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Crystalline Alcoholamine Borates and the Triborate Monoanion

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The triborate and pentaborate compounds 3-hydroxy-2,2-dimethylpropylammonium triborate(1+), $[HOCH_2C(CH_3)_2NH_3][B_3O_3(OH)_4]$ (**1**), and 2-hydroxyethylammonium pentaborate(1−), $[HOCH_2CH_2NH_3][B_5O_6(OH)_4]\cdot H_2O$ (**2**), were prepared by crystallization from concentrated aqueous boric acid solutions containing the respective alcoholamines at a boric acid−alcoholamine mole ratio of 3.33:1.00. Compound **1** crystallized in the triclinic space group $P\bar{1}$ with $a = 5.9595(9)$ Å, $b = 6.3024(9)$ Å, $c = 15.594(2)$ Å, $\alpha = 91.218(2)°$, $\beta = 91.138(2)°$, $\gamma = 118.034(2)°$, $V = 516.56(13)$ Å^3, and $Z = 2$; **2** crystallized in the monoclinic space group $P2_1/n$ with $a = 11.2469(8)$ Å, $b = 9.5091(6)$ Å, $c = 11.5422(8)$ Å, $\beta = 90.175(1)°$, $V = 1234.41(15)$ Å^3, and $Z = 4$. Compound **1** contains a rare example of a structurally characterized hydroxyl-hydrated triborate monoanion. Comparisons are made with other known examples of this anion.

Introduction

Alcoholamine borate solutions have many commercial applications, especially in industrial fluids and agricultural products. As components of lubricants, metal-working fluids, and hydraulic fluids, borates may serve as buffers, corrosion inhibitors, lubricants, or biostats.[1] As a necessary element for plant life, boron is an important agricultural micronutrient, and boric acid dissolved in solvents such as monoethanolamine−water are used as liquid fertilizer concentrates.[1–3] In the latter case, the alcoholamine serves primarily to solubilize boric acid, which has limited solubility in pure water. In fact, alcoholamines and glycols are among the most effective solubilizers for borates. Concentrated borate solutions are also used as fire-retardant treatments for cellulosic materials and as wood preservatives.

Although dilute aqueous borate solutions contain $B(OH)_3$ and $B(OH)_4^-$ as the only significant boron species, concentrated borate solutions also contain significant amounts of polyborate anions, most notably $B_5O_6(OH)_4^-$, $B_3O_3(OH)_4^-$, $B_4O_5(OH)_4^{2-}$, and $B_3O_3(OH)_5^{2-}$.[4–6] These anions are listed in order of increasing basicity and have population distributions dependent upon the boron concentration, pH, and temperature. Mineral and synthetic crystalline salts of these anions are numerous with the exception of the triborate monoanion, $B_3O_3(OH)_4^-$, for which structurally characterized examples are rare. Here we describe the structure and some properties of a crystalline alcoholamine borate containing the triborate monoanion and of another new crystalline alcoholamine borate containing the pentaborate anion.

Experimental Section

$[HOCH_2C(CH_3)_2NH_3][B_3O_3(OH)_4]$ (1). This compound was found to be difficult to crystallize. Initial seed material for further preparation of **1** was obtained by subjecting an aqueous solution containing 50 wt % boric acid and 24 wt % 2-amino-2-methylpropanol (AMP) to temperature cycles between −25 °C and room temperature, whereupon a white microcrystalline mass formed on the bottom of the container after several repetitions. Dispersing a small amount of **1** obtained in this fashion into solutions of the same composition resulted in the precipitation of more **1** within a few hours. The precipitated solid was separated from the mother liquor by filtration, washed with methanol, and air-dried to give a

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Table 1. Crystallographic Data and Structure Refinement Parameters for **1** and **2**

