A combined X-ray and NMR study of borate esters of furanoidic cis-1,2-diols[☆]

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Abstract

Crystals of $K[B(AnErytH_{-2})_2] \cdot 2\ H_2O$ (AnEryt = 1,4-anhydroerythritol) form from aqueous alkaline solutions containing a double molar amount of diol over borate. The spiro-type monoanions are the main borate species in the mother liquors of crystallisation according to ^{11}B and ^{13}C NMR spectroscopy. Ribofuranosides form analogous borate esters using their 1,4-anhydroerythritol core. Crystals of $Na[B(Me\beta\text{-D-Rib}f\ 2,3H_{-2})_2] \cdot 2\ H_2O$ were grown from alkaline methyl β-D-ribofuranoside solutions that had attacked boron-containing Duran vessels. NMR spectra show closely resembling borate–ester speciation in solutions of diols with the 1,4-anhydroerythritol core — 1,4-anhydroerythritol itself, methyl β-D-ribofuranoside and guanosine. © 2000 Published by Elsevier Science Ltd. All rights reserved.

Keywords: Borate esters; 1,4-Anhydroerythritol; Methyl β-D-ribofuranoside; Guanosine

1. Introduction

Recent investigations of the van Bekkum group and others on borate ester formation of mono- and disaccharides led to the assumption of highest complex stabilities for furanoidic cis-1,2-diols [2]. More recently in a study dealing with the molecular origin of boron usage by plants, O'Neill and co-workers demonstrated that cis-1,2-furanoidic diol groups of apiosyl residues of rhamnogalacturonan II are the boron-binding functional groups of this cell-wall polysaccharide [3]. Despite the increasing insight, which mainly stems from ^{11}B and ^{13}C NMR spectroscopy, into the rules and the significance of carbohy-drate–borate ester formation, the metric properties of the boron–carbohydrate linkage remain unexplored. To the best of our knowledge, not a single crystal-structure investigation on borate esters of pyranoidic or furanoidic carbohydrates or derivatives thereof, has been published [4]. Hence, we tried to extend our structural work on carbohydrate–metal complexes in aqueous solution to the field of borate esters. Within this work, we report on the structures of bis-diol esters of methyl β-D-ribofuranoside and of 1,4-anhydroerythritol. The latter comprises the chelating core of a furanoidic cis-1,2-diol without any further substituents.

2. Results and discussion

1,4-Anhydroerythritol complexes.—Orthorhombic needles of $K[B(AnErytH_{-2})_2] \cdot 2\ H_2O$ (**1**) were grown from alkaline aqueous
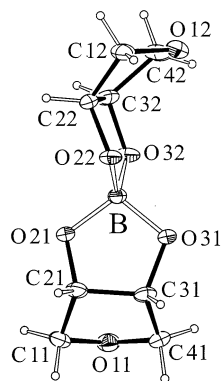

Fig. 1. The bis(diolato)borate anions in **1** (ORTEP plot, 50% probability ellipsoids). Distances (Å): B–O-21 1.477(2), B–O-22 1.478(2), B–O-31 1.466(2), B–O-32 1.468(2), C-11–O-11 1.435(2), C-21–O-21 1.429(2), C-31–O-31 1.428(2), C-41–O-11 1.441(2), C-11–C-21 1.521(2), C-21–C-31 1.558(2), C-31–C-41 1.527(2), C-12–O-12 1.437(2), C-22–O-22 1.429(2), C-32–O-32 1.428(2), C-42–O-12 1.443(2), C-12–C-22 1.521(2), C-22–C-32 1.557(2), C-32–C-42 1.529(3); mean endocyclic oxolane bond angle: 104.06°; mean endocyclic chelate bond angle: 106.64°; diol torsion angles: O-21–C-21–C-31–O-31 11.96(16)°, O-22–C-22–C-32–O-32 12.04(17)°; puckering parameters [10]: O-11–C-11–C-21–C-31–C-41: $Q_2 = 0.410(2)$ Å, $\phi_2 = 191.8(3)°$, O-12–C-12–C-22–C-32–C-42: $Q_2 = 0.410(2)$ Å, $\phi_2 = 192.5(3)°$, O-21–C-21–C-31–O-31–B: $Q_2 = 0.244(2)$ Å, $\phi_2 = 351.5(4)°$, O-22–C-22–C-32–O-32–B: $Q_2 = 0.245(2)$ Å, $\phi_2 = 351.7(4)°$.

