ordination geometry. **1**, Cu(II)-doped **2**, and methanolic **1** exhibit nearly identical electronic spectra, and the last two systems exhibit nearly identical ESR spectra. Similar behavior is exhibited by the corresponding complexes of BIBENZ.

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Registry No. **1**, 87494-83-5; **2**, 87494-85-7; **3**, 87508-96-1; **4**, 87517-34-8; **5**, 87494-87-9; **6**, 87517-36-0; 4,5-Me_2Im, 2302-39-8; BIM, 492-98-8; Me_4BIM, 69286-06-2; BIBENZ, 87508-94-9; NH_3, 7664-41-7; imidazole, 288-32-4; 1,2-cyclohexanedione, 765-87-7; glyoxal, 107-22-2.

Supplementary Material Available: Tables of calculated hydrogen atom positions, anisotropic thermal parameters, observed and calculated structure factors, and deviations from least-squares planes for **1** and **2** (32 pages). Ordering information is given on any current masthead page.

Contribution from Chevron Research Company,
Richmond, California 94802

High-Field ^{11}B NMR of Alkali Borates. Aqueous Polyborate Equilibria

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Received March 3, 1983

The 127- and 160-MHz ^{11}B NMR spectra of aqueous solutions of $KB_5O_8{\cdot}4H_2O$, $K_2B_5O_8(OH){\cdot}2H_2O$, $K_2B_4O_7{\cdot}4H_2O$, and $NaB_5O_8{\cdot}5H_2O$ are reported. Separation of all three signals in solutions of the MB_5O_8 (M = Na, K) pentaborates resulted in calculation of the formation constants for $B(OH)_4^-$ and the polyborates $B_3O_3(OH)_4^-$ and $B_5O_6(OH)_4^-$. All solid samples yielded substantial concentrations of $B_3O_3(OH)_4^-$ and low-to-moderate concentrations of $B_5O_6(OH)_4^-$ in aqueous solution, both detected easily by their resonances at 13 and 1 ppm, respectively. The presence of $B_5O_6(OH)_4^-$ in solutions of pH up to 9.7 was unexpected. The $B_4O_5(OH)_4^{2-}$ ion, though certainly present at pH 9.7, was not detected in these studies. Variable-temperature spectra from 5 to 80 °C and concentration-dependent spectra supported previous observations of the dissociation of the polyborate complexes at high temperature or high dilution. The $B_5O_6(OH)_4^-$ ion gives one signal in its spectrum apparently due only to the tetrahedral boron atom. The trigonal boron resonances for this ion were not observed.

The structural and solution chemistry of the hydrated alkali and alkaline-earth borates remains a topic of current interest,[1] largely due to a history of conflicting reports that are not yet totally resolved. A variety of experimental methods have unequivocally established the existence of polyborate anions in aqueous solution;[2] these ions also occur as discrete entities in the solid state, but the relationship between solid and solution structures is complex due to rapid interconversions of polyborates in solution. The pioneering work of Ingri[3] yielded formation constants from potentiometric titration for the major species postulated to be present in solution. Spectroscopic techniques subsequently lent support with more direct evidence; aqueous polyborate equilibria were studied by ^{11}B NMR[4,5] and more recently by Raman spectroscopy.[6,7] The latter proved successful, and formation constants for $B_3O_3(OH)_4^-$, $B_4O_5(OH)_4^{2-}$, and $B_5O_6(OH)_4^-$ were reported:[6]

$$B(OH)_3 + OH^- \rightleftharpoons B(OH)_4^- \quad K_1 \qquad (1)$$

$$2B(OH)_3 + B(OH)_4^- \rightleftharpoons B_3O_3(OH)_4^- + 3H_2O \quad K_3 \qquad (2)$$

$$2B(OH)_3 + 2B(OH)_4^- \rightleftharpoons B_4O_5(OH)_4^{2-} + 5H_2O \quad K_4 \qquad (3)$$

$$4B(OH)_3 + B(OH)_4^- \rightleftharpoons B_5O_6(OH)_4^- + 6H_2O \quad K_5 \qquad (4)$$

Previous ^{11}B NMR studies[4,5] of the polyborate equilibria at 14 and 80 MHz were limited by the signal broadening typically associated with this method. We now report new ^{11}B NMR data at 127 and 160 MHz. The higher field strengths provided excellent resolution of signals with concomitant identification and quantification of species not previously possible by NMR. We also include the first variable-temperature ^{11}B NMR study of the polyborate equilibria. This report should clarify, at least in part, some of the conflicting data reported on aqueous polyborate chemistry over the past several decades.[1f]

