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Journal of Solid State Chemistry 177 (2004) 4648–4654

JOURNAL OF SOLID STATE CHEMISTRY

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Syntheses and crystal structures of two new organically templated borates

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Received 14 July 2004; received in revised form 24 August 2004; accepted 30 August 2004

Abstract

Two new organically templated borates, $[H_3N(C_6H_{10})NH_3][B_4O_5(OH)_4]$ **(1)** and $[H_3N(C_6H_{10})NH_3][B_5O_8(OH)]$ **(2)** have been synthesized in the presence of *trans*-1,4-diaminocyclohexane acting as a structure-directing agent under mild solvothermal conditions. The structures were determined by single crystal X-ray diffraction and further characterized by FTIR, elemental analysis and thermogravimetric analysis. Compound **1** crystallizes in the monoclinic system, space group $C2/c$ (No. 15), $a = 9.1325(3)$ Å, $b = 11.4869(3)$ Å, $c = 12.2756(5)$ Å, $\beta = 105.258(6)^\circ$, $V = 1242.37(7)$ Å^3, $Z = 4$. The structure contains supramolecular hydrogen-bonded network formed by isolated $[B_4O_5(OH)_4]^{2-}$ polyanions. **2** is monoclinic, space group $P2(1)/n$ (No. 14), $a = 6.5176(2)$ Å, $b = 16.8861(5)$ Å, $c = 11.1522(7)$ Å, $\beta = 91.897(6)^\circ$, $V = 1226.70(9)$ Å^3, $Z = 4$. The structure consists of layers of 3,9-membered boron rings constructed from pentaborate anion groups $[B_5O_8(OH)]^{2-}$. The adjacent borate layers are further linked with each other by hydrogen bond to form a 3D supramolecular network. It is the first example of layered borates templated by an organic amine.

Keywords: Borates; Crystal structure; Templated synthesis; Hydrothermal synthesis

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1. Introduction

In the past decades, much interest has been focused on the studies of borate compounds not only due to their rich structural chemistry but also because of their potential applications in mineralogy and industry [1–7]. From the perspective of structure, boron atoms coordinate with oxygen not only in four-fold coordination (tetrahedral, BO_4) but also in three-fold coordination (triangular, BO_3). These BO_3 and BO_4 groups may further link together via common oxygen atoms to form isolated rings and cages or polymerize into infinite chains, sheets and networks. So far, different borate systems concerning alkali metal, alkaline earth metal, rare earth and transition metal have been widely studied [7].

Surprisingly, very few information is available regarding the borate system containing organic amines. To date, only a few examples with polyanions such as $[B_4O_5(OH)_4]^{2-}$ [8], $[B_5O_6(OH)_4]^{1-}$ [9] and $[B_9O_{12}(OH)_6]^{3-}$ [10] have been reported. Based on the linkage of BO_3 triangles and BO_4 tetrahedral to form fundamental building blocks (FBBs) [3,6] that polymerize to form the structure unit, above-mentioned polyanions can be described as “2△2□:〈△2□〉=〈△2□〉”, “4△1□:〈2△□〉–〈2△□〉” and “6△3□:〈2△□〉–〈△2□〉–〈△2□〉–〈2△□〉”, where △ is the BO_3 triangle and □ is the BO_4 tetrahedron. The delimiters 〈 〉 denote that included polyhedra share corners to form a ring. When rings are linked together, the number of polyhedra common for both rings is indicated by –, = etc. Understanding how various amine cations direct borate

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doi:10.1016/j.jssc.2004.08.039

structural units in borate compounds is fundamental to the rational design of novel borates having useful properties. During our investigations of such borate materials, we apply self-assembly process of organic and inorganic moieties under solvothermal conditions. Herein, we first describe the syntheses and crystal structures of two new organically templated borate compounds, $[H_3N(C_6H_{10})NH_3]$ $[B_4O_5(OH)_4]$ **(1)** and $[H_3N(C_6H_{10})NH_3]$ $[B_5O_8(OH)]$ **(2). 1** is a tetraborate, and **2** provides the first instance of layered borates templated by organic amines.

