

catena-Poly[sodium(I)- μ -tetraethoxyborato]

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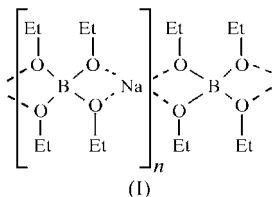
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The title compound, $[\text{Na}(\text{C}_8\text{H}_{20}\text{BO}_4)]_n$, has twofold crystallographic symmetry, with the Na^+ cations bound by four O atoms [$\text{Na}-\text{O} = 2.251(3) \text{ \AA}$]. The tetraethoxyborate anion acts as a bridging ligand to form one-dimensional polymers running along the twofold crystal axis. The crystal was treated as a racemic twin.

Comment

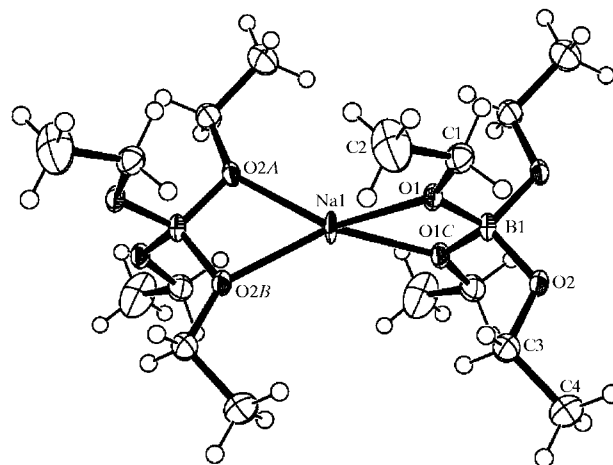
This study is part of a programme aimed at investigating boron diolates and alkoxides, particularly those containing sodium cations [Cambridge Structural Database (Allen, 2002) refcodes GAKLAG (Gainsford & Kemmitt, 2004) and FEFHOO (Gainsford & Kemmitt, 2005a); Gainsford & Kemmitt, 2005b; Bishop *et al.*, 2000]. Although borates form a range of diolate complexes (Bachelier & Verchere, 1995; Springsteen & Wang, 2002), structural data are sparse. There are no reported structures for tetraethoxyborate salts (Allen, 2002), though a large number of tetramethoxyborate salts have been reported (see Gainsford & Kemmitt, 2005b) [two guanidinium salts have since been reported, *viz.* FEWJOH and FEWJUN (Abrahams *et al.*, 2005)].



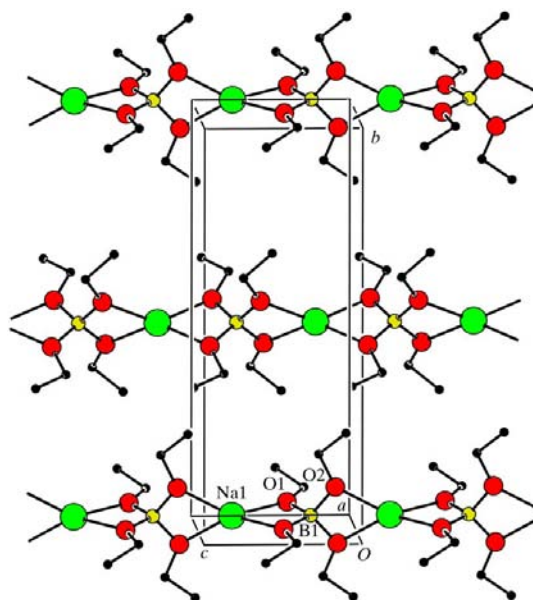
The basic polymeric fragment of the title compound, (I), with asymmetric unit formula $[\text{Na}_{0.5}(\text{C}_4\text{H}_{10}\text{B}_{0.5}\text{O}_2)]$, has twofold crystallographic symmetry, with the symmetry (*c*) axis passing through the Na and B atoms. The molecules crystallized in a racemically twinned crystal. Enantiomeric resolution was not expected from the synthesis or from the small anomalous dispersion effects.

The sodium cations are four-coordinate in a highly distorted tetrahedral arrangement, with mean $\text{Na}-\text{O}$ distances of $2.251(3) \text{ \AA}$, and $\text{O}-\text{Na}-\text{O}$ angles of $138.18(8)$ and $60.62(12)^\circ$. This $\text{Na}-\text{O}$ distance is at the short end of the range of those reported when the bound O atoms are not

structurally constrained; one example of the latter case is POGDAQ01 (Caselli *et al.*, 2000), where the $\text{Na}-\text{O}$ distances range from 2.243 to 2.355 \AA in a niobium-tetraoxycalix[4]-arene compound. The $\text{Na1}/\text{O1}/\text{O1C}/\text{B1}$ and $\text{Na1}/\text{O2A}/\text{O2B}/\text{B1B}$ coordination planes (see Fig. 1, which also gives the symmetry codes) are at right angles [$89.98(12)^\circ$]. These parameters are at the extremes of values for four-coordinate O-bound sodium cations, for which the interplanar angles are usually in the range $55-80^\circ$, for example, bis(μ_2 -triphenylmethoxy)dihydridobis(tetrahydrofuran)aluminiumsodium (JISHIC; Noth *et al.*, 1998) with an interplanar angle of 64.7° and $\text{Na}-\text{O}$ distances of $2.289-2.350 \text{ \AA}$. When the four-coordinate arrangement approaches square planar because of the

**Figure 1**

An ORTEP-3 (Farrugia, 1997) view, showing the asymmetric unit and part of the polymeric unit of (I), with 50% probability displacement ellipsoids. The asymmetric unit atoms, plus symmetry-generated atoms O2A, O2B, O1C and B1B, are labelled. [Symmetry codes: (A) $-x+2, -y, z+1$; (B) $x, y, z+1$; (C) $-x+2, -y, z$.]

