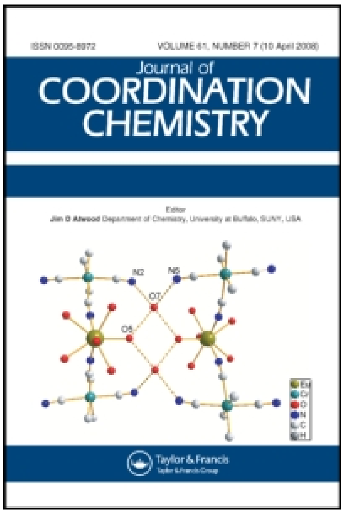


Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

High Field ^{11}B and ^{13}C Nmr Investigations of Aqueous Borate Solutions and Borate-Diol Complexes

J. M. Coddington[a]; M. J. Taylor[a]
[a] Department of Chemistry, University of Auckland, Auckland, New Zealand

To cite this Article Coddington, J. M. and Taylor, M. J.(1989) 'High Field^{11}B and ^{13}C Nmr Investigations of Aqueous Borate Solutions and Borate-Diol Complexes', Journal of Coordination Chemistry, 20: 1, 27 — 38
To link to this Article: DOI: 10.1080/00958978909408845
URL: http://dx.doi.org/10.1080/00958978909408845

J. Coord. Chem. 1989, Vol. 20. pp. 27–38
Reprints available directly from the publisher
Photocopying permitted by license only

HIGH FIELD ^{11}B AND ^{13}C NMR INVESTIGATIONS OF AQUEOUS BORATE SOLUTIONS AND BORATE-DIOL COMPLEXES

J. M. CODDINGTON and M. J. TAYLOR*

Department of Chemistry, University of Auckland, Auckland, New Zealand

(Received August 25, 1988; in final form September 30, 1988)

^{11}B nuclear magnetic resonance spectra of concentrated aqueous solutions of boric acid and the tetrahydroxyborate $B[OH]_4^-$ ion, or of borax, $Na_2B_4O_7$, at 128.4 MHz, reveal substantial amounts of triborate species in the pH range 8–10.5 and enable equilibria such as $B_3O_3(OH)_4^- + OH^- \rightleftharpoons B_3O_3(OH)_5^{2-}$ and the hydrolytic dissociation of these ions to be studied.

Addition of the polyhydroxy-compounds ethane-1,2-diol, propane-1,2-diol, propane-1,3-diol and glycerol results in the formation of a variety of mono- and bis-chelated complexes, among which are spirocyclic anions with five- and six-membered rings sharing a common boron atom. Complexes in which boron atoms of triborate anions are coordinated by diol ligands are also identified. ^{11}B chemical shifts characteristic of chelated and hydroxylic boron centres in mono- and triborate species are reported, taking into account the trends accompanying a change from trigonal to tetrahedral coordination. ^{1}H and ^{13}C NMR spectra of borate solutions containing the complexes $LB(OH)_2^-$ and L_2B^-, where L represents propane-1,2-diol as a chelating ligand, reveal all the possible stereoisomers of this system

Keywords: Boron-11 nmr, carbon-13 nmr, borax, borate complexes, diol complexes

INTRODUCTION

The equilibria which exist in aqueous boric acid-borate solutions have been widely investigated by methods including cryoscopic measurements, conductance studies, pH titrations, Raman spectroscopy, and nuclear magnetic resonance.[1–8] In dilute solutions the results can be explained by a pH dependent equilibrium between the species $B(OH)_3$ and $B(OH)_4^-$:

$$B(OH)_3 + OH^- \rightleftharpoons B(OH)_4^-$$

At intermediate pH values and concentrations greater than about 0.025 mol dm^{-3} polyborate ions are formed, and there is general agreement that the principal species is the triborate $B_3O_3(OH)_4^-$. Other polynuclear anions $B_3O_3(OH)_5^{2-}$, $B_4O_5(OH)_4^{2-}$, and $B_5O_6(OH)_4^-$, have been identified but not fully characterised in solution by the structural methods of Raman[2,3] and ^{11}B NMR spectroscopy.[7] These species are among the many polymeric borate structures known in the solid state from X-ray crystallographic analysis of a wide variety of metal borates.[9–12]

The formation of complexes between borate and polyhydroxy compounds provides an important tool in conformational analysis of carbohydrates, and is used in a variety of separation and chromatographic techniques.[13,14] The reaction with polyols is also known as a means of increasing the strength of boric acid for its

---

* To whom correspondence should be addressed.

volumetric analysis. These systems have been studied over a long period and the structural principles involved are fairly well understood, particularly as a result of recent vibrational and NMR spectroscopic investigation.[15–23] This has established that borate is complexed by diols to give both mono-chelated and bis-chelated, or spirocyclic, anions. 1,2-diols form five-membered ring complexes and 1,3-diols form six-membered rings, and these two situations are readily distinguished by ^{11}B NMR spectroscopy.[6,19]

