

## Poly[di- $\mu_2$ -methanolato-di- $\mu_2$ -tetramethoxyborato-disodium(I)]

Graeme J. Gainsford\* and Tim Kemmitt

Industrial Research Limited, PO Box 31-310, Lower Hutt, New Zealand

Correspondence e-mail: g.gainsford@irl.cri.nz

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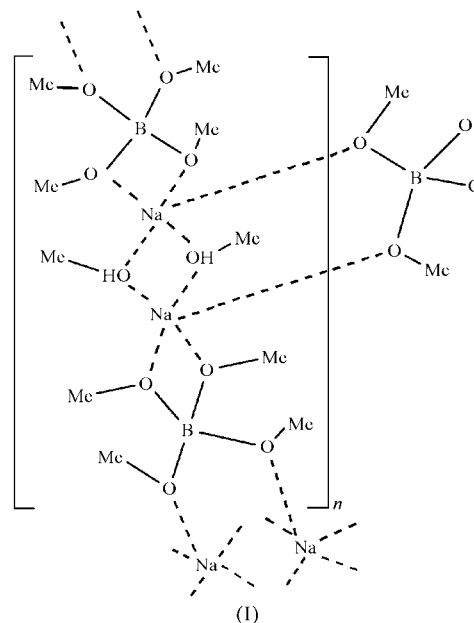
In the polymeric title compound,  $[\text{Na}_2(\text{C}_4\text{H}_{12}\text{BO}_4)_2(\text{CH}_4\text{O})_2]_n$ , the two independent sodium cations are bound by five O atoms. All the O atoms of one tetramethoxyborate anion bind cations, forming a tetrameric cluster around a tetragonal inversion centre [ $\text{Na}-\text{O} = 2.2777(18)$ – $2.3907(16)$  Å]. Two methanol O atoms bridge the two Na atoms [ $\text{Na}-\text{O} = 2.3590(15)$ – $2.4088(18)$  Å] and provide the hydrogen-bonding H atoms. The second tetramethoxyborate anion provides two O atoms to one Na atom [mean  $\text{Na}-\text{O} = 2.31(2)$  Å] and two O atoms as donors for crosslinking hydrogen bonds to adjacent tetramers, which complete the three-dimensional packing. The crystal was treated as a racemic twin.

### Comment

This study is part of a programme aimed at investigating boron diolates and alkoxides, particularly those containing sodium cations (Gainsford & Kemmitt, 2004, 2005). Although borates form a range of diolate complexes (Bachelier & Verchere, 1995; Springsteen & Wang, 2002), structural data are sparse. Tetramethoxyborate salts with organic cations, such as piperidinium tetramethoxyborate [Cambridge Structural Database (CSD; Allen, 2002) refcode BAZFAJ (Alcock *et al.*, 1982)] and others [CSD refcodes RAVPAF (Clegg *et al.*, 1997) and NEMYOT (Kuhn *et al.*, 2001)], have been reported. There are some defined mixed-metal complexes [*e.g.* HOSXES; neodymium(III)–sodium; Gajadhar-Plummer *et al.*, 1999] but only one reported sodium salt of this borate, which also contains bound water molecules (TMXBNA; Heller & Horbat, 1977). The NMR spectrum in  $d_8$ -tetrahydrofuran showed the presence of both methoxide and methanol groups, spurring our investigation, and we were also interested to confirm the absence of water.

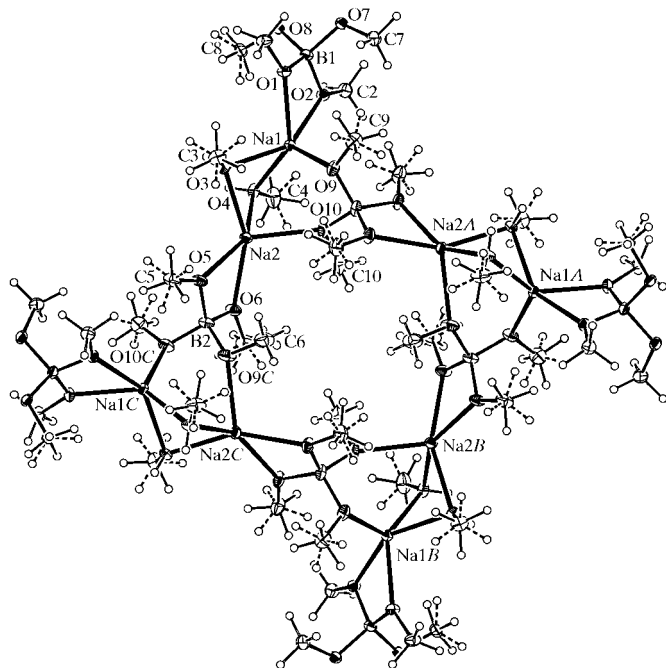
The basic polymeric fragment of the title compound, (I), with asymmetric unit formula  $[\text{Na}_2(\text{C}_4\text{H}_{12}\text{BO}_4)_2(\text{CH}_3\text{OH})_2]_4$  (Table 1 and Fig. 1), crystallized in a racemically twinned crystal. Enantiomeric resolution was not expected from the synthesis and could not be established by anomalous dispersion effects.