solutions of boric acid, 1,4-anhydroerythritol (AnEryt) and potassium hydroxide in a 1:2:5 molar ratio. The structure of the complex monoanion is shown in Fig. 1; significant distances and angles are compiled in the legend. The structure closely resembles one of the analogous beryllium dianion in $Na_2[Be-(C_4H_6O_3)_2]\cdot 5$ H_2O [5]. Both types of central atoms are small, hence the diol torsion angles of the rather flexible five-ring diol also being

small to allow for a small 'bite' of the ligand. The alkoxo-*O* atoms establish bonds to four neighbouring atoms, which are arranged tetrahedrally. Besides the boron and a carbon atom, two potassium ions (in the case of O-31, O-32) or one potassium ion and a hydrogen bond with a water donor (O-21, O-22) stabilise the negative charge of the alkoxo groups in the crystal. Thus, despite the high polarising power of the boron atom, the number of contacts to the formal O^- function is the same as usually found with diolato metallates. However, the O···O distance of the hydrogen bond is rather large, indicating the negative charge on the acceptor atom to be smaller than usual. The principles of hydrogen bonding (Table 1) resemble other polyolatometallates. The water molecules are linked by cooperative hydrogen bonds to an extended network, hence providing donor sites not used for the network for bonds towards alkoxo acceptors. In **1**, the water network is a simple isolated chain along [001]. Despite the well-ordered branches of the network towards the alkoxo acceptors, the infinite cooperative chain itself exhibits disorder of hydrogen atoms. Both point-symmetry elements of the space group, the centre of inversion ($\bar{1}$) and the twofold axis (2) along [010] ($Pbcn \equiv P2_1/b$ $2/c$ $2_1/n$) are involved in the disordered hydrogen-bond array. In a statistical model, the bonding scheme of the hydrogen-bonded chain of water molecules is ($h \equiv 1/2$ H):

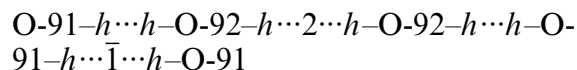O-91–h···h–O-92–h···2···h–O-92–h···h–O-91–h···$\bar{1}$···h–O-91

Table 1
Hydrogen bonds towards alkoxo acceptors (distances in Å, angles in °) [a]

D	H	A [b]	D–H	H···A	D···A	D–H···A
Compound **1**						
O-91	H-911	O-21	0.81(2)	2.01(2)	2.819(2)	173(2)
O-92	H-912	O-22	0.83(2)	2.02(2)	2.833(2)	168(2)
Compound **2**						
O-51	H-851	O-21^i	0.83(2)	1.87(2)	2.682(2)	166(3)
O-52	H-852	O-22^{ii}	0.83(2)	1.93(2)	2.742(2)	163(3)
O-91	H-911	O-31	0.83(2)	1.87(2)	2.693(2)	169(3)
O-92	H-921	O-32^{iii}	0.87(2)	1.93(2)	2.798(3)	176(3)