compound	**1**	**2**
empirical formula	$C_4H_{16}B_3NO_8$	$C_2H_{14}B_5NO_{12}$
fw	238.61	298.19
temperature (K)	298(2)	298(2)
wavelength (Å)	0.71073	0.71073
cryst syst	triclinic	monoclinic
space group	$P\bar{1}$	$P2(1)/c$
unit cell dimensions:		
a (Å)	5.9595(9)	11.2469(8)
b (Å)	6.3024(9)	9.5091(6)
c (Å)	15.594(2)	11.5422(8)
α (deg)	91.218(2)	90
β (deg)	91.138(2)	90.1750(10)
γ (deg)	118.034(2)	90
V (Å^3), Z	516.56(13), 2	1,234.41(15), 4
D_{calcd} (g/cm^3)	1.534	1.605
abs coeff (mm^{-1})	0.138	0.154
$F(000)$	252	616
cryst size (mm)	0.50 × 0.30 × 0.20	0.50 × 0.45 × 0.10
data collection θ range (deg)	2.61−28.28	1.81−28.30
limiting indices	$-7 \le h \le 7, -8 \le k \le 8, -20 \le l \le 20$	$-14 \le h \le 14, -12 \le k \le 12, -14 \le l \le 15$
reflns collected/unique	4533/2393 [$R_{\mathrm{int}} = 0.0144$]	108 39/3000 [$R_{\mathrm{int}} = 0.0190$]
completeness to $\theta_{\max}$ (%)	93.5	97.9
abs correction	SADABS	SADABS
refinement method	full-matrix least squares on F^2	full-matrix least squares on F^2
data/restraints/param	2393/0/194	3000/0/213
GOF on F^2	1.016	0.694
final R indices [$I > 2\sigma(I)$]	R1 = 0.0397, wR2 = 0.1198	R1 = 0.0307, wR2 = 0.0852
R indices (all data)	R1 = 0.0412, wR2 = 0.1209	R1 = 0.0352, wR2 = 0.0914
extinction coeff	0.008(7)	0.0033(13)
largest diff peak, hole (e/Å^3)	0.387, −0.201	0.210, −0.238

white microcrystalline product. Anal. Calcd for $C_4H_{16}B_3NO_8$: C, 20.14; H, 6.76; N, 5.87; B, 13.59. Found: C, 20.10; H, 6.69; N, 5.80; B, 13.43.

$[HO(CH_2)_2NH_3][B_5O_6(OH)_4]\cdot H_2O$ (2). Precipitation of **2** from an aqueous solution containing 60 wt % boric acid and 19.8 wt % 2-aminoethanol was accomplished by layering the viscous solution with methanol in an evaporating dish. The resulting crystals were washed with methanol and air-dried. Dispersal of seed crystals of **2** into supersaturated solutions of boric acid in 2-aminoethanol–water sometimes resulted in the precipitation of more **2**, but less reliably than with **1**. Anal. Calcd for $C_2H_{14}B_5NO_{12}$: C, 8.06; H, 4.73; N, 4.69; B, 18.13. Found: C, 8.20; H, 4.68; N, 4.74; B, 18.00.

X-ray Data Collection and Structure Determinations. For each compound, a colorless cut parallelepiped was mounted on a glass fiber and data were collected at 25 °C on a Bruker SMART 1000 CCD diffractometer using Mo Kα radiation. Unit cell parameters were determined from a least-squares fit of 3821 reflections ($5.23° < 2\theta < 56.56°$) for **1** and 6656 reflections ($5.55° < 2\theta < 56.51°$) for **2**. These dimensions and other parameters of the data collection are summarized in Table 1. Of 2393 unique reflections measured for **1**, 2270 were considered to be observed [$I > 2\sigma(I)$], but all reflections were used in the subsequent structure analysis. Of 3000 unique reflections measured for **2**, 2654 were considered to be observed [$F_o > 4\sigma(F_o)$], but all reflections were used in the structure analysis. Data for both compounds were corrected for Lorentz and polarization effects and for absorption and extinction, and the structures were solved by statistical methods. Programs used in this work are those supplied with the Bruker SMART CCD diffractometer. In each case, atoms were located by use of statistical methods. All non-hydrogen atoms were included with anisotropic displacement parameters. For **1**, position parameters for all hydrogen atoms were refined. Isotropic displacement parameters for hydrogen atoms were based on values for attached atoms. For **2**, hydrogen atoms bound to carbon were placed in calculated positions and position parameters for all other hydrogen atoms were refined. Also for **2**, isotropic displacement parameters for hydrogen atoms were also based on values for attached atoms. Scattering factors for hydrogen were obtained from Stewart et al.[7] and for other atoms were taken from *The International Tables for X-ray Crystallography*.[8]

Results and Discussion

The alcoholamine−boric acid–water system is complex. Because of the weak acidity of boric acid and the basicity of alcoholamines, these reagents react in aqueous media to produce equilibrium mixtures containing both protonated and free base alcoholamine together with the various polyborate anions appropriate for the pH and concentration, where pH is largely a function of the basicity of the specific alcoholamine and the boric acid−alcoholamine mole ratio. Boric acid also forms esters with alcoholamine hydroxyl groups and to an increasing extent with decreasing water concentration. These borate esters are labile in the presence of water and exist in rapid equilibrium with the nonesterified alcoholamine and borate species.

