Acta Crystallographica Section C
**Crystal Structure
Communications**
ISSN 0108-2701

Poly[tetrasodium(I)-tetra-μ_2-bis(butane-1,4-diyldioxy)borato-μ_2-1,4-butanediol]

Graeme J. Gainsford* and Tim Kemmitt

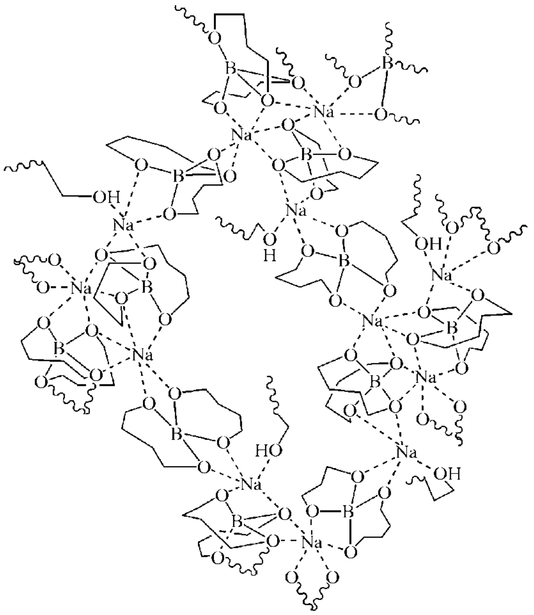
Industrial Research Limited, PO Box 31-310, Lower Hutt, New Zealand
Correspondence e-mail: g.gainsford@irl.cri.nz

Received 18 January 2005
Accepted 24 January 2005
Online 28 February 2005

In the title compound, $[\mathrm{Na_4(C_8H_{16}BO_4)_4(C_4H_{10}O_2)}]_n$, there are two coordination types for the four independent Na$^+$ cations: two Na$^+$ cations bond to six diolate O atoms [Na—O = 2.305 (2)–2.609 (2) Å], while the other two are five-coordinate *via* one 1,4-butanediol [2.289 (2) and 2.349 (3) Å] and four diolate O atoms [2.295 (2)–2.408 (2) Å]. Corresponding to this, there are three- and four-coordinate diolate O atoms, the latter bridging Na atoms. The 1,4-butanediol molecules lie on inversion centres. The boron stereochemistry shows minor local perturbations from its usual tetrahedral state [B—O = 1.457 (4)–1.503 (4) Å]. The resulting polymer packs as sheets parallel to the $(10\overline{1})$ plane crosslinked by the butanediol molecules. The structure was solved using data from a multiple crystal.

Comment

This study is part of a programme aimed at investigating boron diolates and alkoxides (Gainsford & Kemmitt, 2004). Although borates form a range of diolate complexes (Bachelier & Verchere, 1995; Springsteen & Wang, 2002), structural data are sparse and no 1,4-diolates have been reported to date. Low solubility prevented us from obtaining useful NMR data, and the presence of hydroxyl groups of a 'free' diol molecule in the structure made it difficult to determine the coordination mode of the diolate ligands by other techniques. Thus, in order to confirm the chelating nature of the 1,4-diolate ligand, we have carried out the present single-crystal X-ray analysis of the title compound, (I).



(I)

The basic polymeric fragment of (I), with asymmetric unit formula $[\mathrm{Na_4(C_8H_{16}BO_4)_4(C_4H_{10}O_2)}]_n$, is illustrated in Fig. 1. The use of the word 'bound' in this discussion indicates atoms that are within either covalent or ionic attractive distances of each other. The Na$^+$ cations are of two types. Cations Na1 and Na3 are bound to six O atoms, with four of these being monocoordinate diolate O atoms [Na—O = 2.305 (2)–2.499 (2) Å] and two being shared with adjacent Na$^+$ cations [2.459 (2)–2.609 (2) Å]. Cations Na2 and Na4 are five-coor-