Table I. ^{11}B NMR Data

compd	concn, M	temp, °C	chem shift, ppm[a] (% rel area)
$KB_5O_8{\cdot}4H_2O$	0.15	5	18.1 (63.1), 12.6 (29.7), 0.8 (7.2)
	0.15	25	17.9 (60.4), 12.8 (34.8), 0.9 (4.8)
	0.10	25	17.6 (66.6), 13.0 (31.6), 0.9 (1.8)
	0.05	25	16.7, 12.7
	satd	41	17.7, 13.0, 0.9
	satd	83	16.9, 1.7
$K_2B_5O_8(OH){\cdot}2H_2O$	0.2	22	11.7 (97.0), 0.9 (3.0)
	0.4	25	11.7 (91.0), 0.9 (9.0)
	satd	6	11.5, 0.6
	satd	61	12.7, 1.9
$K_2B_4O_7{\cdot}4H_2O$	0.2	5	11.9, 7.5 (98.4), 1.0 (1.6)
	0.2	25	12.2, 8.3 (99.0), 0.9 (1.0)
	0.4	25	11.6, 7.6 (98.2), 0.9 (1.8)
	0.6	41	10.0, 1.4
	0.6	61	10.3
	0.6	80	10.8
$NaB_5O_8{\cdot}5H_2O$	0.15	5	18.7 (65.6), 13.1 (26.1), 1.2 (8.3)
	0.15	25	18.2 (62.8), 13.0 (32.3), 1.1 (4.9)
	0.30	25	18.7 (62.8), 13.2 (24.6), 1.1 (12.6)
	0.40	25	18.9 (58.7), 13.2 (24.9), 1.0 (16.4)

[a] Referenced to external $Et_2O{\cdot}BF_3$; solvent is H_2O.

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(1) (a) Christ, C. L.; Clark, J. R. *Phys. Chem. Miner.* **1977**, *2*, 59. (b) Wan, S. G. C.; Clark, J. R. *Am. Mineral.* **1978**, *63*, 160. (c) Corti, H.; et al. *J. Chem. Soc., Faraday Trans. 1* **1980**, *76*, 2179. (d) Silins, E.; Schwarz, E.; Ozolins, G. *J. Struct. Chem.* (*Engl. Transl.*) **1981**, *22*, 414. (e) Farmer, J. *Chem. Ind.* (*London*) **1982** (March 6), 145. (f) Farmer, J. B. *Adv. Inorg. Chem. Radiochem.* **1982**, *25*, 187–237.

(2) Mellor, J. W. "A Comprehensive Treatise on Inorganic and Theoretical Chemistry,"; Longmans, Green and Co.: London, 1980; Vol. 5, Part A, Supplement 1, pp 259–71, 409–17.

(3) Ingri, N. *Sven. Kem. Tidskr.* **1963**, *75*, 199 and references therein.

(4) Momii, R. K.; Nachtrieb, N. H. *Inorg. Chem.* **1967**, *6*, 1189.

(5) Smith, H. D., Jr.; Wiersema, R. J. *Inorg. Chem.* **1972**, *11*, 1152.

(6) Maya, L. *Inorg. Chem.* **1976**, *15*, 2179.

(7) Maeda, M.; et al. *J. Inorg. Nucl. Chem.* **1979**, *41*, 1217.

0020-1669/83/1322-3920$01.50/0

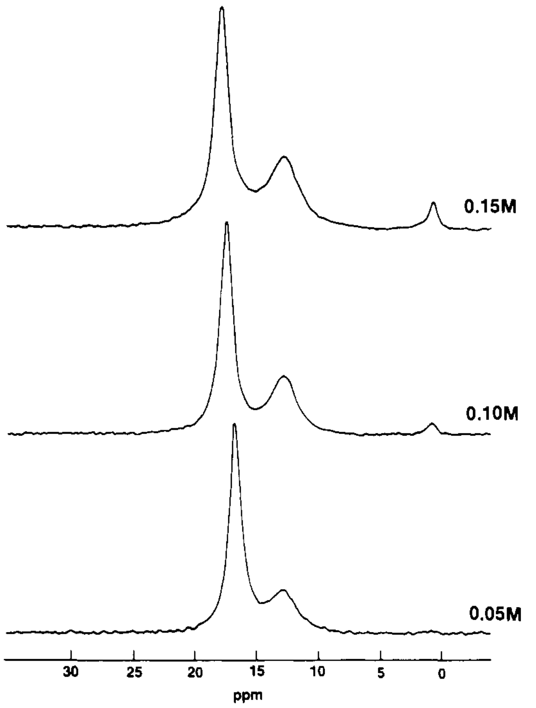

Figure 1. ^{11}B NMR spectra (127 MHz) of $KB_5O_8 \cdot 4H_2O$ at 25 °C, with concentrations as indicated.