Even at high levels of supersaturation, many alcoholamine−boric acid–water solutions are very stable and may be stored for years without phase separation. However, we found that certain alcoholamine−boric acid solutions containing a significant excess of boric acid can be induced to precipitate crystalline alcoholammonium borate salts. Here we describe the preparation and structural characterization of two examples of such compounds, one derived from AMP and another from 2-aminoethanol.

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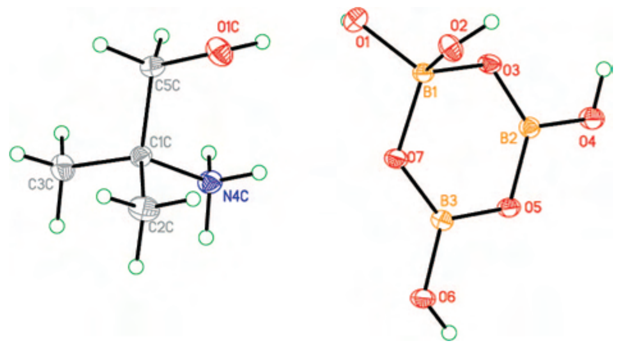
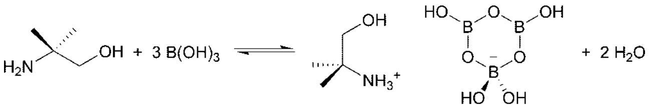


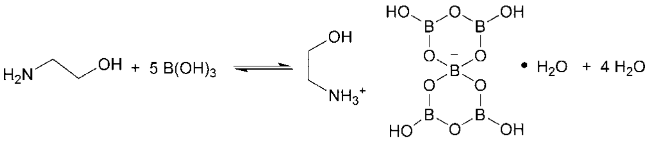
Figure 1. Structure of **1**.

We found that the product obtained from a concentrated aqueous boric acid−AMP solution at a 3.33:1 mole ratio was an unusual triborate of composition $[HOCH_2C(CH_3)_2NH_3][B_3O_3(OH)_4]$ (**1**), formed according to eq 1. However, the corresponding 3.33:1 mole ratio of the boric acid−2-aminoethanol solution instead yielded a pentaborate of composition $[HO(CH_2)_2NH_3][B_5O_6(OH)_4]\cdot H_2O$ (**2**), formed according to eq 2.



1

(1)



2

(2)

Crystal Structures. The asymmetric unit in **1** contains a $HOCH_2C(CH_3)_2NH_3^+$ cation paired with a $[B_3O_3(OH)_4]^-$ anion, as shown in Figure 1. Selected interatomic distances and angles for **1** are listed in Table 2.

As with all hydroxy-hydrated borates, hydrogen bonding is an important feature of **1**, as is partially shown in Figure 2 and listed completely in Table 3.

All four anion hydroxyl hydrogen atoms are involved in hydrogen bonds directed to oxygen atoms in four different surrounding anions, two to hydroxyl oxygen atoms, and two to $(BO)_3$ ring oxygen atoms. Six of the seven anion oxygen atoms are involved in hydrogen bonding. These are with hydroxyl hydrogen atoms of four different anions, one with the cation hydroxyl hydrogen atom, and three with the cation ammonium hydrogen atoms of three different cations. Cation ammonium hydrogen atoms link the nitrogen atom with oxygen atoms of three different anions, two hydroxyl oxygen atoms, and one $(BO)_3$ ring oxygen atom. The cation hydroxyl hydrogen atom is hydrogen bonded to one anion hydroxyl oxygen atom attached to the tetrahedral boron atom.

Table 2. Selected Interatomic Distances (Å) and Angles (deg) for **1**

B1−O2	1.447(2)
B1−O1	1.467(2)
B1−O7	1.480(2)
B1−O3	1.495(2)
B2−O3	1.346(2)
B2−O4	1.362(2)
B2−O5	1.399(2)
B3−O6	1.376(2)
B3−O5	1.392(2)
O2−B1−O1	108.30(13)
O2−B1−O7	108.67(13)
O1−B1−O7	110.21(13)
O2−B1−O3	111.17(13)
O1−B1−O3	108.26(13)
O7−B1−O3	110.20(12)
O3−B2−O4	123.03(15)
O3−B2−O5	120.73(14)
O4−B2−O5	116.24(14)
O7−B3−O6	118.57(15)
O7−B3−O5	122.55(14)
O6−B3−O5	118.88(15)
B2−O3−B1	123.65(12)
B3−O5−B2	118.34(13)
B3−O7−B1	121.87(13)

Typical of such rings, the $(BO)_3$ ring in **1** deviates significantly from planarity and exhibits a half-chair conformation. The four-coordinate boron atom (B1) and ring oxygen atom O7 are displaced 0.096(1) and 0.097(1) Å, respectively, from the plane passing through the six ring atoms and lie on opposite sides of this plane. The four-coordinate boron atom lies 0.206(2) Å from the plane passing through the three oxygen atoms of the ring. Bond angles about this boron atom are in the 108.3(1)–111.2(1)° range. Bond angles about B2 and B3 are in the 116.2(1)–120.7(1)° and 118.6(2)–122.6(1)° ranges, respectively.

