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A new hydrated ammonium hydroxyborate, $(NH_4)_2[B_{10}O_{14}(OH)_4]\cdot H_2O$

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The structure of a new synthetic compound, diammonium tetrahydroxydecaborate monohydrate, has been determined by single-crystal X-ray diffraction. It crystallizes in triclinic space group $P\overline{1}$ and all atoms occupy general sites. The title compound is composed of $[B_{10}O_{15}(OH)_4]^{4-}$ ions as the fundamental building blocks, and these are linked end-to-end by sharing two common O atoms, thus producing infinite chains of composition $[B_{10}O_{14}(OH)_4]_n^{2n-}$. These chains are linked by hydrogen bonds, thus forming borate sheets. Water molecules and ammonium ions between these sheets connect adjacent sheets *via* hydrogen bonds.

Comment

Borates are conventionally obtained by high-temperature solid-state or hydrothermal reactions. In order to enrich the field of borate chemistry and explore more practical materials, an unusual synthetic method involving a flux of molten boric acid was proposed for the synthesis of new borates (Williams *et al.*, 1998; Li *et al.*, 2002). The present work is part of a series of studies aimed at synthesizing new borates from boric acid flux. Several natural or synthetic ammonium borates, *e.g.* larderellite $\{NH_4[B_5O_7(OH)_2]\cdot H_2O$; Merlino & Sartori, 1969} and ammonioborite $\{(NH_4)_3[B_{15}O_{20}(OH)_8]\cdot 4H_2O$; Merlino & Sartori, 1971}, have been found previously, but the title compound, (I), obtained from a boric acid flux, differs from all known ammonium borates. The experimental powder pattern, IR spectrum and ICP analysis of (I) are in good agreement with the results of single-crystal X-ray diffraction analysis.

The basic structural unit in (I) is a double ring consisting of one BO_4 tetrahedron and four BO_3 triangles. This unit was first found in $K[B_5O_6(OH)_4]\cdot 2H_2O$ as an isolated ion (Zachariasen, 1937). In larderellite, these structural units are linked to form infinite chains, while in ammonioborite, three of these structural units are connected to give trimeric ions with $C_2\overline{2}$ symmetry. However, in (I), two of the basic structural units with no symmetric relation are connected, thus forming a dimeric ion. Including H atoms bonded to the terminal O atoms, this dimeric ion is $[B_{10}O_{15}(OH)_4]^{4-}$, which is the fundamental building block (FBB) of (I) (Fig. 1). After making a careful inspection of known borates, we believe that this ion is a new borate FBB.

The FBBs in (I) are linked end-to-end by sharing two O atoms, thus forming infinite chains along the *b* axis with the composition $[B_{10}O_{14}(OH)_4]_n^{2n-}$. Two symmetry-equivalent chains pass through the unit cell. These parallel chains are aligned along the *a* axis and are linked *via* hydrogen bonds, thus forming infinite sheets approximately parallel to the *ab* plane (Fig. 2). Ammonium ions and water molecules are located between these sheets, which are connected to one another *via* hydrogen bonds. The O atoms of the water molecules are disordered, presumably as a result of the large space between the sheets.

The general structural features and the composition are very similar in (I) and in larderellite, but the configurations of their borate chains are different. In (I), the two chains running through the unit cell are parallel, but in larderellite, they

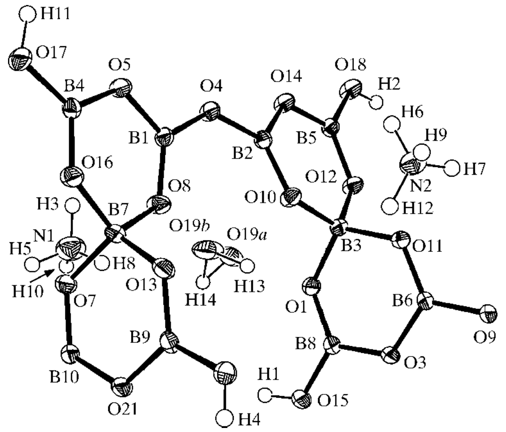

Figure 1
The fundamental building block in (I). Displacement ellipsoids are drawn at the 50% probability level and H atoms are drawn as small spheres of arbitrary radii.

