



Supramolecular hydrogen-bonded structure of a 1:2 adduct of melamine with boric acid

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Abstract

Boric acid (B) forms a 2:1 hydrogen-bond adduct, M-2B, with melamine (M), wherein, a finite tetrameric ribbon of boric acid forms hydrogen bonds with the nitrogen donor sites of M. Hydrogen-bonded layers of B and M in the *bc*-plane are connected by boric acid units along the *a*-axis to give a three dimensional structure. Interestingly, one of the amino groups of M does not participate in hydrogen bonding unlike all the hydroxyl groups of B. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Boric acid; Melamine; Hydrogen bonding; Supramolecular chemistry; Hydrothermal synthesis

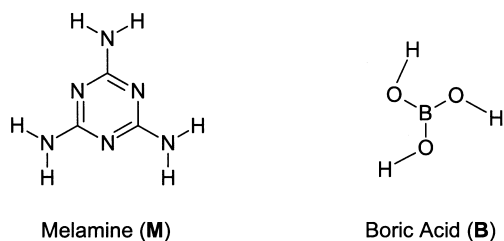
1. Introduction

Boric acid, B(OH)₃, would be expected to be a good building block for supramolecular hydrogen bonded structures by virtue of the presence of three –OH groups oriented in a planar triangular fashion. Boric acid is known to behave as a Lewis acid with the formation of the tetrahedral anion [B(OH)₄][–] rather than as a Brønsted acid with the formation of the conjugate base anion [BO(OH)₂][–]. In dilute aqueous solution B(OH)₃ exist as an equilibrated mixture of the undissociated acid and [B(OH)₄][–] anion. At higher concentrations monomeric borate species undergo condensation to give a variety of oligomeric hydroxo (oxo) borate anions [1]. Accordingly, several

interesting supramolecular hydrogen-bonded architectures involving tetrahydroxy pentaborate and boric acid incorporating a tertiary or quaternary ammonium ion have been isolated and characterized [2–5]. Hydrogen-bonded structures involving only monomeric borate species is, however rare. In (CH₃)₄N⁺(BO(OH)₂)₂[–]·2(NH₂)₂CO·H₂O and (NEt₄)₂[BO(OH)₂]₂·B(OH)₃·5H₂O, [BO(OH)₂][–] is present in the host lattice [6,7]. [(PPh₃)₂N⁺·Cl[–]]₂·B(OH)₃ and [(C₂H₅)₄N⁺]₂CO₃^{2–}·(NH₂)₂CO·2B(OH)₃·H₂O seems to be the only two structures known to date containing the undissociated B(OH)₃ unit [7,8]. We wanted to study supramolecular hydrogen-bonded assemblies formed by boric acid with organic amines and such compounds (Scheme 1) under aqueous conditions. We have found that melamine (M) which is well known to yield excellent hydrogen-bonded structures also forms a stable 1:2 adduct with boric acid (M-2B). Importantly, this adduct is a precursor for making BN nanotubes [9–11]. We have carried out a study of

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M·2B prepared by the hydrothermal technique, to examine the features of this supramolecularly hydrogen-bonded structure.

2. Experimental

0.1295 g of H_3BO_3 was dissolved in 2 ml distilled water. To this solution, 0.1317 g of melamine was added with stirring. The stirring was continued for another 30 min to get a homogenous solution. The reaction mixture with a composition of $2\text{H}_3\text{BO}_3/\text{melamine}/100\text{H}_2\text{O}$ was then sealed in a 23 ml capacity teflon-lined stainless steel autoclave and heated at 150°C for 2 d. It was subjected to natural cooling (~ 4 h). The product containing rod-shaped crystals suitable for single crystal X-ray diffraction was filtered and washed with chilled de-ionized water. The initial pH of the mixture was seven and there was no appreciable change in the pH of the supernatant in the final mixture. Heating the reaction mixture for a longer time (3 d) makes the supernatant highly alkaline (pH ~ 10.5), probably due to the evolution of the ammonia gas which is produced due to the decomposition of melamine under hydrothermal condition as indicated by the smell of ammonia upon opening the autoclave. The product was subsequently characterized by powder X-ray diffraction (PXRD), single crystal X-ray diffraction, thermogravimetric analysis (TGA) and IR spectroscopy. The PXRD immediately revealed that the product is a 1:2 (M·2B) adduct of melamine and boric acid [9]. Our attempts to synthesize 1:1 adduct under similar condition led to recrystallization of melamine. On the other hand attempts to synthesize a composition of 1:3 under similar condition gives back the 1:2 adduct of melamine and boric acid.

