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Structural characterization of borate esters in which sodium acts as a support to the structural framework

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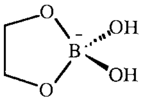
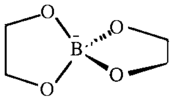
The borate ester derivatives of phenol, *trans*-cyclohexane-1,2-diol and mandelic acid have been prepared from $NaBH_4$ and structurally characterized by X-ray crystallography. The product from the reaction with phenol appears as a crystallographic disorder of $[(THF)_2Na\{B(OPh)_3H\}]_2$ (**1**) and $[(THF)_2Na\{B(OPh)(OH_2)H\}]_2$ (**2**). Both compounds are dimeric with bridging borate groups linking the Na cations. The reaction with *trans*-cyclohexane-1,2-diol in DMSO yields the infinite polymer, $[(DMSO)Na\{B(O_2C_6H_{10})_2\}]_\infty$ (**3**), in which the Na cations link $[B(O_2C_6H_{10})_2]^-$ anions. The unusual 5-coordinate geometry of the sodium is completed by the coordination of a disordered DMSO molecule. In a similar manner, mandelic acid reacts to form an infinite lattice $[Na(py)_2][B\{O_2CC(O)Ph\}_2]$ (**4**), in which each sodium is coordinated to three $[B\{O_2CC(O)Ph\}_2]^-$ anions, one through two interactions involving the alkoxide and carboxylate groups of a chelate mandelic acid, and two interactions involving the carboxylate groups of adjacent anions. The role of the Group 1 cation in supporting the structural framework of the borate anions is discussed.

Introduction

In aqueous solution, borate ions react with polyhydroxy compounds to form ionized complexes, *e.g.*, **I** and **II**. The formation of similar borate ester complexes has been employed in the configurational and chromatographic analysis of carbohydrates.[1] The same reaction is also used in the cross-linking or "gelation" of partially hydrolyzed polysaccharides.[2] Despite being known since 1910[3] and extensively studied by NMR spectroscopy,[4] there are surprisingly few anionic borate esters, $[B(OR)_4]^-$, structurally characterized,[5,6] and the role of the cation, most commonly an alkali metal, is rarely discussed.


(**I**)


(**II**)

We have recently become interested in the ability of boron to act as a cross-linking agent between 1,2- and 1,3-diols as well as naturally occurring polyalcohols.[7] Addition of NaOH to a solution of boric acid, $B(OH)_3$, and a variety of diols results in cross-linking of two diols within the pH range 7–9. In all cases the ability to cross-link and the stability of the borate ester appears dependent on the concentration of sodium or other Group 1 cations. Based upon ^{11}B NMR spectroscopic studies we have found that species similar to both **I** and **II** are formed with a variety of naturally occurring polyalcohols.[4,7] Thus, the boron tetraalkoxides anion, $[B(OR)_4]^-$, appears preferable to the neutral borate ester, $B(OR)_3$. However, solution NMR does not indicate the role, if any, of the Group 1 cation. In this regard, we have investigated the structural characterization of the borate esters of phenol, *trans*-cyclohexane-1,2-diol and mandelic acid.

Results and discussion

Phenol

Reaction of $NaBH_4$ with four equivalents of HOPh yields a white crystalline product whose ^1H NMR spectrum is consistent with the formulation $(THF)_2Na[B(OPh)_2H_2]$, in which two types of phenyl group are present, see Experimental section. However, X-ray crystallographic analysis indicates the crystalline product to consist of a 3:1 mixture of $[(THF)_2Na\{B(OPh)_3H\}]_2$ (**1**) and $[(THF)_2Na\{B(OPh)(OH)_2H\}]_2$ (**2**) as a crystallographic disorder. Attempts to refine the structure as $[(THF)_2Na\{B(OPh)_2H_2\}]_2$ were not successful, suggesting the solution formulation is due to a rapid exchange or that the crystals are not representative of the bulk material. The presence of a crystallographic disorder suggests that partial hydrolysis of either the starting $NaBH_4$ or the borate ester has occurred.

The molecular structures of $[(THF)_2Na\{B(OPh)_3H\}]_2$ (**1**) and $[(THF)_2Na\{B(OPh)(OH)_2H\}]_2$ (**2**) are shown in Fig. 1(a) and (b), respectively; selected bond lengths and angles are given in Table 1. The structures of both compounds **1** and **2** consist of crystallographically centrosymmetric dimers. The geometry about B(1) is close to tetrahedral, while that about Na(1) is highly distorted from octahedral; the O–Na(1)–$O_{(trans)}$ angles range from 143.9(1) to 165.8(1)°.