Results and Discussion

$KB_5O_8 \cdot 4H_2O$. Figure 1 shows the effect of boron concentration on polyborate formation in solutions of potassium pentaborate at 25 °C. This data supports previous work[4,5] in the assignment of the resonances at 18, 13, and 1 ppm to $B(OH)_3/B(OH)_4^-$, $B_3O_3(OH)_4^-$, and $B_5O_6(OH)_4^-$, respectively.[8] The pentaborate anion concentration at 0.05 M $KB_5O_8 \cdot 4H_2O$ is essentially zero, while the triborate anion concentration is still appreciable. This is in close agreement with the temperature-jump studies of Eyring et al.,[9] who found no B_5 anion at 0.2 M total boron concentration and a very small amount at 0.3 M. Further dilution would also decrease the B_3 anion concentration, eventually to an immeasurable amount. It is interesting to point out that the boron enters the solution from the solid state[10] entirely in the form of the $B_5O_6(OH)_4^-$ ion. Over 90% dissociates by hydrolysis to give the triborate and monoborate species. Table I lists the ^{11}B NMR data for all the alkali borates reported here.

At this point a discussion of the source of the two polyborate resonances is in order. The resonance at 13 ppm arises from the $B_3O_3(OH)_4^-$ ion, which undergoes a rapid exchange to equalize all three boron sites as discussed by Momii and Nachtrieb.[4] This exchange, involving a somewhat bulky molecule, naturally results in a broad NMR resonance as observed. The average boron environment is 67% trigonal, and the chemical shift is likewise about one-third of the distance from pure trigonal (~19 ppm) to pure tetrahedral (~2 ppm).[5] The resonance at 1 ppm is due to the $B_5O_6(OH)_4^-$ ion. It has a narrower line width with a chemical shift about 1 ppm *upfield* of pure $B(OH)_4^-$. The line width differences are shown most clearly in the spectrum of sodium pentaborate (Figure 6). In light of these observations, it is reasonable to assume that this resonance arises from the tetrahedral boron atom in the pentaborate anion and that this anion does not undergo a rapid exchange of all five boron atoms on the NMR time scale. Previous workers[4] assigned this resonance to all five boron atoms in $B_5O_6(OH)_4^-$, though they could offer no mechanism for the exchange. That assumption, based on data at 14 MHz, must now be considered unlikely. From this arises the possibility of a separate resonance from the four trigonal boron atoms in $B_5O_6(OH)_4^-$ and the question of its location. It is not likely to fall under the triborate peak, as this peak represents an environment of 33% tetrahedral boron. It may either fall close to the monoborate peak or be too broad to observe. In connection with this, Lal and Petch[11] measured the electric quadrupole coupling constants for the tetrahedral and trigonal boron sites in the pentaborate anion and found that the triangular borons have eqQ/h values over 1 order of magnitude higher than that of the unique tetrahedral boron atom. Since line width is proportional to the square of the quadrupole coupling constant, it is likely that the trigonal boron resonance in the pentaborate anion is sufficiently quadrupolar broadened to prevent its observation. Related to this, it is interesting that an additional broad resonance around 19 ppm was observed in the low-temperature 160-MHz spectra of the K_2B_4 and K_2B_5 salts (discussed below) as shown in Figure 2. The chemical shift corresponds to a trigonal boron environment, although the origin of this broad resonance is unknown and could arise from another polyborate species. To summarize the assumptions used in the following calculations, the 1 ppm resonance was assigned to one boron atom in $B_5O_6(OH)_4^-$ and the 18 ppm resonance to $B(OH)_3/B(OH)_4^-$ only.

