Intermolecular dihydrogen- and hydrogen-bonding interactions in diammonium *closo*-decahydrodecaborate sesquihydrate

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The asymmetric unit of the title salt, $2NH_4^+ \cdot B_{10}H_{10}^{2-} \cdot 1.5H_2O$ or $(NH_4)_2B_{10}H_{10} \cdot 1.5H_2O$, (I), contains two $B_{10}H_{10}^{2-}$ anions, four NH_4^+ cations and three water molecules. (I) was converted to the anhydrous compound $(NH_4)_2B_{10}H_{10}$, (II), by heating to 343 K and its X-ray powder pattern was obtained. The extended structure of (I) shows two types of hydrogen-bonding interactions (N—H···O and O—H···O) and two types of dihydrogen-bonding interactions (N—H···H—B and O—H···H—B). The N—H···H—B dihydrogen bonding forms a two-dimensional sheet structure, and hydrogen bonding (N—H···O and O—H···O) and O—H···H—B dihydrogen bonding link the respective sheets to form a three-dimensional polymeric network structure. Compound (II) has been shown to form a polymer with the accompanying loss of H_2 at a faster rate than $(NH_4)_2B_{12}H_{12}$ and we believe that this is due to the stronger dihydrogen-bonding interactions shown in the hydrate (I).

Comment

Dihydrogen-bonded compounds, such as NH_3BH_3 (Klooster *et al.*, 1999) and $(NH_3)_2Mg(BH_4)_2$ (Soloveichik *et al.*, 2008), give off H_2 when heated. Since the ammonium cation in $(NH_4)_2B_{10}H_{10}$ has protonic hydrogen and the B—H hydrogen on the boron cage ($B_{10}H_{10}^{2-}$) is hydridic, it is a potential material for hydrogen storage. $(NH_4)_2B_{10}H_{10}$ has been mentioned in the literature as an additive in rocket fuel (Goddard *et al.*, 1978), a hydrogen generator for a fuel cell (Kelly *et al.*, 2005; Goddard *et al.*, 1978), and its polymeric product as a neutron shield material (Yolles *et al.*, 1969). The syntheses of anhydrous $(NH_4)_2B_{10}H_{10}$ (Muetterties *et al.*, 1964) and the dihydrate $(NH_4)_2B_{10}H_{10} \cdot 2H_2O$ (Ivanov *et al.*, 1992) have been reported but their structures remain

unknown. The reported synthesis of anhydrous $(NH_4)_2B_{10}H_{10}$ involves a sulfur-containing precursor ($B_{10}H_{12} \cdot 2SMe_2$) which is undesirable for hydrogen-storage materials because the sulfur poisons the fuel cell catalyst. The single-crystal X-ray structure of the reported B_{12} analogue, $(NH_4)_2B_{12}H_{12}$, has weak N—H···H—B dihydrogen-bonding interactions (Tiritiris & Schleid, 2003). We report here the sulfur-free synthesis of the dihydrogen-bonded compound $(NH_4)_2B_{10}H_{10} \cdot 1.5H_2O$, (I), and its anhydrous analog $(NH_4)_2B_{10}H_{10}$, (II), and their characterization by NMR, IR, single-crystal X-ray diffraction analysis, powder X-ray diffraction analysis, differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA).

