

## The first example of a mixed alkoxide hydride of boron: sodium boron isopropoxide trihydride

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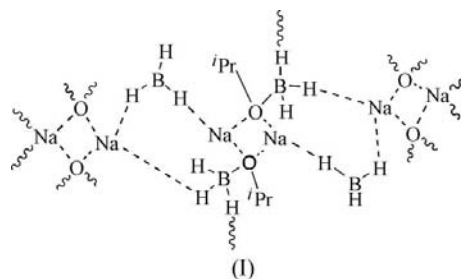
The title compound, poly[[ $\mu$ -trihydro(isopropoxy)borato]-sodium(I)],  $[\text{Na}(\text{C}_3\text{H}_7\text{BO})]_n$ , forms unique polymeric layers normal to the  $c$  axis via  $\text{Na}^+\cdots\text{O}$  [2.3405 (15) Å] and  $\text{Na}^+\cdots\text{H}$  (borane) [2.22 (3) and 2.28 (3) Å] interactions. This arrangement builds on distorted tetrahedral  $\text{Na}^+$ , oxygen and boron environments, with one of the borane hydride units uncoordinated, and highlights potential  $\text{H}_3\text{B}-\text{O}$ -based chemistry.

### Comment

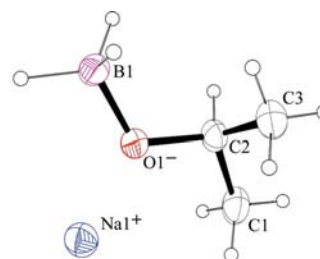
This study is part of a programme aimed at investigating boron diolates and alkoxides with potential applications in hydrogen storage/recycling systems (Kemmitt & Gainsford, 2009; Gainsford & Kemmitt, 2005). There are no previous reports of boron trihydride ( $\text{BH}_3$ ) structures where the boron is bonded to oxygen, although there are 113 compounds containing  $\text{C}-\text{BH}_3$  (principally cyanoboranes) and 186 reports of  $\text{N}-\text{BH}_3$  adducts [Cambridge Structural Database (CSD); Version 5.30 with February 2009 updates; Allen, 2002]. Likewise,  $\text{BH}_3$  units bound to P are common (324 hits), whilst the  $\text{S}-\text{BH}_3$  entity is only found three times.

The asymmetric unit contents of the title compound, (I), with formula  $[\text{Na}(\text{C}_3\text{H}_7\text{BO})]$ , are shown in Fig. 1. The polymeric unit is built around a highly distorted tetrahedral arrangement of the sodium cations through bridging O atoms (Table 1 and Fig. 2) and adjacent  $\text{BH}_3$  hydride atoms. The mean  $\text{Na}\cdots\text{O}$  and  $\text{Na}\cdots\text{H}$  distances are 2.3405 (15) and 2.25 (2) Å, with angles subtended at the Na atoms ranging from 97.8 (11) to 133.6 (7)° (Fig. 2). Bridging hydrides ( $\text{B}-\text{H}\cdots\text{A}$ , where A is an alkali metal) are well known in tetrahydroborates (Ruiz *et al.*, 2008). The  $\text{Na}\cdots\text{H}$  distance parameters in (I) are within the ranges noted by Ruiz *et al.* (2008) {e.g. CSD refcodes HIWXUH [2.28 (2) Å] and HIWZOD [2.32–2.39 Å]} and in the singly-bound  $\text{Na}\cdots\text{H}$  contact in

