4830 *Inorg. Chem.* **2010**, *49*, 4830–4835
DOI: 10.1021/ic902525s

Inorganic Chemistry
Article

Synthesis, Characterization, and Crystal Structure of a New Trisodium Triborate, $Na_3[B_3O_4(OH)_4]$

Jérôme Andrieux, Christelle Goutaudier,* Laetitia Laversenne, Erwann Jeanneau, and Philippe Miele

Laboratoire des Multimatériaux et Interfaces, Université Lyon 1, Villeurbanne, CNRS, UMR 5615, Université de Lyon, F-69622, Lyon, France

Received December 18, 2009

The preparation of a new trisodium triborate, $Na_3[B_3O_4(OH)_4]$, and its complete characterization in terms of molecular structure and thermal behavior are reported. Synthesis of this compound was achieved either by $NaBH_4$ hydrolysis or by thermal treatment of $Na[B(OH)_4]\cdot 2H_2O$. The crystal structure was determined by single-crystal X-ray diffraction. The trisodium triborate crystallized in the monoclinic system ($a = 12.8274(6)$ Å, $b = 7.7276(4)$ Å, $c = 6.9690(3)$ Å, and $\beta = 98.161(3)°$), space group Cc, $Z = 2$. The structure of $Na_3[B_3O_4(OH)_4]$ comprised $[B_3O_4(OH)_4]^{3-}$ polyanions, based on B−O-containing rings with two tetracoordinated boron atoms and one tricoordinated boron atom in the fragments $BO_2(OH)_2$ and BO_3, respectively. These polyanions are interconnected by four intermolecular hydrogen bonds and presented a tilt of 10.470(4)° compared to the *a* axis. Thus, they are stacked by rotation of about 180° around an axis defined by the three-coordinated boron atoms and parallel to the *c* axis. Such polyanions were only observed previously in two synthetic compounds, $M_3[B_3O_4(OH)_4]\cdot 2H_2O$ with M = K and Rb, which were isostructural. The originality of the present work was the synthesis and the description of a different crystallographic structure containing this polyanion. Characteristic peaks ranging from 500 to 1500 cm^{-1} and around 3300 cm^{-1} highlighted the presence of the B−O rings and hydroxyl groups, respectively. The decomposition temperature $T = 155$ °C was obtained by thermogravimetric analysis, and the following equivalent formula in terms of hydration degree was proposed: $NaBO_2\cdot {}^2/_3H_2O$. $Na_3[B_3O_4(OH)_4]$ decomposed into $Na_3[B_3O_5(OH)_2]$ in equilibrium with its vapor.

Introduction

Borate compounds have been widely studied due to their applications as antiseptics or components in glass composition. Among all these compounds, sodium metaborate, $Na_3[B_3O_6]$ (equivalent formula $NaBO_2$), and the related borates formed in the presence of water, $NaBO_2\cdot xH_2O$, are of new interest since they constitute the products of $NaBH_4$ hydrolysis (Scheme 1). This reaction is considered as a promising method for solid-state hydrogen storage. Some of these compounds such as $Na[B(OH)_4]\cdot 2H_2O$ (equivalent formula $NaBO_2\cdot 4H_2O$, sodium metaborate tetrahydrate) or $Na[B(OH)_4]$ (equivalent formula $NaBO_2\cdot 2H_2O$, sodium metaborate dihydrate) are well identified and their structures are defined.[1−3] On the other hand, the stability of low hydration degree metaborates remains an important subject of discussion,[1,4,5] one of the reasons being that characterizations are based only on experimental XRD patterns.[1] Thus, the complete description of these low hydration degree metaborates is of fundamental interest in particular in the above-mentioned hydrogen storage context. In fact, the gravimetric hydrogen storage capacity, ρ_m, expressed as the mass of hydrogen generated over the total mass of reactants ratio (eq 1), is directly linked to the pseudo hydration degree of sodium borate compound, *x*, as exemplified in Scheme 1.

$$\rho_m = \frac{m_{H_2}\cdot 100}{m_{NaBH_4} + m_{H_2O}} \tag{1}$$

In this article we report on the synthesis, the crystal structure determination, and the characterization of a new trisodium triborate, $Na_3[B_3O_4(OH)_4]$.

Experimental Section

$Na[B(OH)_4]\cdot 2H_2O$ (ACROS, white powder >98%) and $NaBH_4$ (ACROS, white powder, 97%) were used without further purification. However, the XRD experiment (not shown here) reveals that commercial $Na[B(OH)_4]\cdot 2H_2O$ is constituted of both $Na[B(OH)_4]\cdot 2H_2O$ and $Na[B(OH)_4]$. Water was freshly distilled and deoxygenized prior to use. Two syntheses routes to $Na_3[B_3O_4(OH)_4]$ have been studied: thermal treatment of $Na[B(OH)_4]\cdot 2H_2O$ and hydrolysis of $NaBH_4$. For the thermal treatment, a double-wall glass oven has been used. $Na_3[B_3O_4(OH)_4]$ was synthesized by

---

*Corresponding author. Tel: +33 472431052. Fax: +33 472440618. E-mail: christelle.goutaudier@univ-lyon1.fr.