2. Experimental section

2.1. Synthesis

Single crystals of title compounds were prepared from a mixture of H_3BO_3, $[H_2N(C_6H_{10})NH_2]$, pyridine and H_2O in the molar ratio of 1:2:40:30 and 1:4:60:88, respectively. The resulting mixture was sealed in Teflon-lined autoclaves and heated at 170 °C for 7 days under autogenous pressure and then cooled to room temperature. The prismatic colorless single crystals were easily separated by sonication from a mixture phase containing white powder and further washed by distilled water and then air-dried. The white powder is an unknown phase and not further characterized (26.7% yield based on boron for **1** and 18.6% for **2**).

Elemental analyses (wt%) found (calcd.) for $[H_3N(C_6H_{10})NH_3]$ $[B_4O_5(OH)_4]$ **(1)** and $[H_3N(C_6H_{10})NH_3]$ $[B_5O_8(OH)]$ **(2)**: C 23.36 (23.43), H 6.60 (6.56), N 9.14 (9.11) and C 22.81 (22.86), H 5.48 (5.44), N 8.83 (8.89), respectively. All the experimental results are consistent with the calculated values.

2.2. Characterization

Infrared spectra were obtained from sample powder pelletized with KBr on an ABB Bomen MB 102 series FTIR spectrophotometer over a range 400–4000 cm^{-1}. The thermogravimetric analysis (TGA) was performed on a Mettler Toledo TGA/SDTA 851e analyzer in N_2 atmosphere with a heating rate of 10 °C/min. The elemental analysis was carried out on an Elemental Vario EL *III* CHNOS elemental analyzer.

2.3. Determination of crystal structure

Crystals of **1** (prism, dimensions $1.20 \times 0.50 \times 0.20\,mm^3$) and **2** (prism, dimensions $0.46 \times 0.14 \times 0.10\,mm^3$) were carefully selected under an optical microscope and glued to thin glass fiber with epoxy resin. Crystal structure determination by X-ray diffraction was performed on a Siemens SMART CCD diffractometer with graphite-monochromated Mo $K\alpha$ ($\lambda = 0.71073\,Å$) in the ω and φ scanning mode at room temperature. An empirical absorption correction was applied using the SADABS program [11]. The structures were both solved by direct methods. The boron, oxygen, carbon and nitrogen atoms were found in the final difference Fourier map. All hydrogen atoms in **1** and **2** were geometrically placed. The structures were refined on F^2 by a full-matrix least-squares methods using the SHELXL-97 program package [12]. All non-hydrogen atoms were refined anisotropically. Crystallographic data for **1** and **2** are presented in Table 1. The final atomic coordinates and the thermal motion parameters are listed in Tables 2 and 3; selected bond distances and angles are listed in Tables 4 and 5, respectively. CCDC 248279 and 241402 contain the supplementary crystallographic data for this paper.

Table 1
Crystal data and structure refinement for **1** and **2**

Compounds	**1**	**2**
Empirical formula	$C_6H_{20}N_2B_4O_9$	$C_6H_{17}N_2B_5O_9$
Formula weight	307.48	315.27
Crystal system	Monoclinic	Monoclinic
Space group	$C2/c$	$P2(1)/n$
a/Å	9.1325(3)	6.5176(2)
b/Å	11.4869(3)	16.8861(5)
c/Å	12.2756(5)	11.1522(7)
β/°	105.258(6)	91.897(6)
V/Å^3	1242.37(7)	1226.70(9)
Z	4	4
D_c/g cm^{-3}	1.644	1.707
μ(Mo-$K\alpha$)/mm^{-1}	0.142	0.145
Reflection collected	4893	7441
Independent reflections	1527	2161
Parameters refined	96	199
Final R_1, w$R_2[I>2\sigma(I)]$	0.0399, 0.1148	0.0381, 0.0893

3. Results and discussion

3.1. Infrared (IR) spectra

The IR spectra of **1** and **2** are similar. The medium bands at ~3000, 1587, and 1485 cm^{-1} are attributed to the terminal NH_3^+ stretch, and bands at ~2951 and 2919 cm^{-1} are due to the stretching vibrations of $–CH_2–$ groups. The strong band at ~1345 cm^{-1} in the spectra is consistent with the existence of trigonally coordinated boron, while the bands at ~1130, 1000, and 830 cm^{-1} are characteristic of tetrahedral boron [13].