We have studied solutions of borax (sodium tetraborate) which is frequently used in the complexing of polyhydroxy compounds, as well as those of the borate ion, $B(OH)_4^-$, with the hydroxy compounds ethane-1,2-diol (ethylene glycol), propane-1,2-diol, propane-1,3-diol, and propane-1,2,3-triol (glycerol), by means of their ^{11}B NMR spectra. Our work has revealed several new species and structures in addition to those recognised in the previous investigations of borate–diol systems. These include bis-chelates in which boron simultaneously forms both a five- and a six-membered ring. Other complexes, which are present in substantial amounts in borax solutions containing diols, appear to be derived from triborate and possibly pentaborate anions. These findings assist in the identification of the various borate species existing in aqueous solution. They also suggest that the variety of structures to be considered in interpreting borate–polyol or borate–carbohydrate complex formation is greater than has previously been appreciated.

EXPERIMENTAL

The compounds ethane-1,2-diol, propane-1,2-diol, propane-1,3-diol and glycerol were commercial materials. Borax solutions were prepared from sodium tetraborate, $Na_2B_4O_7$, (BDH Lab. Reagent) and adjusted to various pH values by adding small amounts of sodium hydroxide or hydrochloric acid solution. Solutions of $NaB(OH)_4$ were prepared from equimolar quantities of NaOH and $B(OH)_3$ in water. The solutions contained 10% D_2O to provide the NMR locking signal.

NMR spectra were obtained using a Bruker AM400 spectrometer. ^{11}B spectra at 128.4 MHz were collected using a 10 mm broadband probe with 8K data points over 6000 Hz using a 60° pulse (10 μs). Typically, the pulse repetition rate was 0.7 s and data were processed using a line broadening of 0.3 Hz. ^{13}C spectra at 100.62 MHz were collected using a 10 mm broadband or 5 mm ^{1}H-^{13}C switchable probe, with 64K data points over 20,000 Hz using a 45° pulse. The pulse repetition rate was typically 6.2 s and spectra were line broadened by 3.0 Hz. DEPT spectra used a 135° editing pulse. ^{1}H spectra at 400.13 MHz were collected using a 5 mm ^{1}H-^{13}C switchable probe with 32K data points over 4000 Hz using a 45° pulse. The pulse repetition rate was typically 4.1 s and spectra were line broadened by 0.25 Hz. ^{1}H and ^{13}C spectra were referenced to internal 3-(trimethylsilyl)propanoic acid as the sodium salt.

^{11}B spectra were referenced to external $Et_2O.BF_3$. On this scale, aqueous $B(OH)_3$ appears at 19.2 ppm. Spectra were recorded at 22°C.

RESULTS AND DISCUSSION

Aqueous Borate Solutions

A solution of $NaB(OH)_4$, with a concentration of 0.50 M, gives a ^{11}B signal at

1.7 ppm (linewidth 10 Hz) due to the tetrahedral $B(OH)_4^-$ ion. For the trigonally coordinated boron in $B(OH)_3$, resonance occurs at 19.2 ppm as a much broader peak having a linewidth of 80 Hz. Both the chemical shift and the linewidth have been shown previously to be independent of concentration over a wide range in dilute solution.[8] When aqueous solutions of $B(OH)_3$ and $NaB(OH)_4$ are mixed the result is a spectrum in which an intense peak at 8 ppm (linewidth 150 Hz) is accompanied by a smaller peak at 12 ppm and a weak signal at 1.1 ppm. A very similar spectrum is obtained when a solution of sodium tetraborate (borax) is examined. The main peak arises from the $B(OH)_3/B(OH)_4^-$ equilibrium. Those near 12 and 1 ppm have been attributed to triborate and pentaborate ions, respectively.[7]

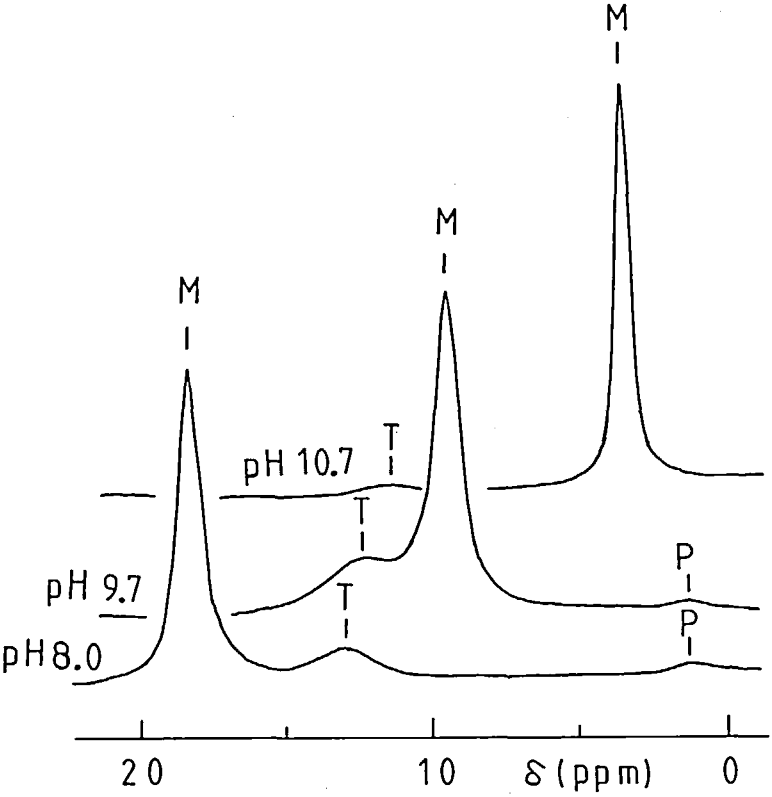
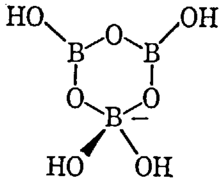
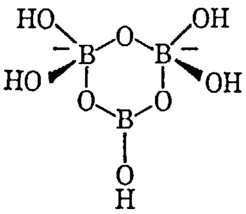