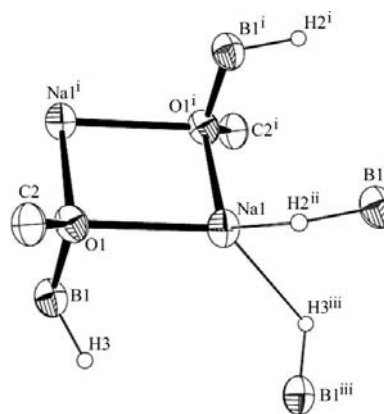
WOCMAD (2.38 Å; Wagler & Hill, 2008). In sodium salts of boron trihydride compounds containing  $\text{S}-\text{B}$  and  $\text{P}-\text{B}$  bonds, the  $\text{Na}\cdots\text{H}$  single contacts are similar at 2.35 (LATSAA; Binder *et al.*, 1993) and 2.32 Å (YILJOT; Izod *et al.*, 2007). The  $\text{B}-\text{O}-\text{C}$  angle and  $\text{B}-\text{O}$ ,  $\text{O}-\text{C}$  and  $\text{Na}\cdots\text{O}$  distances are within the ranges noted previously [Gainsford & Kemmitt, 2004; Knizek *et al.*, 2006 (XEPIIUE)].



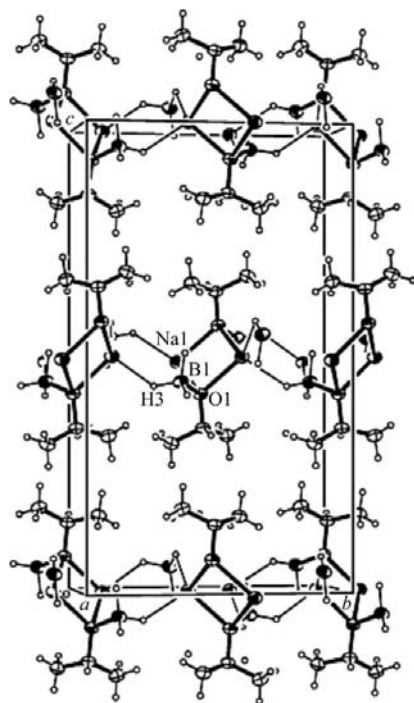
The unique polymeric structure can be described as layers, running parallel to the  $ab$  plane, generated by the four-coordinated Na, B and O atoms, based on the centrosymmetrically related B and O atoms (Figs. 2 and 3) and linked through two of the  $\text{BH}_3$  hydride atoms. These rings can be delineated as  $R_3^2(8)$  rings, taking the  $\text{BH}_3$  H atoms as donors (Bernstein *et al.*, 1995). This arrangement with sodium ions and  $\text{BH}_3$  substituents appears unique, with all other reported structures involving tetrahydroborates. The aliphatic isopropyl groups act as spacer units along the  $c$  axis (Fig. 3), being involved only in van der Waals interactions.



**Figure 1**  
An ORTEP (Farrugia, 1999) view of the asymmetric unit of (I), shown with 30% probability displacement ellipsoids.



**Figure 2**  
An ORTEP (Farrugia, 1999) view showing the fourfold coordination of the Na atoms. Atoms not involved in the coordination environment, except for isopropyl atom C2, have been omitted for clarity. [Symmetry codes: (i)  $-x + 1, -y + 1, -z + 1$ ; (ii)  $x - 1, y, z$ ; (iii)  $x - \frac{1}{2}, -y + \frac{1}{2}, -z + 1$ .]



**Figure 3**  
An ORTEP (Farrugia, 1999) view of the cell contents down the *a* axis, showing the crosslinked layers normal to the *c* axis.

The B...Na distances average 2.904 (2) Å, consistent with the general observation that such longer interactions indicate less bridging of multiple metal atoms by the hydride atoms (Ruiz *et al.*, 2008). This first reported example of a compound containing the O—BH<sub>3</sub> group adds a new dimension to the prolific chemistry of boron hydrides.