[a] Standard deviations in parentheses (consider restraint refinement for H-positions).
[b] Symmetry codes: ^{i} $1/2-x$, $y-1/2$, $-z-1$; ^{ii} $x+1/2$, $3/2-y$, $-z$; ^{iii} $x, y, z+1$.
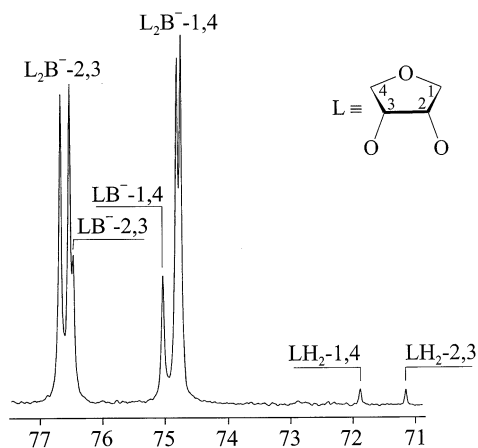
Fig. 2. ^{13}C NMR spectrum of 1,4-anhydroerythritol/borate in a molar ratio of 2:1 at a total borate concentration of ca. 0.9 mol L^{-1}; solution adjusted to pH 13 with sodium hydroxide. δ 71.15, 71.89, 74.78, 74.84, 75.05, 76.70, 76.49, 76.55. Short symbols: LB$^-$ = monodiolato–dihydroxo–borate, L$_2$B$^-$ = bis(diolato)borate, LH$_2$ = free diol.
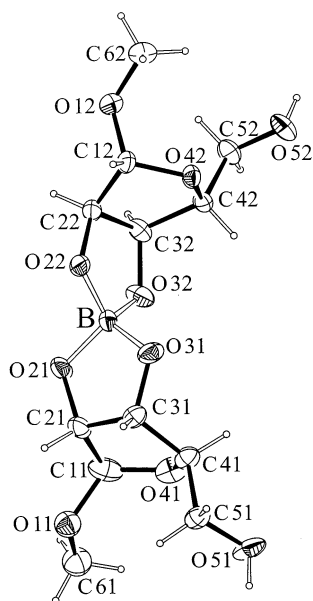

Fig. 3. The bis(diolato)borate anions in **2** (ORTEP plot, 30% probability ellipsoids; only the major form is drawn for the disordered methoxy group with C-61 and O-11). Distances (Å): O-21–B 1.469(3), O-31–B 1.455(3), O-22–B 1.467(3), O-32–B 1.474(3), O-21–C-21 1.408(3), C-21–C-31 1.530(3), O-31–C-31 1.419(3), O-22–C-22 1.418(2), C-22–C32 1.549(3), O-32–C-32 1.411(3); mean endocyclic oxolane bond angle: 106.13°; mean endocyclic chelate bond angle: 107.7°; diol torsion angles: O-21–C-21–C-32–O-31 $-9.2(3)°$, O-22–C-22–C-32–O-32 12.8(2)°; puckering parameters [10]: O-41–C-11–C-21–C-31–C-41: $Q_2 = 0.269(3)$ Å, $\phi_2 = 201.9(13)°$, O-42–C-12–C-22–C-32–C-42: $Q_2 = 0.295(2)$ Å, $\phi_2 = 204.1(4)°$, O-21–C-21–C-31–O-31–B: $Q_2 = 0.101(2)$ Å, $\phi_2 = 201.9(13)°$; O-22–C-22–C-32–O-32–B: $Q_2 = 0.124(2)$ Å, $\phi_2 = 70.2(10)°$.

The bis(diolato)borate anions of **1** are the dominant complex species in both the strongly alkaline mother liquors (pH ca. 13) and in solutions adjusted to the same pH and molar ratios. ^{11}B NMR spectroscopy reveals only a small amount of monodiolato–dihydroxo–borate and a trace of tetrahydroxoborate in addition to the bis(diolato) species. Accordingly, ^{13}C spectra show the two signals of the free diol (about 10% of the total diol amount), two further signals of monodiolato–dihydroxo–borate, and four signals of the bis(diolato) complex, the latter having the highest intensity (Fig. 2). The signals of the carbon atoms that are bearing the *O*-alkoxo atoms are shifted downfield by about 6 ppm, which is slightly less than the value given in Ref. [2]. The shift of the signals of the carbon atoms next to the diolato group is about 3 ppm downfield. The physical origin of the split of the signals in the spiro-type bis(diolato) complex is illustrated in Fig. 1, which shows the spatial inequivalence of, e.g., O-21 and O-31 and hence C-21 and C-31, which are equivalent only in the absence of the spiro centre. As is usual in aqueous borate ester chemistry, the B–O linkages are inert on the NMR timescale, even at a higher temperature of 360 K. When varying the pH value of the solutions at both a constant 2:1 molar ratio of diol and borate and a total concentration of about 1 mol L^{-1}, as a rule, the bis(diolato)borate portion remains the same (about 3/4 throughout the alkaline region) but, the higher the pH, the larger the amount of monodiolato–dihydroxo–borate at the expense of free diol.