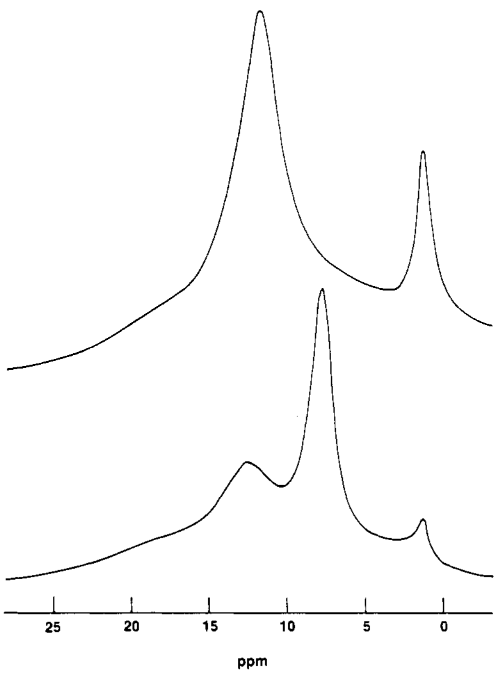

Figure 2. ^{11}B NMR spectra (160 MHz) of 0.4 M $K_2B_5O_8(OH) \cdot 2H_2O$ at 5 °C (top) and 0.4 M $K_2B_4O_7 \cdot 4H_2O$ at 5 °C (bottom).

The complete resolution of all the polyborate resonances in 0.15 M $KB_5O_8 \cdot 4H_2O$ made possible a straightforward calculation of the formation constants K_1, K_3, and K_5. The spectrum directly yielded $[B(OH)_3] + [B(OH)_4^-]$ ($c_1 + c_2$), $[B_3O_3(OH)_4^-]$ (c_3), and $[B_5O_6(OH)_4^-]$ (c_5).[12] The formation constants were calculated by using pH 7.80 for 0.15 M $KB_5O_8 \cdot 4H_2O$ at 25 °C[13] and the charge balance equation c_0 = [$KB_5O_8 \cdot$

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[8] These chemical shifts differ from those of ref 5 for two reasons: (1) use of a different standard, $Et_2O \cdot BF_3$, and (2) reversal of the sign of the chemical shift. Peaks upfield from the reference are now given negative chemical shift values in ^{11}B NMR.

[9] Anderson, J. L.; Eyring, E. M.; Whittaker, M. P. *J. Phys. Chem.* **1964**, *68*, 1128.

[10] Zachariasen, W. H.; Plettinger, H. A. *Acta Crystallogr.* **1963**, *16*, 376.

[11] Lal, K. C.; Petch, H. E. *J. Chem. Phys.* **1965**, *43*, 178.

[12] The following equations were used: $c_1 + c_2 = 5c_0$ (percent of total boron in B_1 peak), where c_0 = initial concentration of $KB_5O_8 \cdot 4H_2O$ = 0.15 M, $c_3 = {}^5/_3c_0$ (percent of total boron in B_3 peak), $c_5 = {}^5/_5c_0$ (percent of total boron in B_5 peak if it were 5 times the area).

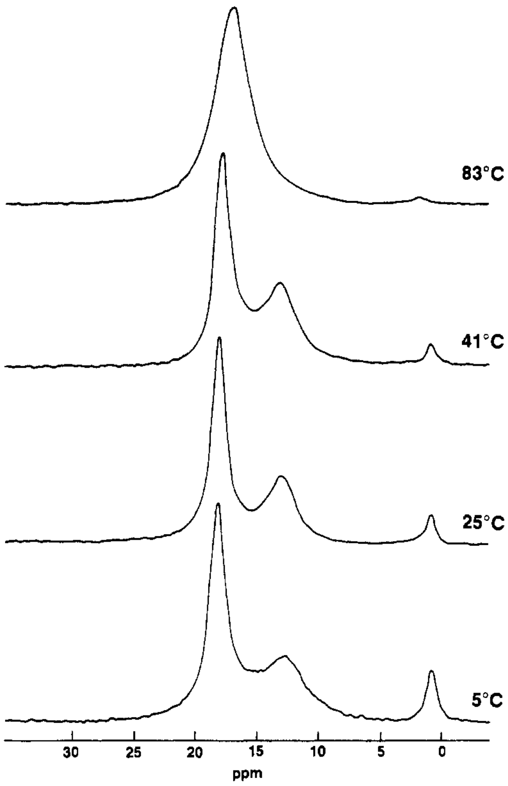

Figure 3. ^{11}B NMR spectra (127 MHz) of saturated, aqueous $KB_5O_8 \cdot 4H_2O$.

$4H_2O] = c_2 + c_3 + c_5$ to determine c_1 and c_2. The concentrations measured at $c_0 = 0.150$ M were $c_1 = 0.333$ (24) M, $c_2 = 0.0468$ (52) M, $c_3 = 0.0730$ (37) M, and $c_5 = 0.0302$ (15) M, yielding $K_1 = (2.23 \pm 0.41) \times 10^5$, $K_3 = 14.1 \pm 4.3$, and $K_5 = 52.5 \pm 23.8$.