3.2. Crystal structures

Structure of ***1***. The asymmetric unit of **1** contains one independent triangularly coordinated boron atom (B–O (av.) 1.375 Å), one unique tetrahedrally coordinated boron atom (B–O (av.) 1.474 Å), five oxygen atoms,

Table 2
Final atomic coordinates ($\times 10^4$) and equivalent thermal isotropic displacement U_{eq} (Å$^2 \times 10^3$) with e.sl.d's in Parentheses of **1** and **2**

Atoms	x	y	z	U_{eq}[a]
$[H_3N(C_6H_{10})NH_3]\ [B_4O_5(OH)_4]$				
B(1)	1932(2)	7411(1)	3286(1)	14(1)
B(2)	−349(2)	8479(1)	3373(1)	13(1)
O(1)	3217(1)	6760(1)	3743(1)	19(1)
O(2)	1042(1)	7812(1)	3950(1)	14(1)
O(3)	0	9221(1)	2500	12(1)
O(4)	−1584(1)	7631(1)	2851(1)	15(1)
O(5)	−811(1)	9136(1)	4218(1)	19(1)
C(1)	1626(2)	5191(1)	441(1)	15(1)
C(2)	664(2)	4783(1)	1213(1)	16(1)
C(3)	−695(2)	4077(1)	534(1)	16(1)
N	2966(1)	5879(1)	1103(1)	16(1)
$[H_3N(C_6H_{10})NH_3]\ [B_5O_8(OH)]$				
B(1)	−1648(3)	6006(1)	4623(2)	17(1)
B(2)	−2496(3)	7416(1)	4862(2)	14(1)
B(3)	846(3)	6914(1)	5668(2)	15(1)
B(4)	2063(3)	7056(1)	7799(2)	15(1)
B(5)	4458(3)	7271(1)	6236(2)	14(1)
O(1)	−2323(2)	5270(1)	4277(1)	30(1)
O(2)	−2931(2)	6618(1)	4356(1)	19(1)
O(3)	233(2)	6122(1)	5173(1)	20(1)
O(4)	−341(2)	7543(1)	5103(1)	15(1)
O(5)	568(2)	6890(1)	6976(1)	18(1)
O(6)	3025(2)	7056(1)	5402(1)	19(1)
O(7)	6397(2)	7500(1)	5999(1)	17(1)
O(8)	4009(2)	7275(1)	7449(1)	21(1)
O(9)	1632(2)	7008(1)	8986(1)	16(1)
C(1)	−5109(3)	5495(1)	1865(2)	25(1)
C(2)	−5243(3)	4600(1)	1700(2)	27(1)
C(3)	−7298(3)	4349(1)	1143(2)	20(1)
C(4)	−9114(3)	4703(1)	1782(2)	25(1)
C(5)	−8889(3)	5596(1)	1952(2)	24(1)
C(6)	−6877(3)	5759(1)	2616(2)	21(1)
N(1)	−7451(2)	3466(1)	1166(1)	22(1)
N(2)	−6662(3)	6610(1)	2936(1)	24(1)

[a] U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 3
Anistropic thermal vibration parameters[a] (Å$^2 \times 10^3$) (e.s.d's in parentheses) for all the atoms of **1** and **2**