A suitable single crystal of M·2B was carefully

Table 1

Crystal data and structural refinement parameters for M·2B

Empirical formula	$\text{C}_3\text{H}_{12}\text{B}_2\text{N}_6\text{O}_6$
Crystal system	Monoclinic
Space group	$P2_1/c$
Crystal size (mm)	$0.33 \times 0.10 \times 0.08$
a (Å)	3.6015 (2)
b (Å)	20.1400 (13)
c (Å)	14.1279 (9)
α (°)	90.0
β (°)	92.134 (2)
γ (°)	90.0
Volume (Å ³)	1024.05 (11)
Z	4
Formula mass	249.81
ρ (g cm ⁻³)	1.620
λ (Mo K α) (Å)	0.71073
μ (mm ⁻¹)	0.144
Temperature of measurement (K)	293 (2)
θ range (°)	1.76–23.32
Total data collected	4170
Index ranges	$-3 \leq h \leq 3$, $-20 \leq k \leq 22$, $-11 \leq l \leq 15$
Unique data	1446
Observed data [$I > 2\sigma(I)$]	923
R_{int}	0.0529
Refinement method	Full-matrix least-squares on F^2
R indices [$I > 2\sigma(I)$]	$R_1 = 0.0490$, $wR_2 = 0.1014^a$
R (all data)	$R_1 = 0.0910$, $wR_2 = 0.1214$
Goodness of fit (S)	1.004
Number of variables	202
Largest difference map peak and hole e Å ⁻³	0.186 and -0.286

^a $R_1 = \|F_0\| - |F_c| / \|F_0\|$; $wR_2 = \{[w(F_0^2 - F_c^2)^2] / [w(F_0^2)^2]\}^{1/2}$, $w = 1 / [\sigma^2(F_0^2) + (aP)^2 + bP]$, $P = [\max(F_0^2, 0) + 2(F_c^2)] / 3$, where $a = 0.0596$ and $b = 0.0000$ for m.2B.

selected under a polarizing microscope and glued to a thin glass fiber with cyanoacrylate (super glue) adhesive. Single crystal structure determination by X-ray diffraction was performed with a Siemens Smart-CCD diffractometer equipped with a normal focus, 2.4 kW sealed tube X-ray source (Mo K α radiation, $\lambda = 0.71073$ Å) operating at 50 kV and 40 mA. A hemisphere of intensity data were collected using SMART software [12] at room temperature in 1321 frames with ω scans (width of 0.30° and exposure time of 20 s per frame) in the 2θ range $3-46.5^\circ$. The total collected data were reduced using SAINT [12] program and the orientation matrix along with the detector and the cell parameters were refined

