^{11}B NMR Spectroscopic Observation of a Borate Ion–Diol Complex with a Seven-Membered Ring and Comparison of Stability among Complexes with Different Ring Sizes

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Synopsis. A ^{11}B NMR signal, which corresponded to a 1:1 complex of the borate ion and 1,4-butanediol (considered to have a seven-membered ring structure), was observed in aqueous solutions. The stability of the complex was lower than those of complexes with five- or six-membered rings between borate ions and structurally similar diols.

The monomeric borate ion ($B(OH)_4^-$: $\mathbf{B}^-$) easily reacts with polyols to form complexes (esters) in aqueous solutions. As structures of the complexes formed, Boeseken[1)] in 1949 proposed five-membered (α,β-bidentate coordination) and six-membered (α,γ-bidentate coordination) ring structures. Since then a number of investigators have supported these structures (See Fig. 1). As for seven-membered (α,δ-bidentate coordination) rings, however, only one report[2)] was made for the complex between $\mathbf{B}^-$ and 1,2-benzenedimethanol (**1**) (Chart 1) and none for complexes between $\mathbf{B}^-$ and aliphatic polyols. In this note, we report the ^{11}B NMR spectroscopic observation of an α,δ-coordinated borate ion–aliphatic diol complex and compare its stability with those of α,β- and α,γ-type complexes of structurally similar aliphatic diols.

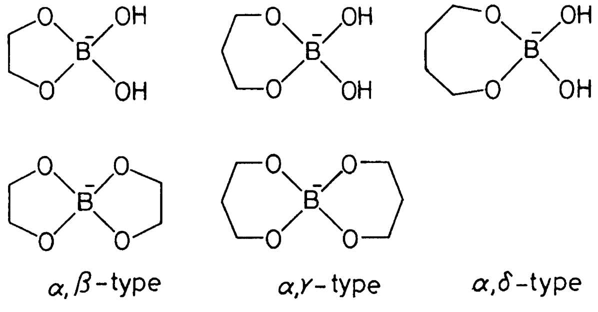

Fig. 1. Structures of α,β-, α,γ-, and α,δ-type complexes corresponding respectively to five-, six-, and seven-membered rings.

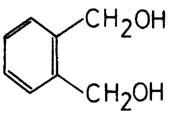

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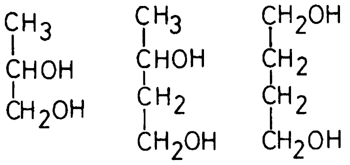
Chart 1.

Experimental

Diols considered in the present study are 1,2-propanediol (**2**), 1,3-butanediol (**3**), and 1,4-butanediol (**4**) (Chart 2). Diols **2** and **3** form α,β- and α,γ-type complexes with $\mathbf{B}^-$, respectively. Diol **4** was the one expected to form an α,δ-type complex. The FT-NMR spectrometer used was a JEOL JNM-GX270, operated at 86.55 MHz and at about 25 °C. All the measurements were made at a constant ionic strength of **3** (in 3 M (M= mol dm^{-3}) NaCl solutions). Peak resolution of overlapping peaks on ^{11}B NMR spectra was performed, when necessary, by using a modified version of a computer program written by Kato et al.[3)] Details of the experimental procedure were given in a previous paper.[4)]



$CH_3\text{–}CHOH\text{–}CH_2OH$ **2** $CH_3\text{–}CHOH\text{–}CH_2\text{–}CH_2OH$ **3** $CH_2OH\text{–}CH_2\text{–}CH_2\text{–}CH_2OH$ **4**

Chart 2.