(1) Bouaziz, R. *Ann. Chim.* **1961**, *6*, 345–393.
(2) Block, S.; Perloff, A. *Acta Crystallogr.* **1963**, *16*, 1233–1238.
(3) Csetenyi, L. J.; Glasser, F. P.; Howie, R. A. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1993**, *49*, 1039–1041.
(4) Toledano, P.; Benhassaïne, A. *C. R. Acad. Sci.* **1970**, *271*, 1577–1580.
(5) Sborgi, U. *Atti. Soc. Toscana Sci. Nat.* **1926**, *35*, 46–51.

Scheme 1. Solid $NaBH_4$ Hydrolysis Reaction

$$NaBH_4(s)+(2+x)H_2O(l)\xrightarrow{cat}NaBO_2\cdot xH_2O(s)+4H_2(g)$$

solid-state decomposition of $Na[B(OH)_4]\cdot 2H_2O$ placed in an alumina boat, under an inert atmosphere (argon) and atmospheric pressure. Powder was regularly homogenized by use of a mortar during heat treatments. After a 12 h plateau at $T = 84$ °C, the temperature of $T = 110$ °C ($\Delta T = \pm 1$ °C) was reached at 1 $°C\cdot min^{-1}$, and isothermal conditions were held for at least 12 h. In the case of the hydrolysis of $NaBH_4$, the $H_2O/NaBH_4$ molar ratio was 3, and the hydrolysis temperature was fixed at $T = 110$ °C. $NaBH_4$ was placed in a Teflon flask under inert atmosphere (glovebox). Then, the flask was connected to a reflux condenser and heated in a constant-temperature oil bath ($\Delta T = \pm 1$ °C). A controlled quantity of water was added, and the hydrolysis was run for one month.

For the phase identification, high-quality X-ray powder diffraction data were collected at room temperature with a Panalytical MPD pro diffractometer, with the parafocusing Bragg–Brentano geometry, using Cu $K_{\alpha 1-\alpha 2}$ radiation (average $\lambda = 1.54187$ Å). The diffraction patterns were collected over the angular range 10–110°(2θ) with a counting time of 500 $s\cdot step^{-1}$ and a step size of 0.008°(2θ). To avoid exposure to air, each sample was placed in a sample holder and covered with hermetic wrap film (Kapton). This results in scattering background intensities in the range 10–30°(2θ) along with a characteristic peak at ~21°(2θ) (see for example Figure 1c). Silicon powder is added as a reference in the sample holder corrections.

A fragment of a single crystal of $Na_3[B_3O_4(OH)_4]$ was mounted on a four-circle Nonius KappaCCD area detector diffractometer, using Mo Kα radiation ($\lambda = 0.71073$ Å) and equipped with a CCD area detector. Intensities were collected at room temperature by means of the COLLECT software.[6] Reflection indexing, Lorentz–polarization correction, peak integration, and background determination were carried out with DENZO.[7] Frame scaling and unit-cell parameter refinement were done with SCALEPACK.[7] The crystal structure was solved by direct methods with SIR97.[8] The crystal structure refinement was achieved with the CRYSTALS software.[9] All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atom positions were all found from successive Fourier difference map analysis. The hydrogen atoms were initially refined using restraints on the bond lengths and angles to regularize their geometry (O–H = 0.82 Å) and isotropic displacement parameters [U(H) in the range 1.2–1.5 times U_{eq} of the adjacent atom]. In the last cycles of the refinement, the hydrogen atoms were refined using a riding mode. More details on data collection and refinement results can be found in the CIF file (see Supporting Information). Drawings were carried out with the software DIAMOND v3.1.[10]

The chemical structure of $Na_3[B_3O_4(OH)_4]$ was investigated by vibrational spectroscopy. The Raman spectrum was obtained by a Jobin Yvon Raman spectrometer, ARAMIS LabRam, equipped with a microscope and a CCD detector. As a source of light, a He–Cd laser ($\lambda = 325$ nm) (IK series He–Cd laser KIMMON) was used. All measurements were done at room temperature, and the typical exposure time for each spectrum was 120 s. Silicon was used as a standard to calibrate wavelengths. The Fourier-transformed infrared (FT-IR) spectrum was recorded on a Nicolet 560 spectrometer equipped with a DTGS/CsI detector by transmission through a KBr pellet containing 1 wt % of $Na_3[B_3O_4(OH)_4]$. KBr powder, preheated at $T = 140$ °C was used to collect background. Prior to pellet preparation, the KBr powder and $Na_3[B_3O_4(OH)_4]$ were mixed together by mechanical grinding. A total of 64 scans were acquired at a 4 cm^{-1} resolution for each sample.