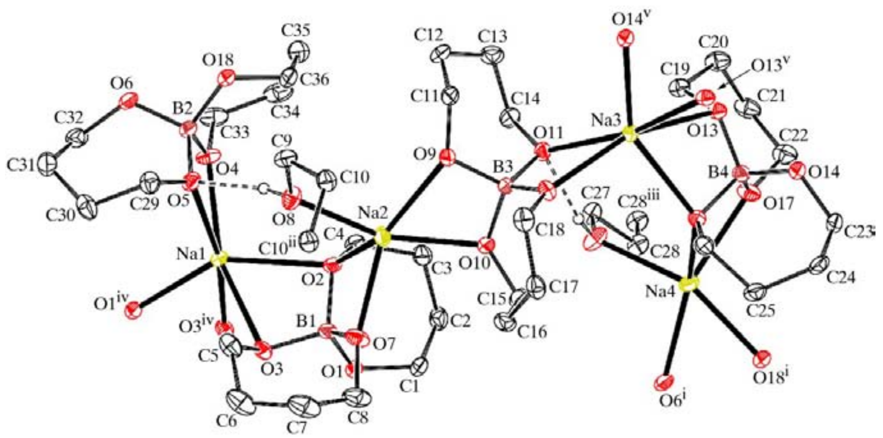


Figure 1
A view of the molecular structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. Atoms of the asymmetric unit and O atoms completing the interaction spheres around the Na atoms are shown. [Symmetry codes: (i) $x, y-1, z$; (ii) $1-x, 2-y, 1-z$; (iii) $2-x, 1-y, -z$; (iv) $1-x, 2-y, -z$; (v) $2-x, 1-y, 1-z$.] Methylene H atoms have been omitted for clarity. The two intramolecular hydrogen bonds are indicated by dashed lines.

DOI: 10.1107/S0108270105002520

dinated through four diolate O atoms, one of which is shared [Na2—O2 = 2.355 (2) Å and Na4—O16 = 2.334 (2) Å], with the other three being monocoordinated [2.342 (2)–2.408 (2) Å]; the fifth position is taken by a singly coordinated butanediol O atom [Na2—O8 = 2.289 (2) Å and Na4—O15 = 2.350 (3) Å]. None of the Na^+-cation geometries approaches an idealized stereochemistry. The butanediol molecules lie on inversion centres (see Fig. 1 and comments below).

The B atoms in the bis(butanedioxy)borate anions show minor perturbations from tetrahedral geometry, with B—O bond length and O—B—O angle ranges of 1.457 (4)–1.503 (4) Å and 101.8 (2)–115.1 (2)°, respectively. These variations can be related to the longer bonds involving O atoms bridging Na atoms (O2, O3, O13 and O16), with a mean B—O distance for these of 1.487 (4) Å, compared with a mean of 1.470 (13) Å for the other 12 three-coordinate O atoms. Thus, four diolate O atoms (O2, O3, O13 and O16) are four-coordinate through bridging two Na^+ cations, and bond to one B atom and one methylene C atom; the remaining O atoms bond to one B atom, one C atom and one Na^+ cation.

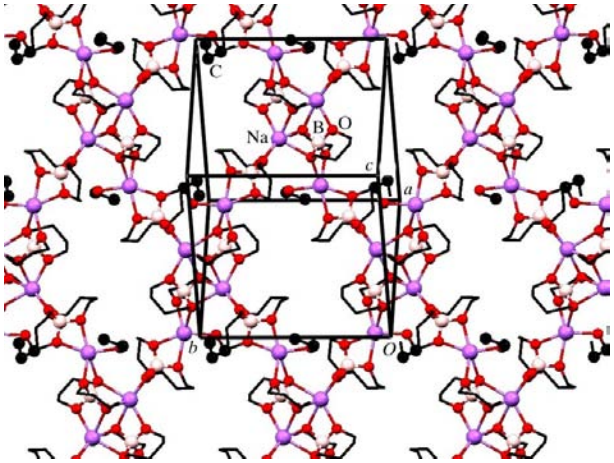


Figure 2
The cell packing in (I), viewed approximately normal to the $(10\overline{1})$ plane. H atoms have been omitted for clarity.

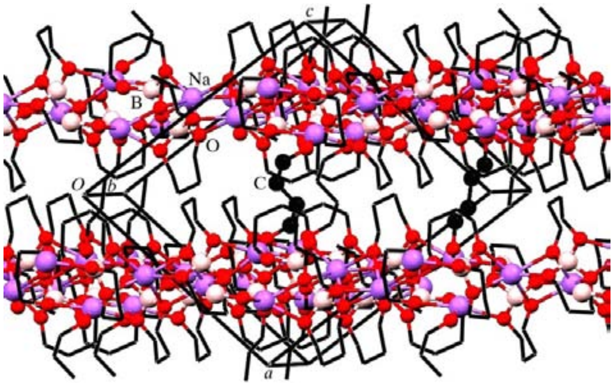


Figure 3
A view of (I), edge on to the polymeric sheet. The C atoms (C10 and C28) which link the sheets are shown as spheres and H atoms have been omitted for clarity.