(I)
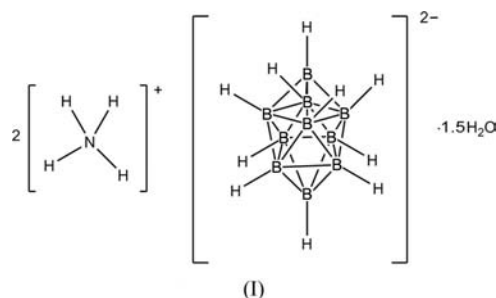
To determine whether the single-crystal structure of (I) is representative of the bulk sample, X-ray powder diffraction of (I) was carried out. The experimental and calculated powder patterns are similar. The small difference in 2θ values is attributed to the temperature difference between the single-crystal collection temperature (150 K) and powder diffraction (297 K) (see supplementary material). The water molecules in
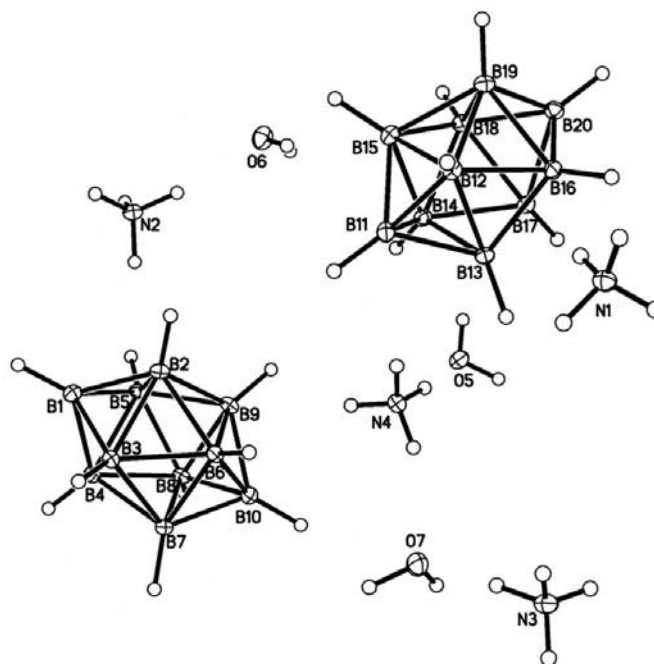

Figure 1
View of the components of the asymmetric unit of (I), shown with 25% probability displacement ellipsoids.
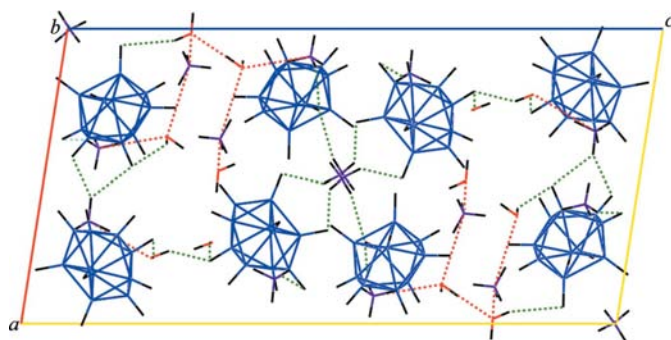
Figure 2
Packing diagram of (I), viewed along the *b* axis. (In the electronic version of this paper, dotted green and dotted red lines represent dihydrogen bonding and hydrogen bonding, respectively.)

(I) were removed by heating to 343 K for 2 h to form (II), where the loss of water was confirmed by IR, DSC and ^{1}H NMR. ^{1}H and ^{11}B NMR also confirmed that no hydrogen was lost as a result of heating of (I) to 343 K. The powder X-ray diffraction pattern of (II) is different from that of (I).