Methyl β-D-ribofuranoside complexes.—The cumbersome procedure of obtaining crystals of diolato–borates with pending functional groups is best highlighted by the experiments that led to the structural analysis of Na[B(Meβ-D-Rib*f*2,3H$_{-2}$)·2 H$_2$O (**2**). **2** was formed in the course of an attempted synthesis of a diolato–silicate. However, under the reaction conditions applied, borate dissolved from the Duran vessels used and formed the borate ester **2**. The crystals were of lower quality than those of **1**. The structure determination revealed borate anions as shown in Fig. 3. The methoxy group of one of the ribose moieties (O-11, C-61) is disordered. The puckering parameters (Fig. 3) of the four

five-rings of the complex anion indicate flatter chelate and oxolane rings when compared with **1** (however, this may be partly due to disorder and higher *U* values, particularly for ribose **1**). Accordingly, the endocyclic bond angles of both ring types are larger in the case of **2**. Hydrogen-bond cooperativity is not as significant as with **1**, which is more typical in this respect. In **2**, the donor sites, which are provided by water molecules and the hydroxymethyl group at position 5 of the ribose skeleton, establish isolated hydrogen bonds towards alkoxo acceptors (Table 1). In **2**, the hydrogen-bond donors are the only neighbours of the *O*-alkoxo atoms besides the carbon and boron atoms. Hence, no counterion–alkoxo contacts are observed.

Though attempts failed to prepare crystals of **2** from riboside–borate solutions in a well-aimed way by combining the riboside and borate in the proper molar ratio, ^{11}B and ^{13}C NMR spectra of the solutions revealed the same species distribution as in 1,4-anhydroerythritol systems. Except for the larger signal number, the ^{13}C spectra, which were assigned in accordance with Ref. [6], show the same features as the spectra in the 1,4-anhydroerythritol solutions. However, enantiomeric forms of the spiro-type bis(diolato) complex, which co-crystallized in the case of the unsubstituted oxolanediol core, now appear as diastereomers. Hence crystallisation may be hampered by the fact that there is no single type of major species to fit into a crystal structure.

NMR study of the guanosine/borate system.—^{13}C NMR spectroscopy has been used as a tool in the study of borate ester formation of the nucleosides [7]. The detection of a 6 ppm downfield shift of the diolato carbon atoms in the adenosine/borate system above pH 6 was obviously not hampered by multiple signals, as the borate–diol molar ratio was adjusted to high values thus giving rise to the formation of monodiolato–dihydroxo–borate as the main species. When adjusting to a 2:1 molar ratio of diol and borate, the ^{13}C spectra reveal the methyl β-D-ribofuranoside spectra regarding number (2 bis(diolato)borate and 1 mono-diolato-dihydroxo-borate signals per carbon atom) and shift of the signals. At a pH

of 14, a 2:4:4 ratio of free guanosine, monodiolato–dihydroxo–borate and bis(diolato)borate shows similar values as for 1,4-anhydroerythritol, again pointing to almost equal ligand properties of diols with the 1,4-anhydroerythritol core.

3. Conclusions

Carbohydrate–borate systems have attracted interest due to their significance for carbohydrate-synthesis and boron-usage in plants [2,3]. NMR spectroscopy reveals furanoidic cis-1,2-diols to be the most suitable ligands for the synthesis of stable complexes [2]. With this work, the first crystal structure analyses of bis(diolato)borate esters of this type are presented. The diols are found with short O···O distances and small torsion angles — the latter being inaccessible with a pyranoidic diol—to assure a small 'bite' suitable for chelate formation with the small boron central atom. From ^{11}B and ^{13}C NMR spectroscopy, the simple parent compound of the furanoidic diols, 1,4-anhydroerythritol, resembles ribofuranose derivatives in terms of ligand strength. It appears to be of importance, for crystallisation, that the spiro-type bis(diolato)-borates derived from 1,4-anhydroerythritol are not apt to the formation of diastereomers. Hence, facilitated crystallisation from these solutions appears to be due to favourable speciation in the mother liquors, which contain co-crystallizing enantiomers instead of diastereomers, as in the case of ribose derivatives.