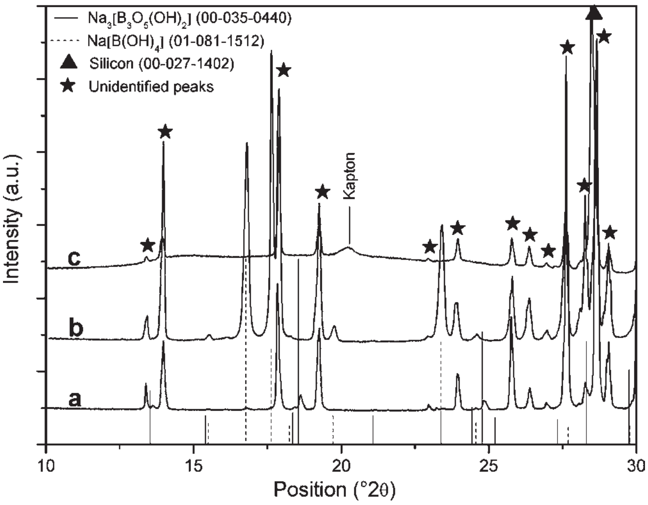


Figure 1. XRD patterns on powders obtained by (a) thermal treatment of $Na[B(OH)_4]\cdot 2H_2O$, (b) $NaBH_4$ hydrolysis ($H_2O/NaBH_4 = 3$), and (c) $NaBH_4$ hydrolysis ($H_2O/NaBH_4 = 3$) + heat treatment for 62 h at $T = 100$ °C. Focus on 10–30°(2θ). Comparison with ICDD reference patterns of $Na[B(OH)_4]$ (ICDD #01-081-1512), $Na_3[B_3O_5(OH)_2]$ (ICDD #00-035-0440), and silicon (ICDD #00-027-1402).

Thermogravimetric analysis of $Na_3[B_3O_4(OH)_4]$ was recorded on a NETZSCH STA 409PC Luxx (Simultaneous Thermal Analysis) apparatus, mounted with TG-DSC sample carriers. Sample was contained in an aluminum crucible (120 μL) capped with a pinhole cover (hole diameter = 600 μm). Measurements were performed using a flow of 40 $mL\cdot min^{-1}$ dry air atmosphere (N_2 30 $mL\cdot min^{-1}$; O_2 10 $mL\cdot min^{-1}$). The sample was preliminary maintained at $T = 100$ °C during 2 h. Then the temperature was increased from $T = 100$ °C to $T = 300$ °C (0.4 $°C\cdot min^{-1}$). TG resolution is given equal to 2 μg, as DSC resolution is lower than 1 μW. Mass losses with a DTG signal lower than 0.01%$\cdot min^{-1}$ are not significant.

Results and Discussion

Syntheses of $Na_3[B_3O_4(OH)_4]$. Figure 1a presents details of a XRD pattern in the range 10–30°(2θ) carried out on the powder obtained by the thermal treatment of $Na[B(OH)_4]\cdot 2H_2O$ compared to ICDD reference patterns. Phase identification confirms the coexistence of $Na_3[B_3O_5(OH)_2]$[11] with an unidentified main phase. Figure 1b shows an XRD pattern (focused at 10–30°(2θ)) performed on powder obtained from the hydrolysis of $NaBH_4$. Phase identification reveals the presence of $Na[B(OH)_4]$[3] in coexistence with a phase that cannot be identified but presents great similarities to the major phase characterized in the thermally treated sample. As a conclusion, the two synthesis pathways lead to the formation of the same phase that does not correspond

---

(6) Nonius, B. V. *COLLECT*; Nonius: Delft, The Netherlands, **1997–2001**.

(7) Otwinowski, Z.; Minor, W. *Methods Enzymol.* **1997**, *267*, 307–326.

(8) Altomare, A.; Burla, M. C.; Camalli, M.; Cascarano, G. L.; Giacovazzo, C.; Guagliardi, A.; Moliterni, A. G. G.; Polidori, G.; Spagna, R. *J. Appl. Crystallogr.* **1999**, *32*, 115–119.

(9) Betteridge, P. W.; Carruthers, J. R.; Cooper, R. I. *J. Appl. Crystallogr.* **2003**, *36*, 1487.

(10) Brandenburg, K. *DIAMOND*, Release 3.1e; Crystal Impact GbR: Bonn, Germany, 1999.

(11) Corazza, E.; Menchetti, S.; Sabell, C. *Acta Crystallogr., Sect. B: Struct. Sci.* **1975**, *31*, 1993–1997.

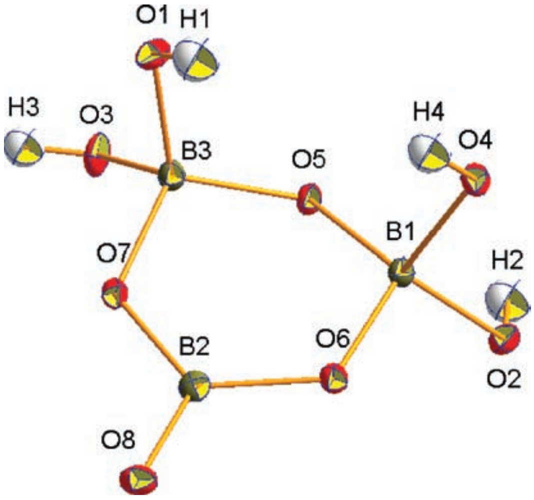


Figure 2. ORTEP diagram of the $[B_3O_4(OH)_4]^{3-}$ anion showing the atom-numbering scheme and the displacement ellipsoids plotted at the 50% probability level.

to any ICDD reference powder pattern and could not be identified. This compound can be considered as being in equilibrium with two other borate compounds depending on the mode of synthesis, suggesting that its hydration degree x is $1/3 < x < 2$. Thus, according to the work of Chiriac et al.,[12] the mixture obtained by $NaBH_4$ hydrolysis (Figure 1b) was heat-treated for 62 h at $T = 100$ °C under an inert atmosphere, and the powder pattern of the resulting product was recorded (Figure 1c). All of the diffraction peaks were unidentified, and no $Na[B(OH)_4]$ was detected, suggesting first that the unidentified compound is stable from room temperature to $T = 100$ °C and second that it is possible to obtain this compound in pure polycrystalline form.

