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Raman Study of Aqueous Monoborate–Polyol Complexes. Equilibria in the Monoborate–1,2-Ethanediol System

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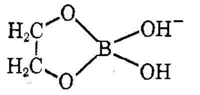
Raman spectra have been obtained of aqueous solutions containing $B(OH)_4^-$ and various polyols, including 1,2-ethanediol, 1,2-propanediol, 1,3-propanediol, 1,3-butanediol, and 1,2,3-propanetriol. Several spectral features arise which can be explained only on the basis of the chelate formation originally postulated by Hermans; there is no evidence of polymerization in the concentrated solutions examined. Assignments are presented for the simplest five-membered (1,2-ethanediol) and six-membered (1,3-propanediol) borate chelates and comparisons made with related ring systems. Spectral changes caused by ring substitution are briefly discussed. A band assigned to B–O ring stretching provides the most reliable indication of ring size, having an average position of 766 cm^{-1} for five-membered and *ca.* 720 cm^{-1} for six-membered chelates. Through quantitative intensity measurements on the aqueous 1,2-ethanediol–$B(OH)_4^-$ system, it is established that 1:1 and 2:1 (diol:boron) complexes exist in concentrated solution; at 30°, the overall equilibrium molarity quotients are $\beta_1 = 1.8 \pm 0.2\ M^{-1}$ and $\beta_2 = 0.65 \pm 0.15\ M^{-2}$.

Introduction

Investigations using a variety of techniques have established that the tetrahedral monoborate ion, $B(OH)_4^-$, reacts with many polyols in aqueous solution to form anionic complexes.[1] In general, equilibrium data support the existence of stepwise complexes having a polyol:boron ratio of 1:1 and 2:1.[2-4] Evidence concerning the *structure* of these solution species is largely indirect, although consistent with the chelate models first proposed by Hermans[5] (I and II below with the simplest 1,2-diol). Dale's[6] examination of the thermal dehydration behavior of a series of crystalline 1:1 complexes has provided information about the configuration of the presumed five- and six-membered chelate rings. Azarova and Sideridu[7] have interpreted partial infrared spectra of solid borate–polyhydroxystearate mixtures as indicating chelate formation. These results, together with Meulenhoff's[8] separation of optical isomers of the 2:1 salicylic acid–monoborate complex, help to understand the structure in the solid state but can be applied only with caution to the essential problem of structure in aqueous solution. In the latter area, Böeseken's[9] conductivity measurements on solutions containing, for example, boric acid and *cis*- or *trans*-cyclopentane-1,2-diol have established certain configurational requirements for complexation. Limited data on proton magnetic resonance coupling constants are compatible with the formation of chelate rings in several borate–carbohydrate solutions.[10] In addition, a recent infrared spectroscopic analysis of aqueous boric acid–lactic acid solutions at pH 2 and 6 reveals that the number of complex species varies with pH and, under these acidic conditions, all complexes contain four-coordinate boron.[11] The spectral assignments point toward the presence of five-membered rings in this system.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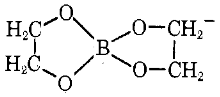
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Raman spectroscopy should be especially helpful in providing direct physical evidence regarding the structure of monoborate–polyol complexes in aqueous solution, although it has never been so used in the past. The present Raman study was undertaken to characterize complexation between monoborate and 1,2- and 1,3-diols and, through use of quantitative intensity measurements, to identify the complex equilibria in the simplest system, monoborate–1,2-ethanediol.

Experimental Section

All chemicals were reagent grade, used without further purification. The source of monoborate was the sodium borate salt $NaB(OH)_4 \cdot 2H_2O$[12] (often written $NaBO_2 \cdot 4H_2O$), except in a few cases when the ion was formed in solution by neutralizing $B(OH)_3$ with NaOH; sodium benzeneboronate, $Na[C_6H_5B(OH)_3]$, was made in solution by neutralizing $C_6H_5B(OH)_2$ with NaOH. In the preparation of deuterated solutions, 99.5% D_2O and 40% NaOD in D_2O (99% minimum isotopic purity) were used. In general, solutions of known concentration were prepared using standard weighing and volumetric techniques and passed through a Millipore filter prior to spectral analysis. For the molar ratio and Job studies on the monoborate–1,2-ethanediol system and for intensity measurements on the separate components, four series of solutions containing 0.25 *M* Na_2SO_4 as internal intensity standard (980-cm^{-1} band) were prepared from stock solutions by quantitative dilution.

