Guanidinium and Imidazolium Borates Containing the First Examples of an Isolated Nonaborate Oxoanion: $[B_9O_{12}(OH)_6]^{3-}$

David M. Schubert,*,[1a] Mandana Z. Visi,[1a] and Carolyn B. Knobler[1b]

U.S. Borax Inc., 26877 Tourney Road, Valencia, California, 91355-1847

Borate compounds in which boron is bound only to oxygen have considerable mineralogical and industrial importance. These contain anionic components composed of BO_3 and BO_4 groups that may link together by sharing oxygen atoms to form isolated rings and cages or polymerize into infinite chains, sheets, and networks. Many examples of isolated boron oxoanions containing one to six borons exist in mineral and synthetic borates. However, isolated boron oxoanions having more than six borons are rare and no previous examples have nine borons.[2] This communication describes the synthesis and structural characterization of crystalline guanidinium and imidazolium borates, $[C(NH_2)_3]_3[B_9O_{12}(OH)_6]$ (**I**) and $[C_3H_5N_2]_3[B_9O_{12}(OH)_6]$ (**II**), containing the first examples of the isolated nonaborate anion, $[B_9O_{12}(OH)_6]^{3-}$. These borates have resolved oxide formulas $[C(NH_2)_3]_2O \cdot 3B_2O_3 \cdot 2H_2O$ and $[C_3H_5N_2]_2O \cdot 3B_2O_3 \cdot 2H_2O$.

Isolated boron oxoanions are found in the commercially significant metaborates ($[B(OH)_4]^-$), tetraborates ($[B_4O_5(OH)_4]^{2-}$), and pentaborates ($[B_5O_6(OH)_4]^-$), as well as in triborates ($[B_3O_3(OH)_4]^-$ and $[B_3O_3(OH)_5]^{2-}$).[3] Also, some mineral and synthetic borates contain the isolated hexaborate anion, $[B_6O_7(OH)_6]^{2-}$.[2] The mineral ammonioborite contains an unusual example of a large isolated anion, $[B_{15}O_{20}(OH)_8]^{3-}$.[2] Polyborate anions can be regarded as products of varying degrees of neutralization of orthoboric acid, $B(OH)_3$, with a strong base in relatively concentrated aqueous solution. The $[B_3O_3(OH)_4]^-$ and $[B_6O_7(OH)_6]^{2-}$ anions, as well as the $[B_9O_{12}(OH)_6]^{3-}$ anion described herein, can all be viewed as products of a $^1/_3$ neutralization with strong base of boric acid to $[B(OH)_4]^-$.

At least three crystalline binary guanidinium borates exist. Guanidinium tetraborate, $[C(NH_2)_3]_2[B_4O_5(OH)_4] \cdot 2H_2O$ (**III**), was reported as early as 1921,[4] and brief references are made to guanidinium pentaborates, including $[C(NH_2)_3][B_5O_6(OH)_4] \cdot 2H_2O$ (**IV**).[5] We have recently found that the novel guanidinium nonaborate **I** crystallizes in the $[C(NH_2)_3]_2O-B_2O_3$ aqueous system at temperatures above ca. 45 °C at $B_2O_3/[C(NH_2)_3]_2O$ mole ratios (defined as q) greater than ca. 2.5 over a range of concentrations. Tetraborate **III** crystallizes at lower temperatures or q values. At $q > 5$ either boric acid or guanidinium pentaborate **IV** crystallizes, depending on concentrations. Nonaborate **I** can be prepared by aqueous stoichiometric or near-stoichiometric

reaction of guanidinium carbonate with boric acid:[6]

$$18B(OH)_3 + 3[C(NH_2)_3]_2CO_3 \xrightarrow[H_2O]{>45 \,°C}$$
$$2[C(NH_2)_3]_3[B_9O_{12}(OH)_6] + 3CO_2 + 21H_2O \quad (1)$$
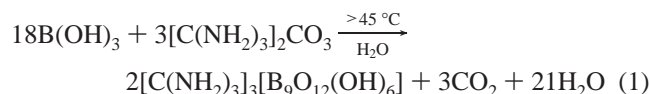
Alternatively, **I** can be prepared by reaction of guanidinium salts with borax and boric acid under appropriate conditions.[7] Nonaborate **I** exhibits temperature-dependent stability in water contact. At 20 °C, an aqueous slurry of **I** converts to tetraborate **III** and boric acid in about 1 day. At elevated temperatures, **I** is stable in aqueous slurry and can be recrystallized from water. Nonaborate **I** can also be prepared by aqueous reaction of tetraborate **III** with boric acid in hot water.[8]