The structure of compound **1** may be considered to be based upon a $[(THF)_2Na(\mu\text{-}OPh)]_2$ dimer in which each face of the Na_2O_2 core is asymmetrically capped by a $B(OPh)_2H$ moiety; resulting in four bridging μ-OPh groups [O(1), O(2) and their symmetry equivalents] and two capping μ_3-OPh groups [O(3) and O(3′)]. The core structure of compound **2** is essentially the same, but with two of the bridging μ-OPh groups and both capping μ_3-OPh are replaced by hydroxide groups, see Fig. 1(b). An alternative view of the core structure in both compounds **1** and **2**, is to consider them consisting of two edge shared NaO_6 octahedra capped on opposite open faces by two BO_3H tetrahedra. A similar structure was reported for $[Li\{Al(CMe_3)(O^iPr)_3(OH)\}]_2$ (**III**),[8] however, in that case the Li atoms are four coordinate.

As noted above, compounds **1** and **2** exist as a crystallographic disorder in the crystal lattice. The disorder of the $Na_2B_2O_6$ cores is clearly seen in Fig. 2. The disorder of the sodium borate core may be considered to be due to reflection in a non-crystallographic mirror plane in the plane defined by Na(1), Na(1′), O(1) and O(1′). Thus, the phenyl ring attached

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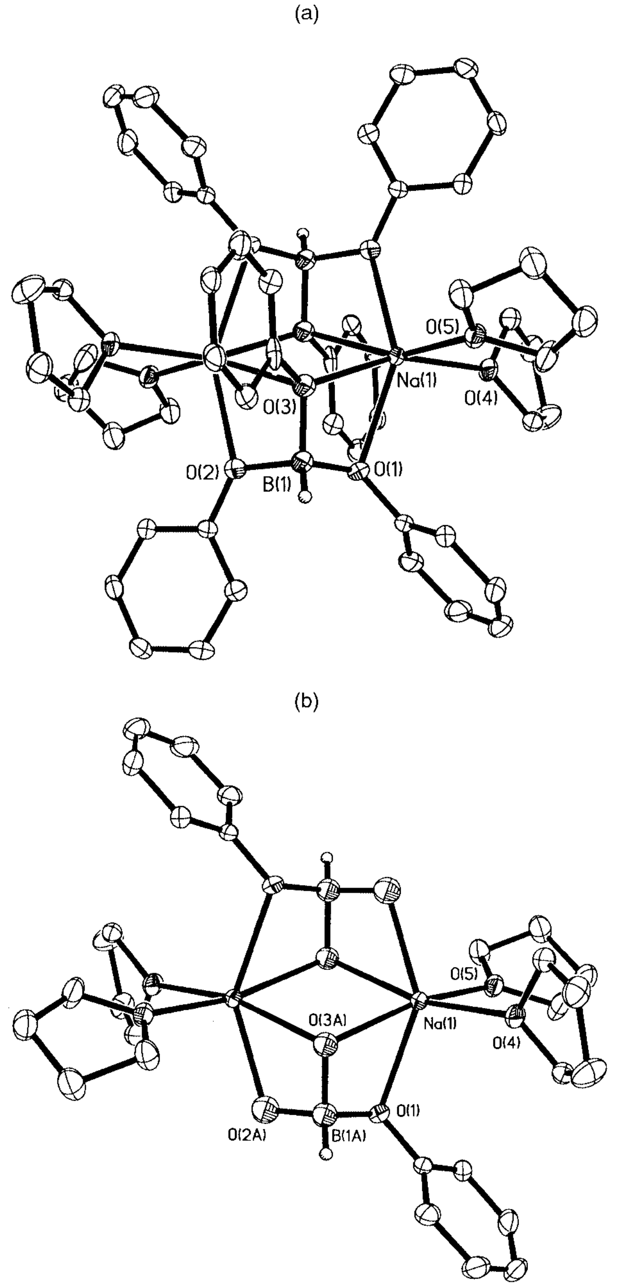
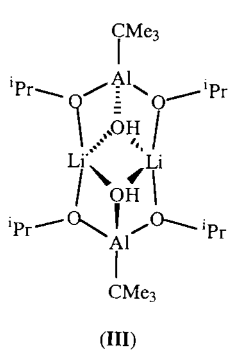


Fig. 1 The molecular structures of (a) $[(THF)_2Na\{B(OPh)_3H\}]_2$ (**1**) and (b) $[(THF)_2Na\{B(OPh)(OH)_2H\}]_2$ (**2**). Thermal ellipsoids are shown at the 20% level and organic hydrogen atoms are omitted for clarity.