Table 2
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for, M:2B

Atom	x	y	z	$U(\text{eq})^a$
B(1)	4507 (11)	3673 (2)	1673 (3)	32 (1)
B(2)	3380 (11)	4891 (2)	6371 (3)	35 (1)
O(1)	3264 (7)	3640 (1)	2576 (2)	37 (1)
O(2)	5998 (7)	4253 (1)	1348 (2)	40 (1)
O(3)	4251 (7)	3137 (1)	1102 (2)	41 (1)
O(4)	2641 (7)	4377 (1)	5776 (2)	48 (1)
O(5)	2512 (7)	4852 (1)	7295 (2)	43 (1)
O(6)	5003 (7)	5459 (1)	6045 (2)	44 (1)
C(1)	8379 (8)	3726 (2)	-1110 (2)	29 (1)
N(1)	9621 (7)	3728 (1)	-1992 (2)	29 (1)
C(2)	10305 (9)	3125 (2)	-2354 (2)	29 (1)
N(2)	9997 (7)	2546 (1)	-1885 (2)	30 (1)
C(3)	8648 (8)	2606 (2)	-1020 (2)	30 (1)
N(3)	7729 (7)	3174 (1)	-595 (2)	30 (1)
N(4)	7727 (9)	4309 (2)	-695 (2)	41 (1)
N(5)	11429 (9)	3098 (2)	-3245 (2)	38 (1)
N(6)	8262 (9)	2043 (2)	-514 (3)	43 (1)
H(1)	7323 (93)	4299 (17)	-54 (26)	52 (11)
H(2)	7977 (105)	4696 (22)	-1059 (27)	73 (14)
H(3)	11804 (82)	3485 (18)	-3544 (22)	34 (10)
H(4)	12162 (88)	2700 (18)	-3500 (22)	43 (11)
H(5)	8396 (107)	1642 (22)	-825 (29)	70 (14)
H(6)	7406 (109)	2069 (19)	31 (28)	59 (13)
H(7)	2254 (100)	3272 (19)	2740 (26)	52 (12)
H(8)	6361 (108)	4539 (22)	1816 (28)	72 (14)
H(9)	5274 (117)	3173 (19)	531 (32)	79 (16)
H(10)	3309 (103)	4455 (19)	5161 (28)	69 (13)
H(11)	1466 (105)	4505 (21)	7486 (25)	62 (14)
H(12)	5675 (100)	5719 (21)	6522 (26)	63 (13)

^a $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

for every 40 frames on all the measured reflections. Pertinent experimental details for the structure determinations are presented in Table 1.

The structure of M:2B was solved by direct methods using SHELXS-86 [13,14] which readily established the position of the light atoms (C, N, O, B and H) from difference Fourier maps. An empirical absorption correction based on symmetry equivalent reflections was applied using the SADABS [15] program. Other effects, such as absorption by glass fiber etc. were simultaneously corrected. All the hydrogen positions for the melamine and boric acid molecules were initially located in the difference Fourier maps, and for the final refinement, the hydrogen atoms were placed in the located position.

Table 3
Selected bond distances and bond angles for M:2B

Moiety	Distance (\AA)	Moiety	Angle ($^\circ$)
B(1)–O(1)	1.370 (4)	O(3)–B(1)–O(1)	120.0 (3)
B(1)–O(2)	1.372 (4)	O(3)–B(1)–O(2)	120.1 (3)
B(1)–O(3)	1.349 (4)	O(1)–B(1)–O(2)	119.9 (3)
B(2)–O(4)	1.352 (4)	O(4)–B(2)–O(5)	120.5 (3)
B(2)–O(5)	1.356 (4)	O(4)–B(2)–O(6)	120.3 (3)
B(2)–O(6)	1.373 (4)	O(5)–B(2)–O(6)	119.2 (3)
C(1)–N(4)	1.339 (4)	N(4)–C(1)–N(1)	118.3 (3)
C(1)–N(1)	1.339 (4)	N(4)–C(1)–N(3)	116.6 (3)
C(1)–N(3)	1.353 (4)	N(1)–C(1)–N(3)	125.0 (3)
N(1)–C(2)	1.344 (4)	C(1)–N(1)–C(2)	115.0 (3)
C(2)–N(5)	1.338 (4)	N(5)–C(2)–N(1)	117.4 (3)
C(2)–N(2)	1.348 (4)	N(5)–C(2)–N(2)	117.4 (3)
N(2)–C(3)	1.338 (4)	N(1)–C(2)–N(2)	125.1 (3)
C(3)–N(3)	1.339 (4)	C(3)–N(2)–C(2)	114.1 (3)
C(3)–N(6)	1.351 (4)	N(2)–C(3)–N(3)	126.3 (3)
		N(2)–C(3)–N(6)	117.0 (3)
		N(3)–C(3)–N(6)	116.6 (3)
		C(3)–N(3)–C(1)	114.1 (3)