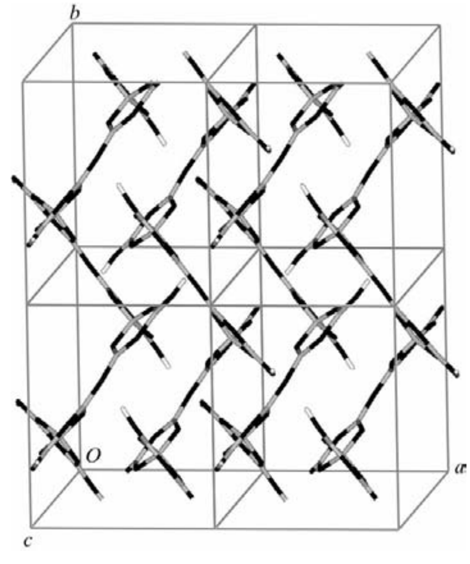

Figure 2
The borate sheet in (I), displayed in stick style. B, O and H atoms are shown as grey, black and white, respectively.

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intersect. Furthermore, in the chains of larderellite, each $[B_5O_{10}]$ unit is obtained from the preceding unit through the operation of a screw diad axis (Merlino & Sartori, 1969), but in (I), adjacent $[B_5O_{10}]$ units in each chain are symmetry distinct.

In (I), the triangular BO_3 groups are slightly distorted, with an average B—O bond length of 1.366 (18) Å (Table 1) and O—B—O angles in the range 113.72 (9)–124.50 (10)°. The BO_4 groups are almost perfect tetrahedra, with a mean B—O distance of 1.469 (4) Å and O—B—O angles in the range 107.65 (9)–111.85 (8)°. These average bond lengths are in agreement with the data reviewed by Hawthorne *et al.* (1996).

The hydrogen bonds within the sheets involve the H atoms of hydroxy groups and O atoms in the sheets, and the hydrogen bonds between the sheets involve the H atoms of the ammonium ions, the water molecules and O atoms in the sheets (Table 2). Each ammonium ion is hydrogen bonded to the two adjacent sheets, but each water molecule is only hydrogen bonded to one neighboring sheet.

Experimental

The title compound was synthesized using a flux of boric acid. All reagents were of analytical grade. A mixture of V_2O_5 (0.22 g), H_2O (1 ml) and $NH_2CH_2CH_2NH_2$ (0.5 ml) was stirred to give a transparent solution, which was mixed with H_3BO_3 (3.09 g), charged into a 50 ml Teflon autoclave and heated at 493 K for 7 d. Excess boric acid was removed by washing the products with hot distilled water, and colorless crystals were isolated easily from the mixture.

Crystal data

$(NH_4)_2[B_{10}O_{14}(OH)_4]\cdot H_2O$
$M_r = 454.23$
Triclinic, $P\overline{1}$
$a = 7.6207\ (15)$ Å
$b = 9.2328\ (18)$ Å
$c = 11.926\ (2)$ Å
$\alpha = 99.46\ (3)°$
$\beta = 105.89\ (3)°$
$\gamma = 91.54\ (3)°$
$V = 793.8\ (3)$ Å^3

$Z = 2$
$D_x = 1.900$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 4431 reflections
$\theta = 2.8$–33.0°
$\mu = 0.18$ mm^{-1}
$T = 293\ (2)$ K
Tablet, colorless
0.4 × 0.2 × 0.1 mm

Data collection

Bruker SMART APEX CCD area-detector diffractometer
ω scans
7470 measured reflections
5466 independent reflections
4462 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.020$
$\theta_{\rm max} = 33.0°$
$h = -9 \rightarrow 11$
$k = -14 \rightarrow 12$
$l = -18 \rightarrow 18$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.044$
$wR(F^2) = 0.118$
$S = 1.01$
5466 reflections
346 parameters

All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.077P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = 0.006$
$\Delta\rho_{\rm max} = 0.52$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.34$ e Å^{-3}

Difference Fourier analysis indicated residual electron density at ~1 Å from positions O19*A* and O19*B*. Further refinement revealed that these two positions corresponded to O atoms with occupancies of 0.64 and 0.36, respectively. In addition, the difference Fourier analysis was able to locate H atoms on these O atoms, forming a disordered water molecule with an occupancy ratio of ~2:1. All of the H atoms were refined without constraints. During the data collection, there was no indication of superstructure reflections.