(III)

Table 1 Selected bond lengths (Å) and angles (°) in $[(THF)_2Na\{B(OPh)_3H\}]_2$ (**1**) and $[(THF)_2Na\{B(OPh)(OH)_2H\}]_2$ (**2**)

Na(1)–O(1)	2.394(3)	Na(1)–O(2)	2.382(3)
Na(1)–O(3)	2.650(3)	Na(1)–O(4)	2.335(3)
Na(1)–O(5)	2.348(3)	Na(1)–O(2A)	2.293(4)
N(1)–O(3A)	2.491(4)	O(1)–B(1)	1.524(4)
O(2)–B(1)	1.496(4)	O(3)–B(1)	1.489(4)
O(1)–B(1A)	1.523(4)	O(2A)–B(1A)	1.425(7)
O(3A)–B(1A)	1.498(9)		
O(1)–Na(1)–O(2)	144.5(1)	O(1)–Na(1)–O(3)	90.47(9)
O(1)–Na(1)–O(4)	100.9(1)	O(1)–Na(1)–O(5)	107.2(1)
O(2)–Na(1)–O(3)	54.76(9)	O(2)–Na(1)–O(4)	94.0(1)
O(2)–Na(1)–O(5)	105.4(1)	O(3)–Na(1)–O(4)	102.1(1)
O(3)–Na(1)–O(5)	158.0(1)	O(4)–Na(1)–O(5)	87.5(1)
O(2A)–Na(1)–O(1)	143.9(1)	O(2A)–Na(1)–O(3A)	55.8(2)
O(2A)–Na(1)–O(4)	110.4(1)	O(2A)–Na(1)–O(5)	91.9(1)
O(3A)–Na(1)–O(1)	59.1(1)	O(3A)–Na(1)–O(4)	98.4(1)
O(3A)–Na(1)–O(5)	165.8(1)	B(1)–O(1)–Na(1)	97.3(2)
B(1)–O(2)–Na(1)	104.6(2)	B(1)–O(3)–Na(1)′	98.7(2)
B(1)–O(3)–Na(1)	93.4(2)	B(1A)–O(1)–Na(1)	98.9(2)
B(1A)–O(3A)–Na(1)	95.75(9)	B(1A)–O(3A)–Na(1)′	95.28(9)
O(1)–B(1)–O(2)	107.4(3)	O(1)–B(1)–O(3)	104.3(3)
O(2)–B(1)–O(3)	102.4(3)	O(2A)′–B(1A)–O(3A)	101.0(3)
O(2A)′–B(1A)–O(1)	101.6(4)	O(3A)–B(1A)–O(1)	106.2(2)
O(1)–B(1A)–Na(1)′	103.9(2)	B(1A)′–O(2A)–Na(1)	106.6(3)

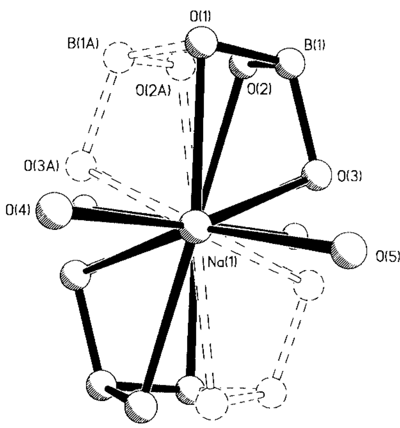


Fig. 2 View of the crystallographically disordered cores in $[(THF)_2Na\{B(OPh)_3H\}]_2$ (**1**) (filled bonds) and $[(THF)_2Na\{B(OPh)(OH)_2H\}]_2$ (**2**) dashed open bonds). Phenyl rings, THF carbon atoms and boron hydrogen atoms are omitted for clarity.

to O(1) remains in both structures, however, the phenyl groups associated with O(2) and O(3) are not present on O(2A) or O(3A). Instead these oxygens are associated with hydroxide groups. Examination of the unit cell packing diagram shows no overlap of disordered groups in the crystal cell, suggesting that the packing is actually dominated by the core, the THF ligands, and the phenyls attached to O(1) and O(1′). While the THF molecules are not disordered with respect to the overall structure, one THF carbon C(42) is disordered in a 1 : 1 ratio.

All bond lengths within compounds **1** and **2** are within the ranges expected. Despite the disorder it is possible to compare the bond lengths in both molecules. The B–O bond lengths [1.425(7)–1.524(4) Å] are within the range previously observed [1.451(3)–1.502(4) Å],[5,6,9,10] and the Na–O distances [2.293(4)–2.650(3) Å] are comparable to those observed for THF complexes and bridging alkoxides [2.24(1)–2.44(1) Å].[11] Although the hydroxide oxygen, O(3A), in compound **2** symmetrically bridges the two sodium atoms [Na(1)–O(3A) 2.491(4) Å, Na(1′)–O(3A) 2.498(4) Å], that associated with the phenoxide in compound **1**, O(3), forms a highly asymmetric bridge [Na(1)–O(3) 2.650(3) Å, Na(1′)–O(3) 2.387(3) Å]. The asymmetry associated with the phenoxide is most likely as a result of intramolecular steric interactions. A similar, but less pronounced, variation is observed for O(2) and O(2A), see Table 1. In contrast, the B–O bond distances appear to be oblivious of any steric variance between OH and OPh ligands. This may be expected given the position of the borate groups at the periphery of the molecular structures.