4. Experimental

X-ray crystallography.—Crystallographic data for **1**: $C_8H_{16}BKO_8$, $M_r = 290.117$ g mol^{-1}, orthorhombic colourless crystal ($1.02 \times 0.22 \times 0.12$ mm), *Pbcn*, $a = 21.9883(12)$, $b = 6.1269(3)$, $c = 18.0038(13)$ Å, $V = 2425.5(2)$ Å^3, $Z = 8$, $D_{calcd} = 1.58898(13)$ g cm^{-3}, $T = 210(2)$ K, μ(Mo K$_\alpha$) = 0.468 mm^{-1}, numerical absorption correction, θ range: 2.26–27.93°, 22,609 reflections, 2870 unique, 2397 with $[I \geq 2\sigma(I)]$, $R_{int} = 0.0970$,

mean $\sigma(I)/I = 0.0409$; C-bonded H atoms refined freely, restraints applied for water H atoms: O–H distance 0.82 Å, H–H distance 1.30 Å (to force the H–O–H angle to 105°), H atoms that are involved in hydrogen bonds to adjacent water molecules are disordered (see text for details), 1 common U_{iso} for water H atoms; 224 parameters, 6 restraints, $R(F)_{obs} = 0.0435$, $R_w(F^2) = 0. 1172$, $S = 1.066$, max/min electron density: $0.479/-0.633$ e Å^{-3}; **2**: $C_{12}H_{24}BNaO_{12}$, $M_r = 394.113$ g mol^{-1}, orthorhombic colourless crystal ($0.60 \times 0.30 \times 0.20$ mm), $P2_12_12$, $a = 15.585(2)$, $b = 15.193(3)$, $c = 7.6324(10)$ Å, $V = 1807.2(5)$ Å^3, $Z = 4$, $D_{calcd} = 1.4485(4)$ g cm^{-1}, $T = 300(3)$ K, $\mu(Mo\ K_\alpha) = 0.147$ mm^{-1}, no absorption correction; θ range: 2.61–27.89° 17,083 reflections, 4139 unique, 2830 with [$I \geq 2\sigma(I)$], $R_{int} = 0.0370$, mean $\sigma(I)/I = 0.0417$, C-bonded H atoms in calculated positions, O-bonded H atoms restrained to a common O–H distance, refined to 0.847 Å, H–O–H angle of water molecules forced to 105°; disordered regions: split positions for O-11 and C-61 (the methoxy function of riboside **1**), which is close to the twofold axis; further split positions were introduced for one hydrogen

atom of each water molecule to allow for disorder along the water···water contacts; attempts to resolve both kinds of disorder in the sense of twin models were unsuccessful; 260 parameters, 14 restraints, $R(F)_{obs} = 0.0386$, $R_w(F^2) = 0.0903$, $S = 0.947$, absolute structure parameter [8]: 0.3(4), max/min electron density: $0.219/-0.240$ e Å^{-3}; equipment used: Stoe PDS, Mo K$_\alpha$ radiation; programs used: SHELXS, SHELXL, ORTEP, PLATON [9]. Lists of positional parameters are provided in Tables 2 and 3.