Atoms	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
$[H_3N(C_6H_{10})NH_3]\ [B_4O_5(OH)_4]$						
B(1)	15(1)	15(1)	12(1)	−1(1)	2(1)	−1(1)
B(2)	13(1)	17(1)	9(1)	0(1)	4(1)	0(1)
O(1)	18(1)	25(1)	13(1)	−1(1)	1(1)	4(1)
O(2)	14(1)	19(1)	9(1)	1(1)	2(1)	1(1)
O(3)	14(1)	14(1)	10(1)	0	4(1)	0
O(4)	15(1)	18(1)	11(1)	1(1)	2(1)	−3(1)
O(5)	22(1)	25(1)	12(1)	−3(1)	8(1)	1(1)
C(1)	18(1)	15(1)	12(1)	0(1)	5(1)	4(1)
C(2)	20(1)	17(1)	11(1)	3(1)	6(1)	4(1)
C(3)	19(1)	16(1)	13(1)	4(1)	6(1)	4(1)
N	18(1)	18(1)	14(1)	1(1)	6(1)	3(1)
$[H_3N(C_6H_{10})NH_3]\ [B_5O_8(OH)]$						
B(1)	17(1)	20(1)	14(1)	−2(1)	1(1)	0(1)
B(2)	12(1)	18(1)	12(1)	1(1)	−1(1)	0(1)
B(3)	11(1)	19(1)	15(1)	0(1)	1(1)	0(1)
B(4)	15(1)	13(1)	15(1)	−1(1)	1(1)	1(1)
B(5)	14(1)	16(1)	13(1)	2(1)	0(1)	2(1)
O(1)	26(1)	19(1)	42(1)	−4(1)	−13(1)	1(1)
O(2)	15(1)	18(1)	23(1)	−3(1)	−4(1)	1(1)
O(3)	19(1)	19(1)	23(1)	−3(1)	−6(1)	3(1)
O(4)	12(1)	18(1)	16(1)	2(1)	0(1)	−1(1)
O(5)	12(1)	28(1)	13(1)	2(1)	0(1)	−3(1)
O(6)	12(1)	31(1)	13(1)	−1(1)	1(1)	0(1)
O(7)	13(1)	25(1)	14(1)	0(1)	2(1)	−3(1)
O(8)	13(1)	36(1)	13(1)	−1(1)	1(1)	−6(1)
O(9)	15(1)	20(1)	13(1)	−2(1)	1(1)	−4(1)
C(1)	19(1)	23(1)	32(1)	−4(1)	−1(1)	−5(1)
C(2)	19(1)	24(1)	37(1)	−5(1)	1(1)	0(1)
C(3)	21(1)	16(1)	23(1)	−2(1)	2(1)	−1(1)
C(4)	18(1)	22(1)	35(1)	−5(1)	3(1)	−3(1)
C(5)	20(1)	20(1)	32(1)	−4(1)	3(1)	1(1)
C(6)	27(1)	17(1)	18(1)	0(1)	−1(1)	−4(1)
N(1)	20(1)	19(1)	26(1)	−4(1)	0(1)	−2(1)
N(2)	27(1)	20(1)	20(1)	−3(1)	0(1)	−4(1)

[a] The form of the anisotropic thermal parameters is $\exp[-2\pi^2(h^2a^{*2}U_{11}+k^2b^{*2}U_{22}+l^2c^{*2}U_{33}+2hka^*b^*U_{12}+2hla^*c^*U_{13}+2klb^*c^*U_{23})$.

three carbons, and one nitrogen atom. The isolated tetraborate polyanion $[B_4O_5(OH)_4]^{2-}$ (Fig. 1), as found in $[C_2H_6N_2]\ [B_4O_5(OH)_4]$ [8], is the basic structural unit of the compound. It is constituted of two $BO_2(OH)$ groups (triangular boron: △) and two $BO_3(OH)$ groups (tetrahedral boron: □), which can be written as 2△2□: ⟨△2□⟩=⟨△2□⟩ with the help of the conception of FBBs after Burns et al. [3,6]. Such an isolated anion is also observed in mineral borate, $Na_2[B_4O_5(OH)_4]\cdot 4H_2O$ and in other synthetic hydrated borates containing alkaline cations, or alkaline and alkaline earth metal cations, for example, $Rb_2[B_4O_5(OH)_4]\cdot 3\cdot 6H_2O$ [14], $NaRb[B_4O_5(OH)_4]\cdot 4H_2O$ [15], $K_2Ca[B_4O_5(OH)_4]_2\cdot 8H_2O$ [16] etc.

It is well known that multipoint hydrogen bond interactions play an important role in the formation and

Table 4
Selected bond length (Å) and angles (deg) for **1**[a]

B(1)–O(1)	1.381(2)	B(2)–O(5)	1.434(2)
B(1)–O(2)	1.373(2)	O(4)–B(1)#1	1.370(2)
B(1)–O(4)#1	1.370(2)	O(3)–B(2)#1	1.469(2)
B(2)–O(2)	1.492(2)	O(1)–H(9)	0.82
B(2)–O(3)	1.469(2)	O(5)–H(10)	0.82
B(2)–O(4)	1.501(2)		
O(4)#1–B(1)–O(2)	121.9(1)	O(3)–B(2)–O(4)	110.4(1)
O(4)#1–B(1)–O(1)	117.3(1)	O(2)–B(2)–O(4)	108.7(1)
O(2)–B(1)–O(1)	120.9(1)	B(1)–O(1)–H(9)	108.5
O(5)–B(2)–O(3)	112.6(1)	B(1)–O(2)–B(2)	117.0(1)
O(5)–B(2)–O(2)	107.7(1)	B(2)#1–O(3)–B(2)	109.0(1)
O(3)–B(2)–O(2)	108.9(1)	B(1)#1–O(4)–B(2)	120.1(1)
O(5)–B(2)–O(4)	108.6(1)	B(2)–O(5)–H(10)	109.5

[a] Symmetry transformations used to generate equivalent atoms: #1 $-x, y, -z+1/2$; #2 $-x, -y+1, -z$.