Table 2 Selected bond lengths (Å) and angles (°) in $[(DMSO)Na\{B(O_2C_6H_{10})_2\}]_\infty$ (**3**)

Na(1)–O(1SA)	2.26(1)	Na(1)–O(1SB)	2.30(4)
Na(1)–O(11)	2.394(5)	Na(1)–O(12′)	2.455(5)
Na(1)–O(22′)	2.473(5)	Na(1)–O(21)	2.571(5)
B(1)–O(21)	1.470(9)	B(1)–O(11)	1.492(8)
B(1)–O(22)	1.49(1)	B(1)–O(12)	1.509(8)
O(1SA)–Na(1)–O(11)	122.7(4)	O(1SB)–Na(1)–O(11)	106(1)
O(1SA)–Na(1)–O(12′)	128.3(4)	O(1SB)–Na(1)–O(12′)	141(1)
O(11)–Na(1)–O(12′)	108.9(2)	O(1SA)–Na(1)–O(22′)	92.4(3)
O(1SB)–Na(1)–O(22′)	89(1)	O(11)–Na(1)–O(22′)	122.5(2)
O(12′)–Na(1)–O(22′)	58.1(2)	O(1SA)–Na(1)–O(21)	90.3(3)
O(1SB)–Na(1)–O(21)	94(1)	O(11)–Na(1)–O(21)	57.4(2)
O(12′)–Na(1)–O(21)	118.5(2)	O(22′)–Na(1)–O(21)	176.6(2)
O(21)–B(1)–O(11)	107.5(5)	O(21)–B(1)–O(22)	106.0(4)
O(11)–B(1)–O(22)	116.0(7)	O(21)–B(1)–O(12)	116.6(6)
O(11)–B(1)–O(12)	105.4(4)	O(22)–B(1)–O(12)	105.7(5)

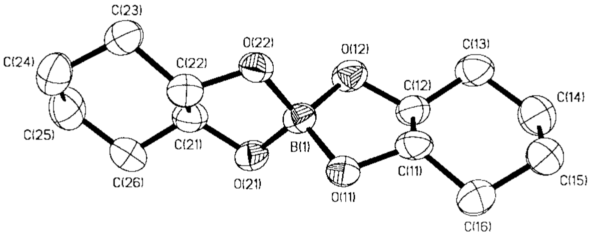


Fig. 3 The structure of the $[B(O_2C_6H_{10})_2]^-$ anion in $[(DMSO)Na\{B(O_2C_6H_{10})_2\}]_\infty$ (**3**). Thermal ellipsoids are shown at the 30% level and hydrogen atoms are omitted for clarity.

trans-Cyclohexane-1,2-diol

Reaction of $NaBH_4$ with two equivalents of *trans*-cyclohexane-1,2-diol in DMSO results in the isolation of $(DMSO)Na[B(O_2C_6H_{10})_2]_\infty$ (**3**) in high yield. The ^1H and ^{13}C NMR spectra reveal no structural details only the ratio of the organic groups in the overall formula. In contrast, the ^{11}B NMR spectrum shows a peak at δ 8.4, consistent with the bis-chelate complexes we have observed previously. The formation of a bis-chelate complex is confirmed by X-ray crystallography; selected bond lengths and angles are given in Table 2.

The structure of the $[B(O_2C_6H_{10})_2]^-$ anion is shown in Fig. 3. The B–O distances are within the range of other borate esters, and the geometry about B(1) is only slightly distorted from ideal tetrahedral; the non-chelate angles, O(11)–B(1)–O(22) and O(12)–B(1)–O(21), being opened up, 116.0(7) and 116.6(6)°, respectively. This is presumably since all other O–B(1)–O angles are involved in a chelate ring, either within the cyclohexane-1,2-diol or the sodium cations, see below. It is interesting that previously, it was assumed that complexation of a *trans*-diol was disfavoured as compared to *cis*-diol, however, the isolation of compound **3**, suggests that the difference in stability is not as significant as expected. We have performed *ab initio* calculations on the model anion, $[B(O_2C_2H_4)_2]^-$ which indicate the *cis–cis* isomer is only 23.3 kJ mol^{-1} favored over the *trans–trans* isomer.[12]

Each $[B(O_2C_6H_{10})_2]^-$ anion is strongly associated with two sodium cations, see Fig. 4, the coordination sphere of each sodium being completed by an adjacent $[B(O_2C_6H_{10})_2]^-$ anion and a DMSO ligand, resulting in a trigonal bipyramidal geometry for the sodium [O(21)–Na(1)–O(22′) 176.6(2)°]. The overall structure of compound **3** consists of an infinite cation · · · anion chain aligned along the *a*-axis of the unit cell, see Fig. 4. Although the –Na–O–B–O– chains appear twisted (Fig. 4), the $[B(O_2C_6H_{10})_2]^-$ anion are actually aligned in a linear fashion along the *a*-axis, and it is the sodium cations that are positioned on alternate sides of the B · · · B chain.