NMR spectroscopy.—NMR spectra were recorded using Bruker AC250 and AC400 spectrometers. ^{11}B δ values listed refer to

Table 2

Fractional positional parameters of non-hydrogen atoms and equivalent thermal parameters (Å^2) [a]; water oxygens are labelled O9n

	x	y	z	U_{eq} [b]
K	0.302888(17)	0.72934(6)	0.123061(18)	0.02137(14)
B	0.35683(8)	0.2300(3)	0.12401(9)	0.0169(3)
C-11	0.38875(9)	0.5851(3)	0.27500(10)	0.0273(4)
C-21	0.39993(7)	0.3727(3)	0.23349(9)	0.0217(3)
C-31	0.34350(8)	0.2314(3)	0.25412(9)	0.0209(3)
C-41	0.30258(9)	0.3926(3)	0.29519(9)	0.0247(4)
O-11	0.32380(6)	0.6073(2)	0.27524(7)	0.0247(3)
O-21	0.39435(5)	0.4075(2)	0.15530(6)	0.0216(3)
O-31	0.31789(6)	0.1590(2)	0.18550(6)	0.0220(3)
C-12	0.39040(8)	−0.1281(3)	−0.02613(9)	0.0258(4)
C-22	0.40174(7)	0.0828(3)	0.01621(9)	0.0204(3)
C-32	0.34716(9)	0.2299(3)	−0.00670(9)	0.0223(4)
O-12	0.32525(6)	−0.1442(2)	−0.02894(7)	0.0254(3)
O-22	0.39363(5)	0.04833(19)	0.09409(6)	0.0197(3)
O-32	0.32026(6)	0.3051(2)	0.06079(6)	0.0227(3)
O-91	0.50049(7)	0.5375(3)	0.07932(9)	0.0379(4)
O-92	0.50198(8)	−0.0700(3)	0.16911(9)	0.0402(4)

[a] Standard deviations in parentheses.
[b] $U_{eq} = 1/3 \Sigma_i \Sigma_j U_{ij} a_i^* a_j^* a_i a_j$.

Table 3

Fractional positional parameters of non-hydrogen atoms and equivalent thermal parameters (Å^2) [a]; water oxygens are labelled O9n

	x	y	z	U_{iso}/U_{eq} [b]
Na	0.40832(5)	0.36447(6)	0.25473(13)	0.0440(2)
O-11 [c]	0.1581(3)	0.4912(3)	−0.6533(6)	0.0556(14)
O-11 [d]	0.1901(4)	0.4606(4)	−0.6819(7)	0.0593(19)
O-21	0.22795(10)	0.63083(10)	−0.3397(3)	0.0534(5)
O-31	0.31628(12)	0.53852(10)	−0.1825(2)	0.0542(5)
O-41	0.31135(12)	0.47113(11)	−0.5619(3)	0.0591(5)
O-51	0.32846(13)	0.28621(11)	−0.5396(3)	0.0640(6)
C-11	0.23685(18)	0.52360(18)	−0.5772(4)	0.0620(8)
C-21	0.20729(13)	0.54462(14)	−0.3928(4)	0.0453(6)
C-31	0.25914(14)	0.48274(13)	−0.2754(3)	0.0413(6)
C-41	0.30880(14)	0.42362(14)	−0.3994(4)	0.0432(6)
C-51	0.27246(14)	0.33225(14)	−0.4236(4)	0.0450(6)
C-61 [c]	0.1729(5)	0.4910(4)	−0.8453(9)	0.0683(18)
C-61 [d]	0.1279(8)	0.5066(6)	−0.7922(14)	0.091(3)
O-12	0.42123(10)	0.83275(11)	0.1698(3)	0.0531(5)
O-22	0.28625(8)	0.68256(10)	−0.0608(2)	0.0444(4)
O-32	0.37701(10)	0.67397(12)	−0.3011(2)	0.0531(5)
O-42	0.46738(8)	0.69092(9)	0.0884(2)	0.0378(4)
O-52	0.63495(10)	0.72897(13)	0.0101(3)	0.0571(5)
C-12	0.39610(12)	0.74673(14)	0.1256(3)	0.0402(5)
C-22	0.34567(13)	0.75267(14)	−0.0431(3)	0.0417(6)
C-32	0.41309(13)	0.73806(16)	−0.1894(3)	0.0427(5)
C-42	0.49341(11)	0.70433(14)	−0.0913(3)	0.0354(5)
C-52	0.57012(12)	0.76555(16)	−0.0981(4)	0.0471(6)
C-62	0.47365(19)	0.8379(2)	0.3231(5)	0.0729(9)
B	0.30190(13)	0.63117(15)	−0.2205(4)	0.0363(6)
O-91	0.41058(11)	0.49348(11)	0.0991(3)	0.0523(4)
O-92	0.47575(11)	0.59206(12)	0.4397(3)	0.0586(5)