The temperature-dependent ^{11}B NMR spectra of a saturated solution of $KB_5O_8 \cdot 4H_2O$ are shown in Figure 3. Titration experiments established that higher temperatures cause dissociation of polyborate anions.[14] Although the spectra seem to support a coalescence at higher temperatures due to rapid exchange, it is possible that polyborate dissociation is also involved.

$K_2B_5O_8(OH) \cdot 2H_2O$. The solid-state structure of the dibasic pentaborate[15] contains the B_5O_6 ring system and differs from that of potassium pentaborate (KB_5) in that these rings are polymerized through external B–O–B bridges in the K_2B_5 salt. Hydrolysis of these bridges would yield the $B_5O_6(OH)_5^{2-}$ ion as the species formed initially in solution. This ion would lose OH^- to form the more stable $B_5O_6(OH)_4^-$ ion.

The temperature-dependent ^{11}B NMR spectra of dibasic potassium pentaborate are shown in Figure 4. Unfortunately, at this K:B ratio the $B(OH)_3/B(OH)_4^-$ resonance is shifted upfield just to the point of overlap with the $B_3O_3(OH)_4^-$ signal at both 127 and 160 MHz. The polyborate temperature dependence here is qualitatively similar to that of the KB_5 salt. In this case, the broadest lines occur at low temperature and the high-temperature singlet is outside the chemical shift range of the two low-temperature peaks. A dissociation is thus more reasonable than a rapid exchange process, though the data cannot clearly distinguish between these two possibilities. A variable-temperature Raman study would nicely complement this work and provide more definitive evidence regarding polyborate dissociation.

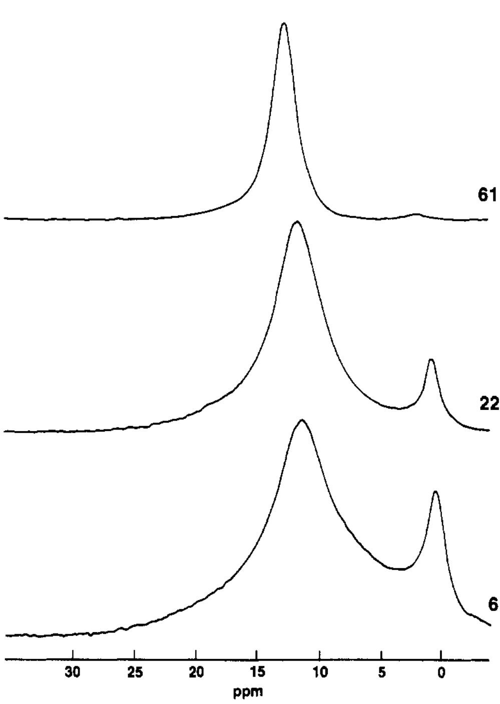

Figure 4. ^{11}B NMR spectra (127 MHz) of saturated, aqueous $K_2B_5O_8(OH) \cdot 2H_2O$.

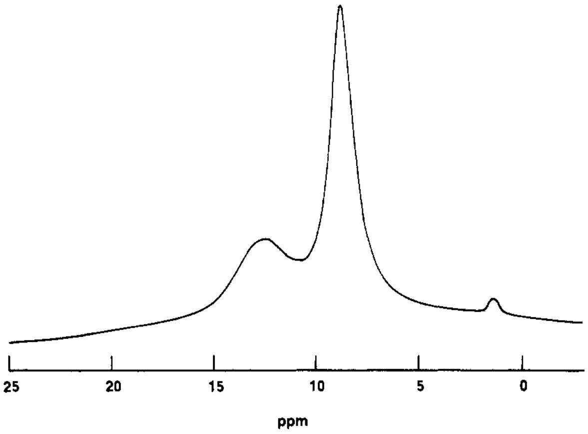

Figure 5. ^{11}B NMR spectrum (160 MHz) of 0.2 M $K_2B_4O_7 \cdot 4H_2O$ at 25 °C.

The resonance at 1 ppm indicates appreciable concentration of the $B_5O_6(OH)_4^-$ ion in solutions of the K_2B_5 salt (pH 9.00, independent of concentration).[16] In a sodium system, Ingri[3] concluded that the pentaborate ion would be absent at this pH and the dominant polyborate would be the $B_4O_5(OH)_4^{2-}$ ion (vide infra).