FIGURE 1 128.4 MHz ^{11}B NMR spectra of borax solutions showing resonances due to $B(OH)_3/B(OH)_4^-$ monomer M, triborate T, and pentaborate P.

Borax at a concentration of 0.30 M has a pH of 9.7. The effect of changing pH on the species in solution was investigated by measuring the spectra of a series from pH 8 to 11.5 (Figure 1). Over this range the main peak moves progressively from 18.2 to 2.0 ppm, *i.e.*, from close to that of trigonal boron in $B(OH)_3$ to the position of tetrahedral boron in the $B(OH)_4^-$ ion. At pH 9.7 the weaker triborate resonance appears at 12.5 ppm, with a linewidth of 250 Hz. This signal was attributed by Salentine[7] to $B_3O_3(OH)_4^-$ (Structure I) who pointed out that it is close to the chemical shift expected for a labile species in which one-third of the boron is



I



II

tetrahedral with two-thirds trigonal. Previous workers have not noticed any change in the position of the triborate peak, but the present study reveals a progressive movement from 13.0 ppm at pH 8.0, to 10.2 ppm at pH 11.3. The latter chemical shift represents an environment in which more than 50% of boron atoms are tetrahedral and suggests that **II** has become the predominant species in solution. The trend with pH can be explained by an equilibrium between triborate ions:

$$\underset{(\mathrm{I}, \delta = 13.3\ \mathrm{ppm})}{B_3O_3(OH)_4^-} + OH^- \rightleftharpoons \underset{(\mathrm{II}, \delta = 7.5\ \mathrm{ppm})}{B_3O_3(OH)_5^{2-}}$$

At higher pH the triborate resonance vanishes and only the peak due to $B(OH)_4^-$ remains, indicating that dissociation has occurred by the reaction below:

$$B_3O_3(OH)_5^{2-} + OH^- + 3H_2O \rightleftharpoons 3B(OH)_4^-$$

The hydrolytic dissociation which is observed below pH 9 is represented by the reaction:

$$B_3O_3(OH)_4^- + H^+ + 2H_2O \rightleftharpoons 3B(OH)_3$$

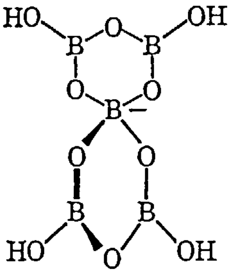
These three reactions give a better picture of the monomer–trimer equilibria in concentrated borate solutions than the single reaction

$$2B(OH)_3 + B(OH)_4^- \rightleftharpoons B_3O_3(OH)_4^-$$

originally put forward by Momii and Nachtrieb[4] and used in most subsequent analyses of this system.

We note that Raman bands at 609 and 565 cm^{-1}, whose relative intensities change with pH, attributed by Maya[2] and Maeda *et al.*[3] to triborate and tetraborate, can equally well be assigned to the triborate ions **I** and **II**, respectively. These should be recognisable as distinct species on the time scale of vibrational spectroscopy, just as are $B(OH)_3$ and $B(OH)_4^-$ in solutions where both are present, whereas they appear as a single averaged peak in the NMR spectrum.

The only other polyborate species for which there is firm structural evidence in aqueous solution is the pentaborate, $B_5O_6(OH)_4^-$ (**III**). Salentine[7] assigned a sharp peak with a chemical shift of 1 ppm to the central, tetrahedral boron atom in this anion, but found difficulty in explaining the absence of any resonance due to the four trigonal boron atoms. In the present work, the tetrahedral boron signal is confirmed at 1.1 ppm. It is detected in solutions of pH 8 to 10 and its position is independent of pH. In contrast, the chemical shift of the other boron atoms can be expected to



III

change with pH since it is likely that pentaborate (III) can coordinate additional hydroxide ions, *e.g.*, to yield $B_5O_6(OH)_6^{3-}$ in which only two boron atoms are trigonal. Since the environments of the trigonal and tetrahedral atoms, other than the central atom, will be averaged by rapid exchange of hydroxyl groups, a broad resonance situated around 10 ppm is anticipated. Such a resonance appears with those of monomer and trimer species in the spectrum of an aqueous borax solution adjusted to pH 8 by addition of HCl. Removal of OH^- ligands from this species to form $B_5O_6(OH)_4^-$ will alter the average chemical shift towards the limiting trigonal value of 19.2 ppm observed in boric acid solutions.