Crystal Structure of $Na_3[B_3O_4(OH)_4]$. Single-crystal X-ray diffraction analysis has been performed using a single crystal extracted from the solid mixture resulting from the hydrolysis of $NaBH_4$ (see Figure S1). According to the single-crystal experiment, the following crystallographic structure has been determined for $Na_3[B_3O_4(OH)_4]$ (Figure 2). This compound crystallizes in the noncentrosymmetric space group *Cc*, monoclinic system. The unit cell parameters are gathered in Table 1, and the values for atom positions are listed in the Supporting Information (Table S2). The unit cell contains $Z = 2$ for a calculated density of $2.267\ g\cdot cm^{-3}$. Finally, the proposed formula for this compound is $Na_3[B_3O_4(OH)_4]$.

$Na_3[B_3O_4(OH)_4]$ is identified as a new trisodium triborate formed by hydrolysis of $NaBH_4$ with water ($n_{H2O}/n_{NaBH4} = 3$) or by decomposition of $Na[B(OH)_4]\cdot 2H_2O$. The structure consists of the isolated $[B_3O_4(OH)_4]^{3-}$ polyanion (Figure 2) with associated sodium cations. This polyanion forms a ring composed by an elementary block of two tetracoordinated boron atoms, containing two hydroxyl groups, $BO_2(OH)_2$, associated with a tricoordinated boron atom, BO_3. The International Union of Pure and Applied Chemistry (IUPAC) system of nomenclature for inorganic compounds advises the name "tetrahydroxydotetraoxidotriborate(3-),trisodium" for $Na_3[B_3O_4(OH)_4]$, whereas Chemical Abstracts Services (CAS, division of the American Chemical Society) recommends "borate(3-),tetrahydroxy[μ-[orthoborato(3-)-O:O′]]-μ-oxodi-,trisodium". However regarding works concerning borate compounds and in order to ensure easier comparison, we have chosen in this paper the usual name of trisodium triborate for $Na_3[B_3O_4(OH)_4]$. The distinction between the two trisodium triborates of the system $NaBO_2-H_2O$, $Na_3[B_3O_4(OH)_4]$ and $Na_3[B_3O_5(OH)_2]$, is done using their structural formulas.

Table 1. Crystallographic Data for Structure Determination of $Na_3[B_3O_4(OH)_4]$

$H_8B_6Na_6O_{16}$	$M_r = 466.86\ g\cdot mol^{-1}$
$a = 12.8274(6)$ Å	C c (9)
$b = 7.7276(4)$ Å	$T = 293$ K
$c = 6.9690(3)$ Å	$\lambda = 0.71073$ Å
$\beta = 98.161(3)°$	$D_{calc} = 2.267\ g\cdot cm^{-3}$
$V = 683.81(6)$ Å^3	$\mu = 0.37\ mm^{-1}$
$Z = 2$	$R[F^2 > 2\sigma(F^2)] = 0.020$[13]
	$R_w(F^2) = 0.024$[14]

Table 2. Selected Geometric Parameters (Å) for the $[B_3O_4(OH)_4]^{3-}$ Polyanion and Their Estimated Standard Deviations[a]

B1−O2	1.484(2)
B1−O4	1.497(2)
B1−O5	1.445(2)
B1−O6	1.492(2)
B2−O6^{ii}	1.399(2)
B2−O7	1.395(2)
B2−O8	1.340(2)
B3−O1	1.486(2)
B3−O3	1.477(2)
B3−O5^{ii}	1.445(2)
B3−O7	1.494(2)

[a] Symmetry code: (ii) $x, 1-y, -1/2+z$.

The bond lengths within $Na_3[B_3O_4(OH)_4]$ are given in Table 2. The average B−O distance is 1.480 Å for the tetrahedrally coordinated boron atoms and 1.378 Å for the trigonal boron atom, which is in good agreement with the expected ones.[15] The ring shows a deviation of the bond angles compared to classical B_3O_6 rings.[16] Indeed the average O−B−O bond angle in the polyanion is 114.07° and the average B−O−B angle is 122.76°, leading to a somewhat distorted B−O hexagon for the overall anion structure. Moreover, one of the other major changes of the structure compared to a classical B_3O_6 ring[16] is the degree of planarity. Whereas boron and oxygen atoms are in the same plane in $Na_3[B_3O_6]$[16] and in $Na_3[B_3O_5(OH)_2]$,[11] the $[B_3O_4(OH)_4]^{3-}$ polyanion cycle is slightly distorted. The atoms B1, B2, B3, O6, O7, and O8 form a plane (largest deviation from the weighted least-squares plane of 0.048 Å for B3), whereas O5, contained in the B−O ring, is located 0.35 Å from this mean plane. This deformation of a boron−oxygen ring has already been observed with a deviation of 0.315 Å for the tetrahedral boron in Ameghinite ($Na[B_3O_3(OH)_4]$).[17] Finally, according to these different structures, we can

---

[12] Chiriac, R.; Sigala, C.; Andrieux, J.; Laversenne, L.; Goutaudier, C.; Miele, P. *Spectra Anal.* **2008**, *264*, 41–43.

