

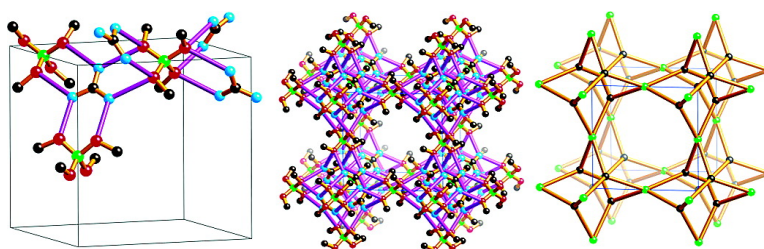
Communication

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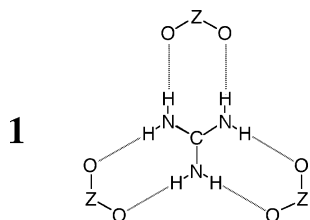
## Guanidinium Ion as a Symmetrical Template in the Formation of Cubic Hydrogen-Bonded Borate Networks with the Boracite Topology

Brendan F. Abrahams, Marissa G. Haywood, and Richard Robson\*

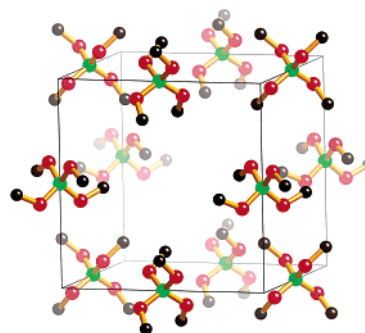
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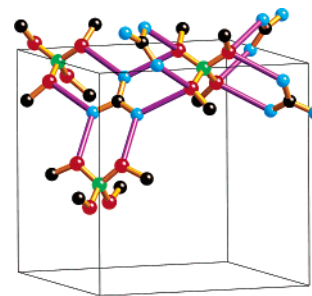
The two major types of interactions employed by supramolecular chemists to engineer a variety of nets, both finite and infinite, are metal–ligand bonding and hydrogen bonding. The guanidinium cation,  $C(NH_2)_3^+$ , is a particularly potent structure-determining template in the formation of both coordination polymer networks and hydrogen-bonded networks. Because of its internal symmetry, it is able to form three pairs of strong hydrogen bonds to various oxyanions, as in **1**, and thus can act as a 3-connecting node in the formation of a number of networks. Outstanding examples are provided by the extensive family of guanidinium sulfonates devised and studied by Ward and co-workers, in which the sulfonate components, as well as the guanidinium units, act as 3-connecting nodes to generate a variety of solids having a common, predictable, yet pliable underlying hydrogen-bonded 3-connected sheet structure with the (6,3) (or hexagonal grid) topology.<sup>1</sup> We have recently discovered<sup>2</sup> a new family of hydrogen-bonded frameworks, of composition  $[C(NH_2)_3][N(CH_3)_4][XO_4]$  ( $X = S, Cr, \text{ or } Mo$ ), related to the guanidinium sulfonates, in which the guanidinium cation again plays the 3-connecting role in **1** and the  $XO_4^{2-}$  ion acts as a second type of 3-connecting node; now, the network generated is the most symmetrical 3D 3-connected network possible, namely, the (10,3)-*a* net,<sup>3</sup> rather than the most symmetrical 2D 3-connected network possible seen in the sulfonates. The guanidinium cation again plays the structural role **1** ( $Z = C$ ) in an extensive family of carbonate-bridged coordination polymers, thereby promoting the generation of highly symmetrical metal–carbonate networks with cubic symmetry and sodalite-like topology.<sup>4</sup> We report here a series of guanidinium borate derivatives in which the guanidinium cation yet again acts as in **1** ( $Z = B$ ), and again, a network of high symmetry (cubic) is formed, in this case with the boracite topology.