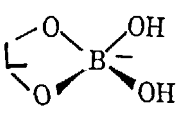
The ^{11}B NMR spectra (at 160 MHz) of solutions of sodium pentaborate $NaB_5O_8.5H_2O$ reported by Salentine[7] consist of peaks at 1.0–1.2, 13.0–13.2, and 18.2–18.9 ppm. At a concentration of 0.30 M the chemical shifts and relative areas are 1.1 ppm (12.6%), 13.2 ppm (24.6%) and 18.7 ppm (62.8%).[7] If the 18.7 ppm peak results from the superposition of signals due to $B(OH)_3$ and the trigonal boron atoms of the pentaborate ion, the boron atoms in different chemical environments are in the proportions: central B of pentaborate 12.6%, other B of pentaborate 50.4%, average B of $B_3O_3(OH)_4^-$ 24.6% and B of $B(OH)_3$ 12.4%. Use of these figures gives the concentrations 0.189 M, 0.123 M and 0.186 M for the pentamer P, trimer T and monomer M, respectively. These values yield an equilibrium constant $K = [T][M]^2/[P] = 2.25 \times 10^{-2}$ for the hydrolytic dissociation of the pentaborate ion:

$$B_5O_6(OH)_4^- + 3H_2O \rightleftharpoons B_3O_3(OH)_4^- + 2B(OH)_3$$

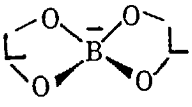
^{11}B NMR Spectra of Borate–Diol Complexes

(i) *Aqueous borate solutions with ethane-1,2-diol*

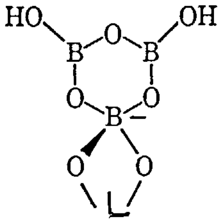
Solutions of $NaB(OH)_4$, also containing ethanediol at various levels, were examined by ^{11}B NMR spectroscopy. Signals were observed at 5.4 and 9.3 ppm, due to the mono-chelate and bis-chelate derived from the $B(OH)_4^-$ anion (Structures IV and V,



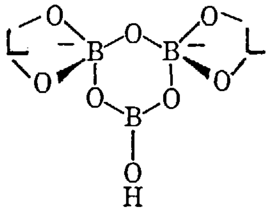
IV



V



VI



VII

respectively). The linewidths, *ca* 15 Hz, are similar to that of B(OH)$_4^-$, which is to be expected since boron has a tetrahedral environment in each case. This result agrees fully with previous studies in which the ^{11}B spectra were measured at lower frequencies of 12.8,[6,18] 28.75[21,22] or 64.2 MHz.[19,20] However, the higher resolution of spectra obtained at 128.4 MHz, now reveals additional resonances of 5.7 and 6.0 ppm. Figure 2 compares the spectra of solutions having diol:borate ratios of 3:1 (in which the major species is the mono-chelate complex), 10:1, and 40:1 (in which the bis-chelate is predominant). Even in the latter solution, some boron atoms remain uncomplexed by the diol ligand, and in an average environment which is close to tetrahedral, as is shown by the weak signal at 2 ppm.

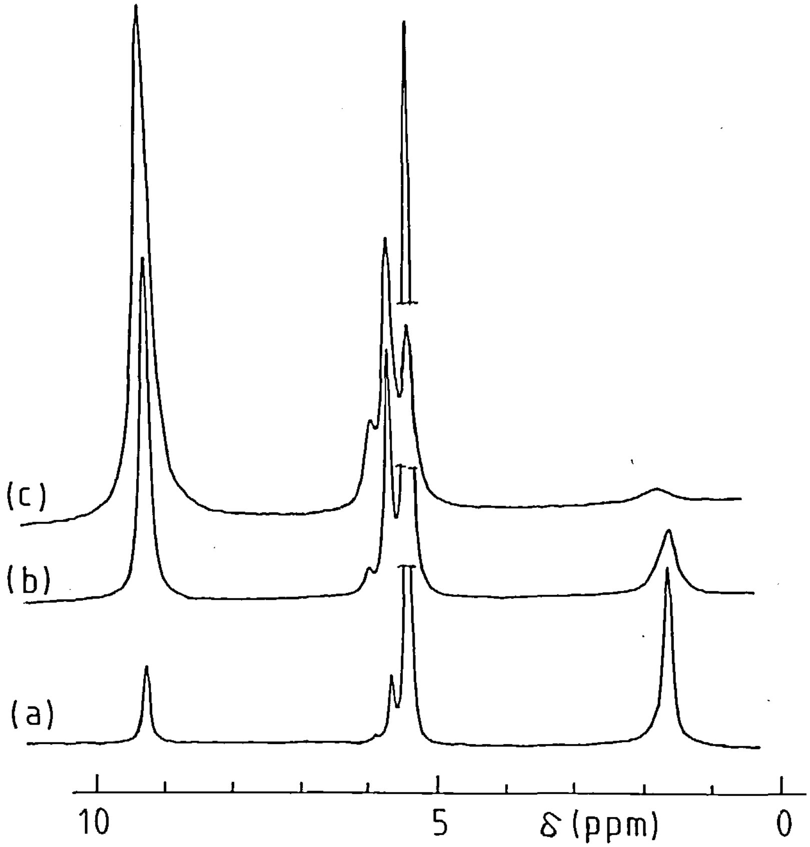
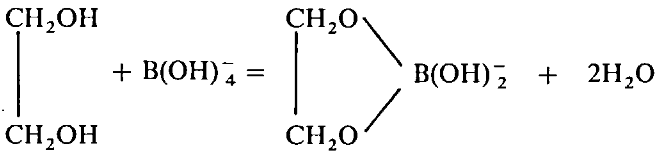


