Intermolecular dihydrogen- and hydrogen-bonding interactions in di-ammonium closo-decahydrodecaborate sesquihydrate

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Abstract
The asymmetric unit of the title salt, 2NH4+_B10H102_—1.5H2O or (NH4)2B10H10_—1.5H2O, (I), contains two B10H102_ anions, four NH4+ cations and three water molecules. (I) was converted to the anhydrous compound (NH4)2B10H10, (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 H2 at a faster rate than (NH4)2B12H12 and we believe that this is due to the stronger dihydrogenbonding interactions shown in the hydrate (I).

Keywords
sesquihydrate, deca, hydrogen, closo, inter, borate, ammonium, bonding, di, molecular, hydro, actions

Disciplines
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The asymmetric unit of the title salt, $2\text{NH}_4^+\text{B}_{10}\text{H}_{10}^2^-\cdot1.5\text{H}_2\text{O}$ or $(\text{NH}_4)_2\text{B}_{10}\text{H}_{10}^2\cdot1.5\text{H}_2\text{O}$, (I), contains two $\text{B}_{10}\text{H}_{10}^2$ anions, four $\text{NH}_4^+$ cations and three water molecules. (I) was converted to the anhydrous compound $(\text{NH}_4)_2\text{B}_{10}\text{H}_{10}$, (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 $(\text{NH}_4)_2\text{B}_{12}\text{H}_{12}$ and we believe that this is due to the stronger dihydrogen-bonding interactions shown in the hydrate (I).

Comment

Dihydrogen-bonded compounds, such as $\text{NH}_3\text{BH}_3$ (Klooster et al., 1999) and $(\text{NH}_3)_2\text{Mg(BH}_4)_2$ (Soloveichik et al., 2008), give off H$_2$ when heated. Since the ammonium cation in $(\text{NH}_4)_2\text{B}_{10}\text{H}_{10}$ has protonic hydrogen and the B—H hydrogen on the boron cage ($\text{B}_{10}\text{H}_{10}^2$) is hydric, it is a potential material for hydrogen storage. $(\text{NH}_4)_2\text{B}_{10}\text{H}_{10}$ 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 synthses of anhydrous $(\text{NH}_4)_2\text{B}_{10}\text{H}_{10}$ (Muetterties et al., 1964) and the dihydrate $(\text{NH}_4)_2\text{B}_{10}\text{H}_{10}\cdot2\text{H}_2\text{O}$ (Ivanov et al., 1992) have been reported but their structures remain unknown. The reported synthesis of anhydrous $(\text{NH}_4)_2\text{B}_{10}\text{H}_{10}$ involves a sulfur-containing precursor ($\text{B}_{10}\text{H}_{12}\cdot2\text{SMe}_2$) which is undesirable for hydrogen-storage materials because the sulfur poisons the fuel cell catalyst. The single-crystal X-ray structure of the reported $\text{B}_{12}$ analogue, $(\text{NH}_4)_2\text{B}_{12}\text{H}_{12}$, has weak N—H···H—B dihydrogen-bonding interactions (Tiritiris & Schleid, 2003). We report here the sulfur-free synthesis of the dihydrogen-bonded compound $(\text{NH}_4)_2\text{B}_{10}\text{H}_{10}\cdot1.5\text{H}_2\text{O}$ (I), and its anhydrous analog $(\text{NH}_4)_2\text{B}_{10}\text{H}_{10}$ (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).
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 $^{13}$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). 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···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$_4$)$_2$B$_{12}$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}$$^{2-}$ anions and two ammonium cations form a dihydrogen-bonded 14-membered ring and this unit is repeated within the sheet. The third dihydrogen bond on N1, H1B···H13, extends the sheet parallel to the a axis and connects two sheets together. The H2C atom on N2 has a bifurcated dihydrogen bond to two B—H H atoms (H2 and H5, Fig. 3) on the same B$_{10}$H$_{10}$$^{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···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···O···H···O···H···N···H···O

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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.)

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) $\frac{1}{2} - x, \frac{3}{2} + y, \frac{1}{2} - z$; (ii) $\frac{1}{2} - x, \frac{3}{2} + y, \frac{1}{2} - z$; (iii) $\frac{3}{2} - x, \frac{1}{2} + y, \frac{3}{2} - z$; (iv) $x, 1 + y, z$; (v) $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$; (vi) $\frac{3}{2} - x, \frac{1}{2} + y, \frac{3}{2} - z$; (vii) $\frac{1}{2} - x, \frac{3}{2} + y, -\frac{1}{2} + z$.]

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) $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$; (ii) $\frac{3}{2} - x, \frac{3}{2} + y, \frac{3}{2} - z$; (iii) $x - 1, y, z$; (iv) $x, 1 + y, z$; (v) $\frac{1}{2} - x, \frac{3}{2} + y, \frac{3}{2} - z$; (vi) $\frac{3}{2} - x, \frac{1}{2} + y, \frac{3}{2} - z$; (vii) $x - 1, 1 + y, z$.]
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···H—N and O—H···O···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 (NH₄)₂B₁₂H₁₂, the kinetics of hydrogen release should be faster. In fact, Yolles et al. (1969) has reported that (NH₄)₂B₁₀H₁₀ releases hydrogen much faster than (NH₄)₂B₁₂H₁₂ when heated under the same conditions.