**Figure 2**

PLATON view (Spek, 2003) of the unit-cell contents of (I) along the *a* axis, showing the one-dimensional polymers along the twofold *c* axis.

constrained O-atom geometry, the Na atoms usually have one (or more) longer 'intramolecular' contact, making a pseudo-square-pyramidal or octahedral description more appropriate [e.g. in the calix[4]arene-sodium compound DONSAA (Bott *et al.*, 1986), with Na—O = 2.274–2.332 Å and a fifth interaction, Na···C = 2.663 Å]. However, in some cases, the fifth available Na⁺ site is shielded by parts of the bound molecule, 'preserving' the approximate square-planar geometry (e.g. in POGDAQ01).

The B—O and C—O bond lengths average 1.416 (4) and 1.467 (4) Å, and the mean B—O—C angle is 117.8 (2)^o, values that fall within normal ranges as reported in GAKLAG. The O—B—O angles are distorted compared with pure tetrahedral values (Table 1) and those in the bis[1,1,1-tris-(hydroxymethyl)propyl]borate salt (108.6–109.9^o; XOCHOM; Zviedre & Belsky, 2001). The borate anions bridge the sodium cations, forming one-dimensional polymers running along the twofold-symmetry *c*-axis direction (Fig. 2). This packing mode was also observed in poly[sodium(I)-μ₃-bis(ethylenedioxy)-borato] (GAKLAG), where the polymers were aligned with the 2₁ screw axis.

Experimental

Sodium metaborate (10 g) was dehydrated in a domestic microwave oven (1000 W) at full power for 10 min. A sample of the resulting NaBO₂ (2.64 g, 0.04 mol) was refluxed in a 2:1 mixture of ethanol and toluene (150 ml), under a nitrogen atmosphere, running the distillate through molecular sieves to remove liberated water. After 8 h, the mixture was filtered and the volume was reduced by distillation. On cooling, the product appeared as plate-shaped crystals. These were filtered off and dried (yield 7.1 g, 83%).

Crystal data

[Na(C ₈ H ₂₀ BO ₄)]	Mo Kα radiation
<i>M_r</i> = 214.04	Cell parameters from 1438 reflections
Orthorhombic, <i>P</i> 2 ₁ 2 ₁ 2	<i>a</i> = 7.633 (3) Å
<i>a</i> = 7.633 (3) Å	<i>b</i> = 15.272 (6) Å
<i>b</i> = 15.272 (6) Å	<i>c</i> = 5.744 (2) Å
<i>c</i> = 5.744 (2) Å	<i>V</i> = 669.6 (4) Å ³
<i>V</i> = 669.6 (4) Å ³	<i>Z</i> = 2
<i>Z</i> = 2	<i>D_x</i> = 1.062 Mg m ⁻³
<i>D_x</i> = 1.062 Mg m ⁻³	

Data collection

Bruker SMART CCD area-detector diffractometer	829 independent reflections
φ and ω scans	648 reflections with <i>I</i> > 2σ(<i>I</i>)
Absorption correction: multi-scan (Blessing, 1995)	<i>R</i> _{int} = 0.068
<i>T</i> _{min} = 0.812, <i>T</i> _{max} = 0.993	<i>θ</i> _{max} = 26.3 ^o
3881 measured reflections	<i>h</i> = -9 → 5
	<i>k</i> = -18 → 19
	<i>l</i> = -7 → 7

Refinement

Refinement on <i>F</i> ²	$w = 1/[\sigma^2(F_o^2) + (0.0421P)^2 + 0.1167P]$
$R[F^2 > 2\sigma(F^2)] = 0.056$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.105$	(Δ/σ) _{max} < 0.001
<i>S</i> = 1.12	Δρ _{max} = 0.18 e Å ⁻³
829 reflections	Δρ _{min} = -0.22 e Å ⁻³
67 parameters	
H-atom parameters constrained	

Table 1

Selected geometric parameters (Å, °).

Na1—O2 ⁱ	2.250 (3)	O1—B1	1.466 (4)
Na1—O1	2.252 (3)	O2—B1	1.469 (4)
O2 ⁱ —Na1—O1	138.18 (8)	O1 ⁱⁱ —B1—O1	101.6 (3)
O1—Na1—O1 ⁱⁱ	60.62 (12)	O1—B1—O2	113.63 (12)
B1—O1—C1—C2	-167.3 (3)	B1—O2—C3—C4	164.5 (2)

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

Friedel pairs were merged after a full data set refinement gave a Flack (1983) parameter that was indeterminate. All H atoms were constrained to their expected geometries (C—H = 0.99 and 0.98 Å) and refined with *U*_{iso}(H) values of 1.2 times *U*_{eq} of their carrier atoms.

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: PLATON (Spek, 2003) and ORTEP-3 (Farrugia, 1997); 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: SF1008). Services for accessing these data are described at the back of the journal.

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