FIGURE 2 128.4 MHz ^{11}B NMR spectra of ethane-1,2-diol (m) – NaB(OH)$_4$ (n) aqueous solutions. (a) m/n = 3, (b) m/n = 10, (c) m/n = 40.

We believe that the resonances at 5.7 and 6.0 ppm arise from chelates in which the boron concerned is part of triborate ion, *i.e.*, Structures **VI** and **VII**, respectively. Complexing by polyols is known to shift the boric acid equilibrium $B(OH)_3 + H_2O \rightleftharpoons B(OH)_4^- + H^+$ to the right since the tetrahydroxyborate ion reacts with diols, *e.g.*, with one mole of ethane diol:



It is reasonable to suppose that similar complexation will affect boron atoms in the species $B_3O_3(OH)_4^-$ and $B_3O_3(OH)_5^{2-}$. Chelation of boron centres appears to stabilise the B_3O_3 ring system, otherwise a solution with a large excess of diol might contain little else but the monomeric bis-chelate complex (V). Previous workers, particularly Dawber and Green[21] who studied solutions of $NaB(OH)_4$ in water with diol:borate ratios up to 40, considered the persistent signal near 2 ppm to represent $B(OH)_4^-$. Tetrahedral boron atoms which carry hydroxyl ligands and are part of a triborate anion are likely to share this resonance and to contribute to this peak.

To investigate complexes of the triborate ion with ethanediol, we used the aqueous solutions of $Na_2B_4O_7$ (0.30 M in boron) adjusted to pH values in the range 8.0 to 11.5 with HCl or NaOH, the ^{11}B NMR spectra of which are shown in Figure 1. Ethanediol was added to give a diol:boron ratio of 5:1. At pH 8 the ^{11}B spectrum of the mixture, with a large signal at 18.4 ppm, differed little from that of the aqueous solution and revealed chiefly $B(OH)_3$. In the more alkaline samples a sharp peak at 9.3 ppm was clearly that of the bis-chelate L_2B^- formed by reaction of the diol with $B(OH)_4^-$. At pH 11.3 this peak was accompanied by broader resonances at 5.3 ppm, attributable to $LB(OH)_2^-$, and 3.4 ppm ($B(OH)_3/B(OH)_4^-$) in line with the previous finding that no triborate remains at this pH. Spectra of the pH 9.7, 10.3 and 10.7 samples contain two broad resonances, one of which moves from *ca.* 14 to 6 ppm, and the other from 6.2 to 5.6 ppm, as the OH^- concentration increases. We interpret this behaviour in terms of mixtures of monoborate complexes L_2B^- and $LB(OH)/LB(OH)_2^-$ and triborate complexes such as $LB_3O_3(OH)_3^{2-}$ in which hydroxyborate centres are exchanging between trigonal and tetrahedral. According to this model of the interaction of ethanediol with 0.3 M borax solutions of pH 9–11, the boron signal of L_2B^- is at 9.3 ppm. Boron atoms which are chelated by only one diol ligand L have an average chemical shift between 6.2 to 5.6 ppm, while those with solely hydroxyl ligands appear in the range 14 to 6 ppm. The much sharper signals which characterise the products of reaction of the diol with $NaB(OH)_4$ solution, described earlier, arise from boron atoms which are predominantly tetrahedral in their coordination. Any attempt to improve on the formation constants for borate-diol complexes obtained in the previous work[6,15,19,21,22] would need to consider all the species present.