**Experimental**

For the synthesis of (I), (NEt₃)₂B₁₀H₁₀ (synthesized from decaborane; Hawthorne & Pilling, 1967) (5.0 g, 15.51 mmol) was passed through an acid exchange resin to form the acidic (H₂O)₂B₁₀H₁₀. Excess ammonia gas was bubbled for 2 min into a water solution of (H₂O)₂B₁₀H₁₀ and (NH₄)₂B₁₀H₁₀.1.5H₂O was crystallized as colorless plate-shaped crystals by evaporation of the water. For the synthesis of (II), compound (I) [(NH₄)₂B₁₀H₁₀·1.5H₂O] was heated at 343 K for 2 h to give anhydrous compound (II) [(NH₄)₂B₁₀H₁₀]. Spectroscopic (IR and H and ¹³B NMR) and thermogravimetric analysis data are available in the archived CIF.

**Crystal data**

2NH₄⁺·B₁₀H₁₀·1.5H₂O

Mᵣ = 181.29

Monoclinic, P2₁/n

a = 11.674 (2) Å

b = 8.6230 (17) Å

c = 23.318 (5) Å

β = 98.97 (3)°

V = 2318.6 (8) Å³

Z = 8

Mo Kα radiation

μ = 0.06 mm⁻¹

T = 150 K

min = 0.38 × 0.31 × 0.12 mm

β = 98.97 (3)°

Data collection

Nonius Kappa CCD diffractometer

10211 measured reflections

5318 independent reflections

3637 reflections with I > 2σ(I)

Rint = 0.042

Refection

R[F² > 2σ(F²)] = 0.045

wR(F²) = 0.121

S = 1.02

5318 reflections

**Table 1**

Hydrogen-bond geometry (Å, °).

<table>
<thead>
<tr>
<th>D···H···A</th>
<th>D···H</th>
<th>H···A</th>
<th>D···A</th>
<th>D···H·D</th>
</tr>
</thead>
<tbody>
<tr>
<td>N2···H20 — O6</td>
<td>0.93 (2)</td>
<td>1.91 (2)</td>
<td>2.837 (2)</td>
<td>171.7 (15)</td>
</tr>
<tr>
<td>N3···H30 — O7</td>
<td>0.968 (19)</td>
<td>1.855 (19)</td>
<td>2.8117 (19)</td>
<td>168.8 (15)</td>
</tr>
<tr>
<td>N4···H40 — O5</td>
<td>0.94 (2)</td>
<td>1.96 (2)</td>
<td>2.896 (2)</td>
<td>168.5 (16)</td>
</tr>
<tr>
<td>N4···H40 — O7</td>
<td>0.98 (2)</td>
<td>2.09 (2)</td>
<td>2.942 (2)</td>
<td>162.7 (17)</td>
</tr>
<tr>
<td>O5···H50 — O6</td>
<td>0.82 (2)</td>
<td>2.01 (2)</td>
<td>2.8557 (18)</td>
<td>170.5 (19)</td>
</tr>
<tr>
<td>O7···H70 — O8</td>
<td>0.93 (2)</td>
<td>1.85 (3)</td>
<td>2.7487 (18)</td>
<td>177 (2)</td>
</tr>
</tbody>
</table>

Symmetry codes: (i) —x + 1/2, y — 1/2, —z + 1/2; (ii) —x + 1/2, y + 1/2, —z + 1/2.

**Table 2**

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

<table>
<thead>
<tr>
<th>D···H···A</th>
<th>D···H</th>
<th>H···A</th>
<th>D···A</th>
<th>D···H·D</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH₄···OH — B13'</td>
<td>2.27 (3)</td>
<td>154 (2)</td>
<td>105 (1)</td>
<td></td>
</tr>
<tr>
<td>NH₄···OH — B16</td>
<td>2.03 (3)</td>
<td>141 (2)</td>
<td>106 (1)</td>
<td></td>
</tr>
<tr>
<td>NH₄···OH — B8''</td>
<td>2.08 (3)</td>
<td>133 (1)</td>
<td>92 (1)</td>
<td></td>
</tr>
<tr>
<td>NH₄···OH — B20''</td>
<td>2.27 (3)</td>
<td>157 (2)</td>
<td>89 (1)</td>
<td></td>
</tr>
<tr>
<td>NH₄···OH — B5'</td>
<td>2.24 (2)</td>
<td>123 (2)</td>
<td>90 (1)</td>
<td></td>
</tr>
<tr>
<td>NH₄···OH — B5'</td>
<td>2.17 (2)</td>
<td>140 (2)</td>
<td>91.0 (9)</td>
<td></td>
</tr>
<tr>
<td>NH₄···OH — B8''</td>
<td>1.99 (3)</td>
<td>150 (2)</td>
<td>104 (1)</td>
<td></td>
</tr>
<tr>
<td>NH₄···OH — B15''</td>
<td>1.92 (3)</td>
<td>154 (2)</td>
<td>101 (1)</td>
<td></td>
</tr>
<tr>
<td>NH₄···OH — B15''</td>
<td>1.89 (3)</td>
<td>144 (2)</td>
<td>95 (1)</td>
<td></td>
</tr>
<tr>
<td>NH₄···OH — B2''</td>
<td>1.92 (3)</td>
<td>146 (2)</td>
<td>97 (1)</td>
<td></td>
</tr>
<tr>
<td>NH₄···OH — B2''</td>
<td>1.50 (2)</td>
<td>126 (2)</td>
<td>101 (1)</td>
<td></td>
</tr>
<tr>
<td>NH₄···OH — B15</td>
<td>1.06 (3)</td>
<td>147 (2)</td>
<td>103 (1)</td>
<td></td>
</tr>
</tbody>
</table>

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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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SQ3215). Services for accessing these data are described at the back of the journal.

**References**


Hoek, H. M. 18, 394–400.


Ysidro et al. • 2NH₄⁺·B₁₀H₁₀·1.5H₂O m3