## Experimental

NaAlH<sub>4</sub> (0.65 g, 12 mmol) was added in small aliquots over a period of 15 min to a flask containing a rapidly stirred solution of NaB[OCH(CH<sub>3</sub>)<sub>2</sub>]<sub>4</sub> (2.70 g, 10 mmol) in tetrahydrofuran (100 ml) at 273 K. The reaction mixture was allowed to return to room temperature and was stirred for 16 h. It was then filtered and the volume reduced under partial vacuum. After the reaction mixture had been left in a freezer (261 K) for 16 h, the product appeared as colourless needles, which were filtered off and dried *in vacuo* (yield 0.8 g, 84%). <sup>1</sup>H NMR (*d*<sub>6</sub>-DMSO): δ 0.9 (*d*, 6.1 Hz, CH<sub>3</sub>, 6H), 2.01 (*q*, 88 Hz, BH<sub>3</sub>, 3H), 3.17 (sept, CH, 1H). <sup>13</sup>C NMR (*d*<sub>6</sub>-DMSO): δ 24.72 (CH<sub>3</sub>), 61.84 (CH). <sup>11</sup>B NMR (*d*<sub>6</sub>-DMSO): δ -9.7 (88 Hz).

### Crystal data

[Na(C <sub>3</sub> H <sub>10</sub> BO)]	<i>V</i> = 1187.6 (4) Å <sup>3</sup>
<i>M<sub>r</sub></i> = 95.91	<i>Z</i> = 8
Orthorhombic, <i>Pbca</i>	Cu Kα radiation
<i>a</i> = 5.5071 (11) Å	<i>μ</i> = 1.19 mm <sup>-1</sup>
<i>b</i> = 11.094 (2) Å	<i>T</i> = 173 K
<i>c</i> = 19.438 (4) Å	0.5 × 0.05 × 0.02 mm

### Data collection

Rigaku SPIDER diffractometer	9917 measured reflections
Absorption correction: multi-scan (ABSCOR; Higashi, 1995)	1119 independent reflections
<i>T</i> <sub>min</sub> = 0.492, <i>T</i> <sub>max</sub> = 1.0	849 reflections with <i>I</i> > 2σ( <i>I</i> )
(expected range = 0.480–0.977)	<i>R</i> <sub>int</sub> = 0.104

### Refinement

$R[F^2 > 2\sigma(F^2)] = 0.070$	85 parameters
$wR(F^2) = 0.194$	Only H-atom coordinates refined
<i>S</i> = 1.08	$\Delta\rho_{\max} = 0.49 \text{ e \AA}^{-3}$
1119 reflections	$\Delta\rho_{\min} = -0.35 \text{ e \AA}^{-3}$

**Table 1**

Selected geometric parameters (Å, °).

Na1...O1 <sup>i</sup>	2.3393 (19)	Na1...H3 <sup>iii</sup>	2.22 (3)
Na1...O1	2.3416 (17)	O1—B1	1.486 (3)
Na1...H2 <sup>ii</sup>	2.28 (3)	C1—C2	1.517 (4)
O1 <sup>i</sup> ...Na1...O1	90.38 (6)	H2 <sup>ii</sup> ...Na1...H3 <sup>iii</sup>	97.8 (11)
O1...Na1...H2 <sup>ii</sup>	104.5 (8)	Na1 <sup>i</sup> ...O1...Na1	89.62 (6)
O1...Na1...H3 <sup>iii</sup>	133.6 (7)		

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

The positional parameters of all H atoms were freely refined, with C—H and B—H distances in the ranges 0.93 (4)–1.05 (4) and 1.14 (3)–1.21 (3) Å, respectively, and with *U*<sub>iso</sub>(H) values fixed at 1.5 or 1.2 (for H4) times *U*<sub>eq</sub> of their carrier atoms. A total of 37 of the 1077 expected reflections within the sinθ/λ limit of 0.60 either could not be processed correctly (25) or were omitted as outliers (12).

Data collection: *CrystalClear* (Rigaku, 2005); cell refinement: *FSProcess* in *PROCESS-AUTO* (Rigaku, 1998); data reduction: *FSProcess* in *PROCESS-AUTO*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP* in *WinGX* (Farrugia, 1999); software used to prepare material for publication: *SHELXL97* and *PLATON* (Spek, 2009).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: DN3110). Services for accessing these data are described at the back of the journal.

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