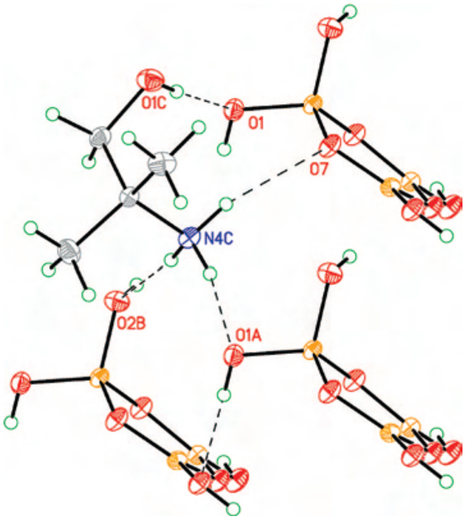


Figure 2. Partial details of cation–anion hydrogen bonding in **1**.

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)	∠DHA	*d*(D···A)
O1−H1···O6#1	0.83(3)	2.07(3)	171(2)	2.9004(18)
O2−H2···O6#2	0.80(3)	2.03(3)	171(2)	2.8140(18)
O4−H4···O3#3	0.84(3)	1.93(3)	175(2)	2.7690(17)
O6−H6···O5#4	0.78(3)	2.03(3)	169(2)	2.8030(17)
N4C−H4C1···O7	0.94(3)	2.34(3)	165(2)	3.260(2)
N4C−H4C2···O1#5	0.93(3)	1.98(3)	169(2)	2.900(2)
N4C−H4C3···O2#6	0.91(3)	1.90(3)	170(2)	2.808(2)
O1C−H1C···O1	0.89(3)	1.86(3)	176(3)	2.7515(19)

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

Table 4. Selected Interatomic Distances (Å) and Angles (deg) for **2**

B1−O1C	1.4709(12)
B1−O1A	1.4711(12)
B1−O1B	1.4712(13)
B1−O1D	1.4791(13)
O1A−B2B	1.3485(13)
O1B−B2A	1.3455(12)
O1C−B2C	1.3553(13)
O1D−B2D	1.3546(13)
B2A−O2D	1.3609(13)
B2A−O3A	1.3885(13)
B2B−O2A	1.3567(13)
B2B−O3A	1.3887(13)
B2C−O2B	1.3515(13)
B2C−O3B	1.3830(13)
B2D−O2C	1.3613(13)
B2D−O3B	1.3736(13)
O1−C2	1.4209(15)
C2−C3	1.5020(16)
C3−N4	1.4804(16)
O1C−B1−O1A	109.41(8)
O1C−B1−O1B	108.51(8)
O1A−B1−O1B	110.91(8)
O1C−B1−O1D	111.19(8)
O1A−B1−O1D	108.15(8)
O1B−B1−O1D	108.69(8)
B2B−O1A−B1	123.37(8)
B2A−O1B−B1	122.98(8)
B2C−O1C−B1	123.09(8)
B2D−O1D−B1	123.53(8)
O1B−B2A−O2D	124.29(9)
O1B−B2A−O3A	121.50(9)
O2D−B2A−O3A	114.21(9)
O1A−B2B−O2A	119.77(9)
O1A−B2B−O3A	121.46(9)
O2A−B2B−O3A	118.75(9)
O2B−B2C−O1C	124.59(9)
O2B−B2C−O3B	114.02(9)
O1C−B2C−O3B	121.38(9)
O1D−B2D−O2C	119.81(9)
O1D−B2D−O3B	120.95(9)
O2C−B2D−O3B	119.23(9)
B2A−O3A−B2B	118.47(8)
B2D−O3B−B2C	119.75(8)
O1−C2−C3	109.18(9)
N4−C3−C2	110.89(9)

Table 5. Specified Hydrogen Bonds for **2** [Å and deg (esds)][a]

