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Article

Synthesis and Structure of a New Heptaborate Oxoanion Isomer: $B_7O_9(OH)_5^{2-}$

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The nonmetal borate $[H_3N(CH_2)_7NH_3][B_7O_9(OH)_5]\cdot H_2O$ (**1**) was prepared via a neat reaction of 1,7-diaminoheptane with excess boric acid under mild nonhydrothermal conditions. Single-crystal X-ray characterization of **1** revealed a new isomer of the heptaborate anion, $B_7O_9(OH)_5^{2-}$. The heptaborate anion in **1** is comprised of four fused $(BO)_3$ rings sharing three four-coordinate boron atoms and a single three-coordinate oxygen atom. This anion is a structural isomer of another recently described heptaborate anion, consisting of a chain of three $(BO)_3$ rings. Compound **1** crystallized in the triclinic space group $P\bar{1}$ with $a = 9.3266(17)$ Å, $b = 10.1222(19)$ Å, $c = 10.847(2)$ Å, $\alpha = 89.422(2)°$, $\beta = 82.349(2)°$, $\gamma = 75.158(2)°$, $V = 980.7(3)$ Å^3, and $Z = 2$.

Introduction

Minerals and synthetic compounds containing boron bonded exclusively to oxygen have found extensive industrial use.[1] The anionic constituents of these ionocovalent compounds are made up of BO_3 and BO_4 polyhedra that may link together by oxygen sharing to form isolated rings and cages, or extended chains, sheets, and networks. In these compounds, the negative charge of the borate or polyborate component is balanced by the net positive charge of interstitial cations.[1–3] Although the vast majority of characterized borate compounds contain metal cations, an increasing number of synthetic borates containing nonmetal interstitial cations have been reported in recent years. In some cases, the presence of these nonmetal cations can result in the formation of unusual borate anions under mild nonhydrothermal conditions.[4,5]

Two crystalline metal borate compounds were recently reported, both formed under hydrothermal conditions, con-

taining topologically the same heptaborate anion, $B_7O_9(OH)_5^{2-}$.[6,7] Here we describe the synthesis and structural characterization of a crystalline nonmetal borate, $[H_3N(CH_2)_7NH_3][B_7O_9(OH)_5]\cdot H_2O$ (**1**), which forms under nonhydrothermal conditions and contains a new structural isomer of the heptaborate anion.

Experimental Section

Materials. Boric acid was produced by U.S. Borax Inc., Rio Tinto Minerals, and 1,7-diaminoheptane was obtained from Sigma-Aldrich Chemical Co. Both reagents were used without further purification.

Synthesis of $[H_3N(CH_2)_7NH_3][B_7O_9(OH)_5]\cdot H_2O$ (1). Boric acid (4.33 g, 0.07 mol) and 1,7-diaminoheptane (1.30 g, 0.01 mol) were ground together with a mortar and pestle. The resulting gummy mass was placed in a glass tube, sealed with a Teflon screw cap, and heated at 80 °C for 16 h. The resulting white solid product was suspended in 50 mL of MeOH, separated by vacuum filtration, and dried in a 60 °C oven to give 4.37 g of **1** (96% yield). Anal. Calcd for $C_7H_{26}B_7N_2O_{17}$: C, 18.48; H, 5.98; N, 6.16; B, 16.63. Found: C, 18.14; H, 6.24; N, 6.02; B, 16.9.

The same procedure was repeated with heating at 120, 150, and 250 °C. White solid products were obtained in each case except for the 250 °C experiment, which yielded a clear, viscous syrup

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Table 1. Crystallographic Data and Structure Refinement Details for **1**