Table 1
Selected interatomic distances (Å).

O1—B8	1.3478 (14)	O9—B6	1.3813 (14)
O1—B3	1.4751 (14)	O10—B2	1.3443 (14)
O2—B9	1.3879 (14)	O10—B3	1.4714 (14)
O2—B10	1.3893 (14)	O11—B6	1.3399 (13)
O3—B6	1.3820 (14)	O11—B3	1.4638 (14)
O3—B8	1.3909 (15)	O12—B5	1.3536 (14)
O4—B1	1.3703 (14)	O12—B3	1.4699 (15)
O4—B2	1.3775 (14)	O13—B9	1.3424 (14)
O5—B4	1.3812 (14)	O13—B7	1.4676 (15)
O5—B1	1.3811 (14)	O14—B5	1.3761 (14)
O6—B9	1.3673 (15)	O14—B2	1.3801 (14)
O7—B10	1.3374 (13)	O15—B8	1.3602 (14)
O7—B7	1.4652 (14)	O16—B4	1.3501 (14)
O8—B1	1.3387 (13)	O16—B7	1.4702 (14)
O8—B7	1.4652 (15)	O17—B4	1.3595 (14)
O9—B10$^{\rm vii}$	1.3785 (13)	O18—B5	1.3596 (14)

Symmetry code: (vii) $x, y-1, z$.

Table 2
Hydrogen-bonding geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N1—H3···O4$^{\rm iii}$	0.90 (2)	2.16 (2)	3.039 (2)	168 (2)
N1—H5···O11$^{\rm v}$	0.89 (4)	2.38 (4)	3.231 (2)	159 (3)
N1—H8···O15$^{\rm viii}$	0.87 (3)	2.22 (3)	2.909 (2)	136 (3)
N1—H10···O16$^{\rm i}$	0.94 (4)	2.22 (4)	3.098 (2)	154 (3)
N2—H6···O18$^{\rm vi}$	0.91 (3)	1.83 (3)	2.745 (2)	179 (2)
N2—H7···O7$^{\rm vii}$	0.81 (4)	2.22 (3)	2.992 (2)	160 (3)
N2—H9···O12$^{\rm ix}$	0.95 (3)	2.24 (3)	3.117 (2)	154 (2)
N2—H12···O2$^{\rm iv}$	0.92 (4)	2.04 (4)	2.945 (2)	165 (3)
O6—H4···O10$^{\rm iv}$	0.79 (2)	2.29 (2)	2.991 (2)	147 (2)
O15—H1···O6$^{\rm i}$	0.86 (2)	2.06 (2)	2.846 (1)	153 (2)
O17—H11···O19*A*$^{\rm iii}$	0.92 (2)	1.70 (2)	2.576 (2)	160 (2)
O18—H2···O17$^{\rm ii}$	0.82 (2)	1.85 (2)	2.637 (1)	158 (2)
O19*A*—H13···O1	0.95 (3)	1.81 (3)	2.693 (2)	153 (3)
O19*A*—H14···O13$^{\rm i}$	0.85 (3)	1.87 (3)	2.710 (2)	170 (3)

Symmetry codes: (i) $x-1, y, z$; (ii) $x-1, y-1, z$; (iii) $1-x, 1-y, -z$; (iv) $2-x, 1-y, 1-z$; (v) $x, 1+y, z$; (vi) $1-x, -y, -z$; (vii) $x, y-1, z$; (viii) $1-x, 1-y, 1-z$; (ix) $1+x, y, z$.

Data collection: *SMART* (Bruker, 1997); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 1997); structure solution: *SHELXS*97 (Sheldrick, 1997); structure refinement: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 (Farrugia, 1997) and *ViewerLite* (Accelrys, 2001).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: IZ1036). Services for accessing these data are described at the back of the journal.

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