Reaction between boric acid and guanidinium salts in methanolic solution at room temperature in the presence of various bases and anions gives well-formed crystals of composition  $\{[B(OCH_3)_4]_3-[C(NH_2)_3]_4\}^+X^- \cdot \text{solvate}$ .<sup>5</sup> Products in which  $X^- = Cl^-$  or  $PF_6^-$  are characterized here by single-crystal X-ray diffraction,<sup>6</sup> powder X-ray diffraction, and elemental analysis, and several other crystalline products with the same unit cell but with different anions are readily obtained. The crystals obtained directly from the reaction mixtures are suitable for single-crystal X-ray diffraction studies, which reveal a common hydrogen-bonded network with cubic symmetry ( $a = \sim 10.6 \text{ \AA}$ ). As shown in Figure 1, boron centers are located at the midpoints of the 12 edges of the cubic unit cell. One methoxy group from each  $B(OCH_3)_4^-$  unit projects into each



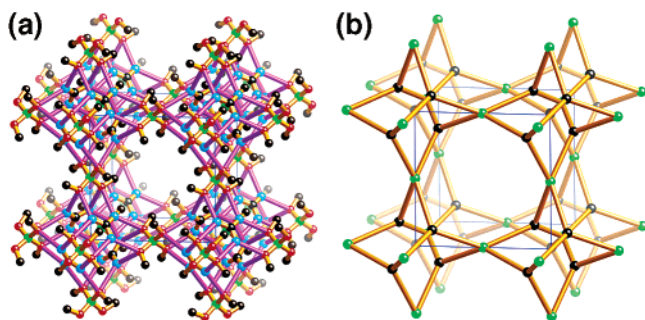
**Figure 1.** Cubic unit cell of the  $\{[B(OCH_3)_4]_3[C(NH_2)_3]_4\}^+$  framework showing only the  $B(OCH_3)_4^-$  anions located at the midpoints of the cell edges.



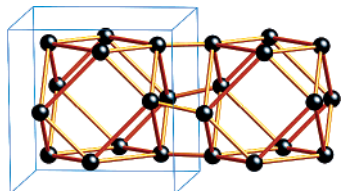
**Figure 2.** Arrangement of the hydrogen bonds, represented in purple. Blue centers = N; green = B; black = C; red = O. All  $C(NH_2)_3^+$  cations are equivalent as are all  $B(OCH_3)_4^-$  anions. The  $C(NH_2)_3^+$  cation seen on the left is connected by six hydrogen bonds to three  $B(OCH_3)_4^-$  anions. The  $B(OCH_3)_4^-$  anion seen at the midpoint of the top, front cell edge is connected by eight hydrogen bonds to four  $C(NH_2)_3^+$  cations.

of the four cells that share that particular edge. Guanidinium ions with their planes perpendicular to the 3-fold axes of the cubic cell are found in four of the eight corners of each cell. As can be seen in Figure 2, the guanidinium ion forms a pair of hydrogen bonds ( $N \cdots O$ , 2.91  $\text{\AA}$ ) to each of its three near-neighbor borate ester anions and, therefore, acts as a 3-connecting node. Each borate ion in turn is doubly hydrogen bonded to four guanidinium cations, as shown in Figure 2, and therefore acts as a 4-connecting node. The infinite (3,4)-connected net thereby generated, shown in Figure 3, has the  $(6^3)(6^28^4)$  topology (or boracite topology). By coincidence, we saw precisely this connectivity some time ago in a coordination polymer of  $Cu^I$  and tripyridyltriazine,<sup>7</sup> and almost simultaneously, the structure of  $Na_2Zn_3(CO_3)_4 \cdot 3H_2O$  was reported<sup>8</sup> which we note has the same topology. The atoms in the framework are crystallographically well defined, but the remaining contents of the crystal are highly disordered. The presence of the  $X^-$  anion is not clearly indicated by the crystallography, but analytical data and, in some cases, IR data confirm it.