(ii) *Aqueous borate solutions with propane-1,3-diol, ethane-1,2-diol plus propane-1,3-diol, or propane-1,2-diol plus propane-1,3-diol*

Except for higher resolution resulting from the increased NMR operating frequency, and the change from boric acid to $Et_2O.BF_3$ as the chemical shift origin, our ^{11}B

NMR spectra of the propane-1,3-diol-$NaB(OH)_4$ system at ratios of 2:1, 3:1 and 10:1 are similar to those obtained before.[21] They reveal a 1:1 borate–diol complex at 0.9 ppm, a 1:2 borate–diol at 0.5 ppm and a hydroxyborate signal at 2–3 ppm. The interesting fact that ^{11}B signals for boron atoms which are part of a six-membered chelate ring indicate a more shielded environment than that of $B(OH)_4^-$, whereas those associated with five-membered ring chelates are less shielded, is well established.[6,18–23]

In the earliest ^{11}B study of the interaction of borate with diols Kennedy *et al.*[6] considered the formation of a mixed spirocyclic anion, with five- and six-membered rings on the same boron atom, and deduced its likely presence by summing the areas of peaks which were unresolved at their NMR frequency of 12.8 MHz. Figure 3 shows the ^{11}B NMR spectrum at 128.4 MHz of a borate solution containing ethane diol plus propane-1,3-diol. A new peak at 4.75 ppm, midway between the peaks at 9.2 and 0.3 ppm of the bis-chelate complexes formed by ethanediol and propane-1,3-diol, respectively, can be assigned with confidence to the mixed ligand species. It is worth noting that the signals due to mono-chelated complexes occur at 5.65 and 1.1 ppm (not 5.4 and 0.9 ppm) and are rather broad. The explanation is that triborate, as well as simple $B(OH)_4^-$ based species with diol ligands are contributing to these peaks in this particular sample. A mixture of propane-1,2-diol and propane-1,3-diol borate complexes, shows the signal due to the mixed ligand spirocyclic anion as a separate peak at 4.8 ppm. An intense peak at 5.4 ppm is that of the monochelate formed by reaction of propane-1,2-diol with $B(OH)_4^-$ to give $LB(OH)_2^-$. A shoulder at 5.7 ppm is attributed to the corresponding chelate of $B_3O_3(OH)_4^-$.

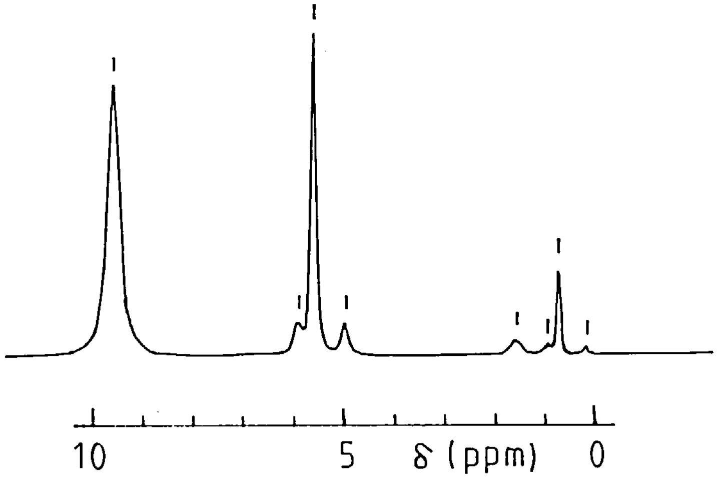


FIGURE 3 128.4 MHz ^{11}B NMR spectrum of an aqueous solution of $NaB(OH)_4$ containing ethane-1,2-diol and propane-1,3-diol.

(iii) *Aqueous borate solutions with propane-1,2,3-triol (glycerol)*

Glycerol (propane-1,2,3-triol) has the capacity to form borate complexes of all the types considered so far, and Figure 4 shows that it does so. In this ^{11}B NMR spectrum of 0.5 M $NaB(OH)_4$ solution, with a glycerol:borate ratio of 3:1, the outer

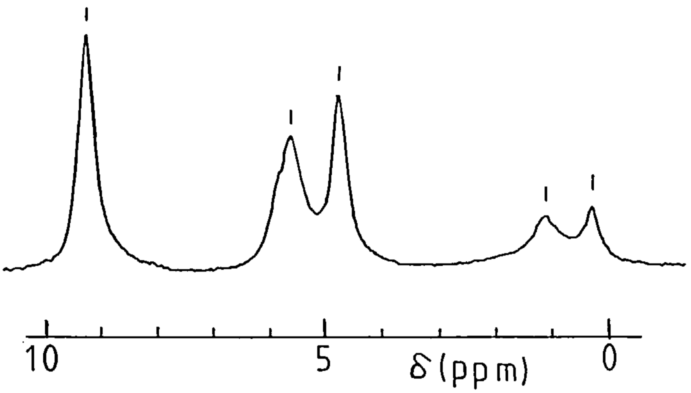
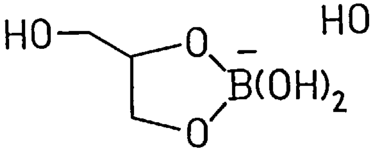
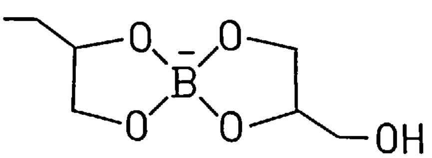


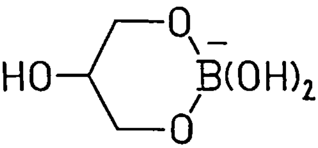
FIGURE 4 128.4 MHz ^{11}B NMR spectrum of an aqueous solution of $NaB(OH)_4$ containing propane-1,2,3-triol.