We recently found that imidazolium nonaborate **II** crystallizes from aqueous mixtures of boric acid and imidazole between room temperature and 100 °C:[9]

$$9B(OH)_3 + 3C_3H_4N_2 \xrightarrow{H_2O}$$
$$[C_3H_5N_2]_3[B_9O_{12}(OH)_6] + 9H_2O \quad (2)$$
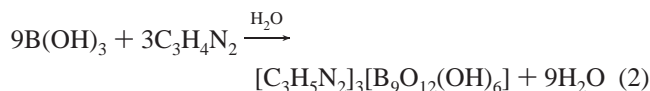
In contrast to **I**, nonaborate **II** is stable in contact with water at room temperature. The guanidine−borate and imidazole−borate systems contrast with the extensively studied ammonia−borate system, where ammonium tetraborate and pentaborate occur under comparable conditions under which **I** and **II** are formed.[5]

Single-crystal X-ray structures of **I** and **II** are shown in Figures 1 and 2.[10] The $[B_9O_{12}(OH)_6]^{3-}$ anion found in each consists of four B_3O_3 rings sharing three tetrahedral boron centers in a linear arrangement. The remaining six boron centers are trigonal with one attached hydroxyl group. The two inner B_3O_3 rings each contain one trigonal and two tetrahedral borons, and the two outer

* To whom correspondence should be addressed. Phone: (661)287-6074. Fax: (661)287-6014. E-mail: dave.schubert@borax.com.

(1) (a) U.S. Borax Inc. (b) McCullough Crystallographic Laboratory, Department of Chemistry and Biochemistry, University of California, Los Angeles.

(2) Grice, J. D.; Burns, P. C.; Hawthorne, F. C. *Can. Mineral.* **1999**, *37*, 731−762.

(3) The sodium salt of the tetraborate anion, known as borax pentahydrate ($Na_2[B_4O_5(OH)_4] \cdot 3H_2O = Na_2O \cdot 2B_2O_3 \cdot 5H_2O$), has by far the greatest industrial significance with annual world production in excess of one million metric tons.

(4) (a) Rosenheim, A.; Leyser, F. *Z. Anorg. Allg. Chem.* **1921**, *119*, 1−38. (b) Weakley, T. J. R. *Acta Crystallogr.* **1985**, *C41*, 377−379.

(5) Bowden, G. H. In *Supplement to Mellor's Comprehensive Treatise on Inorganic and Theoretical Chemistry, Volume V, Boron, Part A: Boron−Oxygen Compounds*; Longman Group Ltd.: London, 1980.

(6) To a solution of 360.3 g (2.0 mol) guanidinium carbonate in 1.00 L of water at 45 °C was added 742.0 g (12.0 mol) of boric acid. Mild effervescence occurred. The mixture was heated to 90 °C, maintained with stirring for 1 h, then cooled to 45 °C and filtered (pH 8.1). Product was washed with water and dried at 105 °C, giving 668.4 g (88% yield) white powder (**I**). Anal. Calcd: C, 6.30%; H, 4.27%; N, 22.06%; B, 17.02%. Found: C, 6.25%; H, 4.33%; N, 21.46%; B, 17.32%. Crystals precipitated from the filtrate upon standing (38 g), identified as guanidinium tetraborate, **II**, by XRD analysis.

(7) To a solution of 47.8 g (0.50 mol) guanidinium chloride in 225 mL of water at 40 °C was added 30.9 g (0.50 mol) of boric acid and 72.8 g (0.25 mol) of $Na_2B_4O_7 \cdot 5H_2O$. The mixture was heated to 90 °C, maintained with stirring for 1 h, then cooled to 45 °C and filtered (pH 8.2). The resulting powder was dried at 105 °C and identified as **I** by XRD and titration analysis.