An analogous structure has been reported for $(^iPrOH)_2K[Al(O^iPr)_4]$ in which the potassium is six-coordinate.[13] A related structure is observed for $(DME)K[Al(O_2C_2H_4)\{CH(SiMe_3)_2\}_2]$ with a four-coordinate potassium as a consequence of the presence of only a single ethylene glycolate per aluminium.[14]

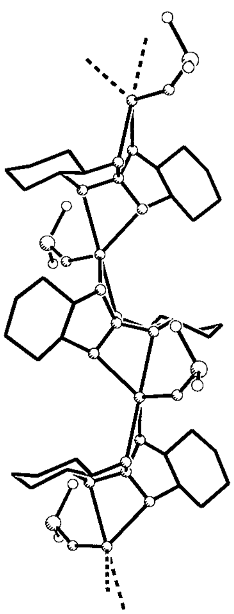
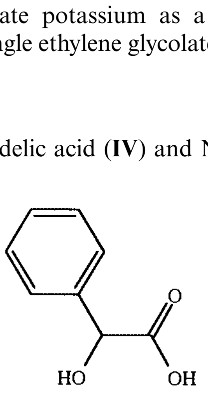


Fig. 4 A view of the structural linkage between the $[B(O_2C_6H_{10})_2]^-$ anion and sodium cations in a section of one of the infinite chains of $[(DMSO)Na\{B(O_2C_6H_{10})_2\}]_\infty$ (**3**). The cyclohexane rings are shown as line representations and all hydrogen atoms are omitted for clarity.

Mandelic acid

The reaction of mandelic acid (**IV**) and $NaBH_4$ in acetonitrile



(IV)

yielded an insoluble product, however, recrystallization in the presence of pyridine allowed for the isolation of $[Na(py)_2][B\{O_2CC(O)Ph\}_2]$ (**4**) in good yield, see Experimental section.

The structure of compound **4** was determined by X-ray crystallography and selected bond lengths and angles are given in Table 3. The structure of the $[B\{O_2CC(O)Ph\}_2]^-$ anion is shown in Fig. 5. The B–O distances are within the range of other borate esters, and there is no variation between the $B(1)–O_{(alkoxide)}$ and $B(1)–O_{(carboxylate)}$ distances. This would suggest that the carboxylate is highly localized rather than delocalized. This is confirmed by the asymmetry in the carboxylate C–O distances [Δ(C–O) = 0.11 Å, see Table 3]. The geometry about B(1) is only slightly distorted from ideal tetrahedral; as with compound **3** it is the non-chelate angles, O(12)–B(1)–O(21A) and O(22)–B(1)–O(11A), that are opened up, 114.5(3) and 115.1(3)°, respectively. The Na–N distances [2.498(3) and 2.509(3) Å] are comparable to examples in the literature [2.450(5)–2.63(2) Å] for pyridine complexes.[15]

Each $[B(O_2C_6H_{10})_2]^-$ anion is associated with three sodium cations. One is associated *via* the two alkoxide oxygens, O(12) and O(22), in a similar manner to that observed for compound **3**, see Fig. 6. The coordination sphere of the sodium is completed by two *trans*-pyridine ligands, and the carboxylate oxygens, one each, from two adjacent $[B(O_2C_6H_{10})_2]^-$ anions. The coordination about Na(1) is a highly distorted octahedron

Table 3 Selected bond lengths (Å) and angles (°) in $[Na(py)_2][B\{O_2CC(O)Ph\}_2]$ (**4**)

Na(1)–O(12)	2.597(3)	Na(1)–O(22)	2.434(2)
Na(1)–N(31)	2.509(3)	Na(1)–N(41)	2.498(3)
Na(1)–O(11B)	2.342(3)	Na(1)–O(21B)	2.348(3)
B(1)–O(12)	1.443(4)	B(1)–O(22)	1.448(4)
B(1)–O(11A)	1.495(4)	B(1)–O(21A)	1.504(4)
O(22)–Na(1)–O(12)	56.61(7)	N(31)–Na(1)–O(12)	82.3(1)
N(41)–Na(1)–O(12)	85.8(1)	O(11B)–Na(1)–O(12)	137.8(1)
O(21B)–Na(1)–O(12)	116.53(9)	O(11B)–Na(1)–O(22)	85.56(9)
O(21B)–Na(1)–O(22)	164.1(1)	N(41)–Na(1)–N(31)	161.5(1)
O(22)–Na(1)–N(31)	103.6(1)	O(11B)–Na(1)–N(31)	90.3(1)
O(21B)–Na(1)–N(31)	88.8(1)	O(22)–Na(1)–N(41)	81.1(1)
O(11B)–Na(1)–N(41)	108.0(1)	O(21B)–Na(1)–N(41)	84.1(1)
O(11B)–Na(1)–O(21B)	104.7(1)	O(22)–B(1)–O(12)	111.5(3)
O(22)–B(1)–O(11A)	115.1(3)	O(12)–B(1)–O(11A)	104.9(3)
O(22)–B(1)–O(21A)	103.9(3)	O(12)–B(1)–O(21A)	114.5(3)
O(11A)–B(1)–O(21A)	107.1(3)	B(1)–O(12)–Na(1)	92.5(2)
B(1)–O(22)–Na(1)	99.3(2)		