$K_2B_4O_7 \cdot 4H_2O$. Figure 5 shows the 160-MHz spectrum of 0.2 M potassium tetraborate.[17] At this K:B ratio, the $B(OH)_3/B(OH)_4^-$ resonance is between the triborate and pentaborate resonances at 12 and 1 ppm, respectively. The resolution of all three peaks at 160 MHz was a considerable improvement over the spectra at 80 MHz,[5] which showed only shoulders on the large monoborate resonance. Surprisingly, the pentaborate ion was detected in 0.2 M $K_2B_4O_7 \cdot 4H_2O$ (pH 9.34)[18] at 25 °C, though as expected its concentration was diminished compared to that at pH 9.00.

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(13) U.S. Borax and Chemical Corp. Technical Data Sheet IC-10, 1983. The various constants were calculated as follows: $K_1 = c_2/c_1[OH^-]$, $K_3 = c_3/c_1^2c_2$, $K_5 = c_5/c_1^4c_2$, $K_w = 10^{-14}$.

(14) (a) Spessard, J. E. *J. Inorg. Nucl. Chem.* **1970**, *32*, 2607. (b) Mesmer, R. E.; Baes, C. F.; Jr.; Sweeton, F. H. *Inorg. Chem.* **1972**, *11*, 537.

(15) Marezio, M. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1969**, *B25*, 1787.

(16) Carpêni, G. *Bull. Soc. Chim. Fr.* **1955**, *22*, 1327.

(17) Marezio, M.; Plettinger, H. A.; Zachariasen, W. H. *Acta Crystallogr.* **1963**, *16*, 975.

(18) U.S. Borax and Chemical Corp. Technical Data Sheet IC-9, 1979.

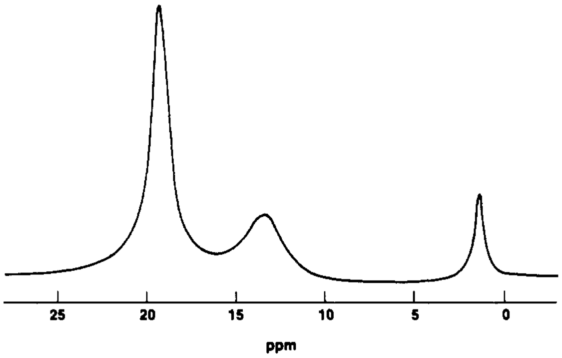

Figure 6. ^{11}B NMR spectrum (160 MHz) of 0.3 M $NaB_5O_8 \cdot 5H_2O$ at 25 °C.

Table II. Borate Ion Formation Constants

cation	$[MB_5O_8]$, M	pK_1	pK_3	pK_5
K	0.15	−5.35	−1.15	−1.72
Na	0.15	−5.39	−1.05	−1.64
Na	0.30	−6.00	−0.49	−1.23
Na	0.40	−6.26	−0.42	−1.16

No resonance attributable to the tetraborate dianion could be detected in these solutions. At pH 9.0–9.5 this ion is the most abundant polyborate in solution according to Ingri.[3] Its invisibility here could be a result of exchange effects.

The temperature-dependent 127-MHz ^{11}B NMR spectra of 0.6 M $K_2B_4O_7 \cdot 4H_2O$ paralleled those of the other systems. The triborate and monoborate resonances collapsed to a single line at 41 °C (width at half-height 700 Hz), which sharpened with increased temperature. At 61 °C the pentaborate resonance at 1 ppm disappeared, and at 80 °C the signal width at half-height was 180 Hz.

$NaB_5O_8 \cdot 5H_2O$. The 127- and 160-MHz ^{11}B NMR spectra of sodium pentaborate were qualitatively similar to those of the potassium salt (see Figure 6). Data at 0.15 M were used to calculate c_1 = 0.342 (25) M, c_2 = 0.0518 (49) M, c_3 = 0.0675 (34) M, and c_5 = 0.0307 (15) M and the formation constants $K_1 = (2.45 \pm 0.41) \times 10^5$, $K_3 = 11.1 \pm 3.2$, and $K_5 = 43.3 \pm 18.8$ at 25 °C. Within experimental error, these values are equivalent to those obtained in the potassium system. We conclude, as did Barrês,[19] that the alkali cation has very little, if any, effect on the formation equilibria at 25 °C.