(8) To 86.9 g (0.25 mol) of guanidinium tetraborate, **III**, in 225 mL of water at 40 °C was added 30.9 g (0.50 mol) of boric acid. The mixture was heated to 90 °C and maintained with stirring for 1 h, then cooled to 45 °C and filtered. The resulting product was dried at 105 °C and identified as **I** by XRD and titration analysis.

(9) To a solution of 70.0 g (1.0 mol) imidazole in 225 mL of water at 40 °C was added 185.5 g (3.0 mol) of boric acid. The mixture was heated to 90 °C and maintained with stirring for 1 h, cooled to 45 °C, and filtered (pH 7.8). The resulting white powder (**II**) was washed with water and dried at 105 °C. Anal. Calcd: C, 18.06%; H, 3.53%; N, 14.04%; B, 16.25%. Found: C, 18.13%; H, 3.49%; N, 14.12%; B, 16.67%.
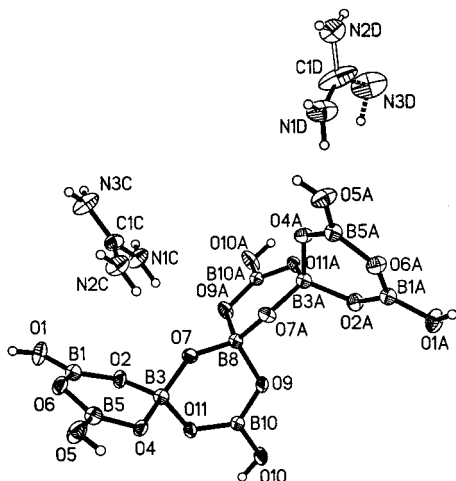
Figure 1. Structure of guanidinium nonaborate, **I**, drawn at 50% probability level. One of the three guanidinium cations, which has a 2-fold axis passing through the carbon atom causing a disorder, has been omitted.
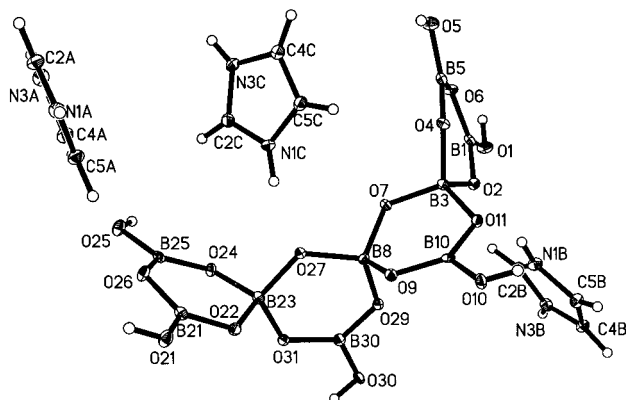

Figure 2. Structure of imidazolium nonaborate, **II**, drawn at 50% probability level.

rings each contain one tetrahedral and two trigonal borons. In **I**, there is a crystallographic 2-fold axis passing through the centermost boron atom (B8) relating halves of the anion. This 2-fold axis also passes through the carbon atom (CD) of one guanidinium cation, causing a disorder in this cation. The anion in **II** has no crystallographically required symmetry. The nonaborate anions **I** and **II** are stereochemically equivalent.

In the anion of **I**, the average B−O interatomic distances around tetrahedral and trigonal borons are 1.471 and 1.363 Å, respectively. The interatomic distance between tetrahedral boron centers, B3 and B8, is 2.548 Å. Extensive O−H···O and N−H···O hydrogen bonding involving all hydroxyl and guanidine hydrogens links anions and cations as well as adjacent anions. In **II**, the

average B−O distances around tetrahedral and trigonal borons are 1.480 and 1.370 Å, respectively. The interatomic distances between the tetrahedral boron centers B3 and B8 and B8 and B23 are 2.548(4) and 2.604(4) Å, respectively. Compound **II** also exhibits extensive hydrogen bonding linking adjacent anions as well as anions and cations. There is no significant difference between intracyclic and exocyclic B−O bond lengths in either **I** or **II**.