The polymeric units of (I) form sheets parallel to the $(10\overline{1})$ plane and are linked by two bound butanediol links per cell (Fig. 3). The butanediol H atoms are involved in strong intramolecular binding, thus strengthening these links (Fig. 1 and Table 2). The contents of one sheet are shown in Fig. 2. The internal ring consists of 12 B—O and 16 Na—O bonds, involving eight Na and eight B atoms. The links between the sheets involve crystallographic inversion centres at the centres of the butanediol molecules (so the asymmetric unit shown in Fig. 1 reflects incomplete links), through Na2—O8—C9—C10—$C10^{ii}$—$C9^{ii}$—$O8^{ii}$—$Na2^{ii}$ and Na4—O15—C27—C28—$C28^{iii}$—$C27^{iii}$—$O15^{iii}$—$Na4^{iii}$ [symmetry codes: (ii) $1 - x$, $2 - y$, $1 - z$; (iii) $2 - x$, $1 - y$, $-z$].

The title compound has a unique structure, with no directly comparable compounds containing seven-membered dioxygenboron rings; the closest two are a bis[ethylborandiyl-bis(oxy)]cyclobutane compound (Yalpani *et al.*, 1983) and sodium scylloinositoldiborate decahydrate (Grainger, 1981). In the latter, the B—O bond lengths are in the range 1.486–1.502 Å, but the Na^+ cations are completely surrounded by water molecules. The long Na—O distances in (I), involving the asymmetric bridging of the five- and six-coordinate Na atoms by atoms O2 and O16, are unique with respect to the subtended angles at the O atoms (Table 1), which are usually around 90°. Examples of such bridging distances are found in bis[(μ_2-hydrogentriphenylborato)bis(tetrahydrofuran)sodium] (Bishop *et al.*, 2000) and (μ_2-dibenzo-30-crown-10)aquamethanoldisodium bis(tetraphenylborate) methanol solvate (Steed *et al.*, 2003), with Na—O distances and Na—O—Na angles of 2.386/2.650 Å and 94.16°, and 2.380/2.648 Å and 103.24°, respectively, compared with averages (for O2 and O16) of 2.345 (15)/2.606 (5) Å and 134 (2)° in (I).

Experimental

The title compound was prepared by the addition of excess 1,4-butanediol (75 ml) to a solution of sodium metaborate (0.1 mol, 13.8 g) in distilled water (10 ml). Water and excess diol were removed on a rotary evaporator equipped with a high-temperature oil bath, leaving a white solid. A sample was redissolved in a minimum of 1,4-butanediol and an equal volume of anhydrous acetonitrile was added, causing the slow growth of crystals of (I) over a period of 4 d.

Crystal data

$[Na_4(C_8H_{16}BO_4)_4(C_4H_{10}O_2)]$
$M_r = 930.15$
Triclinic, $P\overline{1}$
$a = 12.813\ (4)$ Å
$b = 13.349\ (4)$ Å
$c = 14.381\ (5)$ Å
$\alpha = 89.282\ (5)°$
$\beta = 79.966\ (4)°$
$\gamma = 89.837\ (4)°$
$V = 2421.9\ (14)$ Å^3

$Z = 2$
$D_x = 1.273$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 7356 reflections
$\theta = 2.3$–$26.4°$
$\mu = 0.13$ mm^{-1}
$T = 163\ (2)$ K
Block, colourless
0.75 × 0.42 × 0.15 mm

Data collection

Bruker SMART CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (Blessing, 1995)
$T_{min} = 0.685$, $T_{max} = 0.981$
7185 measured reflections

7185 independent reflections
5247 reflections with $I > 2\sigma(I)$
$R_{int} = 0.000$
$\theta_{max} = 26.6°$
$h = -15 \rightarrow 16$
$k = -16 \rightarrow 16$
$l = 0 \rightarrow 18$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.060$
$wR(F^2) = 0.154$
$S = 0.99$
7185 reflections
565 parameters