Raman spectra were recorded on a Cary 81 spectrophotometer using the 5145-Å line from a Coherent Radiation Laboratories Model 52 Ar^+ laser as excitation source and R136 photomultiplier tubes for detection. Throughout the investigation, the laser power at the sample was *ca.* 70 mW and the spectral slit width *ca.* 7 cm^{-1} at 5145 Å. The frequency scale was calibrated using indene, CCl_4, and C_6H_6; except for very broad bands and shoulders, positions of band maxima are expected to be accurate to ±2 cm^{-1}. The 180° excitation–viewing mode was used to obtain spectra of samples contained in 1.3-mm i.d. Kimax capillaries. For quantitative intensity measurements a single capillary was used for all solutions in a particular series;

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TABLE I

RAMAN FREQUENCIES (CM^{-1}) FOR AQUEOUS MONOBORATE–POLYOL SYSTEMS AND THE CORRESPONDING POLYOLS[a]

4M 1,2-ethanediol	2M B(OH)$_4^-$ + 4M 1,2-ethanediol	2M 1,2-propanediol	2M B(OH)$_4^-$ + 4M 1,2-propanediol	2M 1,2,3-propanetriol	1M B(OH)$_4^-$ + 2M 1,2,3-propanetriol	2.8M 1,3-propanediol	2M B(OH)$_4^-$ + 4M 1,3-propanediol	2M 1,3-butanediol	1M B(OH)$_4^-$ + 2M 1,3-butanediol
~ 2960 sh,p	~ 2970 sh,s,p	2984 s,dp	2977 s,dp	2950 vs,p	2972 sh,s,p	2966 sh,vs,p	2965 sh,vs,p	2979 vs,dp	2977 vs,dp
2946 vs,p	2945 vs,p	2942 vs,p	2936 vs,p	~ 2920 ms,dp	2942 vs,p	~ 2936 sh,vs,dp	2945 sh,vs,dp	2938 vvs,p	2937 vvs,p
2889 s,p	2882 vs,p	2914 ms,dp	~ 2905 ms	2895 vs,p	~ 2910 sh	2922 vvs,p	2932 vs,dp	2917 vs,p	2916 vs,p
2729 w,p	2727 w,p	2891 s,p	2877 s,p	2753 b,vw,p	2888 vs,p	2900 vs,p	2921 vvs,p	~ 2898 sh,vs,p	2883 vs,p
1463 ms,dp	1482 s,dp	2738 w,p	2760 w,p	1465 s,dp	2770 b,vw,p	2762 b,w,p	~ 2893 sh,p	2742 mw,p	2737 m,p
~ 1418 b,w,dp	1465 m,dp	1461 s,dp	2739 mw,p	~ 1371 b,w,dp	1482 s,dp	2742 vw	2881 vs,p	1479 m,dp	1479 ms,dp
1294 mw,dp	~ 1410 b,w	~1415 b,mw,dp	1479 ms,dp	1315 mw,dp	1468 s,dp	1477 s,dp	2761 b,vw,p	1460 ms,dp	1456 s,dp
1275 m,dp	1370 mw,p	1368 mw,dp	1459 ms,dp	1261 m,dp	1389 mw,dp	1442 ms,dp	2736 w,p	1443 sh,m,dp	1435 ms,dp
1213 w,dp	1355 sh,w,dp	1344 mw,dp	1380 w,dp	1210 w,dp	1344 m,dp	~ 1428 sh,w,dp	1480 sh,ms,dp	1430 sh,mw,dp	1376 m,dp
1087 ms,p	1295 w,dp	1299 mw,dp	1345 mw,dp	1111 ms,p	1290 m,dp	1322 sh,mw,dp	1474 s,dp	~ 1415 sh,w,dp	1351 m,dp
1068 mw,dp	1276 mw,dp	1245 mw,dp	1321 mw,dp	1089 ms,dp	1249 m,dp	1298 s,dp	~ 1445 sh,m,dp	1374 w,dp	1316 m,dp