[13] R factor definition: $R = \frac{\sum ||F_{obs}| - |F_{calc}||}{\sum |F_{obs}|}$

[14] R_w factor definition: $R_w = \sqrt{\frac{\sum w((F_{obs})^{\overset{2}{2}} - (F_{calc})^2)}{\sum w(F_{obs})^2}}$

[15] Hawthorne, F. C.; Burns, P. C.; Grice, J. D. *Rev. Mineral.* **1996**, *33*, 41–115.

[16] Marezio, M.; Plettinger, H. A.; Zachariasen, W. H. *Acta Crystallogr.* **1963**, *16*, 594–595.

[17] Salentine, C. *Inorg. Chem.* **1987**, *26*, 128–132.

conclude that this deviation is a function of the 4-fold coordinated boron atom number present in the polyanion, since the B–O–B atoms will not be in the same plane as the others atoms of the ring due to the tetrahedral configuration of the boron atom.

Taking into consideration the atom coordination in the structure of $Na_3[B_3O_4(OH)_4]$, the simplest case is a trigonal boron atom linked to three oxygen atoms of the ring with an average $B_{(3)}$–O length of 1.378 Å. The two 4-fold coordinated boron atoms are linked by covalent bonding to four oxygen atoms, two from endo-ring oxygen atoms and two exo-ring hydroxyl groups (average $B_{(4)}$–O length 1.488 Å). According to Table 3, it is worth noting that the B1–O5 and B3–O5 bond lengths, belonging to the B–O ring, are slightly shorter than the other ones: 1.445 Å instead of 1.488 Å.

The coordination type of the oxygen atoms differs depending on whether the oxygen atom belongs to the boron–oxygen ring or to the hydroxyl groups. The first (O5, O6, and O7) are linked to two boron atoms and two sodium atoms placed at the vertex of a tetrahedron, that leads to an atom coordination number of 4. Oxygen atoms from exo-ring hydroxyl groups have a coordination number of 5 with a pyramidal geometry. A deformed quadrate composed of one boron atom and three sodium atoms is the base of the pyramid with hydrogen atoms at the opposite vertex.

The three sodium cations are crystallographically independent; each of them is placed at general positions (Figure 3). Two of them display a unique coordination configuration. Na1 is six-coordinated and is surrounded by six oxygen atoms from four anions (three oxygen atoms of the ring and three hydroxyl groups out of the ring). The Na1–O distances range from 2.314(2) to 2.943(2) Å, fixing the maximum value for the Na–O distance at 3.1 Å. With the same coordination, Na2 interacts with three oxygen atoms of the ring and three of the exo-ring hydroxyl groups. Finally, Na_3 is seven-coordinated, with five hydroxyl groups and two endo-ring oxygen atoms in its first coordination sphere.

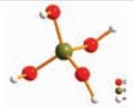
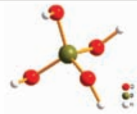
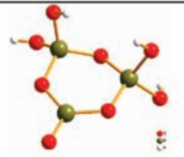
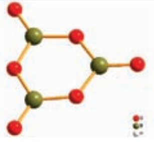
The three-dimensional framework is further interconnected by four intermolecular hydrogen bonds (Figure 4).

Lastly, the packing of atoms in the crystallographic structure of $Na_3[B_3O_4(OH)_4]$ is shown along the *b* axis (Figure 5a) and along the *c* axis (Figure 5b) for four unit cells. Boron polyhedra (green) are represented by means of the B–O bonds.

According to the possible boron coordination, two polyhedral geometries are observed. The first, a flat polyhedron (see Figure 5b), is due to three-coordinated boron atoms, while the second, a pyramidal polyhedron (see Figure 5a and b), is related to tetracoordinated boron atoms. In agreement with the projection of the crystallographic structure along the *b* axis (Figure 5a), a packing of $[B_3O_4(OH)_4]^-$ polyanions is observed along the *c* axis. All the polyanions are tilted by 10.470(4)° compared to the *a* axis. Moreover, according to the crystallographic structure view along the *c* axis (Figure 5b), we conclude that the polyanions are stacked by rotation of about 180° around an axis defined by the three-coordinated boron atoms and parallel to the *c* axis.

Other boron–oxygen-based structures have already been mentioned for other sodium borate species. $Na[B(OH)_4]$[3] is based only on tetracoordinated boron atoms linked to four hydroxyl groups, $Na_3[B_3O_5(OH)_2]$[11] is composed of two tricoordinated boron and one tetracoordinated boron linked to a hydroxyl group, leading to a boron–oxygen-based polyanion $[B_3O_5(OH)_2]^{3-}$, and $Na_3[B_3O_6]$[16] is composed of three tricoordinated boron.

Table 3. Borate Clusters for Sodium Borate Compounds with Their Corresponding B–B Graph and Algebraic Descriptor, after Burns et al.,[18] Hawthorne et al.,[15] and Touboul et al.[19]

Descriptor	Formula	B-B connectivity diagram	[Ref.]
1:[(1:□)]	$Na[B(OH)_4]\cdot 2H_2O$		2
1:[(1:□)]	$Na[B(OH)_4]$		3
3:[(3:Δ+2□)]	$Na_3[B_3O_4(OH)_4]$		This work
3:[(3:2Δ+□)]	$Na_3[B_3O_5(OH)_2]$		11
3:[(3:3Δ)]	$Na_3[B_3O_6]$		16

A hierarchical classification of complex borate minerals has been proposed[15,18] according to the polymerization of cation coordination polyhedra with higher bond valences, meaning the fundamental building block (FBB) of the structure. This FBB is based on the boron atoms contained in the polyanion ring. A three-coordinated boron atom is represented by the symbol Δ, while the symbol □ indicates a tetracoordinated boron atom. On the basis of the work of Touboul et al.,[19] a simplified notation (eq 2) allows the description of the number of crystallographically independent boron atoms and their surrounding configuration.

$$n{:}[(m{:}b\Delta + c\square)] \qquad (2)$$

where *n* means the total number of FBB boron atoms, *b* the number of three-coordinated boron atoms, and *c* the number of tetracoordinated boron atoms contained in the FBB. Thus, $m = b + c$.