Table 5
Selected bond length (Å) and angles (deg) for **2**[a]

B(1)–O(1)	1.369(2)	B(3)–O(6)	1.480(2)
B(1)–O(2)	1.357(2)	B(4)–O(5)	1.345(2)
B(1)–O(3)	1.367(2)	B(4)–O(8)	1.390(2)
B(2)–O(2)	1.484(2)	B(4)–O(9)	1.365(2)
B(2)–O(4)	1.437(2)	B(5)–O(6)	1.347(2)
B(2)–O(9)#1	1.479(2)	B(5)–O(7)	1.356(2)
B(2)–O(7)#2	1.487(2)	B(5)–O(8)	1.393(2)
B(3)–O(3)	1.495(2)	O(7)–B(2)#3	1.487(2)
B(3)–O(4)	1.446(2)	O(9)–B(2)#4	1.479(2)
B(3)–O(5)	1.476(2)	O(1)–H(1A)	0.82
O(2)–B(1)–O(3)	121.7(2)	O(5)–B(4)–O(9)	118.8(2)
O(2)–B(1)–O(1)	116.1(2)	O(5)–B(4)–O(8)	120.7(2)
O(3)–B(1)–O(1)	122.2(2)	O(9)–B(4)–O(8)	120.5(2)
O(4)–B(2)–O(9)#1	112.2(1)	O(6)–B(5)–O(7)	124.9(2)
O(4)–B(2)–O(2)	112.3(1)	O(6)–B(5)–O(8)	120.6(2)
O(9)#1–B(2)–O(2)	106.4(1)	O(7)–B(5)–O(8)	114.6(2)
O(4)–B(2)–O(7)#2	108.9(1)	B(1)–O(1)–H(1A)	109.5
O(9)#1–B(2)–O(7)#2	108.3(1)	B(1)–O(2)–B(2)	120.0(1)
O(2)–B(2)–O(7)#2	108.6(1)	B(1)–O(3)–B(3)	121.3(1)
O(4)–B(3)–O(5)	111.7(1)	B(2)–O(4)–B(3)	118.6(1)
O(4)–B(3)–O(6)	107.3(1)	B(4)–O(5)–B(3)	124.0(1)
O(5)–B(3)–O(6)	110.6(1)	B(5)–O(6)–B(3)	123.6(1)
O(4)–B(3)–O(3)	111.3(2)	B(5)–O(7)–B(2)#3	128.4(1)
O(5)–B(3)–O(3)	107.5(1)	B(4)–O(8)–B(5)	119.7(2)
O(6)–B(3)–O(3)	108.5(1)	B(4)–O(9)–B(2)#4	121.0(1)

[a] Symmetry transformations used to generate equivalent atoms: #1 $x-1/2$, $-y+3/2$, $z-1/2$; #2 $x-1$, y, z; #3 $x+1$, y, z; #4 $x+1/2$, $-y+3/2$, $z+1/2$.

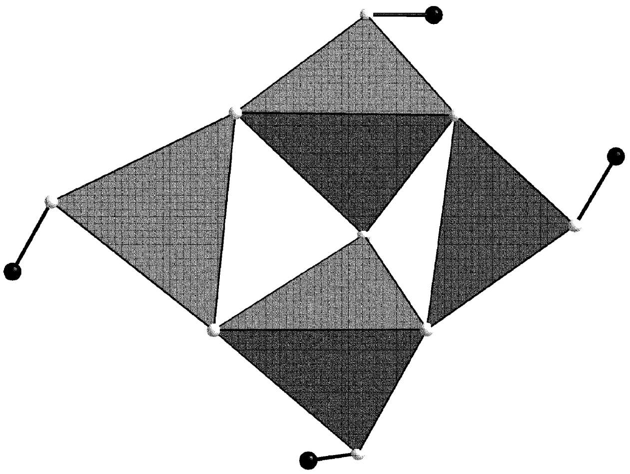

Fig. 1. Polyhedral representation of the tetraborate unit $[B_4O_5(OH)_4]^{2-}$. H atoms: black ball.