empirical formula	$C_7H_{27}B_7N_2O_{15}$
fw	454.98
temperature (K)	293(2)
wavelength (Å)	0.710 73
cryst syst, space group	triclinic, $P\bar{1}$
unit cell dimensions	
a, b, c (Å)	9.3266(17), 10.1222(19), 10.847(2)
α, β, γ (deg)	89.422(2), 82.349(2), 75.158(2)
volume (Å³), Z	980.7(3), 2
calcd density (g/cm³)	1.541
abs coeff (mm⁻¹)	0.137
$F(000)$	476
cryst size (mm)	$0.40 \times 0.40 \times 0.40$
data collection θ range (deg)	4.15−29.11
limiting indices	$-12 \leq h \leq 12, -13 \leq k \leq 13,$
	$-14 \leq l \leq 14$
reflns collected	9099
indep reflns	5037 [R(int) = 0.0169]
completeness to θ = 29.11° (%)	95.6
abs corrn	none
max and min transmn	0.9473 and 0.9473
refinement method	full-matrix least squares on F^2
data/restraints/param	5037/0/321
GOF on F^2	0.936
final R indices [$I > 2\sigma(I)$]	R1 = 0.0368, wR2 = 0.1004
R indices (all data)	R1 = 0.0439, wR2 = 0.1071
largest diff peak and hole (e/Å³)	+0.309 and −0.230

Scheme 1. Isolated Borate Anions Occurring in a Concentrated Aqueous Solution

Scheme 2. Heptaborate Anion in **1** is Formally Composed of Both the Tetraborate (**4**) and Heptaborate (**7**) Anions
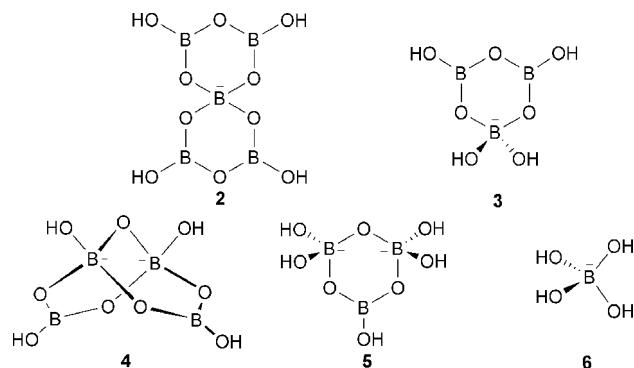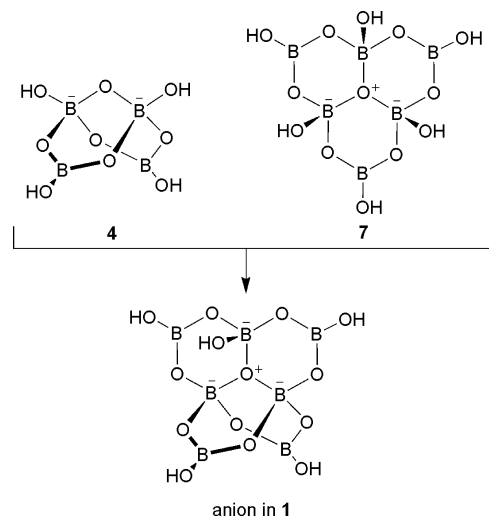

anion in **1**

that slowly devitrified to a white solid upon conditioning at 120 °C. The products of each experiment exhibited a powder X-ray diffraction (XRD) pattern characteristic of **1**, matching the pattern generated from single-crystal X-ray data.

X-ray Data Collection and Structure Determination. A colorless parallelepiped of **1** prepared at 80 °C was mounted on a glass fiber, and XRD data were collected on a Bruker SMART CCD diffractometer using Mo Kα radiation. Table 1 summarizes details of this data collection and subsequent refinement. Programs used in this work are those supplied with the Bruker SMART CCD diffractometer.

Atoms were located using statistical methods. All non-hydrogen atoms were included with anisotropic displacement parameters. Position parameters of the hydrogen atoms on nitrogen and oxygen were refined. Hydrogen atoms bonded to carbon were placed in calculated positions. For the water molecule, hydrogen positions and isotropic displacement parameters were allowed to vary. All other hydrogen atoms were included, with parameters based on the values for the attached atoms. Scattering factors for hydrogen were obtained from Stewart et al.[8] and for other atoms were taken from *The International Tables for X-ray Crystallography*.[9]