As a consequence, a classification of each sodium borate compound in terms of FBB is presented in Table 3. The new trisodium triborate is based on $[B_3O_4(OH)_4]^{3-}$ as

---

[18] Burns, P. C.; Grice, J. D.; Hawthorne, F. C. *Can. Mineral.* **1995**, *33*, 1131–1151.

[19] Touboul, M.; Penin, N.; Nowogrocki, G. *Solid State Sci.* **2003**, *5*, 1327–1342.

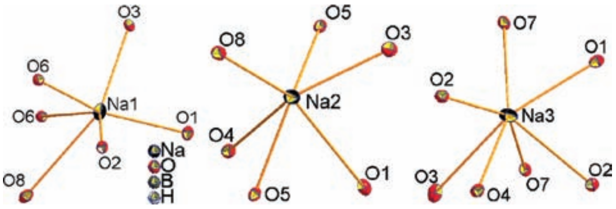


Figure 3. ORTEP diagrams of the coordination spheres of the three independent sodium cations in $Na_3[B_3O_4(OH)_4]$.

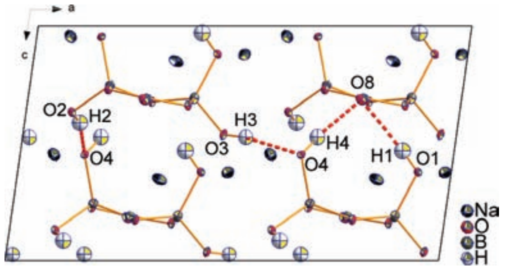


Figure 4. Arrangement of boron−oxygen polyanions in the unit cell along the *b* axis. The four crystallographically independent hydrogen bonds are indicated by red dotted lines. Hydrogen bond parameters: O1−H1 = 0.81 Å, O2−H2 = 0,78 Å, O3−H3 = 0.74 Å, O4−H4 = 0.80 Å, H1···O8^{iii} = 2.00 Å, H2···O4^{i} = 1.99 Å, H3···O4^{ii} = 1.96 Å, H4···O8 = 1.84 Å, O1···O8^{iii} = 2.808 Å, O2···O4^{i} = 2.760 Å, O3···O4^{ii} = 2.694 Å, O4···O8 = 2.629 Å, O1−H1···O8^{iii} = 177°, O2−H2···O4^{i} = 166°, O3−H3···O4^{ii} = 170°, O4−H4···O8 = 172°. Symmetry codes: (i) *x*, 2−*y*, 1/2+*z*; (ii) 1/2+*x*, −1/2+*y*, *z*; (iii) *x*, 1−*y*, −1/2+*z*.

FBB and, as a consequence, belongs to the descriptor $3:[(3:\Delta+2\square)]$. A natural mineral, Solongoite ($Ca_2[B_3O_4(OH)_4]Cl$), presents this polyanion as fundamental building block.[20] The only works that mention the synthesis of such a polyanion concerns solid potassium and rubidium triborate, $K_3[B_3O_4(OH)_4]\cdot 2H_2O$[21−23] and $Rb_3[B_3O_4(OH)_4]\cdot 2H_2O$,[24] which are isostructural.

Regarding B−B connectivity diagrams presented in Table 3, the different boron−oxygen rings correspond to different borate compounds. The lower the hydration degree of borate, the lower the quantity of hydroxyl groups in the ring. The ratio of tri/tetracoordinated boron is also a function of the hydration degree of the compounds, which increases with the lowering of the hydration degree. The formation of these different boron−oxygen rings leads to an increase of the unit cell volume with the hydration ratio.

To conclude, for sodium borate species, the only complex B−O ring-based compound characterized in the solid-state form for a 1:1 Na/B ratio was $Na_3[B_3O_5(OH)_2]$ until the recent synthesis of $Na_3[B_3O_4(OH)_4]$.

Characterization of $Na_3[B_3O_4(OH)_4]$. Thermal analyses were performed on a mixture described previously (see Figure 1b, mixture of $Na[B(OH)_4]$ and $Na_3[B_3O_4(OH)_4]$). In order to study the new compound, a heat treatment at 20 °C·min^{-1} until T = 100 °C is first imposed as a consequence of the results mentioned above. Then an isothermal period of two hours at T = 100 °C is used in order to avoid kinetic effects and to ensure that all the $Na[B(OH)_4]$ is decomposed, reaching the thermodynamic equilibrium of the decomposition products. Heat treatment from T = 100 °C to T = 300 °C is then applied at a heating rate of 0.4 °C·min^{-1}.