The use of the word 'bound' here indicates atoms that are within either covalent or ionic attractive distances of each other. Both sodium cations are five-coordinate in a highly distorted square-pyramidal arrangement; the basal atoms deviate from the square plane by 0.1020 (6)–0.1792 (8) Å, with the Na atoms 0.80 (Na1) and 0.57 Å (Na2) above and towards the pyramidal O atoms (O9 and O10, respectively). Both distorted trigonal-bipyramidal [EDUNUM (Onada *et al.*, 2002) and GOLSIJ (Hauptmann *et al.*, 1999)] and square-pyramidal (OGEBEH; Fukin *et al.*, 2002) environments around oxygen-bridged sodium cations have been observed previously.



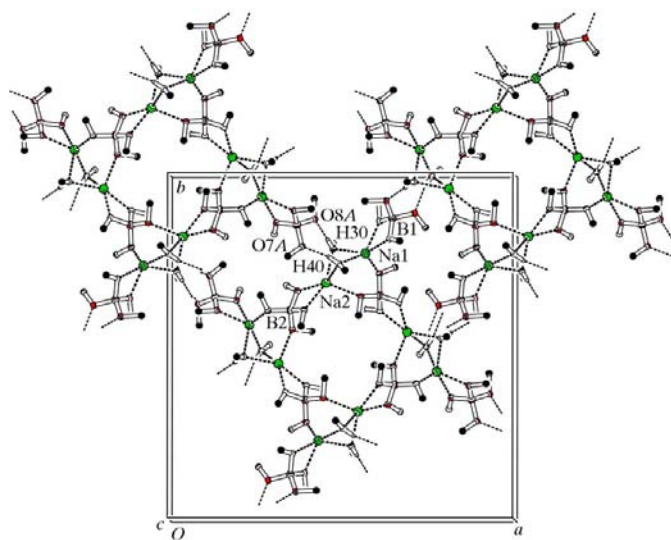
Each Na atom is bound by two shared methanol O-atom bridges [O3 and O4;  $\text{Na}-\text{O} = 2.3590(15)$ – $2.4088(18)$  Å] and two O atoms from adjacent tetramethoxyborate groups [O5/O6 and O1/O2, respectively;  $\text{Na}-\text{O} = 2.2994(14)$ – $2.3159(15)$  Å] making up the square basal planes. A wider range of  $\text{Na}-\text{O}$ (methanol) distances was observed in TMXBNA (2.358–2.611 Å), with similar  $\text{Na}-\text{O}$ (tetramethoxyborate) distances of 2.282 and 2.386 Å. For the two Na atoms in (I), the fifth coordination position is occupied by one of two O atoms from one fourfold roto-inversion symmetry-related tetramethoxyborate group (atoms O9 and O10, respectively). This arrangement results in the tetrameric unit with fourfold inversion symmetry shown in Fig. 1. Rather than bind to sodium cations, the two remaining tetramethoxyborate O atoms (O7 and O8) on atom B1 provide the acceptor sites for two strong hydrogen bonds that link adjacent clusters into a complete three-dimensional network (Table 2 and Fig. 2). This structural binding has some similarity to the TMXBNA structure, in which one of the two tetramethoxyborate groups is bound through two O atoms to one of the Na atoms; however, in that case, the second (charged) tetramethoxyborate group is only retained in the lattice by hydrogen bonds to the water and bound methanol molecules.

Our interest in these structures concerns the lengthening or otherwise of the B—O bonds in relation to different appended alkyl groups. In (I), the longest B—O—C bonds involve the



**Figure 1**

A PLATON (Spek, 2003) view of the polymeric unit of (I), shown with 50% probability displacement ellipsoids. Labels of asymmetric unit atoms, all Na atoms, and atoms O9C and O10C are shown. Atoms labelled with the suffixes A, B and C are at the symmetry positions ( $y, 1-x, 1-z$ ), ( $1-x, 1-y, -z$ ) and ( $1-y, x, 1-z$ ).



**Figure 2**

A PLATON (Spek, 2003) view of (I), showing two representatives of the hydrogen bonds (dashed lines) that link the polymeric units (shown in Fig. 1) into a three-dimensional network. All H atoms, except H3O and H4O, have been excluded for clarity. Atoms O7A and O8A are at the symmetry position ( $y - \frac{1}{2}, \frac{3}{2} - x, \frac{3}{2} - z$ ).

non-bridging 'free' O atoms O8 and O7 bound to B1, with mean B—O and O—C distances of 1.474 (7) and 1.418 (3) Å compared with averages of 1.464 (6) and 1.409 (2) Å for the other six bond sets. These differences are statistically insignificant, although they suggest that intermolecular hydrogen bonding may influence the covalent binding at the B atom. Although cell-packing interactions (Table 2) can be important, steric requirements may play the dominant role. Indeed, the Na—O(methanol) bridging distances (2.359–2.409 Å) are shorter than those found in *catena*-poly[hexakis( $\mu_2$ -methanolato)disodium ditelluride] (2.432 Å; Thiele *et al.*, 1996) and a bis(trimethanolsodium) salt [2.45 (3) Å; Brničević *et al.*, 1991]. Examination of previous structures of organic salts (with 'free' O atoms; BAZFAJ, NEMYOT and RAVPAF) shows that these have a wide range of B—O and C—O distances, while in the comparable sodium salt (TMXBNA), the ranges are 1.461–1.482 and 1.426–1.440 Å, respectively. Ranges in other metal salts [HOSXES and the lithium complex KAJPOA (Al-Juaid *et al.*, 1989)] are similar, with slightly lower minimum values (1.440–1.481 and 1.418–1.443 Å). We conclude that no definitive conclusions can be made about variations in bond strengths on the basis of current studies.