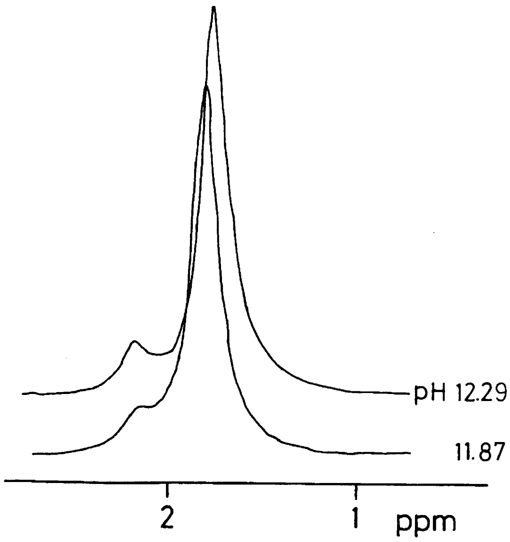


Fig. 2. ^{11}B NMR spectra observed for the boric acid–1,4-butanediol aqueous solutions. The concentration of boric acid was 0.1 M, that of the diol 2.0 M, the ionic strength **3** (3 M NaCl), temperature 25 °C, and the reference was diethyl ether–boron trifluoride (1/1) (δ=0.0).

Table 1. ^{11}B NMR Spectroscopic Data for Boric Acid–1,3-Butanediol (**3**) Solutions

pH$^{a)}$	B concn	**3** concn	Chemical shift/ppm			Peak area/%		
	M	M	$\mathbf{B}^\circ+\mathbf{B}^-$	B^-L	B^-L_2	$\mathbf{B}^\circ+\mathbf{B}^-$	B^-L	B^-L_2
12.05	0.101	0.503	1.66	1.10	0.93	57.29	13.39	29.32
11.05	0.093	0.463	1.66	1.10	0.94	61.36	14.34	24.31
10.07	0.093	0.467	2.30	1.19	1.01	66.52	14.71	18.77
9.22	0.101	0.505	4.28	1.13	—	70.83	29.17	0.00
8.96	0.101	0.503	6.17	2.31$^{b)}$	—	78.85	21.15	0.00
8.66	0.100	0.499	8.07	2.45$^{b)}$	—	80.02	19.98	0.00

a) Measured with a pH meter. b) $B^-L+B^\circ L$ (?).

Table 2. ^{11}B NMR Spectroscopic Data for Boric Acid–1,4-Butanediol (**4**) Solutions

pH$^{a)}$	B concn	**3** concn	Chemical shift/ppm		Peak area/%	
	M	M	$\mathbf{B}^\circ+\mathbf{B}^-$	B^-L	$\mathbf{B}^\circ+\mathbf{B}^-$	B^-L
12.29	0.099	1.98	1.70	2.16	91.58	8.42
11.87	0.100	2.00	1.80	2.25	91.14	8.86
10.23	0.100	2.00	2.23	—	100.00	—

a) Measured with a pH meter.

Table 3. Stability Constants of Borate Ion–Diol Complexes with Different Coordination

diol	Coordination type	K_{BL} mol^{-1} dm^3	K_{BL2} mol^{-1} dm^3	Reference
1,2-Propanediol	α,β	4.4	0.57	4
1,3-Butanediol	α,γ	0.87	3.9	This work
1,4-Butanediol	α,δ	0.049	—	This work

Results and Discussion

The equilibria expected among the boric acid molecule ($\mathbf{B}^\circ$), $\mathbf{B}^-$, a diol (L) and possible esters of $\mathbf{B}^-$ with the diol in the boric acid–diol aqueous solutions are as follows:

$$\mathbf{B}^\circ + OH^- = \mathbf{B}^- \qquad K_B = [\mathbf{B}^-]/([\mathbf{B}^\circ][OH^-])$$
$$\mathbf{B}^- + L = B^-L + 2H_2O \qquad K_{BL} = [B^-L]/([\mathbf{B}^-][L])$$
$$B^-L + L = B^-L_2 + 2H_2O \qquad K_{BL2} = [B^-L_2]/([B^-L][L])$$
$$(L = \mathbf{2},\ \mathbf{3} \text{ or } \mathbf{4})$$

where [A] represents the concentration of species A and K's are equilibrium (stability or formation) constants. The value of K_B is known. The coordination structures of B^-L and B^-L_2 are conceivable in a rather straightforward fashion (cf. Fig. 1), since other structures are hardly viable.

The ^{11}B NMR spectra obtained for the boric acid–**4** system are drawn in Fig. 2 with the omission of the signal at δ=0.0 from the reference (diethyl ether–boron trifluoride (1/1)).