TGA/DSC results are presented in Figure 6. The bold solid curve is the TGA experiment (the dotted curve is the calculated DTG, based on the TGA experiment), and the dashed curve is the DSC experiment. Two weight losses are clearly identified in Figure 6. The first decomposition, occurring at T = 155 °C, leads to a total weight loss of 13.4% of the sample. This weight loss corresponds to the decomposition of $Na_3[B_3O_4(OH)_4]$. Hydration degree calculation for this weight loss leads to an equivalent formula, $NaBO_2\cdot 2/3H_2O$, that agrees with theoretical hydration degree deduced from the crystallographic structure described previously. In terms of hydration degree, the authors propose the name "sodium metaborate two-thirds hydrate". The second decomposition step involves a total weight loss of 6.7%, starting at T = 247 °C. Hydration degree calculation leads to the identification of $Na_3[B_3O_5(OH)_2]$ by thermal analysis (equivalent formula $NaBO_2\cdot 1/3H_2O$). The obtained temperature of decomposition for this compound is in good agreement with a previous work.[12]

As $Na_3[B_3O_4(OH)_4]$ is characterized by XRD at room temperature (see Figure 1), thermal analyses permit us to conclude that $Na_3[B_3O_4(OH)_4]$ is stable from room temperature until 155 °C. At this temperature, thermal analysis allows the identification of a dehydration reaction, which can also be described as a peritectic reaction according to Scheme 2.

Lastly regarding the structure of $Na_3[B_3O_4(OH)_4]$ and $Na_3[B_3O_5(OH)_2]$, we concluded that this decomposition is related to the loss of one molecule of water per unit cell by breaking one B−OH bond and one O−H bond. This leads to the transformation of one tetracoordinated boron in $Na_3[B_3O_4(OH)_4]$ into a tricoordinated boron in $Na_3[B_3O_5(OH)_2]$.

As the first synthetic synthesis of $Na_3[B_3O_4(OH)_4]$, the infrared and Raman spectra are of interest and are reported in Figure 7. These spectra show sharp peaks, especially in the region 400−2000 cm^{-1}, which are characteristic of a low-symmetry crystalline structure allowing different vibrational modes.

Two regions are observed in Figure 7. The first exhibits a strong absorption band in the range 2250 to 3400 cm^{-1} due to the stretching vibration of the hydroxyl group. A maximum is located around 3300 cm^{-1}, in accordance with results published by Tobin et al.[25] The second region, from 400 to 1500 cm^{-1}, is related to boron−oxygen bonds. The main peak in the Raman spectrum (~630 cm^{-1}, Figure 7) is due to the symmetric pulse of the triborate anion. A strong doublet, attributed to the asymmetric stretching mode of $B_{(3)}$−O, is observed at 1300−1400 cm^{-1} (respectively 1320 and 1370 cm^{-1}), whereas the weak band at ~900 cm^{-1} could be assigned to the symmetric stretching mode of $B_{(3)}$−O.[26,27]

---

(20) Yamnova, N. A.; Simonov, M. A.; Belov, N. V. *Kristallografiya* **1997**, *22*, 624–626.

(21) Ozols, J. *Latv. PSR Zinat., Akad. Vestis, Kim. Ser.* **1977**, *3*, 356–357.

(22) Zviedre, I.; Belsky, V. L. *Latv. Kim. Z.* **1993**, *2*, 131–141.

(23) Zhu, L. X.; Gao, S. Y.; Wang, B.; Xia, S. P. *Chin. J. Inorg. Chem.* **2003**, *19*, 333–336.

(24) Zviedre, I. I.; Ievin'sh, A. F. *Latv. PSR Zinat., Akad. Vestis, Kim. Ser.* **1974**, 395.

(25) Tobin, M. C. *Laser Raman Spectroscopy*; Wiley Interscience: New York, 1971.

(26) Jun, L.; Shuping, X.; Shiyang, G. *Spectrochim. Acta, Part A* **1995**, *51*, 519–532.

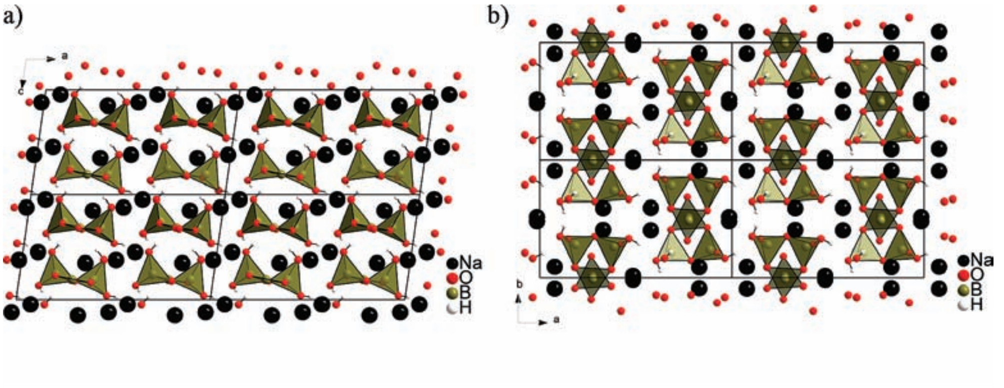


Figure 5. Packing of boron polyhedra (green) (a) along the *b* axis and (b) along the *c* axis, for four unit cells. Boron polyhedra are represented by means of the B−O bonds.