Results and Discussion

Isolated borate anions found in industrial-scale borates include pentaborate $B_5O_6(OH)_4^-$ (**2**), tetraborate $B_4O_5(OH)_4^{2-}$ (**4**), and tetrahydroxyborate $B(OH)_4^-$ (**6**). Along with the triborate anions $B_3O_3(OH)_4^-$ (**3**) and $B_3O_3(OH)_5^{2-}$ (**5**), these anions exist in substantial concentrations in concentrated aqueous borate solutions.[10,11] These anions are shown in Scheme 1 in order of increasing basicity (**2** < **3** < **4** < **5** < **6**) of their associated solutions. A number of other isolated borate anions are found in crystalline mineral and synthetic borates. For example, the isolated hexaborate anion B_6O_7-$(OH)_6^{2-}$ (**7**; see Scheme 2) is found in several compounds, including $Mg[B_6O_7(OH)_6]\cdot5H_2O$,[12] $Mg[B_6O_7(OH)_6]\cdot2H_2O$ (aksaite),[13] $Mg_2[B_6O_7(OH)_6]_2\cdot9H_2O$ (mcallisterite),[14] and Na_6-$Mg[B_6O_7(OH)_6]_4\cdot10H_2O$ (rivadavite).[15]

Polyborate anions can be regarded as resulting from both Lewis neutralization of boric acid with OH⁻, to produce tetrahedral anionic boron centers, and condensation of BOH groups to form rings and cages. Extended 1-D chain, 2-D sheet, and 3-D network borate structures also occur through further condensation but generally require solvothermal conditions to form. Isolated polyborate anions containing more than six boron atoms are relatively rare.[16]

Although $B(OH)_3$ is a Lewis acid, its reactions with ammonia or organoamines in aqueous media typically result in the formation of salts of polyborate anions rather than B−N adducts. The pentaborate anion, **2**, is most frequently encountered in these systems, but salts of the tetraborate

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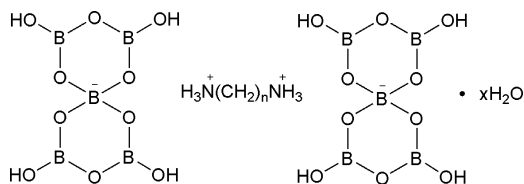(16) Grice, J. D.; Burns, P. C.; Hawthorne, F. C. *Can. Mineral.* **1999**, *37*, 731–762.
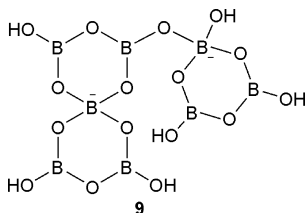
Figure 1. Type **8** compounds.

Figure 2. Octaborate dianion **9** in [H$_3$N(CH$_2$)$_7$NH$_3$][B$_8$O$_{10}$(OH)$_7$]·2B(OH)$_3$.

anion, **4**, and rarely the triborate monoanion, **3**, also occur.[17] For example, ammonium pentaborate, NH$_4$[B$_5$O$_6$(OH)$_4$]·2H$_2$O, and ammonium tetraborate, (NH$_4$)$_2$[B$_4$O$_5$(OH)$_4$]·2H$_2$O, are well-defined crystalline compounds that have been manufactured on an industrial scale for many years using reactions of boric acid with aqueous ammonia at appropriate stoichiometries.[1]

We recently reported structures of crystalline borates resulting from reactions of excess boric acid with **1** and *n*-diaminoalkanes (*n* = 5−12) in aqueous media under mild conditions.[18] In most cases, these reactions resulted in pentaborate salts, [H$_3$N(CH$_2$)$_n$NH$_3$][B$_5$O$_6$(OH)$_5$]$_2$·*x*H$_2$O (**8**), shown in Figure 1.

Although nonmetal borates of type **8** are comprised of only pentaborate anions and protonated diaminoalkane cations, these systems are complex. The pentaborate anion is capable of forming a range of hydrogen-bonded supramolecular frameworks, the type of which is controlled by the number of carbon atoms in the interstitial cation alkyl chain. The conformation of the cation alkyl chain is, in turn, controlled by the arrangement of the pentaborate anion framework.[18]

An exception to the formation of compounds of type **8** was found for the reaction of 1,7-diaminoheptane with excess boric acid in an aqueous solution, which results in the formation of [H$_3$N(CH$_2$)$_7$NH$_3$][B$_8$O$_{10}$(OH)$_6$]·2B(OH)$_3$. This compound contains the unusual octaborate anion **9**, shown in Figure 2, formed by formal condensation of pentaborate **2** and triborate **3** monoanions.