The asymmetric unit of (I) contains two crystallographically independent $B_{10}H_{10}^{2-}$ anions, four NH_4^+ cations and three water molecules (Fig. 1) and the unit cell contains four asymmetric units (Fig. 2). There are nine different N—H···H—B dihydrogen-bonding interactions (Table 2) that lead to the formation of a two-dimensional dihydrogen-bonded sheet which lies parallel to the *ab* plane (Fig. 3, and supplementary Figs. S3 and S4). The range of H···H distances in these interactions is 1.99 (3)–2.27 (3) Å and either two (N2) or three (N1 and N3) of the four H atoms of the ammonium cation are involved. In addition, four different O—H···H—B interactions are observed, with H···H distances in the range 2.06 (3)–2.23 (3) Å. An examination of 18 X-ray structures from the Cambridge Structural Database (CSD, Version 5.30,
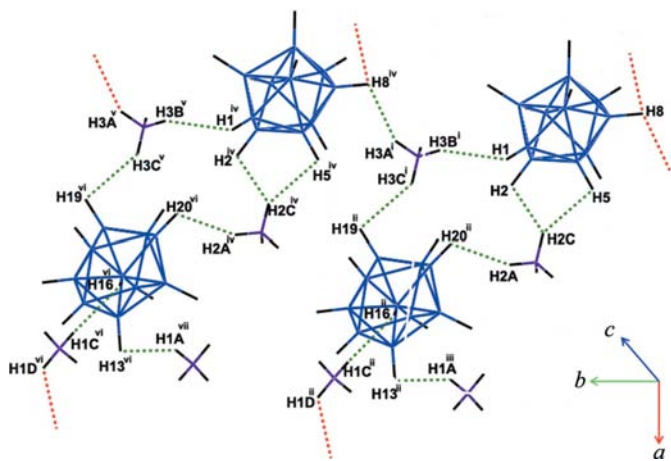

Figure 3
The two-dimensional sheet structure of (I), showing N—H···H—B dihydrogen-bonding interactions. (In the electronic version of this paper, red dotted lines show the contacts for the extended structure.) [Symmetry codes: (i) $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$; (ii) $\frac{3}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$; (iii) $\frac{1}{2} + x, \frac{3}{2} - y, -\frac{1}{2} - z$; (iv) $x, 1 + y, z$; (v) $\frac{1}{2} - x, \frac{3}{2} + y, \frac{1}{2} - z$; (vi) $\frac{3}{2} - x, \frac{3}{2} + y, \frac{1}{2} - z$; (vii) $\frac{1}{2} + x, \frac{5}{2} - y, -\frac{1}{2} + z$.]
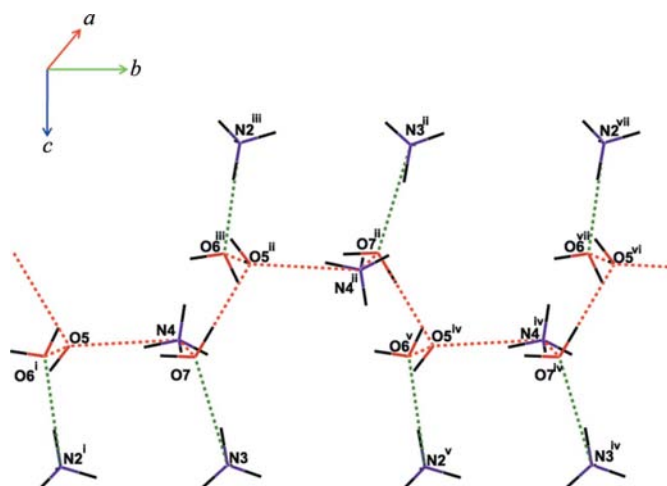

Figure 4
A one-dimensional chain of O—H···O and N—H···O hydrogen bonding. (In the electronic version of this paper, dotted red lines represent the main chain of hydrogen bonding and dotted green lines represent hydrogen bonding branching from the main chain.) [Symmetry codes: (i) $\frac{3}{2} - x, -\frac{1}{2} + y, \frac{1}{2} - z$; (ii) $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$; (iii) $x - 1, y, z$; (iv) $x, 1 + y, z$; (v) $\frac{3}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$; (vi) $\frac{1}{2} - x, \frac{3}{2} + y, \frac{1}{2} - z$; (vii) $x - 1, 1 + y, z$.]