1049 m,dp	1235 ms,dp	1137 m,dp	1237 m,dp	1055 s,p	1224 m,dp	1243 mw,dp	1433 ms,dp	1356 w,dp	1302 sh,w,dp
1032 sh,mw,p	1134 w,p	1108 m,p	1142 m,p	976 w,dp	~ 1124 sh,m,dp	1196 mw,dp	1391 w,dp	1326 w,dp	1262 m,dp
884 sh,m,dp	1084 m,p	1084 ms,dp	1106 mw,dp	922 m,dp	1097 ms,dp	~ 1099 sh,w,p	1375 vw,dp	1310 mw,dp	1228 mw,dp
865 vs,p	1068 m,dp	1043 m,p	1081 mw,dp	910 sh,mw,dp	1062 ms,p	1062 s,dp	1349 vw,dp	1252 w,dp	1166 mw,dp
~ 800 b,w	1049 m,dp	990 mw,p	1052 mw,p	~ 870 sh,m,p	1044 ms,p	~ 1050 sh,m,p	1324 sh,w,dp	1210 w,dp	1140 m,dp
523 mw,dp	1032 sh,mw,p	944 mw,dp	1020 w,dp	850 s,p	968 mw,dp	1028 m,p	1294 s,dp	1136 mw,dp	1109 ms,p
481 m,p	942 s,p	924 ms,dp	991 w,p	820 m,p	922 mw,dp	981 m,p	1252 m,dp	1109 sh,mw,p	~1090 sh,m,dp
348 mw,p	884 sh,m,p	840 vs,p	951 w,dp	786 vw,p	856 s,p	936 sh,mw,dp	1221 mw,dp	1093 m,dp	1058 m,dp
	866 ms,p	803 ms,p	924 mw,dp	674 mw,p	819 mw,p	920 ms,p	~ 1190 vw,dp	1054 m,dp	~1000 sh,w,p
	764 sh,mw,p	657 vw,dp	864 mw,p	553 w,dp	768 ms,p	872 s,p	1150 w,dp	997 m,p	983 ms,p
	747 ms,p	523 ms,p	838 ms,p	484 ms,p	~ 745 sh,w,p	849 s,p	1093 ms,p	987 m,p	966 ms,p
	~720 vw	478 mw,p	804 mw,p	~ 440 sh,w	729 w,dp	~ 814 w,p	1065 ms,dp	967 m,p	941 w,dp
	623 m,dp	447 mw,dp	766 m,p	417 m,p	710 vw,dp	781 mw,dp	1028 m,p	941 w,dp	907 mw,dp
	523 w, dp	386 m,p	~ 747 sh,mw,p	~ 386 sh,mw,dp	~ 662 b,vw,p	528 m,p	981 mw,p	906 mw,dp	893 mw,dp
	482 mw,p		710 w,dp		~ 618 b,vw,dp	413 m,p	966 mw,dp	851 s,p	851 s,p
	407 m,p		633 sh,w,dp		530 vw,dp	388 m,p	938 mw,dp	~ 820 w,p	829 s,p
	348 w,p		620 sh,w,p		484 mw,p		923 mw,p	~ 796 mw,p	~ 796 mw,p
			596 mw,p		417 mw,p		~ 874 sh,m,p	783 s,p	783 s,p
			527 mw,p		~ 356 b,vw,p		857 s,p	540 mw,p	732 ms,p
			~ 488 w,p				782 vw,dp	488 m,p	622 ms,p
			452 w,dp				743 m,p	420 mw,dp	530 m,p
			385 mw,p				707 ms,p	353 m,p	508 m,dp
			364 mw,p				613 w,p		488 ms,p
			292 w,dp				~ 570 vw,p		418 ms,p
							528 mw,p		355 ms,p
							497 m,dp		
							455 m,dp		
							414 m,p		
							383 m,p		
							~ 329 b,w,p		

[a] All spectra were examined down to 250 cm^{-1}. Qualitative intensities refer to heights of unresolved bands. Abbreviations: p, polarized; dp, depolarized; s, strong; m, medium; w, weak; v, very; sh, shoulder; b, broad.

this capillary was not sealed, since the sample temperature in the laser beam was 30° and negligible evaporation occurred during the time of spectral recording.