The inclusion of 2 mol equiv of interstitial boric acid maintains a boron−amine molar ratio of 10:1, as is found in related compounds of type **8**.

When reactions of diaminoalkanes with excess boric acid were carried out under limiting water conditions, a number of crystalline pentaborate-based compounds, containing coordinative covalent B−N bonds, were obtained. These include zwitterions of type **10** and salts of type **11**, as shown in Figure 3.[19,20]
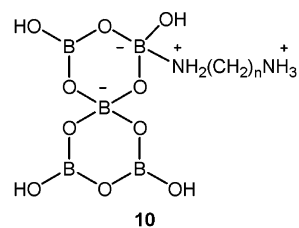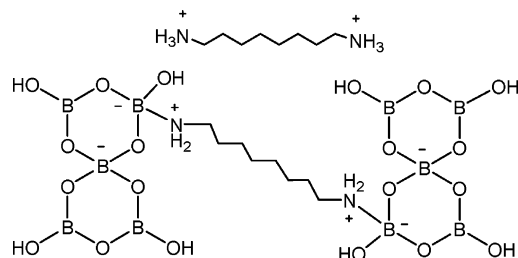
Figure 3. Coordinative covalent B−N bonds containing pentaborate-based zwitterions (**10**) and salt (**11**, shown for *n* = 8).
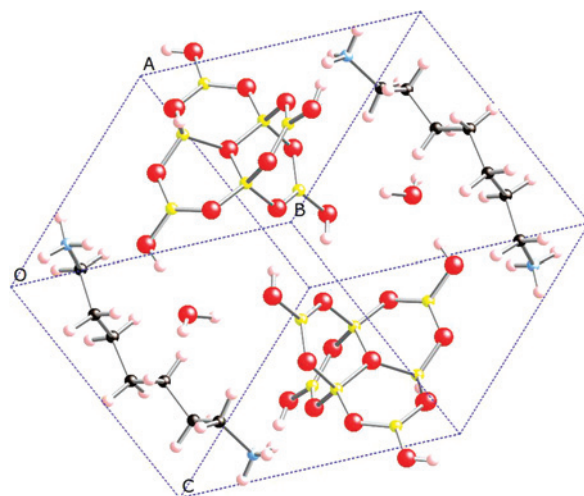

Figure 4. View of the unit cell of **1**.

Structures determined by single-crystal X-ray crystallography for several compounds of types **10** and **11** will be described in more detail separately.

In another anomaly, the reaction under limiting water conditions of 1,7-diaminoheptane with excess boric acid yielded the crystalline compound **1**, according to eq 1.

$$H_2N(CH_2)_7NH_2 + 7B(OH)_3 \xrightarrow[\textbf{1}]{-6H_2O} [H_3N(CH_2)_7NH_3] - [B_7O_9(OH)_5] \cdot H_2O \quad (1)$$
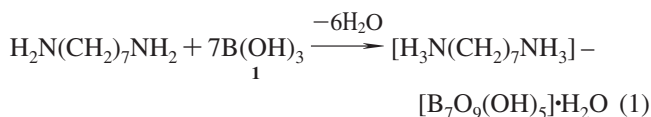
Structure Description. The asymmetric unit for **1** contains one diamminoheptane dication, one heptaborate dianion, and one water molecule. Contents of the unit cell (*Z* = 2) are shown in Figure 4. The heptaborate anion in **1** is shown in Figure 5, and selected interatomic distances and angles for this anion are listed in Table 2. This anion contains four fused (BO)$_3$ rings having one three-coordinate oxygen atom

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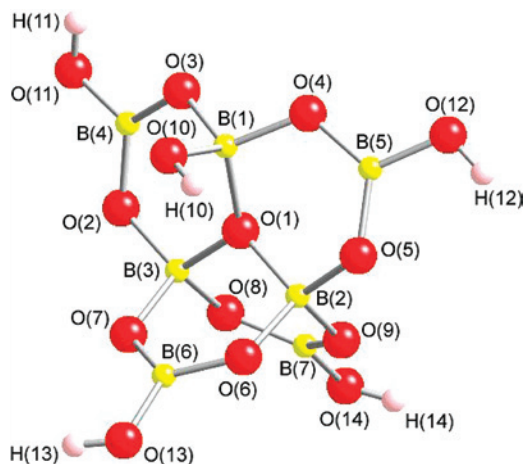
Figure 5. Heptaborate anion $B_7O_9(OH)_5^{2-}$ in **1**.