D−H···A	d(D−H)	d(H···A)	d(D···A)	∠DHA
O2A−H2A···O1S	0.817(18)	1.881(18)	2.6930(12)	172.5(18)
O2B−H2B···O2A#1	0.881(17)	1.822(17)	2.6711(11)	161.1(15)
O2C−H2C···O1	0.856(15)	1.812(16)	2.6675(11)	177.0(14)
O2D−H2D···O2C#2	0.836(16)	2.155(16)	2.9223(11)	152.7(14)
O1−H1···O1D#3	0.851(17)	1.871(17)	2.7161(11)	172.4(16)
N4−H41···O1S#4	0.862(17)	2.301(16)	2.9602(15)	133.5(13)
N4−H41···O3B	0.862(17)	2.536(16)	3.0464(12)	118.8(12)
N4−H42···O3A#4	0.918(16)	2.072(16)	2.9679(12)	164.9(13)
N4−H43···O1B#5	0.813(18)	2.305(17)	2.9991(13)	143.8(14)
N4−H43···O2B	0.813(18)	2.618(15)	3.0795(13)	117.6(13)
O1S−H1S1···O1C#6	0.834(17)	2.004(17)	2.8367(11)	176.3(16)
O1S−H1S2···O1A#7	0.906(17)	1.976(17)	2.8819(12)	179.1(14)

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

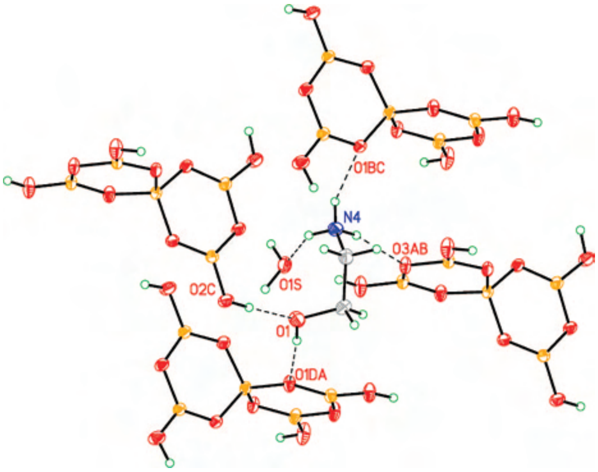


Figure 3. View of the structure of **2** showing partial details of hydrogen bonding.

The asymmetric unit in **2** contains one $HO(CH_2)_2NH_3^+$ cation, one $[B_5O_6(OH)_5]^-$ anion, and one water molecule. Selected interatomic distances and angles are listed in Table 4. The pentaborate anion can be viewed as two triborate monoanions sharing one tetrahedral boron atom. One of the six-membered $(BO)_3$ rings in the pentaborate anion in **2** deviates more from planarity than does the other. This ring exhibits a slightly twisted envelope conformation, with the tetrahedral boron atom lying 0.1285 Å from the plane passing through the three ring oxygen atoms and 0.0600 Å from the least-squares plane of six ring atoms. This tetrahedral boron atom lies only 0.0360 Å from the plane passing through the three oxygen atoms of the second $(BO)_3$ ring of which it is a member and 0.0168 Å from the least-squares plane of this ring. Many pentaborate anions have been structurally characterized, and the anion in **2** is fairly typical of other previously described examples.[9]

Details of hydrogen bonding in **2** are listed in Table 5. All four hydrogen atoms of the pentaborate anion are involved in hydrogen bonding, one to the water oxygen atom, two to hydroxyl oxygen atoms of two different anions, and one to the cation hydroxyl oxygen atom. All four anion oxygen atoms adjacent to the central four-coordinate boron atom participate in hydrogen bonding, one with the cation hydroxyl hydrogen atom, two with hydrogen atoms of two different water molecules, and one with an amine hydrogen atom. Three of the four anion hydroxyl oxygen atoms participate in hydrogen bonding, two with anion hydroxyl hydrogen atoms of two different anions and one with an amine hydrogen atom. Both of the anion distal oxygen atoms participate in hydrogen bonding with amine hydrogen atoms of two different cations. Details of anion−cation hydrogen bonding are shown in Figure 3. All three amine hydrogen atoms participate in a total of five hydrogen bonds, one with a water oxygen atom, two with the anion distal oxygen atoms of different anions, one with an anion hydroxyl oxygen atom, and one with an anion oxygen atom adjacent to the tetrahedral boron atom. Two of these are bifurcated bonds, one involving both water and an anion distal oxygen atom and another involving an anion hydroxyl oxygen atom and an oxygen atom adjacent to the tetrahedral boron atom. The cation oxygen atom participates in hydrogen bonding with an anion hydroxyl hydrogen atom. The water oxygen atom is linked via two hydrogen bonds with amine and anion hydroxyl hydrogen atoms. The two hydrogen atoms of the