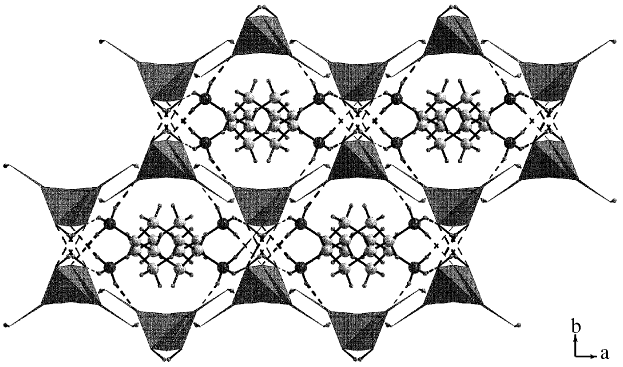

Fig. 2. Polyhedral view of the structure of **1** along the *c*-axis showing 10-membered boron rings constructed by H-bonding. N atoms: middle gray; C atoms: gray; H atoms: small black.

stability of low-dimensional structures. In the present compound, all H atoms of the hydroxyl and ammonium groups participate in hydrogen bond, forming a three-dimensional network. As shown in Fig. 2, the tetraborate anions are linked together by hydrogen bonds, O(5)–H(10)…O(5), O(1)–H(9)…O(2), to form a complex supramolecular network containing 10-memered boron rings channels along the [001] direction. The organic moieties reside in the channels and interact with the polyborate network through N–H(3)…O(5), N–H(2)…O(3), N–H(1)…O(4) hydrogen bonds. The details of H-bonds are given in Table 6.

Structure of **2**. The asymmetric unit of **2** contains 22 independent non-hydrogen atoms, including five boron atoms, nine oxygen atoms, six carbons, and two nitrogen atoms. As found in several known borates, such as $Na_2[B_5O_8(OH)]\cdot 2H_2O$ [17], $Ce[B_5O_8(OH)]NO_3\cdot 3H_2O$ [18], pentaborate $[B_5O_8(OH)]^{2-}$ is the basic unit of the compound (Fig. 3). It contains a double ring composed of two different rings, ⟨2△□⟩ and ⟨△2□⟩, that link together through a common tetrahedron. Different from the $[B_5O_6(OH)_4]^{1-}$ polyanion [9], $[B_5O_8(OH)]^{2-}$ anion can be written as 3△2□:⟨2△□⟩–⟨△2□⟩ in terms of description of boron–oxygen groups [6]. The B–O bond lengths and O–B–O bond angles are in the range of 1.345(2)–1.495(2) Å and 106.4(1)–124.9(2)°, which are in good agreement with those reported previously for other borate compounds.

The structure of **2** can be described as borate sheets that stack one over another, forming the polyborate structures. These layers are constructed from pentaborate groups $[B_5O_8(OH)]^{2-}$, which are linked together through exocyclic oxygen atoms [O(7), O(9)] to neighboring units. A common feature of these borate layers is that they all contain 3, 9-membered boron rings, as shown in Fig. 4. Such nine-membered window systems have also been found in some lamellar or microporous germanates [19–21], which shows that nine-membered rings is a common structural geometry existing in different systems. Adjacent sheets are further connected with each other through strong H-bonding interaction [O(1)–H(1A)…O(3)]. Thus a 3D polyborate supramolecular framework (Fig. 5), formed between the B–OH

Table 6
Details of hydrogen bonds for **1**[a]

D–H…A	d(D–H) (Å)	d(H…A) (Å)	d(D…A) (Å)	∠(DHA) (deg)
O(5)–H(10)…O(5) [#1]	0.82	2.14	2.885(2)	151.4
O(1)–H(9)…O(2) [#2]	0.82	1.96	2.778(1)	174.7
N–H(3)…O(5) [#3]	0.89	2.02	2.821(1)	148.8
N–H(2)…O(3) [#4]	0.89	2.02	2.889(1)	163.4
N–H(1)…O(4) [#5]	0.89	1.98	2.854(1)	167.5

Symmetry transformations used to generate equivalent atoms: [#1] $-x$, $-y+2$, $-z+1$; [#2] $-x+1/2$, $-y+3/2$, $-z+1$; [#3] $x+1/2$, $-y+3/2$, $z-1/2$; [#4] $x+1/2$, $y-1/2$, z; [#5] $-x$, y, $-z+1/2$.