Table 2. Selected Interatomic Distances (Å) and Angles (deg) for the Heptaborate Anion in **1**

O(1)−B(3)	1.4937(13)	B(7)−O(8)−B(3)	120.02(9)
O(1)−B(2)	1.5121(13)	B(7)−O(9)−B(2)	120.93(9)
O(1)−B(1)	1.5123(14)	O(4)−B(1)−O(3)	111.97(9)
O(2)−B(4)	1.3551(15)	O(4)−B(1)−O(10)	112.37(9)
O(2)−B(3)	1.4335(13)	O(3)−B(1)−O(10)	106.70(9)
O(3)−B(4)	1.3718(14)	O(4)−B(1)−O(1)	107.03(8)
O(3)−B(1)	1.4613(13)	O(3)−B(1)−O(1)	107.21(8)
O(4)−B(5)	1.3650(14)	O(10)−B(1)−O(1)	111.50(9)
O(4)−B(1)	1.4431(14)	O(5)−B(2)−O(6)	112.36(9)
O(5)−B(5)	1.3740(15)	O(5)−B(2)−O(9)	110.61(9)
O(5)−B(2)	1.4309(13)	O(6)−B(2)−O(9)	109.95(9)
O(6)−B(6)	1.3672(14)	O(5)−B(2)−O(1)	109.86(8)
O(6)−B(2)	1.4685(14)	O(6)−B(2)−O(1)	107.38(8)
O(7)−B(6)	1.3639(14)	O(9)−B(2)−O(1)	106.47(8)
O(7)−B(3)	1.4808(14)	O(2)−B(3)−O(8)	111.00(9)
O(8)−B(7)	1.3674(14)	O(2)−B(3)−O(7)	109.76(9)
O(8)−B(3)	1.4686(14)	O(8)−B(3)−O(7)	109.55(9)
O(9)−B(7)	1.3684(14)	O(2)−B(3)−O(1)	111.06(9)
O(9)−B(2)	1.4742(14)	O(8)−B(3)−O(1)	106.99(8)
O(10)−B(1)	1.4620(15)	O(7)−B(3)−O(1)	108.41(8)
O(11)−B(4)	1.3729(14)	O(2)−B(4)−O(3)	123.20(10)
O(12)−B(5)	1.3686(14)	O(2)−B(4)−O(11)	116.52(10)
O(13)−B(6)	1.3721(15)	O(3)−B(4)−O(11)	120.24(10)
O(14)−B(7)	1.3689(15)	O(4)−B(5)−O(12)	117.05(10)
B(3)−O(1)−B(2)	111.73(8)	O(4)−B(5)−O(5)	123.00(10)
B(3)−O(1)−B(1)	123.13(8)	O(12)−B(5)−O(5)	119.94(10)
B(2)−O(1)−B(1)	119.98(8)	O(7)−B(6)−O(6)	123.14(10)
B(4)−O(2)−B(3)	123.34(9)	O(7)−B(6)−O(13)	121.50(10)
B(4)−O(3)−B(1)	121.20(9)	O(6)−B(6)−O(13)	115.35(10)
B(5)−O(4)−B(1)	119.11(9)	O(8)−B(7)−O(9)	122.51(10)
B(5)−O(5)−B(2)	121.00(8)	O(8)−B(7)−O(14)	116.88(10)
B(6)−O(6)−B(2)	120.09(8)	O(9)−B(7)−O(14)	120.60(10)
B(6)−O(7)−B(3)	119.86(9)		

and two four-coordinate boron atoms in common. This heptaborate anion in **1** contains both the tetraborate anion **4**, as found in compounds such as tincal (borax decahydrate) and tincalconite (borax pentahydrate),[21,22] and the hexaborate anion **7**,[12–15] as illustrated in Scheme 2.

