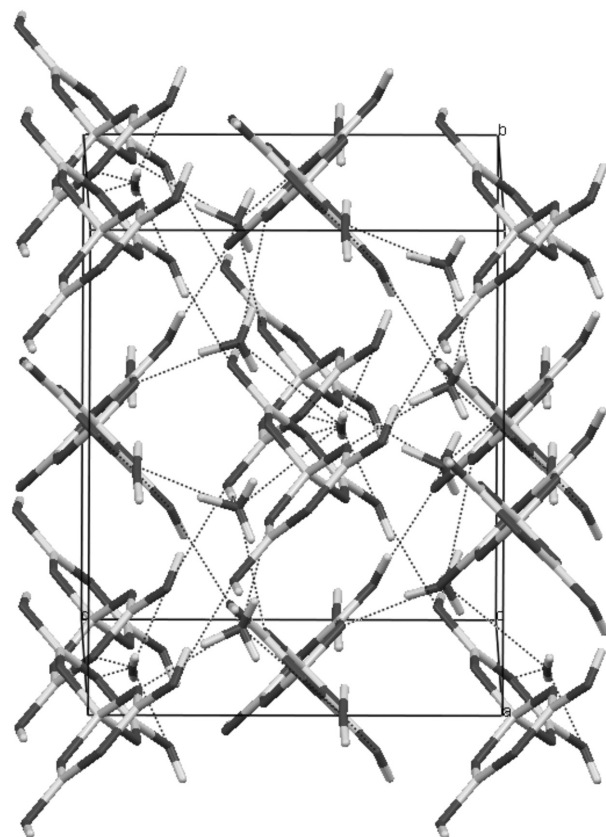


Fig. 3. Three-dimensional packing of the molecules in the crystal structure; hydrogen bonds are shown as dotted lines

possesses the prerequisites for potential (non-linear) optical application. Unfortunately we could not grow sufficiently large crystals for performing such investigations. The structural parameters (bond lengths and angles) of the title compound are comparable with those reported earlier [12, 13]. The boroxin ring systems (B1/O1/B2/O2B3/O3) is essentially planar with r.m.s. deviation of 0.0038(4) Å. The two hydroxy groups (O4 and O5) are also situated in the plane of the boroxin ring (OH groups are strong π -donor). In the three-dimensional arrangement of the molecules of **1** all possible donors and acceptors are involved in hydrogen bonding interactions (Fig. 2, 3 and Table 3). A closer inspection of the short distances and contacts present in crystal structure of **1** could not locate $\pi \dots \pi$ or other weak interactions. The ^{11}B NMR shifts are consistent with O_4B^- and O_3B arrangement [14] ^{11}B NMR (THF- D_8 , 160.4 MHz): $\delta = -4.8$ (O_4B^-), 16.9 (BO_3).

The observed formation of the title compound (pentaboric acid) in the presence of triethylbenzylammonium chloride can be explained with the assumption that the alkylammonium salt enhances the solubility of orthoboric acid and prevents crystallization of orthoboric acid. In addition, the bulky and less polar cation locally decreases the medium polarity and favors the equilibrium shift to pentaboric acid.

SUPPLEMENTARY MATERIALS

ICSD 425613 contains the supplementary crystallographic data for this paper. Further details of the crystal structure investigation(s) may be obtained from Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: (+49)7247-808-666; e-mail: crysdata(at)fiz-karlsruhe.de, http://www.fiz-karlsruhe.de/request_for_

deposited_data.html) on quoting the appropriate ICSD number.

Acknowledgments: The authors thank the financial support of the Bulgarian National Science Fund through contract DRNF 02/1.

REFERENCES

1. M. A. Beckett, P. N. Horton, M. B. Hursthouse, J. L. Timmis, K. Sukumar Varma, *Collect. Czech. Chem. Commun.*, **75**, 971 (2010).
2. Y. Yang, J. B. Sun, M. Cui, R. B. Liu, Y. Wang, C. G. Meng, *J. Sol State Chem.*, **184**, 1666 (2011).
3. V. Dyulgerov, R. P. Nikolova, L. T. Dimova and B. L. Shivachev, *Acta Cryst. E*, **68**, o2320 (2012).
4. M. D. Apostolova, R. P. Nikolova and B. L. Shivachev, *Acta Cryst. E*, **66**, o1273(2010).
5. B. Shivachev, R. Petrova, E. Naydenova, *Acta Cryst. E*, **62**, o3887 (2006).
6. Agilent. CrysAlisPro (version 1.171.35.15). Agilent Technologies Ltd, Yarnton England, 2010.
7. G. M. Sheldrick, *Acta Cryst. A*, **64**, 112 (2008).
8. L. J. Farrugia, *J. Appl. Cryst.*, **32**, 837 (1999).
9. L. J. Farrugia, *J. Appl. Cryst.*, **30**, 565 (1997).
10. I. J. Bruno, J.C. Cole, P. R. Edgington, M. Kessler, C. F. Macrae, P. McCabe, J. Pearson, R. Taylor, *Acta Cryst. B*, **58**, 389 (2002).
11. B. Shivachev, *Bull. Chem. Comm.*, **45**(4), 461 (2013).
12. R. A. Baber, J. P. H. Charmant, N. C. Norman, A. G. Orpen, J. Rossi, *Acta Cryst. E*, **60**, o1086 (2004).
13. Hong-Xia Zhang, Jie Zhang, Shou-Tian Zheng, Guo-Yu Yang, *Cryst. Growth Des.*, **5**, 157 (2005).
14. B. Wrackmeyer, NMR Spectroscopy of Boron Compounds Containing Two-, Three- and Four-Coordinate Boron, *Annu. Rep. NMR Spectrosc.*, **20**, 61 (1988).

СИНТЕЗ И КРИСТАЛНА СТРУКТУРА НА ОКСОНИЕВ 2,4,8,10-ТЕТРАГИДРОКСИ-1,3,5,7,9,11-ХЕКСАОКСА-2,4,6,8,10-ПЕНТА- БИСПИРО[5.5]УНДЕКАН-6-ОИД ХИДРАТ

Л. Димова, К. Косев, Х. И. Сбиркова, Р. П. Николова, Б. Л. Шивачев

*Институт по минералогия и кристалография „Акад. Иван Костов“,
Българска академия на науките, ул. „Акад. Георги Бончев“,
блок 107, София 1113, България*

Постъпила февруари, 2013 г.; приета май, 2013 г.

(Резюме)

Синтезираният оксониев 2,4,8,10-тетрагидрокси-1,3,5,7,9,11-хексаокса-2,4,6,8,10-пентабиспиро[5.5]ундекан-6-оид хидрат бе охарактеризиран посредством монокристална рентгенова дифракция и ¹¹N ЯМР анализи. Така наименуваното вещество, В₃Н₉О₁₂, кристализира в орторомбична кристална система и *Aba2* пространствена група, с параметри на елементарната клетка $a = 11.3286(5) \text{ \AA}$, $b = 11.0118(4) \text{ \AA}$, $c = 9.2314(4) \text{ \AA}$, $Z = 4$ and $V = 1151.60(8) \text{ \AA}^3$. Триммерната кристална структура е стабилизирана от мрежа от водородни връзки, като всички потенциални донори и акцептори участват в стабилизиращи взаимодействия.