[a] Standard deviations in parentheses.
[b] $U_{eq} = 1/3 \Sigma_i \Sigma_j U_{ij} a_i^* a_j^* a_i a_j$; U_{iso} is given for disordered positions.
[c] Site occupancy: $k = 0.57(1)$.
[d] Site occupancy: $1 - k = 0.43(1)$.

boron trifluoride diethyl etherate as an external standard. The ^{13}C signals of 1,4-anhydroerythritol and its complexes have been assigned by means of DEPT spectra. The following short symbols are used in the listings: B$^-$ = tetrahydroxoborate, LB$^-$ = monodiolato–dihydroxo–borate, L$_2$B$^-$ = bis(diolato)borate.), LH$_2$ = diol.

*Potassium-bis(*meso*-oxolanediolato)borate dihydrate* (**1**).—1,4-Anhydroerythritol (0.41 g, 3.9 mmol) and potassium hydroxide (0.56 g, 10 mmol) were dissolved in 2.5 mL water. Boric acid (0.12 g, 1.9 mmol) was added. The solutions were concentrated. Crystals formed within 4 weeks. The ^{11}B NMR spectrum of the mother liquor: δ 11.10 (L$_2$B$^-$), 6.31 (LB$^-$), 1.32 (B$^-$). A typical ^{13}C spectrum of a diol–borate solution in a 2:1 molar ratio is shown in Fig. 2.

Sodium-bis(methyl β-D-ribofuranosid-2, 3-ato)-borate dihydrate (**2**).—Methyl β-D-ribofuranoside (0.66 g, 4.0 mmol) and sodium hydroxide (0.16 g, 4 mmol) were dissolved in 8.0 mL of water. Tetramethoxysilane (0.32 g, 2.0 mmol) was added under stirring. The solution was heated to 100 °C for 60 h in a Duran vessel in an autoclave (Büchi Tinyclav). After having filtered off a slight precipitate, the solution was concentrated. Few crystals formed within half a year. Boron obviously was dissolved from the Duran vessels. Attempts to prepare **2** using boric acid as the source for borate resulted in the formation of syrup or glassy products (work on quaternary systems diol/borate/silicate/water is in progress).

NMR spectra of a riboside–borate solution in a 2:1 molar ratio at pH 13: ^{11}B: δ 11.10 (L$_2$B$^-$), 6.49 (LB$^-$); ^{13}C (note splitting of the L$_2$B$^-$ signals; the signals of LB$^-$–C2 and LB$^-$–OCH$_3$ are not given since they coincide with the stronger L$_2$B$^-$ signals): δ 110.26 (LB$^-$–C-1), 110.01, 109.96 (L$_2$B$^-$–C-1), 109.24 (LH$_2$–C-1), 88.34 (LB$^-$–C-4), 88.11, 88.09 (L$_2$B$^-$–C-4), 84.66 (LH$_2$–C-4), 81.46, 81.21 (L$_2$B$^-$–C-2), 77.41, 77.22 (L$_2$B$^-$–C-3), 77.18 (LB$^-$–C-3), 75.30 (LH$_2$–C-2), 71.67 (LH$_2$–C-3), 63.65 (LH$_2$–C-5), 63.62 (LB$^-$–C-5), 63.47, 63.45 (L$_2$B$^-$–C-5), 55.20 (LH$_2$–OCH$_3$), 54.92,

54.89 (L$_2$B$^-$–OCH$_3$). Molar ratios of species about 7:1:2 for L$_2$B$^-$, LB$^-$, and LH$_2$.

5. Supplementary material

Tables of atomic coordinates, atomic distances and bond angles have been deposited with the Cambridge Crystallographic Data Centre. These tables may be obtained on request, from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, deposition numbers: CCDC 140096 (**1**) and 140095 (**2**).

Acknowledgements

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