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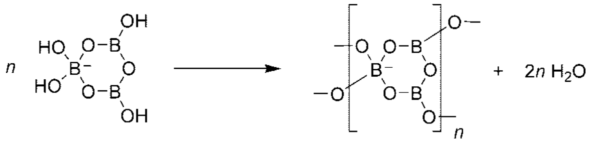
(9) Visi, M. Z.; Knobler, C. B.; Owen, J. J.; Khan, M. I.; Schubert, D. M. *Crystal Growth Des.* **2006**, *6*, 538–545.

water molecule are linked to anion oxygen atoms adjacent to the tetrahedral boron of two different anions.

Thermal Properties. Thermogravimetric analysis of **1** shows decomposition with release of approximately 2 mol equiv of water in the 105–120 °C range, a process accompanied by melting to a viscous liquid. Because **1** contains no interstitial water, this water loss results either from further condensation of the triborate anion, for example, eq 3, or from an esterification reaction between the anion and cation.



(3)

Compound **2** exhibits weight loss of about 16% in the 110–170 °C range, corresponding to the loss of 5 mol equiv of water. This includes both interstitial water and water resulting from condensation of hydroxyl groups. Gradual weight loss continues to about 400 °C, at which point the viscous char begins to darken and puff, apparently as a result of ethanolamine pyrolysis.

Solubility. Solubility measurements for compounds that readily form supersaturated solutions are difficult. In order to estimate the water solubility of **1**, a precipitation approach was used. Although supersaturated solutions of **1** are very stable, seeding these solutions with small amounts of crystalline **1** reproducibly initiates precipitation of more **1**. By seeding aqueous solutions containing different concentrations of boric acid and AMP at a 3.33:1 mole ratio, respectively, it was found that 41 g of **1** dissolves in 59 g of water at room temperature. This corresponds to an equivalent boric acid concentration of about 32 wt % for a saturated solution of **1**. Compound **2** appears to have higher water solubility than **1**. However, because **2** could not be reliably precipitated by seeding, its solubility could not be accurately measured.

The pentaborate monoanion $B_5O_6(OH)_4^-$ is frequently encountered in borate compounds involving a wide range of cations. With nonmetal cations, borate compounds other than pentaborates are often difficult to crystallize under mild conditions. Although the $B_3O_3(OH)_4^-$ anion is thought to be abundantly present in concentrated aqueous borate solutions in the intermediate pH range, this anion is rarely observed in solid-state compounds.[4–6] We are aware of only two other structurally characterized examples of this isolated anion and of no previous examples containing nonmetal cations. These are found in the mineral ameghinite, $NaB_3O_3(OH)_4$,[10] and the synthetic borate $KB_3O_3(OH)_4$.[11] The structure of the $B_3O_5(OH)_2^{3-}$ anion, related by formal deprotonation of the $B_3O_3(OH)_4^-$ anion, was also reported.[12] The fundamental building block of the triborate monoanion, denoted 3:2△1□ in the notation of Burns et al.,[13] is found in some anhydrous borates and notably as part of extended networks in so-called enneaborates, such as CsB_9O_{14} ($Cs_2O \cdot 9B_2O_3$).[14] Nevertheless, the isolated $B_3O_3(OH)_5^{2-}$ triborate dianions, having a six-membered $(BO)_3$ ring containing one trigonal and two tetrahedral boron atoms, is encountered far more frequently in both mineral and synthetic borates. This is also true of condensed cage, chain, and sheet borates, where the 3:1△2□ fundamental building block is the most common structure motif found in borate chemistry.[15]

Many borate compounds exhibit incongruent solubility behavior, wherein the composition of the mother liquid differs from the solid borate with which it is in equilibrium. Thus, even when a solution possesses the composition of a particular crystalline borate salt, the borate that crystallizes often has a different composition. This is usually the case for solutions having the cation-to-boron mole ratio corresponding to the triborate monoanion. Such solutions generally yield salts of either the pentaborate monoanion or the tetraborate anion, $B_4O_5(OH)_4^{2-}$, rather than the triborate monoanion. As suggested by Salentine, this may be because salts of the triborate monoanion are generally more soluble than those of the pentaborate and tetraborate anions.[11] Salentine used a solid-state method to prepare $KB_3O_3(OH)_4$, allowing a mixture of solid potassium pentaborate and tetraborate to react under high humidity conditions, and reported that this compound could not be crystallized from aqueous solution.[11] This suggests that $KB_3O_3(OH)_4$ may be thermodynamically favored but is more soluble in water than the corresponding tetraborate and pentaborate.