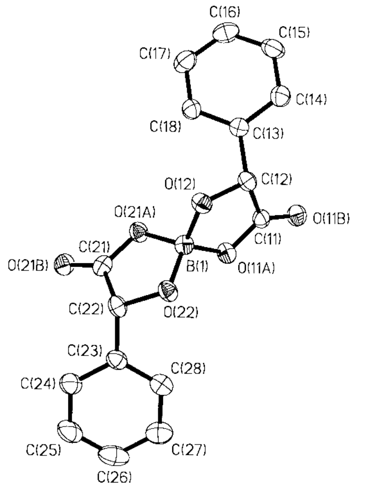


Fig. 5 The structures the $[B(\{O_2CC(O)Ph\}_2]^-$ anion in $[Na(py)_2][B\{O_2CC(O)Ph\}_2]$ (**4**). Thermal ellipsoids are shown at the 30% level and hydrogen atoms are omitted for clarity.

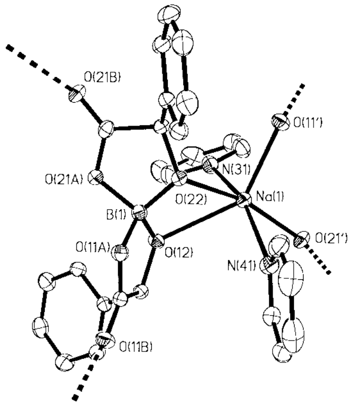


Fig. 6 A view of the structural linkage between the $[B\{O_2CC(O)Ph\}_2]^-$ anion and sodium cations in $[Na(py)_2][B\{O_2CC(O)Ph\}_2]$ (**4**). Atoms are shown as shaded spheres and hydrogen atoms are omitted for clarity.

with the $X–Na(1)–X_{(trans)}$ angles ranging from 137.8(1) to 164.1(1)°. The overall structure of compound **4** consists of an infinite two-dimensional sheet, see Fig. 7. The crystal lattice also contains pyridine molecules of solvation.

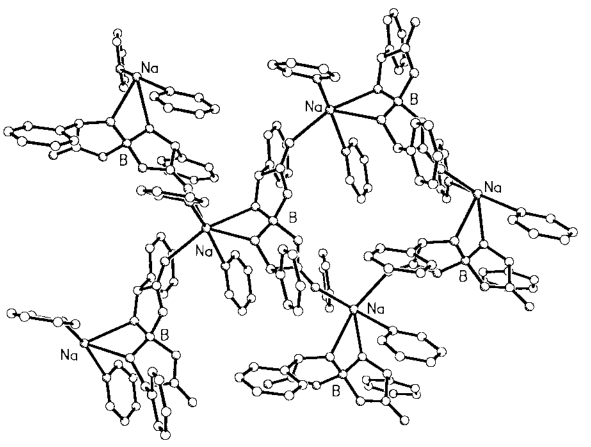
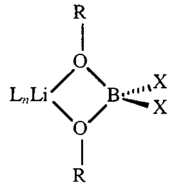


Fig. 7 A view of a section of the infinite two-dimensional sheet in $[Na(py)_2][B\{O_2CC(O)Ph\}_2]$ (**4**). Atoms are shown as shaded spheres, the pyridines of solvation and hydrogen atoms are omitted for clarity.



X = R, OR

(**V**)

Sodium as a support to the structural framework of borate esters

In all the structures discussed above the sodium counter ion for the borate ester (or carboxylate ester) has been involved in a four-membered ring involving the boron and two of the oxygen atoms of the alkoxide or carboxylate ligands. Based on these results and comparison with other structures discussed above, we propose that the sodium (or presumably other Group 1 cation) acts as a support to the framework of a borate ester.

A review of the literature indicates that dialkylboroxides behave in a similar manner to alkoxides or siloxides.[16] In contrast, borate anions, $[B(OR)_4]^-$ or $[B(OR)_2R_2]^-$ (R = alkyl, aryl), form either dimetallic monomeric structures (**V**)[17] or oligomeric arrays.