The high solubility of sodium pentaborate allowed spectral collection at 0.3 and 0.4 M. The relative pentaborate anion concentration increased progressively at the higher boron concentrations while the relative triborate anion concentration decreased as compared to 0.15 M (Table I). At 0.3 M, c_1 = 0.534 (42) M, c_2 = 0.0925 (104) M, c_3 = 0.0818 (41) M, c_5 = 0.126 (6) M, $K_1 = (9.96 \pm 1.89) \times 10^5$, $K_3 = 3.10 \pm 0.99$, and $K_5 = 16.8 \pm 7.9$ (25 °C). At 0.4 M, c_1 = 0.607 (51) M, c_2 = 0.102 (15) M, c_3 = 0.100 (5) M, c_5 = 0.198 (10) M, $K_1 = (1.80 \pm 0.41) \times 10^6$, $K_3 = 2.66 \pm 0.97$, and $K_5 = 14.3 \pm 7.6$ (25 °C). All the equilibrium data are summarized in Table II. At 0.15 M MB_5O_8 concentration, we obtained pK_1 values slightly lower than those found by Momii and Nachtrieb[4] (−5.0, Na) and Barrês[19] (−5.08, K) but comparable within experimental error to Ingri's value[3] (−5.31, Na). Generally, our values for K_3 and K_5 (0.15 M MB_5O_8) are about 50% to 1 order of magnitude lower than those reported previously by spectroscopic methods.[4,6] However, inspection of Table II reveals an important point often overlooked in previous studies: *The formation "constants" are a function of total boron concentration.* This is to be expected from the increase in the ionization constant of boric acid with concentration[1f,2] (K_a = 4.6×10^{-10} at 0.1 M $B(OH)_3$ and 408×10^{-10} at 0.75 M $B(OH)_3$). Increasing K_a would correspondingly increase K_1 at higher concentrations, as experimentally observed (Table II). It follows that increasing K_1 would decrease K_3 and K_5, also as observed.

Interestingly, one reaction seems independent of concentration, the hydrolysis of the pentaborate ion to produce the triborate ion:

$$B_5O_6(OH)_4^- + 3H_2O \rightleftharpoons B_3O_3(OH)_4^- + 2B(OH)_3 \qquad K_{35} \quad (5)$$

Table II shows that pK_{35} ($pK_3 - pK_5$) is, within experimental error, equal at all concentrations.

It is interesting also that the pentaborate ion showed a temperature effect opposite from that of the triborate ion in the 5–25 °C range. Above 25 °C, both ions seemed to dissociate as the temperature rose. In both the sodium and potassium systems at 0.15 M $MB_5O_8 \cdot xH_2O$, c_3 decreased ~25% while c_5 increased ~45% in progressing from 25 to 5 °C. Since c_1 also decreased slightly at 5 °C compared to the case at 25 °C, the reverse of eq 5 may be favored at low temperature. However, other sources for the additional $B_5O_6(OH)_4^-$ produced at lower temperature cannot be ruled out. In any case, the difference in low-temperature behavior between the triborate and pentaborate anions is clearly evident.

The combined sodium and potassium data obtained here by ^{11}B NMR can most directly be qualitatively compared to the data of Maya,[6] who measured polyborate ion concentrations in a sodium system (with no added salts)[20] by Raman spectroscopy at 25 °C. Maya detected the pentaborate anion only up to pH 8.0 whereas it was detected up to at least pH 9.7 by ^{11}B NMR spectroscopy. The Raman and ^{11}B NMR data both established the presence of the $B_3O_3(OH)_4^-$ anion in solution in the pH range 7.0–9.0. The tetraborate dianion, $B_4O_5(OH)_4^{2-}$, was detected by Raman spectroscopy in the pH range 8.0–10.0 in agreement with Ingri.[3] Apparently, the ^{11}B NMR signals for this ion are either very broad or are not observable by this method due to time-scale limitations.

The lack of detection of polyborates other than the B_3^- and B_5^- ions, with the resulting simplistic assumptions that only these ions are present, limits the overall accuracy of equilibrium data determined by ^{11}B NMR spectroscopy. Despite these limitations, it has been shown that ^{11}B NMR can be a powerful tool and a useful supplementary method in the study of aqueous boron chemistry.

Experimental Section

Physical Measurements. The 126.9-MHz ^{11}B spectra were obtained with an instrument designed by Professor F. A. L. Anet of UCLA. The 160.4-MHz ^{11}B NMR spectra were recorded on a Bruker WM-500 instrument at the California Institute of Technology. Spectra are referenced to external $Et_2O \cdot BF_3$. The chemical shift of 0.5 M boric acid was +19.3 ppm at 22 °C. The NMR solvent was deionized water, boiled to expel CO_2 and cooled under nitrogen. Spectra of all the borates were recorded at both 127 and 160 MHz. The relative areas were measured by integration of the 160-MHz spectra, where peak separation was excellent and agreed within a few percent to values estimated from the 127-MHz spectra. Due to the nature of the spectra, a generous ±5% relative error was assigned to all peak areas, which is reflected in the errors expressed in the concentrations and equilibrium constants. Infrared spectra were recorded on a Nicolet MX-1 FTIR instrument.