The “internal surfaces” presented by the 3D polymer consist almost entirely of hydrophobic methyl groups from the borate ester units, with no less than 12 of them per cell; their disposition is



**Figure 3.** (a) Extended network of hydrogen bonds represented in purple. (b) The  $(6^3)(6^2 8^4)$  net (or boracite net) generated by linking the 3-connecting guanidinium carbon nodes (black) to the 4-connecting boron nodes (green), seen from the same angle as that in Figure 3a.



**Figure 4.** Disposition of the methyl carbon centers in two adjacent cells, showing two distorted cuboctahedral  $(\text{CH}_3)_{12}$  chambers and the  $[(\text{CH}_3)_4]_2$  access port between them. The distorted cuboctahedral arrangement is indicated by gold connections.

represented in Figure 4. The methyl carbon centers are found at the corners of a distorted cuboctahedron consisting of six rectangular faces with  $\text{C}\cdots\text{C}$  edges of 5.57 and 4.51 Å, and eight equilateral triangular faces, four of them with  $\text{C}\cdots\text{C}$  edges of 5.57 Å and four with edges of 4.51 Å. The four guanidinium ions per cell are associated with the larger of the equilateral triangles of methyl groups. Each of these  $(\text{CH}_3)_{12}$  “chambers” is connected to six other chambers by “access ports” consisting of two  $(\text{CH}_3)_4$  rectangles ( $\text{C}\cdots\text{C}$  edges 5.57 and 4.51 Å) on opposite sides of the cell face, with closest  $\text{C}\cdots\text{C}$  contacts between rectangles of 3.57 Å; an example of such an access port can be seen in Figure 4. The generation of nonpolar regions within crystals resulting from the assembly of hydrophilic units has been observed in a number of diverse systems.<sup>9</sup> This labyrinthine system of chambers and access ports, more or less continuously surfaced with methyl groups, does seem to offer prospects of interesting inclusions; for example, addition of excess iodine in methanol to a solution of boric acid, guanidinium chloride, and base causes the rapid separation of deep red-brown tetrahedral crystals; single-crystal X-ray diffraction studies of which reveal the same hydrogen-bonded network as that observed in the  $\text{Cl}^-$  and  $\text{PF}_6^-$  crystals above, with the iodine highly disordered.

It is interesting that the boric acid becomes completely esterified, even in aqueous methanolic reaction mixtures containing as much as 25%  $\text{H}_2\text{O}$ . Possibly this esterification is “driven” by the very favorable multiple hydrogen bonding of the  $\text{B}(\text{OCH}_3)_4^-$  anion to the highly complementary guanidinium cation in the crystal. This complementarity can be viewed as a 3D analogue of that existing between the guanidinium cation and sulfonate anions in the extensive series of 2D guanidinium sulfonates referred to above.<sup>1</sup> Although high symmetry nets that generate significant channels and cavities are now becoming more common in coordination polymers, they remain rare in hydrogen-bonded networks, and the present examples are noteworthy in this regard. The systems described here are immediately suggestive of many attractive variants; for example, guanidinium-templated networks with  $\text{B}(\text{OH})_4^-$  in place of  $\text{B}(\text{OCH}_3)_4^-$ , if achievable, would possess a considerably enlarged system of channels and cavities with internal surfaces now

lined with polar groups, in contrast to the nonpolar methylated internal surfaces described above, possibly with quite different preferences for inclusions. Moreover, models suggest that the imaginary linking of methyl carbon to methyl carbon, say via an appropriate polymethylene connection, while leaving the hydrogen-bonded network intact, might be a realistic prospect; in other words, it may be possible to use appropriate diols, triols, and polyols in place of methanol, together with the templating guanidinium cation to promote the formation of novel crystalline borate ester polymers. We note, however, that despite the encouragement provided by models, preliminary attempts to grow crystals of a related compound using ethanol instead of methanol have thus far proven to be unsuccessful.