It appears that the formation of monomers *versus* oligomerization is generally dependent on the identity of the Group 1 cation rather than the steric bulk of the borate substituents, *i.e.*, Li salts are dimetallic monomeric structures while heavier metal salts (Na, K, *etc.*) are oligomeric. The extent of oligomerization is, however, dependent on the steric bulk of the borate substituents and also the identity of the ligands bound to the Group 1 metal. The only exceptions to this observation are compounds in which the Group 1 anion is bound inside a cryptand which limits its interaction to a single borate center.[18]

Table 4 Summary of X-ray diffraction data

Compound	$3[(THF)_2Na\{B(OPh)_3H\}]_2\cdot[(THF)_2Na\{B(OPh)(OH)_2H\}]_2$ **31·2**	$[(DMSO)Na\{B(O_2C_6H_{10})_2\}]_\infty$ (**3**)	$[Na(py)_2][B\{O_2CC(O)Ph\}_2](py)$ (**4**)
Empirical formula	$C_{46}H_{60}B_2Na_2O_{10}$	$C_{14}H_{26}BNaO_5S$	$C_{31}H_{27}BN_3NaO_6$
M_w	420.27	340.21	571.36
Crystal system	Triclinic	Orthorhombic	Orthorhombic
Space group	$P\bar{1}$	$P2_12_12_1$	$P2_12_12_1$
a/Å	10.264(2)	11.175(2)	7.574(2)
b/Å	11.013(2)	8.913(2)	14.331(3)
c/Å	12.600(3)	18.521(4)	27.131(5)
a/°	109.93(3)		
β/°	108.35(3)		
γ/°	96.60(3)		
V/Å^3	1230.8(4)	1844.7(6)	2945(1)
Z	1	4	4
μ/mm^{-1}	0.092	0.216	0.102
No. collected reflections	5583	8260	13377
No. independent reflections	3497	2648	4219
No. observed reflections [($\lvert F_o\rvert > 4.0\sigma F_o$)]	2915	1249	2673
Weighting scheme SHELXTL parameters	0.189, 0.631	0.08, 0.0	0.0375, 0.0
R	0.0895	0.082	0.0463
R_w	0.252	0.171	0.0880

While all the structures discussed herein are specifically limited to the solid state, we propose that it is important to consider the role of the cation in supporting the structural framework of the borate anions in the formation of "cross-linked" structures between boron and 1,2- and 1,3-diols as well as naturally occurring polyalcohols including polysaccharides.

Experimental section

Mass spectra were obtained on a Finnigan MAT 95 mass spectrometer operating with an electron beam energy of 70 eV for EI mass spectra. IR spectra (4000–400 cm^{-1}) were obtained using an Nicolet 760 FT-IR infrared spectrometer. Samples were prepared as Nujol mulls between NaCl plates unless otherwise stated. NMR spectra were obtained on a Bruker Avance 200 spectrometer. Chemical shifts are reported relative to internal solvent. Phenol, *trans*-cyclohexane-1,2-diol and mandelic acid were obtained from Aldrich and were used without further purification.

Reaction of PhOH with NaBH$_4$ in THF

PhOH (1.92 g, 20.4 mmol) was added to a stirred solution of NaBH$_4$ (0.19 g, 5.0 mmol) in THF (50 mL) and the reaction mixture was stirred at room temperature overnight. The reaction mixture was concentrated and cooled to −22 °C for several days. The resulting white crystals were collected by filtration. The only crystals suitable for X-ray diffraction showed a disorder between $[(THF)_2Na_2\{B(OPh)_3H\}_2]$ (**1**) and $[(THF)_2Na_2\{B(OPh)(OH)_2H\}_2]$ (**2**), however, the ^{1}H NMR spectra is consistent with either a fluxional mixture of the species or $[(THF)_2Na_2\{B(OPh)_2(OH)H\}_2]$ ^{1}H NMR (CDCl$_3$): δ 7.10 [2H, t, J(H–H) = 7.5 Hz, *m*-CH), 7.11 [2H, t, J(H–H) = 7.5 Hz, *m*-CH], 6.97 [2H, d, J(H–H) = 7.5 Hz, *o*-CH], 6.86 [1H, t, J(H–H) = 7.0 Hz, *p*-CH], 6.82 [1H, t, J(H–H) = 7.0 Hz, *p*-CH], 6.79 [1H, d, J(H–H) = 7.5 Hz, *o*-CH], 3.69 (8H, m, OCH$_2$), 1.72 (8H, m, OCH$_2$CH$_2$). ^{13}C NMR (CDCl$_3$): δ 157.9 (OC), 129.1 (*o*-CH), 119.7 (*p*-CH), 118.7 (*m*-CH), 67.9 (OCH$_2$), 25.3 (OCH$_2$CH$_2$).