The average B−O distances around three- and four-coordinate boron atoms are 1.470 and 1.368 Å, respectively. These distances are within the typical range for borate compounds.[23] The average B−O distance around the central three-coordinate oxygen atom, O(1), is 1.506 Å, significantly longer that the other [4]B−O distances. This is in agreement with the comparable B−O distances in structurally characterized examples of the hexaborate anion **7**.[12–15] The average B−O distance around the four-coordinate boron atoms in
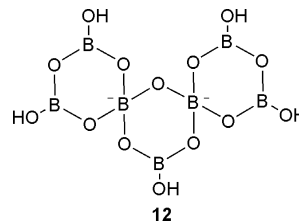

Figure 6. $B_7O_9(OH)_5^{2-}$ anion, **12**, an isomer of the heptaborate anion in **1**.

Table 3. Specified Hydrogen Bonds for **1** (Å and deg), Where D and A Are Hydrogen-Bond Donor and Acceptor Atoms, Respectively[a]

D−H⋯A	d(D−H)	d(H⋯A)	d(D⋯A)	∠(DHA)
O(10)−H(10)⋯O(6)#1	0.811(18)	2.013(18)	2.7780(12)	157.1(16)
O(11)−H(11)⋯O(3)#2	0.84(2)	1.89(2)	2.7271(13)	174.3(18)
O(12)−H(12)⋯O(1W)	0.87(2)	1.82(2)	2.6873(14)	177.9(18)
O(13)−H(13)⋯O(11)#3	0.84(2)	2.10(2)	2.9021(13)	160.2(18)
O(14)−H(14)⋯O(9)#4	0.82(2)	1.99(2)	2.8024(13)	174(2)
N(1)−H(1A)⋯O(10)#3	0.94(2)	1.77(2)	2.7018(14)	173.3(18)
N(1)−H(1B)⋯O(1W)#5	0.86(2)	2.45(2)	3.1388(18)	137.3(17)
N(1)−H(1C)⋯O(7)	0.92(2)	2.02(2)	2.8832(15)	156.5(17)
N(2)−H(2A)⋯O(10)#6	0.86(2)	2.15(2)	2.9053(15)	146.1(17)
N(2)−H(2B)⋯O(13)#7	0.90(2)	2.00(2)	2.8282(16)	153.0(17)
N(2)−H(2C)⋯O(12)#4	0.94(2)	1.87(2)	2.7544(16)	156.8(17)
O(1W)−H(1W)⋯O(14)#4	0.88(2)	2.02(2)	2.8513(16)	156(2)
O(1W)−H(2W)⋯O(8)#8	0.78(2)	2.06(2)	2.8195(14)	165(2)

[a] Symmetry transformations used to generate equivalent atoms: #1, −x + 1, −y + 1, −z + 2; #2, −x, −y + 2, −z + 2; #3, −x, −y + 1, −z + 2; #4, −x + 1, −y + 1, −z + 1; #5, x − 1, y, z; #6, x, y − 1, z − 1; #7, −x + 1, −y, −z + 1; #8, x + 1, y, z.

bonds to O(1) is 1.458 Å. The B₃O moiety including the three-coordinate oxygen atom O(1) is slightly pyramidal. Exhibiting an average B−O−B angle of 118.28°, O(1) is distorted from an idealized triangular geometry.

The heptaborate anion in **1** is an isomer of another heptaborate anion, **12**, reported in 2006, consisting of a chain of three six-membered (BO)₃ rings connected by two tetrahedral boron centers shared between pairs of rings, shown in Figure 6.[6,7]

Hydrogen Bonding. As with all hydroxy-hydrated borates, hydrogen bonding is an important feature of **1**. Details of hydrogen bonding involving the cation, anion, and interstitial water in **1** are listed in Table 3.

All five hydroxy hydrogen atoms of the anion are involved in hydrogen bonding, four to oxygen atoms of four other heptaborate anions and one to a water oxygen atom. A total of 10 of the 14 oxygen atoms of the anion are involved in hydrogen bonding, five with hydroxyl hydrogen atoms of five different neighboring anions, two with water hydrogen atoms, and five with N−H atoms of five different cations. The N−H⋯O bonds involve five anions and one water molecule.