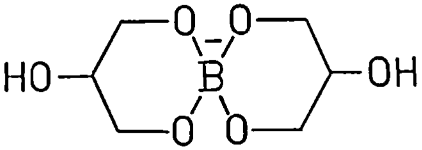
VIII δ 5.6



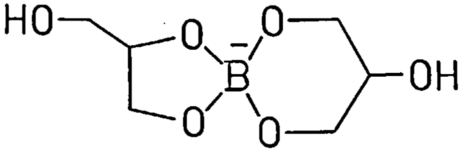
IX δ 9.6



X δ 0.75



XI δ 0.2



XII δ 4.95

resonances of 9.6 and 0.2 ppm are due to spirocyclic anions with five- or six-membered rings, respectively (Structures IX and XI). The central peak at 4.95 ppm is that of the anion in which one glycerol ligand has formed a five-membered and the other a six-membered ring (Structure XII). With the advantage of hindsight, the signal attributable to this species can be detected as a shoulder in the spectrum obtained at 28.75 MHz in previous work.[21] The peaks at 5.6 and 0.75 ppm arise from monoborate complexes, each with a single glycerol ligand which is involved in five-membered ring chelation in one case and six-membered ring formation in the other (Structures VIII and X, respectively). We attribute the smaller peaks to similarly chelated atoms, except that here the boron is part of the triborate ion, *i.e.* 1.0 ppm to Structure VI, 5.9 ppm to Structure VI and the shoulder at 6.2 ppm to Structure VII. This assignment is supported by the fact that the intensity ratio of the small peak to that of the adjacent larger peak is the same for both 5- and 6-membered ring systems. This should be the case because the ratio will be that of triborate to monoborate ions in the solution. The remaining signal, at 1.6 ppm, has the chemical shift expected of tetrahedral borate species with hydroxyl ligands. Its intensity, compared with the combined intensity of peaks due to the chelated boron atoms of Structure VI, suggests that it arises from the non-chelated borons of these triborate complexes. There may be very little free $B(OH)_4^-$ in this mixture, which is contrary to the assumption of earlier workers,[6,19–21] but should not be surprising because glycerol is present in excess, and the spectrum shows that strong complexing takes place. We note that mixtures with glycerol:borate ratios of 1:1 and 2:1 have a weak broad signal at *ca* 4 ppm attributable to the $B(OH)_3/B(OH)_4^-$ equilibrium, in addition to the full set of resonances present in the 3:1 system.

^1H and ^{13}C NMR Spectra of Borate–Diol Complexes

^1H and ^{13}C NMR spectroscopy can reveal the manner in which the ligand is incorporated in borate–diol complexes. Dawber *et al.*[22] have recently studied a variety of polyols in combination with $B(OH)_4^-$, using ^{13}C resonance at 22.52 MHz. They confirm the findings of complexation by ethanediol and propanediol ligands. For glycerol, the three ^{13}C signals indicate complexing across C_1:C_2 and C_1:C_3 with the greater extent of complexation across adjacent carbon atoms. It has also been reported that the ^{13}C spectrum of ethanediol in D_2O is unaffected by the addition of sodium tetraborate;[17] however the explanation suggested (that the ligand conformation was unfavourable to complexing) is unlikely to be correct. It is probable that the pH of the borax solution was not high enough for complexation to occur.

We have studied the ^{13}C NMR spectra at 100.62 MHz of solutions containing $NaB(OH)_4$ and propane-1,2-diol taking advantage of the fact that the methyl group of this ligand provides a convenient label to identify the different isomers of mono- and bis-chelates. Solutions with borate:diol ratios of 1:1, 1:2, 1:3, and 1:10 were examined. The ^{11}B NMR spectra show that these systems, in which L is derived from $CH_3CH(OH)CH_2OH$, consist of the bis-chelate L_2B^- (δ 9.2 ppm), $LB(OH)_2^-$ (δ 5.4 ppm; the major component), and $B(OH)_4^-/B(OH)_3$. Very little of the $B(OH)_4^-/B(OH)_3$ component remains in the solution with a large excess of the diol. The ^{13}C NMR spectra comprise sharp signals due to the free diol at δ 18.95 (CH_3), 67.45 (CH_2) and 68.80 ppm (CH), and of the ligand within the $LB(OH)_2^-$ complex at 20.01, 69.65 and 70.07 ppm. The increases in the chemical shifts of 1 to 2 ppm upon complexation are of similar magnitude to the substituent effects upon borate ester formation in a range of polyhydroxycarboxylates.[24]