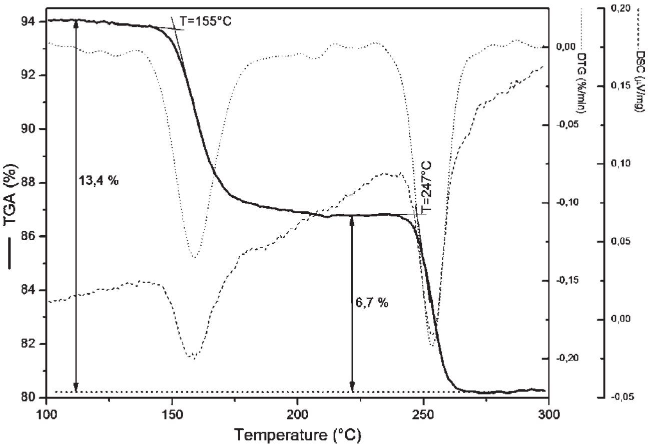


Figure 6. TGA-DSC experiment on powder synthesized by $NaBH_4$ hydrolysis ($H_2O/NaBH_4 = 3$), thermal treated 2 h at 100 °C.

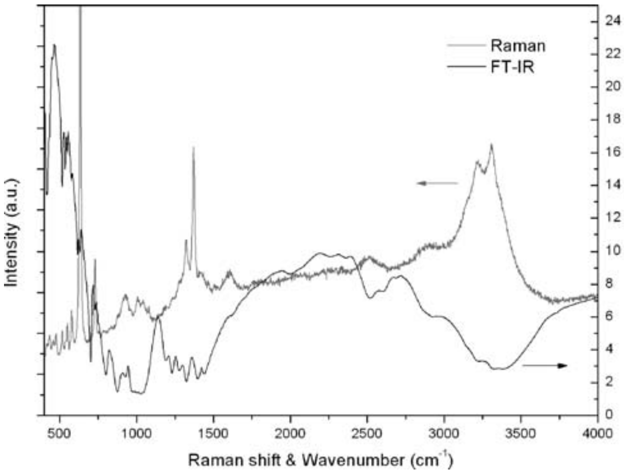


Figure 7. FT-IR/Raman spectra of $Na_3[B_3O_4(OH)_4]$.

Scheme 2. Peritectic Reaction Occurring at $T = 155$ °C

$$Na_3[B_3O_5(OH)_2] + Vap. \xrightarrow{T=155°C} Na_3[B_3O_4(OH)_4]$$

Thus, out-of-plane bending of $B_{(3)}$−O is related to the sharp peak at 730 cm^{-1}. The infrared spectrum shows more defined peaks as well as peaks described in the Raman spectrum. Characteristic peaks for symmetric and asymmetric stretching modes of $B_{(4)}$−O might be located around 740−890 and 940−1060 cm^{-1} (literature data stated 1000−1150 cm^{-1}[26]), respectively. Moreover, bending of $B_{(3)}$−O and $B_{(4)}$−O appears in the range 400−590 cm^{-1}. These results are in good agreement with those reported for $K_3[B_3O_4(OH)_4]\cdot 2H_2O$ spectroscopic characterizations.[22] The low infrared and Raman regions have not been plotted here because they mainly convey lattice vibration or M−O stretching vibration modes. The evidence of both tetracoordinated and tricoordinated boron atoms is in accordance with previous results obtained for other borate polyanions[26,27] and with the structure previously described.

Conclusion

A new trisodium triborate, $Na_3[B_3O_4(OH)_4]$, has been synthesized at ambient pressure in the binary system $NaBO_2$−H_2O either by $NaBH_4$ hydrolysis or by thermal treatment of $Na[B(OH)_4]\cdot 2H_2O$. It has been characterized in terms of crystallographic structure by single-crystal X-ray diffraction. We have demonstrated the formation of the rare polyanion $[B_3O_4(OH)_4]^{3-}$. Concerning thermal behavior, $Na_3[B_3O_4(OH)_4]$ presents a hydration degree of $NaBO_2\cdot 2/3H_2O$ (equivalent formula). It is stable from room temperature up to $T = 155$ °C, where it decomposes into $Na_3[B_3O_5(OH)_2]$. According to its low hydration degree ($x = 2/3$), this new trisodium triborate could play a significant role in hydrogen storage through $NaBH_4$ hydrolysis. In fact, the lower the hydration degree of borate formed, the higher the gravimetric hydrogen storage capacity.

Acknowledgment. The authors acknowledge the Rhone-Alpes region (CLUSTER 7 ENERGIES) and the French National Research Agency ANR (ANR Project CASTAFHYOR) for a fellowship and financial support. The authors also thank the group of Prof. B. Champagnon (CECOMO, Lyon 1) for the advice and the availability of the ARAMIS Raman spectrometer, and Julien Pansiot (Ph.D. student, Lyon 1) for the formation on the NETZSCH STA 409PC apparatus.

Supporting Information Available: (1) Picture of a crystal of $Na_3[B_3O_4(OH)_4]$ (Figure S1), (2) compounds cited in the paper (Table S1), and (3) positional parameters of atoms contained in the unit cell (Table S2). In addition, crystallographic data of the trisodium triborate $Na_3[B_3O_4(OH)_4]$ are available in the crystallographic information file (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

---

(27) Chryssikos, G. D.; Kapoutsis, J. A.; Patsis, A. P.; Kamitsos, E. I. *Spectrochim. Acta, Part A* **1991**, *47*, 1117–1126.