[a] D and A signify donor and acceptor oxygens, respectively.

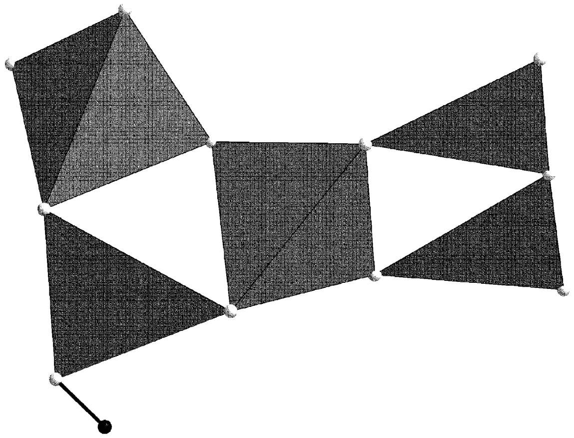

Fig. 3. Polyhedral representation of the pentaborate unit $[B_5O_8(OH)]^{2-}$. H atoms: black ball.

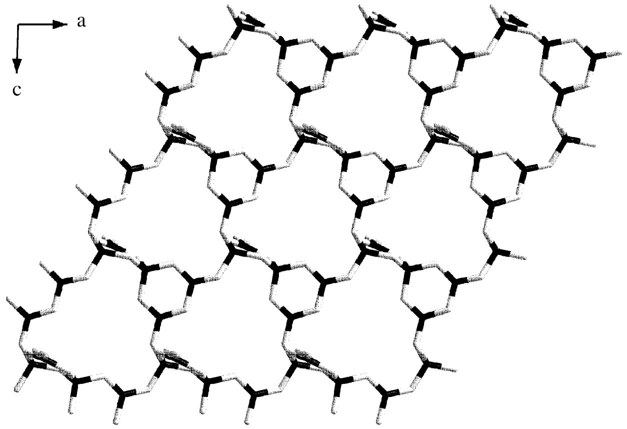

Fig. 4. View along the b-axis of **2** showing layers with 3, 9-membered boron rings.

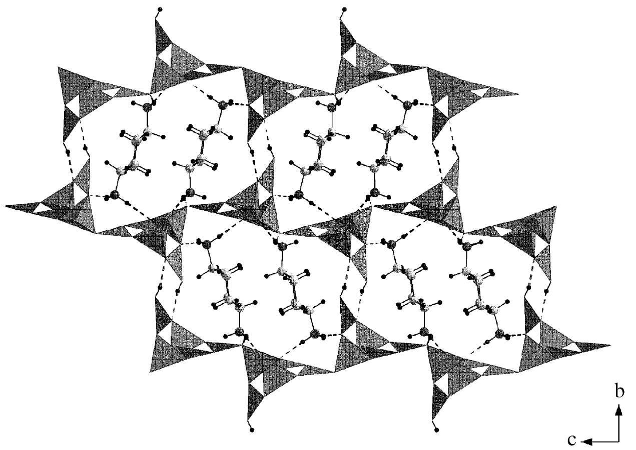

Fig. 5. Polyhedral view of the structure of **2** along the a-axis showing 14-membered boron rings constructed by H-bonding. N atoms: middle gray; C atoms: gray; H atoms: small black.

and ring oxygen atoms of neighboring sheets, can be viewed along the a-axis with extra large channels containing 14-membered boron rings. The diprotonated organic molecules reside in the channels and interact with the inorganic framework through hydrogen bonding interactions as N(1)–H(1D)…O(4) [$d = 1.95$], N(1)–H(1E)…O(9) [$d = 2.06$], N(2)–H(2F)…O(7) [$d = 2.12$], N(2)–H(2C)…O(2) [$d = 1.98$]. To our knowledge, this compound is the first example of layered borate with an organic amine as template. The details of H-bonds are given in Table 7.