**Acknowledgment.** We thank the Australian Research Council for support.

**Supporting Information Available:** X-ray powder diffraction patterns; X-ray crystallographic data in CIF format. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (5)  $[\text{B}(\text{OCH}_3)_3]_3[\text{C}(\text{NH}_2)_3]_4\text{Cl}\cdot 5\text{H}_2\text{O}$ : A solution of  $\text{C}(\text{NH}_2)_3\text{Cl}$  (620 mg, 6.46 mmol) in methanol (7 mL) was added to a solution containing  $\text{H}_3\text{BO}_3$  (200 mg, 3.23 mmol) and  $\text{NEt}_3$  (0.45 mL, 3.23 mmol) in MeOH (8 mL). Colorless crystals began to separate after 15 min. The crystals were filtered off after 4 h, washed quickly with the minimum amount of MeOH, and dried in air. Yield: 240 mg, 31%. Anal. Found: C, 24.6; H, 7.9; N, 21.8. Calcd: C, 24.9; H, 9.2; N, 21.8.  $[\text{B}(\text{OCH}_3)_3]_3[\text{C}(\text{NH}_2)_3]_4\text{PF}_6\cdot 2\text{H}_2\text{O}$  was prepared by a closely similar procedure to that described above for the chloride, except that  $\text{Bu}_4\text{NPF}_6$  (1.25 g, 3.23 mmol) was dissolved together with the  $\text{C}(\text{NH}_2)_3\text{Cl}$  (gentle heating was required) prior to addition to the  $\text{H}_3\text{BO}_3/\text{NEt}_3$  solution. Yield: 260 mg, 30.6%. Anal. Found: C, 22.8; H, 7.9; N, 20.3; Cl, nil. Calcd: C, 23.3; H, 7.8; N, 20.3; Cl, nil. It is interesting that this product contains zero chlorine, which indicates that the cationic guanidinium/borate framework has a distinct preference for the inclusion of  $\text{PF}_6^-$  rather than  $\text{Cl}^-$ . Strong bands (844 and 561  $\text{cm}^{-1}$ ) in the IR spectrum indicate the presence of  $\text{PF}_6^-$ . X-ray powder diffractograms of both the  $\text{Cl}^-$  and  $\text{PF}_6^-$  derivatives were in excellent agreement with those generated from the single-crystal data. Well-formed tetrahedral crystals were readily obtained from reaction mixtures closely similar to those above, except that guanidinium nitrate was used in place of guanidinium chloride; a strong sharp band in the IR spectrum at 1385  $\text{cm}^{-1}$  confirmed  $\text{NO}_3^-$  in the crystal, and single-crystal X-ray diffraction indicated essentially the same unit cell as those for the  $\text{Cl}^-$  and  $\text{PF}_6^-$  derivatives.
- (6) Crystal data for  $[\text{C}(\text{NH}_2)_3]_4[\text{B}(\text{OCH}_3)_3]_3\text{PF}_6\cdot 2\text{CH}_3\text{OH}$  and  $[\text{C}(\text{NH}_2)_3]_4[\text{B}(\text{OCH}_3)_3]_3\text{Cl}\cdot 4\text{CH}_3\text{OH}$  (in parentheses):  $M_r$  854.2 (776.8), space group  $P4_3m$  ( $P4_3m$ ),  $a = 10.5722(4)$ ,  $(10.6139(4))$  Å;  $V = 1181.67(8)$ ,  $(1195.71(8))$  Å<sup>3</sup>;  $Z = 1$ ;  $T = 293(2)$ ,  $(293(2))$  K;  $\mu(\text{Mo K}\alpha) = 0.142$ ,  $(0.145)$   $\text{mm}^{-1}$ ; reflections measured, unique which were used in all calculations. The final values for  $wR2$  (all data) and  $R1$  [ $I > 2\sigma(I)$ ] were 0.2476 (0.3097) and 0.1048 (0.1153), respectively. Due to severe disorder within the large cavity of the unit cell, it was not possible to model the methanol or  $\text{PF}_6^-$  and  $\text{Cl}^-$  anions. When the structure was refined on “squeezed” data obtained using the PLATON program,<sup>10</sup>  $R1 = 0.0469$  (0.0415). The crystal structures were solved and refined using SHELX-97.<sup>11</sup> Full details are included in the CIF files (Supporting Information).
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