Four of the five hydrogen atoms of each heptaborate anion are involved in hydrogen bonds with adjacent anions, creating an anionic supramolecular framework with cations and water

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molecules positioned in the interstitial space. The cations are tied to the framework by five hydrogen bonds per cation. The remaining hydrogen bond involves a water oxygen. We previously described how borate supramolecular framework structures can control the diamine cation conformation and vice versa.[18] In the case of **1**, the carbon chain of the $[H_3N(CH_2)_7NH_3]^{2+}$ cation is somewhat folded, with a C···C distance between outermost carbon atoms of 6.884(2) Å and an N···N distance of 8.776(2) Å. This compares with C···C and N···N distances of 7.599(2) and 10.019(2) Å, respectively, for the same cation in $[H_3N(CH_2)_7NH_3][\mathbf{9}]\cdot 2B(OH)_3$, which takes on a fully outstretched conformation. These differences in cation conformations appear to be related to how the cations hydrogen bond with the anionic supramolecular framework.

The various hydrogen-bonding roles of interstitial water in borate compounds have been described.[24,25] Borate interstitial water invariably interacts through coordination with metal cations, if present, and by both donating and receiving hydrogen bonds. The water molecule in **1** donates hydrogen bonds to oxygen atoms of two different anions, and hydrogen atoms of one cation and one anion are hydrogen-bonded to the water oxygen atom. Thus, interstitial water in **1** does not change the net number of hydrogen bonds in the system. Therefore, the average coordination number of the oxygen atoms in the heptaborate anion, including hydrogen bonds, is 2.79. This is significantly higher than that observed in structures of the isomeric heptaborate anion **12** ($CN_{ave} = 2.36$) and closer to the range of average oxygen coordination numbers typical of borate minerals having borate fundamental building blocks (FBBs) of similar basicity.[24]

Thermal Properties. Compound **1** was studied by thermogravimetric analysis (TGA). Upon heating, **1** exhibits a weight loss of ca. 4 wt % in the 100−150 °C temperature range, corresponding to elimination of interstitial water. A second weight loss event of ca. 10 wt % occurs in the 150−250 °C range, assignable to water loss resulting from condensation of BOH groups. An additional ca. 30 wt % is lost in the range 375−550 °C, accompanied by darkening and puffing of the sample, apparently due to pyrolysis of the organic component. Continued heating to 700 °C results in a dark-colored vitreous residue.

Further Discussion. Although the reaction producing **1** was conducted without added solvent, the use of a closed system containing product water was found to be necessary. An intimate mixture of boric acid and 1,7-diaminoheptane in a 7:1 molar ratio showed no evidence of reaction by XRD after standing for several days at room temperature. In addition, heating this mixture in an open crucible did not result in the formation of **1**. Only when this mixture was heated in a sealed tube was **1** obtained. It is notable that **1** was obtained as the exclusive product in reactions carried out in a sealed system well above the dehydration temper-

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Table 4. Summary of Ring Geometries for the Heptaborate Anion in **1**

outer plane	max displacement from the outer plane (Å)	inner plane; angle with the normal to the outer plane (deg)
B(1), O(3), B(4), O(2), B(3)	O(3), 0.1117(7)	B(1), O(1), B(3); 28.99(9)
B(1), O(4), B(5), O(5), B(2)	O(5), 0.1919(7)	B(1), O(1), B(2); 38.03(7)
B(2), O(6), B(6), O(7), B(3)	O(9), 0.117(7)	B(1), O(1), B(3); 56.15(10)
B(2), O(9), B(7), O(8), B(3)	O(6), 0.0318(7)	B(1), O(1), B(3); 52.79(6)

ature for this compound, for example, at 150 °C, implying that the dehydration events observed in the TGA experiment are reversible.

Examination of hexaborate anion **7** shows that the three hydroxy groups attached to the four-coordinate boron atoms extend in the same direction and fall in close enough proximity to be bridged by a single atom. Indeed, anion **7** can act as either a bi- or tridentate ligand to metals via coordination with these hydroxy groups, as seen in complexes such as $Ni(H_2O)_4[\eta^2\text{-}B_6O_7(OH)_6]$,[26] $Mg(H_2O)_3[\eta^3\text{-}B_6O_7(OH)_6]$,[12] and $Zn[\eta^3\text{-}B_6O_7(OH)_6]_2$.[27] The heptaborate anion in **1** can be regarded as the result of condensation of **7** with $B(OH)_3$, the product having a BOH group bridging two of these hydroxy groups. This results in a tetracyclic system having four fused $(BO)_3$ rings.