November 2008 release; Allen, 2002) containing either substituted ammonium ions or open-cage boron compounds found that the H···H distances in the N—H···H—B dihydrogen bonds are in the range 1.7–2.2 Å, and H···H—B and H···H—N bond angles are clustered in the ranges 95–115 and 150–170°, respectively. The H···H—B and H···H—N bond angles of the nine dihydrogen-bonded interactions in (I) are similarly clustered in the ranges 90–110 and 130–160° with 5 (H···H—B) and 15° (H···H—N) shifts to smaller angles compared to the 18 X-ray structures from the CSD. The N—H···H—B dihydrogen-bond distances in (I) are much shorter than those in the closely related cage compound $(NH_4)_2B_{12}H_{12}$, which are all the same by symmetry (2.36 Å) and close to the sum of the van der Waals radii of H atoms (~2.4 Å) (Tiritiris & Schleid, 2003).

In the two-dimensional sheet (Fig. 3), two $B_{10}H_{10}^{2-}$ anions and two ammonium cations form a dihydrogen-bonded 14-membered ring and this unit is repeated within the sheet. The third dihydrogen bond on N1, H1*B*···H13, extends the sheet parallel to the *a* axis and connects two sheets together. The H2*C* atom on N2 has a bifurcated dihydrogen bond to two B—H H atoms (H2 and H5, Fig. 3) on the same $B_{10}H_{10}^{2-}$. Two sets of N—H···H—B dihydrogen-bonded sheets are connected to another two sets of sheets by four different (O—H···H—B) dihydrogen-bonding interactions combined with six hydrogen-bonding interactions (four N—H···O and two O—H···O) (Tables 1 and 2) to form a three-dimensional extended network (supplementary Fig. S4). The B15—H15 H atoms have a bifurcated dihydrogen bond with two different water molecules and the O—H···H—B dihydrogen bonds form a one-dimensional zigzag chain (B—H···H—O—H···H—B) connecting the bottom and upper two-dimensional layers (supplementary Fig. S4). The hydrogen bonds also form a continuous chain of H—N—H···O···H—O···H—N—H···O

along the *b* axis. Along the hydrogen-bonded chain (Fig. 4), additional ammonium ions and water molecules hydrogen bond with water on the main chain (O$\cdots$H—N and O—H$\cdots$O$\cdots$H—N) and the end-group ammonium H atoms link the two sheets from above and below by dihydrogen bonding with B—H. The significance of this study is that since the dihydrogen bonds in (I) are stronger than those in $(NH_4)_2B_{12}H_{12}$, the kinetics of hydrogen release should be faster. In fact, Yolles *et al.* (1969) has reported that $(NH_4)_2B_{10}H_{10}$ releases hydrogen much faster than $(NH_4)_2B_{12}H_{12}$ when heated under the same conditions.

Experimental

For the synthesis of (I), $(NEt_3H)_2B_{10}H_{10}$ (synthesized from decaborane; Hawthorne & Pilling, 1967) (5.0 g, 15.51 mmol) was passed through an acid exchange resin to form the acidic $(H_3O)_2B_{10}H_{10}$. Excess ammonia gas was bubbled for 2 min into a water solution of $(H_3O)_2B_{10}H_{10}$ and $(NH_4)_2B_{10}H_{10}\cdot1.5H_2O$ was crystallized as colorless plate-shaped crystals by evaporation of the water. For the synthesis of (II), compound (I) $[(NH_4)_2B_{10}H_{10}\cdot1.5H_2O]$ was heated at 343 K for 2 h to give anhydrous compound (II) $[(NH_4)_2B_{10}H_{10}]$. Spectroscopic (IR and ^1H and ^{11}B NMR) and thermogravimetric analysis data are available in the archived CIF.