The few available structurally characterized examples of the $B_3O_3(OH)_4^-$ anion show a range of $(BO)_3$ ring geometries. In the mineral ameghinite, the $(BO)_3$ ring has an envelope shape, with the tetrahedral boron lying 0.315 Å from the plane of the three oxygen atoms and 0.146 Å from the least-squares plane of the six ring atoms. The $(BO)_3$ ring of the anion in $KB_3O_3(OH)_4 \cdot H_2O$ is also envelope-shaped but is much more planar than the ring in ameghinite, with the four-coordinate boron atom lying 0.062 Å from the plane of the three oxygen atoms and only 0.036 Å from the least-squares plane of the six ring atoms. The triborate anion in **1** presents a twisted (reverse chair) conformation in which the four-coordinate boron atom and an adjacent oxygen atom (O7) lie above and below the least-squares plane of the $(BO)_3$ ring by 0.096(1) and 0.097(1) Å, respectively. The four-coordinate boron atom is displaced 0.206 Å from the plane defined by the three ring oxygen atoms. This ring is more planar than the one in ameghinite and less planar than that in $KB_3O_3(OH)_4$.

The triborate monoanion moiety may occur in other more complex borate structures. For example, we recently de-

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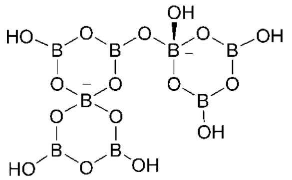


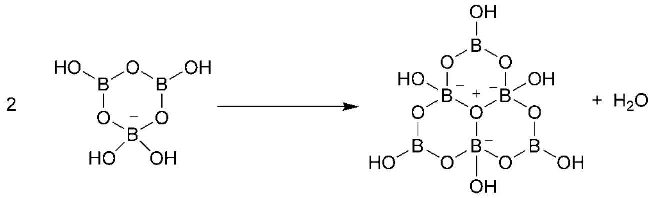
3

Figure 4. Octaborate dianion $B_8O_{10}(OH)_6^{2-}$ (**3**).

scribed the synthesis and structure of the borate $[H_3N(CH_2)_7NH_3][B_8O_{10}(OH)_6]\cdot 2B(OH)_3$, which contains the unusual octaborate dianion, **3**, shown in Figure 4.[9]

This anion contains an appended triborate monoanion moiety ring. This triborate ring displays an envelope conformation, with the tetrahedral boron atom lying 0.1862 Å from the plane of three ring oxygen atoms and 0.0868 Å from the least-squares plane of six ring atoms.

There is a relationship between the triborate monoanion and other anions containing multiples of three boron atoms. The triborate anion belongs to a system including the hexaborate anion, $B_6O_7(OH)_6^{2-}$ (**4**), found in the minerals aksaite, mcallisterite, and rivadavite,[16–19] and the nonaborate anion, $B_9O_{12}(OH)_6^{3-}$ (**5**), found in certain synthetic borates.[20] These anions are related by the formal condensation of water, as represented in eqs 4 and 5. Thus, compounds containing



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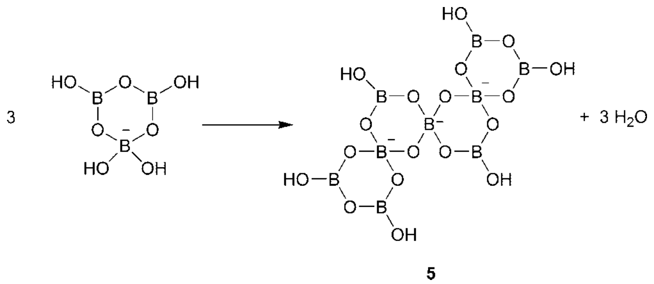
(4)



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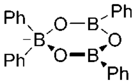
(5)

the triborate monoanion, hexaborate dianion (**4**), and nonaborate trianion (**5**), a monocation, M^+, and no interstitial water have compositions $M_2O\cdot 3B_2O_3\cdot 4H_2O$, $M_2O\cdot 3B_2O_3\cdot 3H_2O$, and $M_2O\cdot 3B_2O_3\cdot 2H_2O$, respective.