One might expect strain in the highly fused ring system of the heptaborate anion in **1**. However, analyses of bond angles and ring geometries indicate that these rings are not significantly distorted compared with the rings of commonly encountered borate anions. The six-membered $(BO)_3$ ring is abundantly found in borate chemistry, and rings of this type formed by corner sharing between two BO_4 tetrahedra and one BO_3 triangle (3:□2Δ) are encountered most frequently as a structural motif. This arrangement, typically having an envelope conformation of the ring atoms, has less ring strain than other arrangements.[28] The heptaborate anion in **1** consists of four such rings, connected in such a way that each ring is not greatly distorted from geometries found in more familiar borate structures, such as **4** and **7**.

Each six-membered ring in the heptaborate anion in **1** exhibits an envelope conformation with the central shared three-coordinate oxygen atom [O(1)] displaced from the average plane of the ring. The non-hydrogen atoms of the anion can be described by a set of seven intersecting average planes. Three inner planes (or envelope flaps) are each defined by two four-coordinate boron atoms and the central oxygen atom O(1). Four outer average planes are described by the normals to each six-membered ring excluding O(1) (see Scheme 2). Some atoms describing the average outer planes are dislocated slightly from these average planes. Two rings share a central plane [B(2), O(1), and B(4)] and display larger angles with the outer planes than the other two rings. Table 4 summarizes geometries of these rings.

A related diamine heptaborate, $[H_3N(CH_2)_6NH_3][B_7O_{10}(OH)_3]$, was recently reported.[29] This compound consists of extended 2-D layers of heptaborate FBBs **13**, shown in Figure 7, composed of hexaborate moieties elaborated with pendant $B(OH)_2$ groups, with interstitial $H_3N(CH_2)_6NH_3^{2+}$ cations. This compound was reported to form in the reaction of 1,6-diaminohexane with 3.8 mol equiv of boric acid under solvothermal conditions (150 °C, 5 days) in ethanol.[29] These
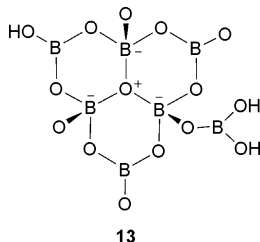
13

Figure 7. Borate FBB in [H₃N(CH₂)₆NH₃][B₇O₁₀(OH)₃].

conditions typically favor the formation of more condensed borate phases that often exhibit 2-D or 3-D extended structures. This reaction is similar to that which produces **1**, but the use of 1,6-diamine and different conditions results in intercluster rather than intracluster condensation, making the bridgeable hydroxy groups unavailable to participate in further cyclization.

Methods for estimating the basicity of borate anions have been described.[24] The average basicity of the $B_7O_9(OH)_5^{2-}$ anion (AB = 0.214) is considerably higher than that of the pentaborate, $B_5O_6(OH)_4^-$ anion (AB = 0.180), which is frequently encountered with nonmetal cations, including those derived from diamines.[18] However, heptaborate anion

in **1** is less basic than the tetraborate anion (AB = 0.311), which is sometimes encountered in nonmetal borates.[5]

Conclusions

The formation of compounds containing polyborate anions via reactions of boric acid with Brønsted bases is a general reaction. The specific polyborate anion formed and the degree of condensation are functions of solvation, temperature, and relative concentrations of boric acid and base. In the case of amine bases, it is apparent that the intrinsic basicity, size, shape, and hydrogen-bonding capabilities of the resulting conjugate acid cation also play important roles. The use of nonmetal bases permits control of these parameters. The formation of the heptaborate anion in **1**, instead of other potential polyborate anions, including more condensed phases or B−N bond-containing products of types **10** and **11**, found in reaction products of other diamines under similar conditions, apparently results from the specific characteristics of the $H_3N(CH_2)_7NH_3^{2+}$ cation.

Crystallographic data for the crystal structure reported in this paper have been deposited with the Cambridge Crystallographic Database (CCDC No. 683747). This material can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K.; fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

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