Materials. Potassium pentaborate, $KB_5O_8 \cdot 4H_2O$, and potassium tetraborate, $K_2B_4O_7 \cdot 4H_2O$, were obtained from U.S. Borax and Chemical Corp. and used as received. A sample of sodium pentaborate, $NaB_5O_8 \cdot 5H_2O$, was obtained from U.S. Borax Research. Boric acid

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(19) Barrês, M. *Rev. Chim. Miner.* **1967**, *4*, 803.

(20) The data of Ingri[3] was obtained at various ionic strengths, all in the presence of added salts such as $NaClO_4$. This has a significant effect on formation constants[19] as compared to aqueous solutions of pure solid borates or $NaB(OH)_4/B(OH)_3$ mixtures.

and potassium hydroxide were purchased from Mallinckrodt. Literature methods[21] served as a guide for the preparation of the elusive $K_2B_5O_8(OH)\cdot 2H_2O$. It is difficult to prepare; we found it necessary to introduce seed crystals to the supersaturated "K_2B_5" solution to prevent formation of a glass. Even this was not always successful. Identification and purity of the microcrystalline product were checked by X-ray powder crystallography.[22] The infrared spectrum is distinct from those of other potassium borates and not previously reported in the literature: 3513 m, br; 1636 w; 1445 m, sh; 1385 s; 1361 s; 1237 s; 1182 w; 1090 m; 1056 m; 979 vs; 928 s; 848 m; 820 w; 752 w; 745 w; 729 w; 702 w; 630 w; 610 w; 596 vw; 555 vw; 498 vw; 463 vw cm^{-1} (KBr disk).

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Registry No. $B(OH)_4^-$, 15390-83-7; $B_3O_3(OH)_4^-$, 17927-68-3; $B_5O_6(OH)_4^-$, 17927-69-4; ^{11}B, 14798-13-1.

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Crystal Structure and Vibrational Spectra of $(TePh_2)HgI_2$

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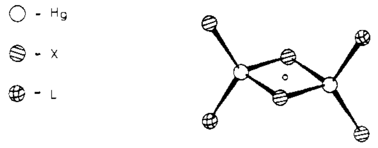
The structure of $(TePh_2)HgI_2$ has been determined by single-crystal X-ray crystallography. The compound crystallizes in the space group $P2_1/c$ with $a = 14.827$ (2) Å, $b = 13.438$ (3) Å, $c = 15.245$ (2) Å, $\beta = 90.32$ (1)°, $Z = 8$, $d_{calcd} = 3.220$ g cm^{-3}, and $d_{obsd} = 3.19$ g cm^{-3}. Intensities were measured for 3987 independent reflections ($2\theta \le 45°$), of which 2734 were classed as observed [$I \ge 2.3\sigma(I)$] and used in subsequent structure determination and refinement ($R = 0.043$). The molecule was found to exhibit a novel tetrameric structure involving two different types of iodine bridges. Low-wavenumber vibrational data for the $(TePh_2)HgX_2$ series (where X = Cl, Br, or I) were also collected and are discussed in relation to the $(TePh_2)HgI_2$ structure.

Introduction

The literature contains numerous reports of 1:1 complexes formed between mercuric halides, HgX_2 (X = Cl, Br, or I), and neutral donor ligands (L) containing group 5B (N, P, As, or Sb) and group 6B (S, Se, or Te) donor atoms.[1-29] For many years the solid-state structure of these compounds was thought to be that of a discrete dimeric halogen-bridged molecule in which Hg atoms lie in a tetrahedral environment and donor ligands lie mutually trans with respect to one another (i).



i

More recent studies have indicated that in addition to the discrete dimeric arrangement[15,17,19-23] other more associated structures also occur.[15-18,24-28]

The $(2,4,6\text{-}Me_3py)HgCl_2$[24] and $(PEt_3)HgCl_2$[15,18] molecules exist as continuous chlorine-bridged chains in which mercury atoms lie in trigonal-bipyramidal environments (ii). The compounds $(C_4H_8S)HgCl_2$[27] and $(PMe_3)HgCl_2$[15,18] have "pseudoionic" structures in which $[L\text{–}Hg\text{–}Cl]^+$ and Cl^- "ions" are alternately arranged giving rise to continuous chlorine-bridged chains (iii). The α-form of $(P\text{-}n\text{-}Bu_3)HgCl_2$, in the

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