The B—O—C angles range from 114.21 (18) to 117.37 (15)°, again consistent with previous observations (114.4–120.5°) in the above-mentioned studies. Finally, it is noted that in the 'closest relative' structure (TMXBNA), the two Na atoms are five- and six-coordinate, the latter coordination involving bridging water and methanol molecules only. The one-dimensional (short) chains in TMXBNA involve a tetramethoxyborate 'capped'  $\{\text{Na}^+\}_4$  unit built with O-atom bridges; however, these O atoms are provided by the three water and two methanol molecules rather than by the tetramethoxyborate molecules.

## Experimental

The title compound was prepared by refluxing a methanol (75 ml) solution of sodium metaborate (0.1 mol, 13.8 g) for 4 h, running the condensate through a bed of molecular sieves to remove water. The crude product was obtained on removal of the solvent. X-ray quality crystals were obtained by recrystallizing the product from a methanol/toluene mixture.

### Crystal data

$[\text{Na}_2(\text{C}_4\text{H}_{12}\text{BO}_4)_2(\text{CH}_4\text{O})_2]$   
 $M_r = 379.96$   
 Tetragonal,  $I\bar{4}$   
 $a = 22.0496$  (19) Å  
 $c = 8.8155$  (15) Å  
 $V = 4286.0$  (9) Å<sup>3</sup>  
 $Z = 8$   
 $D_x = 1.178$  Mg m<sup>-3</sup>

Mo  $K\alpha$  radiation  
 Cell parameters from 4302 reflections  
 $\theta = 2.5$ – $26.3^\circ$   
 $\mu = 0.13$  mm<sup>-1</sup>  
 $T = 98$  (2) K  
 Block, colourless  
 0.65 × 0.54 × 0.50 mm

### Data collection

Bruker SMART CCD area-detector diffractometer  
 $\varphi$  and  $\omega$  scans  
 Absorption correction: multi-scan (Blessing, 1995)  
 $T_{\min} = 0.787$ ,  $T_{\max} = 0.936$   
 6990 measured reflections

2330 independent reflections  
 2070 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.020$   
 $\theta_{\text{max}} = 26.3^\circ$   
 $h = -27 \rightarrow 27$   
 $k = -4 \rightarrow 27$   
 $l = -6 \rightarrow 10$

## Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.027$   
 $wR(F^2) = 0.066$   
 $S = 1.04$   
 2330 reflections  
 238 parameters  
 H atoms: see below

$$w = 1/[\sigma^2(F_o^2) + (0.0368P)^2 + 0.8467P]$$

where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} = 0.001$   
 $\Delta\rho_{\max} = 0.11 \text{ e } \text{\AA}^{-3}$   
 $\Delta\rho_{\min} = -0.13 \text{ e } \text{\AA}^{-3}$

**Table 1**

Selected interatomic distances (Å).

Na1—O9	2.2777 (18)	Na2—O4	2.4088 (18)
Na1—O3	2.3893 (16)	O1—B1	1.453 (3)
Na2—O5	2.3009 (16)	O7—B1	1.479 (2)

**Table 2**

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O3—H3O $\cdots$ O8 <sup>i</sup>	0.79 (2)	1.86 (2)	2.648 (2)	178 (2)
O4—H4O $\cdots$ O7 <sup>i</sup>	0.78 (2)	1.84 (2)	2.596 (2)	162 (3)

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

Friedel pairs were merged after a full data set refinement gave a Flack (1983) parameter of 0.6 (2). The H atoms on methyl C atoms C3, C4, C5, C6, C8 and C9 were modelled as disordered over two sites rotated by 60°; the major site occupancies were 0.73 (3), 0.78 (3), 0.79 (3), 0.52 (3), 0.78 (3) and 0.90 (3), respectively. All methyl H atoms, except those on atom C10, were constrained to their expected geometries (C—H = 0.98 Å). The hydroxy H atoms (H3O and H4O) and the H atoms on atom C10 were freely refined. All H atoms were refined with  $U_{\text{iso}}(\text{H})$  values of 1.2 times  $U_{\text{eq}}$  of their carrier atoms.

Data collection: *SMART* (Bruker, 2001); cell refinement: *SMART*; data reduction: *SAINTE* (Bruker, 2001) and *SADABS* (Sheldrick, 1996); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FA1119). Services for accessing these data are described at the back of the journal.

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