The last cycles of refinement included atomic positions for all the atoms, anisotropic thermal parameters for all the non-hydrogen atoms and isotropic thermal parameters for all the hydrogen atoms. Full-matrix-least-squares structure refinement against $|F^2|$ was carried out using SHELXTL-PLUS [16] package of programs. Details of the final refinements are given in Table 1. The atomic coordinates, bond distances and angles for M:2B is presented in Tables 2 and 3. The experimental powder pattern of the bulk sample is in good agreement with the simulated pattern generated from single crystal data.

FT-IR spectroscopy of M:2B on KBr disc indicates the presence of asymmetric and symmetric $-\text{NH}_2$ stretching frequency at 3495 and 3415 cm^{-1} , respectively. Sharp band around 1607 and 1249 cm^{-1} is due to CN and B–O stretching modes. The O–B–O bending modes are observed at 803 and 652 cm^{-1} , respectively. TGA was carried out in a nitrogen atmosphere in the 25–800 $^\circ\text{C}$ range. The TGA curve indicates that there is a sharp weight loss around 140 $^\circ\text{C}$ due the loss of three molecules of water (calc. = 21.6%, obs. = 22.5%) which is followed by a continuous weight loss till 800 $^\circ\text{C}$, mainly due to the decomposition of the amine moiety. It has been observed earlier by Hagio et al. [9] using

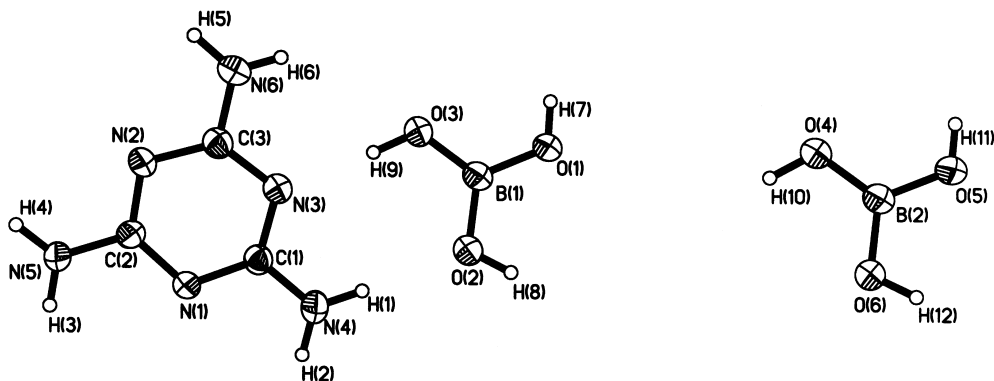


Fig. 1. The ORTEP plot of the asymmetric unit of M-2B. The thermal ellipsoids are given at 50% probability.

TG-mass spectrometry that (M-2B) decomposes with the evolution of NH_3 , CO_2 and H_2NCN . The annealed product remaining at 800°C was amorphous and weakly diffracting and yielded BN nanotubes on further treatment at higher temperatures [10].

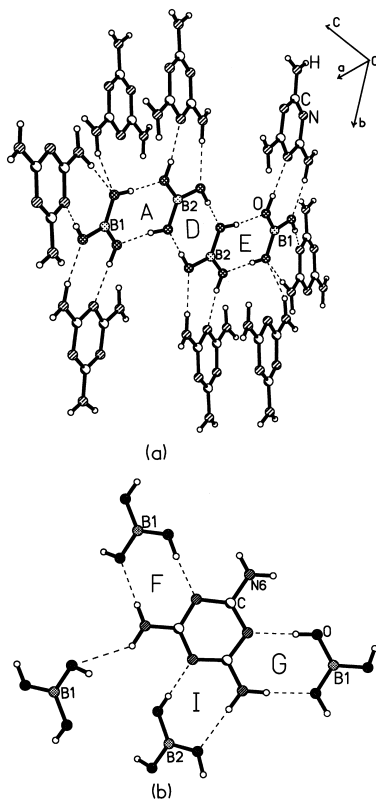


Fig. 2. (a) The finite tetrameric ribbon of boric acid and the environment of each crystallographically distinct boric acid unit. A, D and E denotes the three eight-membered $[\text{R}_2^2(8)]$ ring. (b) The environment around a melamine unit has been shown, F, G and I denotes the three eight-membered $[\text{R}_2^2(8)]$ ring.