$[(DMSO)Na\{B(O_2C_6H_{10})_2\}]_\infty$ (3)

A solution of *trans*-cyclohexane-1,2-diol (2.3 g, 20 mmol) in anhydrous DMSO (50 mL) was added to a stirred slurry of NaBH$_4$ (0.38 g, 10 mmol) in anhydrous DMSO and refluxed overnight. The solution was then concentrated under vacuum and cooled to room temperature. The resulting white crystals were collected by filtration. Yield: *ca.* 80%. ^{1}H NMR (d$_6$-DMSO): δ 3.34 (2H, m, 1,2-CH), 2.61 (6H, s, SCH$_3$), 1.97 (2H, m, 6-CH$_2$), 1.70 (2H, m, 3-CH$_2$), 1.26 (4H, m, 4,5-CH$_2$). ^{13}C NMR (d$_6$-DMSO): δ 75.8 (1,2-CH), 40.9 (SCH$_3$), 32.8 (3,6-CH$_2$), 24.3 (4,5-CH$_2$). ^{11}B NMR: δ 8.4.

$[Na(py)_2][B\{O_2CCH(O)Ph\}_2]$ (4)

Mandelic acid (1.52 g, 10 mmol) and NaBH$_4$ (0.19 g, 5.0 mmol) were refluxed in acetonitrile (100 mL). The reaction mixture was filtered and the white precipitate was dissolved in dichloromethane–pyridine (3 : 1) solution. Colorless crystals were obtained upon cooling to −22 °C. Yield: *ca.* 75%. MS (EI): *m*/*z* 333.9 (M$^+$ − pyridine), 311.9 (M$^+$ − Na − pyridine). DRIFT (cm^{-1}): 3626 (s), 3088 (w), 3062 (s), 3032 (s), 3006 (w), 2910 (s), 1736 (s), 1645 (w), 1600 (s), 1495 (s), 1347 (w), 1316 (s), 1116 (s). ^{1}H NMR (CDCl$_3$): δ 8.62 (2H, m, *o*-CH, py), 7.81 (3H, m, *m*- and *p*-CH), 7.65 (2H, m, *o*-CH), 7.38 (2H, m, *m*-CH, py), 7.33 (1H, m, *p*-CH, py), 5.48 (1H, s, O$_2$CCH). ^{13}C NMR (CDCl$_3$): δ 207.0 (CO$_2$), 146.8 (*o*-CH, py), 139.6 [O$_2$CCH(O)*C*], 138.9 (*p*-CH, py), 128.5 (CH, Ph), 128.4 (CH, Ph), 127.9 (CH, Ph), 126.6 (CH, Ph), 126.4 (CH, Ph), 125.0 (*m*-CH, py), 78.1 [CH(O)].

Crystallographic studies

Crystals of compounds **31·2**, **3** and **4** were sealed in a glass capillaries under argon. Crystal and data collection and solution details are given in Table 4. Standard procedures in our laboratory have been described previously.[19] Data were collected on a Bruker CCDC SMART system, equipped with graphite monochromated Mo-Kα radiation (λ = 0.71073 Å) and corrected for Lorentz and polarization effects. The structures were solved using the direct methods program XS[20] and difference Fourier maps and refined by using full matrix least squares.[21]

One of the THF carbon atoms, C(42), in compound **1** exhibits a 1 : 1 site disorder. As may be seen from Fig. 8, there exists a disorder of the sulfur and oxygen atoms of the DMSO ligand in compound **3**. The methyl groups occupy fixed places in the lattice, while the S and O reside in two positions each in a "slinky-esque" disorder.[22] Refinement of positional and anisotropic thermal parameters led to convergence (see Table 4).

CCDC reference number 186/2104.

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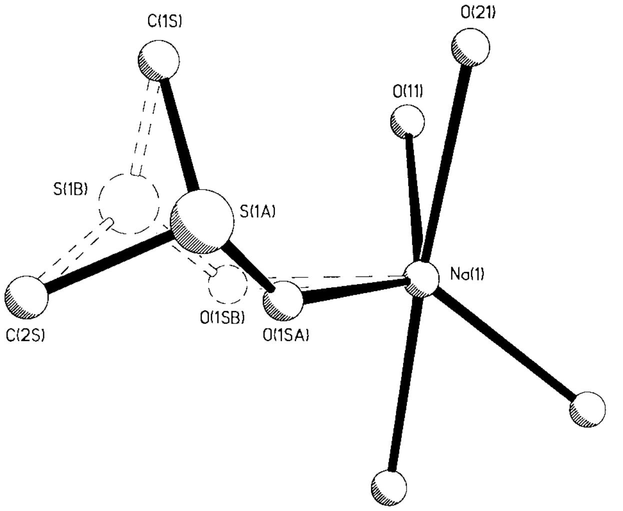

Fig. 8 View of the disordered DMSO in $[(DMSO)Na\{B(O_2C_6H_{10})_2\}]_\infty$ (**3**). Hydrogen atoms are omitted for clarity.

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