A set of weaker peaks in the ^{13}C spectrum is attributable to the bis-chelated borate complex L_2B^-. In the CH_3 resonance region there are four such peaks, in two pairs: δ 20.18, 20.22 and 20.50, 20.54 ppm, and these correspond to the four structural isomers afforded by the unsymmetrical diol, $CH_3CH(OH)CH_2OH$. The signals are of equal size, showing that all four isomers are equally favoured in the formation of the L_2B^- complex. The expected signals due to the carbon atoms of the CH_2O and CHO groups are also observed and their assignment is confirmed by polarisation transfer (DEPT) spectra. For each of these carbon atoms two signals are found, which are at 69.56 and 69.76 ppm for CH_2O and 70.01 and 70.13 ppm for CHO. The differentiation can be associated with the environments which are on the same or the opposite side of the molecule as the CH_3 group of the other ligand. The further inequivalence which could arise from the alternative positions of the CH_3 group on the chelate ring is not detected in these signals, although it is presumably responsible for the small chemical shift difference of 0.04 ppm noticed in the pairs of CH_3 resonances.

^1H NMR spectra at 400.13 MHz of the propane-1,2-diol:borate mixtures generally support the interpretation of complex formation based on the ^{11}B and ^{13}C spectra but are too complicated to warrant extensive analysis. For the case of ethanediol–borate complexation, the ^1H spectrum shows that the CH_2 resonance undergoes a small change from 3.630 to 3.665 ppm, and the peaks are sufficiently well resolved to be used to measure the amounts of free and complexed ligand; however no distinction emerges between the ligands of L_2B^- and $LB(OH)_2^-$ complexes which therefore limits the use of the technique in this instance. The peaks concerned have linewidths of *ca* 6 Hz and some broadening is to be expected due to conformational equilibria involving the diol ligand.

ACKNOWLEDGEMENTS

We thank the New Zealand Universities Grants Committee and Medical Research Council for financial support.

REFERENCES

1. R.E. Mesmer, C.F. Baes, Jr. and F.H. Sweeton, *Inorg. Chem.*, **11**, 537 (1972).
2. L. Maya, *Inorg. Chem.*, **15**, 2179 (1976).
3. M. Maeda, T. Hirao, M. Kotaka and H. Kakihana, *J. Inorg. Nucl. Chem.*, **41**, 1217 (1979).
4. R.K. Momii and N.H. Nachtrieb, *Inorg. Chem.*, **6**, 1189 (1967).
5. H.D. Smith, Jr. and R.J. Wiersema, *Inorg. Chem.*, **11**, 1152 (1972).
6. W.G. Henderson, M.J. How, G.R. Kennedy and E.F. Mooney, *Carbohyd. Res.*, **28**, 1 (1973).
7. C.G. Salentine, *Inorg. Chem.*, **22**, 3920 (1983).
8. R. Balz, U. Brändle, E. Kammerer, D. Köhnlein, O. Lutz, A. Nolle, R. Schafitel and E. Veil, *Z. Naturforsch*, **41a**, 737 (1986).
9. J.B. Farmer, *Adv. Inorg. Chem. Radiochem.*, **25**, 187 (1982).
10. B.P. Tarasevich and E.V. Kuznetsov, *Russ. Chem. Rev.*, **56**, 203 (1987).
11. I. Haiduc and D.B. Sowerby, "*The Chemistry of Inorganic Homo- and Heterocycles*", Academic Press, London (1987).
12. C.G. Salentine, *Inorg. Chem.*, **26**, 128 (1987).
13. J. Böeseken, *Adv. Carbohydr. Chem.*, **4**, 189 (1949).
14. R.J. Ferrier, *Adv. Carbohydr. Chem. Biochem.*, **35**, 31 (1978).
15. R.P. Oertel, *Inorg. Chem.*, **11**, 544 (1972).
16. M. Mazurek and A.S. Perlin, *Can. J. Chem.*, **41**, 2403 (1963).
17. P.A.J. Gorin and M. Mazurek, *Carbohydr. Res.*, **27**, 325 (1973).
18. G.R. Kennedy and M.J. How, *Carbohydr. Res.*, **28**, 13 (1973).
19. M. van Duin, J.A. Peters, A.P.G. Kieboom and H. van Bekkum, *Tetrahedron*, **30**, 2901 (1984); **41**, 3411 (1985).
20. M. Makkee, A.P.G. Kieboom and H. van Bekkum, *Rec. Trav. Chim. Pays-Bas*, **104**, 230 (1985).
21. J.G. Dawber and S.I.E. Green, *J. Chem. Soc., Faraday Trans., I*, **82**, 3407 (1986).

22. J.G. Dawber, S.I.E. Green, J.C. Dawber and S. Gabrail, *J. Chem. Soc., Faraday Trans., I*, **84**, 41 (1988).
23. M. van Duin, J.A. Peters, A.P.G. Kieboom and H. van Bekkum, *J. Chem. Soc., Perkin Trans., II*, 473 (1987).
24. M. van Duin, J.A. Peters, A.P.G. Kieboom and H. van Bekkum, *Rec. Trav. Chim. Pays-Bas*, **105**, 488 (1986).