3. Results and discussion

The asymmetric unit of M-2B contains two crystallographically distinct boric acid molecules and one melamine molecule as shown in Fig. 1. The planar triangular boric acid molecules and the melamine molecule form a three-dimensional hydrogen-bonded supramolecular structure involving $\text{O}-\text{H}\cdots\text{O}$, $\text{N}-\text{H}\cdots\text{O}$ and $\text{O}-\text{H}\cdots\text{N}$ hydrogen bonds. The four $\text{B}(\text{OH})_3$ units are linked to one another to form a finite tetrameric ribbon through strong $\text{O}-\text{H}\cdots\text{O}$ ($d(\text{O}\cdots\text{O})_{\text{av}} = 2.716 \text{ \AA}$) hydrogen bonding with the formation of three eight-membered cyclic $[\text{R}_2^2(8)]$ rings [17] as shown in Fig. 2(a). In the tetramer, $\text{B}(2)(\text{OH})_3$ forms a dimer in the middle while $\text{B}(1)(\text{OH})_3$ is located at the two ends of the dimer. The $\text{B}(1)(\text{OH})_3$ unit interacts with three melamines and one boric acid, $\text{B}(2)(\text{OH})_3$. The $\text{B}(2)(\text{OH})_3$ unit, on the other hand, interacts with two boric acid molecules, $\text{B}(1)(\text{OH})_3$ and $\text{B}(2)(\text{OH})_3$, as well as one melamine molecule through $\text{O}-\text{H}\cdots\text{O}$ and $\text{O}-\text{H}\cdots\text{N}$ interactions, utilizing all the donor and acceptor sites. Of the six oxygens in the two boric acid units, O(6) attached to B(2) does not participate in Hydrogen bonding with the melamine molecule either as donor or an acceptor. The average B–O bond lengths in the two distinct boric acids are

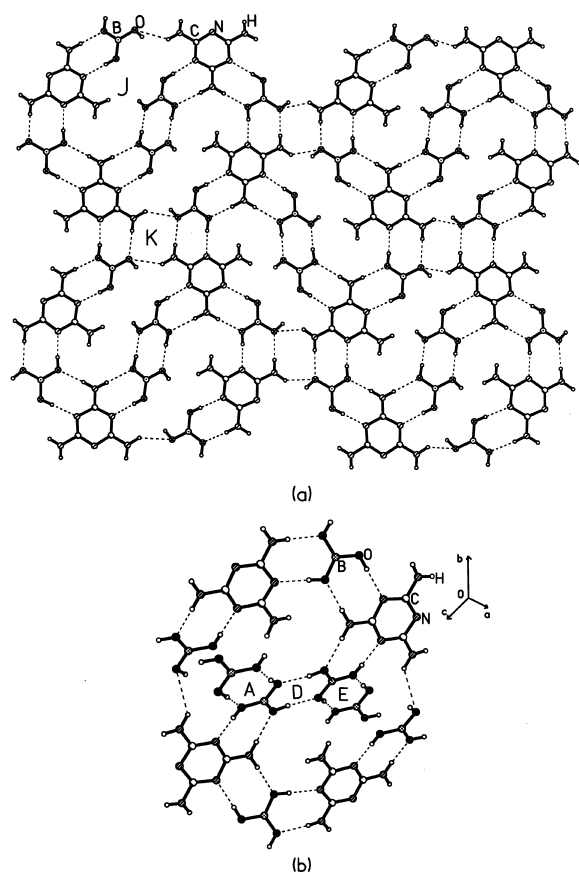


Fig. 3. (a) A projection of a section of the layer-like architecture into the bc -plane has been shown. J and K denotes the 22- and eight-membered $[R_6^7(22)]$ and $[R_2^2(8)]$ ring, respectively. (b) The boric acid unit which connects the layers along the a -axis from top (A) and bottom (E).

comparable ($d(\text{B}(1)-\text{O})_{\text{avg}} = 1.363$ and 1.360 \AA). However, the individual B–O distance in each boric acid moiety varies considerably depending on their participation in hydrogen bonding.