Several examples of organically substituted analogues of the triborate monoanion are found in the literature, each containing $(BO)_3$ rings of the 3:□2Δ type. For example, the $Ph_4B_3O_3^-$ anion (**6**) is found in $[Me_4N][Ph_4B_3O_3]$,[21] $[Me_3N(CH_2)_2OH][Ph_4B_3O_3]$,[22] and $\{[(t\text{-}Bu)_3PAu]_4P\}[Ph_4B_3O_3]$,[23] and the $Ph_3B_3O_3(OH)^-$ anion (**7**) is found in $[Et_3NH][Ph_3B_3O_3(OH)]$.[22] The rings of these anions also typically deviate from planarity, exhibiting envelope or twisted-envelope conformations. For example, the ring of anion **6** in $[Me_3N(CH_2)_2OH][Ph_4B_3O_3]$ exhibits a twisted-envelope shape, with the four-coordinate boron atom lying 0.435 Å from the plane of the ring oxygen atoms. The same anion in $[Me_4N][Ph_4B_3O_3]$ has a flatter envelope conformation with one oxygen atom displaced from the plane of the ring. The anion in $\{[(t\text{-}Bu)_3PAu]_4P\}[Ph_4B_3O_3]$ is planar within experimental error.[23] However, because of the presence of heavy atoms in the cation of this compound, estimated standard deviation values for the ring atom positions are large enough that some deviation from planarity cannot be ruled out. Anion **7** exhibits a 0.334 Å displacement of one three-coordinate boron atom from the plane of the ring oxygen atoms.



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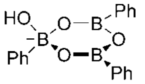

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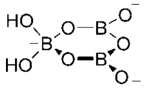

8

The related $B_3O_5(OH)_2^{3-}$ (**8**) anion, structurally characterized in the synthetic borate $Na_3B_3O_5(OH)_2$, presents an unusual example of a partially hydrated borate moiety representing the Brønsted conjugate base of the protonated $B_3O_3(OH)_4^-$ anion.[12] The trianion **8** is structurally similar to the $B_3O_3(OH)_4^-$ anion, but the two trigonal boron atoms each possess a terminal exocyclic oxygen atom without attached hydrogen atoms, in violation of Christ's original third rule, stating that each borate terminal oxygen atom should have an attached hydrogen atom.[24] However, this rule was later modified to accommodate borate structures that are not fully hydrated, such as **8**.[25] In this case, the $(BO)_3$ ring is planar, with all six ring atoms and the two terminal oxygen atoms lying on a crystallographically required mirror plane that relates the two hydroxyl oxygen atoms. The two B−O distances involving trigonal boron and unprotonated oxygen atoms are significantly shorter than those found in the protonated analogue in **1** (1.318 and 1.333 Å versus 1.362 and 1.376 Å for the corresponding B−O distances in **1**), with the longer of these bonds associated with an oxygen atom that accepts a hydrogen bond.

It is notable that the few structurally characterized examples of the triborate anion monoanion involve cations

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having relatively low Lewis acidity, Na^+ and K^+. Schindler and Hawthorne showed that, for borate minerals, there is a correlation between borate anion average basicity (AB) and cation Lewis acidity and described a method of estimating the AB value of borate anions.[26] Although this correlation appears to hold only loosely for synthetic borates, it does describe a general trend. The AB value of the $B_3O_3(OH)_4^-$ anion (0.257) is considerably higher than that of the pentaborate, $B_5O_6(OH)_4^-$, anion (0.180). The pentaborate anion is frequently encountered in the presence of relatively large nonmetal cations, wherein the Lewis acid and base properties of cation and anion are better matched than with other isolated borate anions. The formation of the more basic triborate monoanion in **1** with the $[AMPH]^+$ cation is anomalous. However, the tetraborate anion, $B_4O_5(OH)_4^{2-}$, with still higher AB (0.311), is occasionally encountered in synthetic crystalline compounds together with relatively large nonmetal cations. For example, the synthetic crystalline ethylenediammonium tetraborate, $[H_3N(CH_2)_2NH_3][B_4O_5(OH)_4]$, was structurally characterized.[27]

Finally, it can be noted that, although alcoholamines and borates are used together in many commercial industrial fluids, such as lubricants, anticorrosives, and metal-working fluids, these products typically contain a molar excess of alcoholamine. Even when boric acid is present in molar excess in solutions with alcoholamines, a number of borate species exist in rapid equilibrium.[5,6] Thus, the crystalline compounds described herein do not occur in these systems and have no regulatory significance in the context of these commercial products.

Crystallographic data for the crystal structures reported in this paper have been deposited with the Cambridge Crystallographic Database (CCDC Nos. 676 453 and 676 454). 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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