H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.1104P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.007$
$\Delta\rho_{max} = 0.36$ e Å^{-3}
$\Delta\rho_{min} = -0.30$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Na1—O4	2.338 (2)	Na2—O7	2.342 (2)
Na1—O1^{i}	2.349 (2)	Na2—O2	2.355 (2)
Na1—O3^{i}	2.425 (2)	Na2—O9	2.406 (2)
Na1—O5	2.456 (2)	Na3—O13	2.459 (2)
Na1—O3	2.477 (2)	Na3—O16	2.602 (2)
Na1—O2	2.609 (2)	Na4—O15	2.350 (3)
Na2—O8	2.289 (2)	O1—B1	1.457 (4)
Na2—O10	2.295 (2)	O2—B1	1.491 (4)
O1^{i}—Na1—O3^{i}	58.09 (7)	Na2—O2—Na1	132.65 (8)
O3^{i}—Na1—O5	166.60 (8)	Na1^{i}—O3—Na1	101.83 (7)
O7—Na2—O2	59.44 (7)	Na3—O13—Na3^{ii}	100.37 (7)
O2—Na2—O9	139.66 (9)	Na4—O16—Na3	135.70 (9)
O8—C9—C10—C10^{iii}	−64.6 (4)	O15—C27—C28—C28^{iv}	179.2 (3)

Symmetry codes: (i) $1-x, 2-y, -z$; (ii) $2-x, 1-y, 1-z$; (iii) $1-x, 2-y, 1-z$; (iv) $2-x, 1-y, -z$.

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

D—H···A	D—H	H···A	D···A	D—H···A
O8—H8O···O5	0.85 (4)	2.06 (2)	2.897 (3)	170 (4)
O15—H15O···O11	0.80 (4)	2.14 (4)	2.927 (3)	169 (5)

Details of the handling of the data from the multiple crystal are given in the CIF in the supplementary material. All C-bound H atoms were constrained to their expected geometries (C—H = 0.99 Å). The hydroxyl (H8O and H15O) H atoms were freely refined, with O—H distances restrained (DFIX) to 0.84 (3) Å. All H atoms, except H8O and H15O, were refined with $U_{iso}(H) = 1.2U_{eq}(C)$; the ratio was $1.5U_{eq}$ for H8O and H15O.

Data collection: *SMART* (Bruker, 2001); cell refinement: *SMART*; data reduction: *SAINT* (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: *ORTEP-3* (Farrugia, 1999) and *MERCURY* (Bruno *et al.*, 2002); software used to prepare material for publication: *SHELXL97*.

The authors thank Professor Ward T. Robinson, Dr J. Wikaira and Mr William Lewis of the University of Canterbury for their assistance.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1811). Services for accessing these data are described at the back of the journal.

References

Bachelier, N. & Verchere, J.-F. (1995). *Polyhedron*, **14**, 2009–2017.
Bishop, M., Bolt, S. G. & Barron, A. R. (2000). *J. Chem. Soc. Dalton Trans.* pp. 3100–3105.
Blessing, R. H. (1995). *Acta Cryst.* A**51**, 33–38.
Bruker (2001). *SMART* (Version 5.045) and *SAINT-Plus* (Version 6.22). Bruker AXS Inc., Madison, Wisconsin, USA.
Bruno, I. J., Cole, J. C., Edgington, P. R., Kessler, M. K., Macrae, C. F., McCabe, P., Pearson, J. & Taylor, R. (2002). *Acta Cryst.* B**58**, 389–397.
Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.
Gainsford, G. J. & Kemmitt, T. (2004). *Acta Cryst.* E**60**, m1943–m1944.
Grainger, C. T. (1981). *Acta Cryst.* B**37**, 563–568.
Sheldrick, G. M. (1996). *SADABS*. Version 2.03. University of Göttingen, Germany.
Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
Springsteen, G. & Wang, B. (2002). *Tetrahedron*, **58**, 5291–5300.
Steed, J. W., Johnson, K., Legido, C. & Junk, P. C. (2003). *Polyhedron*, **22**, 769–774.
Yalpani, M., Koster, R. & Wilke, G. (1983). *Chem. Ber.* **116**, 1336–1344.