In contrast to the boric acid moieties, the melamine unit does not utilize all its donor and acceptor sites. Melamine interacts with four boric acid units through the utilization of two N donor sites (N4 and N5) and all the acceptor sites as shown in Fig. 2(b). Out of the four boric acid units, three form cyclic eight-membered $[R_2^2(8)]$ rings [17]. It is interesting that the N(6) of melamine unit does not involve in hydrogen bonding. When viewed along the a -axis, M·2B forms a layer like structure in the bc -plane as shown in Fig. 3(a). Within the layer, four melamine units and four boric acid units are linked alternatively to form an elliptical ring which is bisected along one of the axis by the B(2)(OH)₃ dimer into two 22-membered $[R_6^7(22)]$ rings [17]. The layers are connected along the a -axis in AAAA fashion through B(1)(OH)₃ units as shown in Fig. 3(b) to give the three-dimensional structure. The details of the hydrogen bonding interactions in M·2B are given in Table 4.

There are many interesting features in the M·2B adduct. Besides being a novel precursor for the BN nanotubes, it represents a rather rare hydrogen-bonded solid containing boric acid. The tetrameric ribbon in M·2B is akin to a neutral ribbon of boric acid [18]. A wide variety of supramolecular adducts with melamine, where the amine uses all its donor and acceptor sites, are reported in the literature [19–21], a well-known example being the melamine–cyanuric acid adduct with the hydrogen-bonded rosette structure

Table 4
Selected Hydrogen bond interactions in compound M·2B

D–H···A	D–H	H···A	D···A	D–H···A
N(4)–H(1)···O(2)	0.93 (4)	2.05 (4)	2.977 (4)	175 (3)
N(4)–H(2)···O(2)	0.95 (4)	2.57 (4)	3.308 (5)	135 (3)
N(5)–H(3)···O(4)	0.90 (3)	2.07 (3)	2.964 (5)	180 (3)
N(5)–H(4)···O(3)	0.92 (4)	1.94 (4)	2.853 (4)	172 (3)
O(1)–H(7)···N(2)	0.86 (4)	1.92 (4)	2.781 (4)	180 (4)
O(2)–H(8)···O(5)	0.89 (4)	1.79 (4)	2.671 (4)	174 (4)
O(3)–H(9)···N(3)	0.90 (4)	1.85 (4)	2.747 (4)	174 (4)
O(4)–H(10)···O(6)	0.92 (4)	1.84 (4)	2.759 (4)	174 (3)
O(5)–H(11)···N(1)	0.84 (4)	1.87 (4)	2.702 (4)	174 (4)
O(6)–H(12)···O(1)	0.88 (4)	1.84 (4)	2.718 (4)	172 (4)

[21]. Surprisingly in the present case, one of the NH_2 groups does not participate in hydrogen bonding. There is no proton transfer between the amine and boric acid.

In the hydrogen bonded structures formed by boric acid or by the monomeric borate species reported in the literature, infinite ribbon of $\text{B}(\text{OH})_3$ and $\text{BO}(\text{OH})_2^-$ [6], a rosette-like structure of $\text{B}(\text{OH})_3-\text{CO}_3^{2-}$ –urea linkages [7] and head-to-head dimer of $\text{B}(\text{OH})_3$ [8] are known to occur. Thus, the hydrogen bonded structure in M·2B is quite different, having a finite tetrameric ribbon of $\text{B}(\text{OH})_3$.

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