3.3. Thermal properties

Thermogravimetric (TG) analysis of **1** and **2** was carried out in N_2 atmosphere from 40 to 1000 °C with a heating rate of 10 °C/min. The TG curve of **1** (the curve **I** in Fig. 6) showed a continuous weight loss between 70 and 500 °C, corresponding to the removal of the organic amine and the dehydration of hydroxyls (found: 54.08%; calcd: 54.69%). The TG curve of **2** (curve **II** in Fig. 6) showed that the compound was stable up to ~320 °C. Between 320 and 480 °C, a sharp weight loss of 41.62% occurred, which was attributed to the removal of the organic amine and one water molecule (calcd: 41.93%). The residue after the calcination for **1** and **2** is amorphous, respectively, and its phase is unidentified.

Table 7
Details of hydrogen bonds for **2**[a]

D–H...A	*d*(D–H) (Å)	*d*(H...A) (Å)	*d*(D...A) (Å)	∠(DHA) (deg)
O(1)–H(1A)...O(3) [#1]	0.82	1.99	2.775(2)	159.9
N(1)–H(1D)...O(4) [#2]	0.89	1.95	2.814(2)	162.8
N(1)–H(1E)...O(9) [#3]	0.89	2.06	2.840(2)	145.4
N(2)–H(2F)...O(7) [#4]	0.89	2.12	2.888(2)	143.3
N(2)–H(2C)...O(2)	0.89	1.98	2.858(2)	168.3

Symmetry transformations used to generate equivalent atoms: [#1] $-x, -y+1, -z+1$; [#2] $-x-1/2, -y-1/2, -z+1/2$; [#3] $-x-1, -y+1, -z+1$; [#4] $x-3/2, -y+3/2, z-1/2$.

[a] D and A signify donor and acceptor oxygens, respectively.

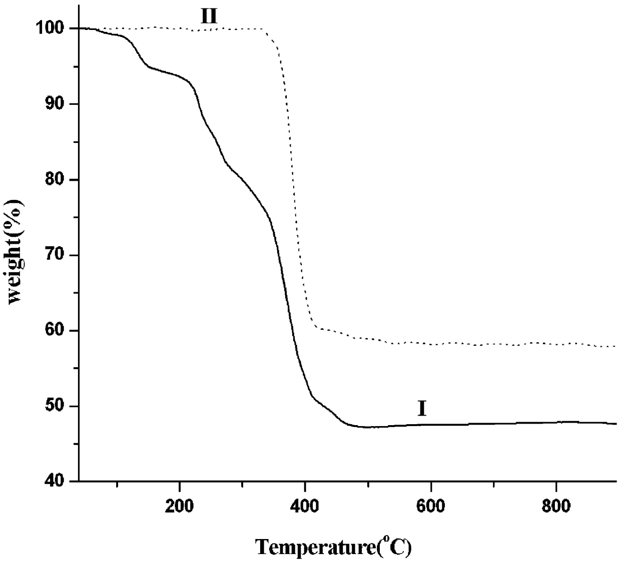

Fig. 6. The TG curve of **1** and **2**.

4. Conclusions

In summary, the syntheses, crystal structures, and thermal properties of two new organically templated borates, $[H_3N(C_6H_{10})NH_3]$ $[B_4O_5(OH)_4]$ **(1)** and $[H_3N(C_6H_{10})NH_3]$ $[B_5O_8(OH)]$ **(2)** have been described. **1** has a tetraborate anion $[B_4O_5(OH)_4]^{2-}$, which is compensated by the diprotonated organic amine. While **2** has 3, 9-membered boron sheets built up from pentaborate groups. It is the first example of layered borate compound containing organic template. It is noteworthy that the concentration of the initial mixture has a critical influence on the final product. In our case, the inorganic dimensionality is increased with a larger $[H_2N(C_6H_{10})NH_2]/[H_3BO_3]$ ratio(0-D: 2; 2-D: 4). The successful syntheses of the two borates provide the possibility for preparing structural complex open-framework borate compounds in the presence of organic amines acting as templates or structure-directing agents (SDAs). Further work on this subject is in progress.

Acknowledgments

This work was supported by the NNSF of China (Grant Nos. 20171045 and 20271050), the Talents Program of Chinese Academy of Sciences, the NSF of Fujian Province (Grant No. E0210029), and State Key Laboratory of Inorganic Synthesis and Preparative Chemistry of Jilin University.

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