Crystal data

$2NH_4^+\cdot B_{10}H_{10}^{2-}\cdot1.5H_2O$	$V = 2318.6\,(8)$ Å^3
$M_r = 181.29$	$Z = 8$
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation
$a = 11.674\,(2)$ Å	$\mu = 0.06$ mm^{-1}
$b = 8.6230\,(17)$ Å	$T = 150$ K
$c = 23.318\,(5)$ Å	$0.38 \times 0.31 \times 0.12$ mm
$\beta = 98.97\,(3)°$	

Data collection

Nonius Kappa CCD diffractometer	10211 measured reflections
Absorption correction: multi-scan	5318 independent reflections
(*SCALEPACK*; Otwinowski &	3637 reflections with $I > 2\sigma(I)$
Minor, 1997)	$R_{int} = 0.042$
$T_{min} = 0.978$, $T_{max} = 0.993$	

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.045$	412 parameters
$wR(F^2) = 0.121$	All H-atom parameters refined
$S = 1.02$	$\Delta\rho_{max} = 0.35$ e Å^{-3}
5318 reflections	$\Delta\rho_{min} = -0.26$ e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N2—H2$D\cdots$O6	0.93 (2)	1.91 (2)	2.837 (2)	171.7 (15)
N3—H3$D\cdots$O7	0.968 (19)	1.855 (19)	2.8117 (19)	168.8 (15)
N4—H4$B\cdots$O5	0.94 (2)	1.96 (2)	2.896 (2)	168.5 (16)
N4—H4$A\cdots$O7	0.88 (2)	2.09 (2)	2.942 (2)	162.7 (17)
O5—H5$B\cdots$O6^i	0.82 (2)	2.01 (2)	2.8357 (18)	176.5 (19)
O7—H7$B\cdots$O5^{ii}	0.90 (3)	1.85 (3)	2.7487 (18)	177 (2)

Symmetry codes: (i) $-x+\frac{3}{2}, y-\frac{1}{2}, -z+\frac{1}{2}$; (ii) $-x+\frac{1}{2}, y+\frac{1}{2}, -z+\frac{1}{2}$.

Table 2
Dihydrogen-bond geometry (Å, °) of (I).

D—H$\cdots$H—X	H$\cdots$H	H$\cdots$H—X	H$\cdots$H—D
N1—H1$A\cdots$H13—B13^i	2.27 (3)	154 (2)	105 (1)
N1—H1$C\cdots$H16—B16	2.03 (3)	141 (2)	106 (1)
N1—H1$D\cdots$H8—B8^{ii}	2.08 (3)	133 (1)	92 (1)
N2—H2$A\cdots$H20—B20^{iii}	2.27 (3)	157 (2)	89 (1)
N2—H2$C\cdots$H2—B2	2.24 (3)	123 (2)	90 (1)
N2—H2$C\cdots$H5—B5	2.17 (2)	140 (2)	91.0 (9)
N3—H3$A\cdots$H8—B8^{ii}	1.99 (3)	150 (2)	104 (1)
N3—H3$B\cdots$H1—B1^v	2.19 (3)	154 (2)	105 (1)
N3—H3$C\cdots$H19—B19^{vi}	2.17 (3)	144 (2)	95 (1)
O5—H5$A\cdots$H7—B7^v	2.12 (3)	146 (2)	97 (1)
O6—H6$A\cdots$H15—B15^{iv}	2.06 (3)	158 (2)	106 (1)
O6—H6$B\cdots$H15—B15	2.06 (3)	147 (2)	103 (1)
O7—H7$A\cdots$H2—B2^v	2.23 (3)	143 (2)	101 (2)

Symmetry codes: (i) $1-x, 1-y, 1-z$; (ii) $\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$; (iii) $\frac{3}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$; (iv) $\frac{3}{2}-x, -\frac{1}{2}+y, \frac{1}{2}-z$; (v) $\frac{1}{2}-x, -\frac{1}{2}+y, \frac{1}{2}-z$; (vi) $-1+x, y, z$.

H atoms were located and refined isotropically. The range of refined B—H distances is 1.090 (14)–1.147 (14) Å.

Data collection: *COLLECT* (Nonius, 2000); cell refinement: *SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *DENZO* (Otwinowski & Minor, 1997) and *SCALEPACK*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL* and *Mercury* (Version 2.2; Macrae *et al.*, 2006).

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