Polymeric borate structures can be described in terms of compact, insular groups, referred to as fundamental building blocks (FBB's), which form the basis of classification schemes for crystalline borates.[11,12] These schemes define FBB's by the number of boron atoms, the number of BO_3 and BO_4 groups, and the mode of polymerization between FBB's to give isolated, modified isolated, chain, modified chain, sheet, modified sheet, and network structures. By use of the classification scheme of Christ and Clark, the nonaborate anion in **I** and **II** is described as "9:6Δ + 3T, isolated", indicating an isolated B_9−FBB having six BO_3 and three BO_4 polyhedra.[11] However, this scheme cannot describe connectivity. The recent refinement of borate classification schemes proposed by Burns describes this anion as "6Δ3□: ⟨2Δ□⟩−⟨Δ2□⟩−⟨Δ2□⟩−⟨2Δ□⟩", where Δ and □ refer to BO_3 and BO_4 polyhedra, respectively, and the ⟨ ⟩−⟨ ⟩ symbols indicate rings of polyhedra connected by sharing one boron center.[12] Referring to these schemes, one finds only one borate possessing a FBB similar to the anion in **I** and **II**. This is the mineral preobrazhenskite, $Mg_3B_{11}O_{15}(OH)_9$, which contains infinite sheets based on a modified B_9−FBB (9:4Δ + 5T) linked by bridging −$O_2B(OH)_2$− groups.[2,13]

It has been shown that B_3O_3 rings having one trigonal and two tetrahedral borons (Δ2□) occur more frequently and are more energetically stable than other configurations.[14] Although reaction of 1 mol of base with 3 mol of boric acid could produce the $[B_3O_3(OH)_4]^-$ (2Δ□) anion, formation of the nonaborate anion allows a larger proportion of boron to participate in Δ2□-type B_3O_3 rings. The larger nonaborate anion may also be favored by the presence of larger cations.

Its B/N mole ratio of 1 suggests that **I** might serve as a boron nitride precursor. It does not melt below 1000 °C and pyrolyzes to a white refractory powder. TGA−MS analysis under inert atmosphere shows that **I** begins weight loss at ca. 220 °C, initially involving elimination of H_2O by condensation of B−OH groups followed by loss of some NH_3 and CO_2 upon further heating, resulting in a ceramic material having a B/N mole ratio greater than 1. Compound **II** exhibits similar thermal decomposition behavior, with elimination of water commencing at ca. 180 °C.

Supporting Information Available: Crystallographic files in CIF format for compounds **I** and **II**. This material is available free of charge via the Internet at http://pubs.acs.org.

IC000217U

(10) Crystal data (297 K) for **I**: $C_3H_{24}B_9O_{18}N_9$, monoclinic, $C2/c$, $a = 16.452$-(7) Å, $b = 9.100(4)$ Å, and $c = 15.266(7)$ Å, $\beta = 95.07(1)°$, $V = 2276.7$-(17) Å^3, $Z = 4$, $\lambda = 0.7107$ (Mo Kα), $R = 0.066$, $R_w = 0.1822$ for 2994 unique reflections, 1257 with $I > 2\sigma(I)$, GOF = 0.941. Crystal data (297 K) for **II**: $C_9H_{21}B_9O_{18}N_6$, monoclinic, $P2_1/c$, $a = 16.622(3)$ Å, $b = 9.3324(15)$ Å, and $c = 15.570(3)$ Å, $\beta = 91.170(3)°$, $V = 2414.8(7)$ Å^3, $Z = 4$, $\lambda = 0.7107$ (Mo Kα), $R = 0.050$, $R_w = 0.074$ for 5756 unique reflections, 2863 with $I > 2\sigma(I)$, GOF = 0.825.

(11) Christ, C. L.; Clark, J. R. *Phys. Chem. Miner.* **1977**, *2*, 59−87.
(12) Burns, P. C. *Can. Mineral.* **1995**, *33*, 1167−1176.
(13) Rumanova, I. M.; Razmanova, Z. P.; Belov, N. V. *Sov. Phys. Dokl.* **1972**, *16*, 518−521.
(14) Burns, P. C.; Grice, J. D.; Hawthorne, F. C. *Can. Mineral.* **1995**, *33*, 1131−1151.