The concentration ratio of boric acid and **4** was 1/20 (0.1 M/2.0 M). Other than the large peak corresponding to the concentration-weighted average of the $\mathbf{B}^\circ$ and $\mathbf{B}^-$ peaks, which was pH-dependent,$^{5)}$ a small peak was observed at about δ=2.2 in the high pH region (pH=11.87 and 12.29). Although not shown in the figure, the peak was not observed at lower pH values (pH=8.98 and 10.23). In addition, Henderson et al.$^{2)}$ reported that the peak was not observed when the concentration ratio of boric acid and **4** was not sufficiently low (2/5) even at a high pH value (pH=12). Thus, this peak is observed only when the polyol concentration is high, the boric acid/polyol concentration ratio is low, and the pH of the solution is high.

The peak at δ=2.2 can be assigned in a straightforward fashion to the borate ion–**4** ester with a seven-membered ring (cf. Fig. 1). The only other possible assignment is the one in which the peak is regarded as being obtained from monodentate complexes such as $B(OH)_3(OCH_2CH_2CH_2CH_2OH)^-$, $B(OH)_2(OCH_2CH_2CH_2CH_2OH)_2^-$, $B(OH)(OCH_2CH_2CH_2CH_2OH)_3^-$, and $B(OCH_2CH_2CH_2CH_2OH)_4^-$. To examine the existence of monodentate esters, ^{11}B NMR spectra of the boric acid–ethanol system with 1/20 mole ratio (0.1 M/2.0 M) were also recorded, but no peak was detected other than those corresponding to $\mathbf{B}^\circ+\mathbf{B}^-$. The possibility of monodentate esters being ruled out, the formation of the α,δ-bidentate complex between the borate ion and **4** was thus confirmed. To the best of our knowledge, this is the first observation of a borate ion–aliphatic diol complex with a seven-membered ring.

^{11}B NMR spectroscopic data obtained for boric acid–**3** and boric acid–**4** solutions are summarized in Tables 1 and 2, respectively. The peak assignments of the former solutions are based on the pH dependences of the peak areas of the ^{11}B NMR signals and reference to the literature on other α,γ-type esters.[6,7] The stability constant values of the three systems (boric acid–**2**, –**3**, and –**4** systems) are summarized in Table 3. The K_{BL} and K_{BL2} values of the boric acid–**2** system were cited from the previous paper,[4] those of the boric acid–**3** were calculated from the peak areas in the ^{11}B NMR spectra between pH=10.07 and 12.05, and K_{BL} of the boric acid–**4** system was from the peak areas at pH=11.87 and 12.29.

The K_{BL} value is larger than the K_{BL2} value in the boric acid–**2** system, while the K_{BL} value is smaller than the K_{BL2} value in the boric acid–**3** system. This shows that $\mathrm{B^-L}$ is more stable than $\mathrm{B^-L_2}$ in the former system where α,β-type complexes are formed, while $\mathrm{B^-L_2}$ is more stable than $\mathrm{B^-L}$ in the latter system where α,γ-type complexes are formed. This result could be due to the difference in structural deformation around the boron atom between α,β-type complexes and α,γ-type complexes. The O–B–O angle in the latter complexes is nearly equal to the tetrahedral angle (the angle for $\mathbf{B^-}$),[5] which means that the α,γ-coordination does not change the electronic circumstances around the ^{11}B nucleus substantially, relative to that in $\mathbf{B^-}$. Unlike the α,γ-coordination, the α,β-coordination deforms the electronic circumstances around the ^{11}B nucleus,[6] which hinders the second α,β-coordination, making K_{BL} smaller than K_{BL2}. Note, however, that the overall stabilities ($K_{\mathrm{BL}} \times K_{\mathrm{BL2}}$) are similar to each other in the two systems ($K_{\mathrm{BL}} \times K_{\mathrm{BL2}}=2.5$ in the boric acid–**2** system and $=3.4$ in the boric acid–**3** system). This result is consistent with the speculation by Henderson et al.[2] that 1,2-diol and 1,3-diol have similar complexing ability.

Compared with the K_{BL} values of the α,β- and α,γ-type complexes, that of the α,δ-type complex is very small. This is attributable, for the most part, to the fact that **4** has to be heavily bent in order to form with $\mathbf{B^-}$ an ester with a seven-membered ring.

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