Depolarization data were obtained using the 90° excitation–viewing mode in conjunction with a multipass liquid cell. The direction of the incident electric vector was changed by rotating a presample half-wave plate; neither an analyzer nor polarization scrambler was placed in the viewing path. This arrangement was tested with CCl_4 and 1,2-ethanediol[13–15] and found to work satisfactorily. A Du Pont Model 310 curve resolver aided in resolving overlapping bands for intensity and depolarization measurements.

Results and Discussion

Spectra.—The tetrahedral structure of the monoborate ion in aqueous solution has been firmly established by the close similarity between its Raman spectrum[16,17] and that of crystalline $Na_2[B(OH)_4]Cl$,[17] in which boron is known to be tetrahedrally surrounded by oxygen atoms.[18] In good agreement with the earlier solution spectra, the frequencies observed for aqueous $B(OH)_4^-$ in the present study are 374 (ν_2, e), 516 (ν_4, f_2), 744 (ν_1, a_1), and *ca.* 940 (ν_3, f_2) cm^{-1}. Several features of the prominent a_1 B–O stretching band were further examined in the concentration range $[B(OH)_4^-]$ = 0.50–4.0 *M;* its frequency (744 cm^{-1}) and width at half-height (22 cm^{-1}) remain unaltered and, compared with the 980-cm^{-1} band of SO_4^{2-} as internal intensity standard, its intensity (height) increases linearly with the stoichiometric $B(OH)_4^-$ concentration. In addition, there is never any sign of a band at *ca.* 875 cm^{-1}, where the planar BO_3 group exhibits strong Raman scattering due to symmetric B–O stretching.[19] These observations uphold the view that $B(OH)_4^-$ does not undergo significant polymerization in the relatively concentrated aqueous solutions being investigated.[16,20]

Table I lists the Raman frequencies observed for several aqueous polyol solutions with and without added monoborate. The polyols, chosen to offer adequate representation of different structure types and yet minimize spectral complexity, include 1,2-ethanediol,[13–15] 1,2-propanediol, 1,3-propanediol,[14] 1,3-butanediol, and 1,2,3-propanetriol[21] (vibrational assignments for three of these appear in the cited references). Spectra of the systems containing the simplest 1,2- and 1,3-diols are shown in Figures 1 and 2, respectively. In these two cases, the new bands resulting from reaction between monoborate and the polyol are listed in Tables II and III, together with vibrational assignments.

Spectra of all the systems reveal several features

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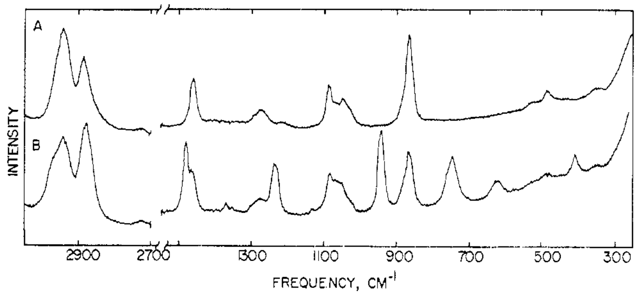


Figure 1.—Raman spectra of (A) 4 *M* 1,2-ethanediol and (B) 2 *M* $B(OH)_4^-$ + 4 *M* 1,2-ethanediol. The instrument sensitivity setting is unchanged throughout spectrum A, but for spectrum B the region above 2700 cm^{-1} is run at two-thirds the sensitivity used for the lower region.

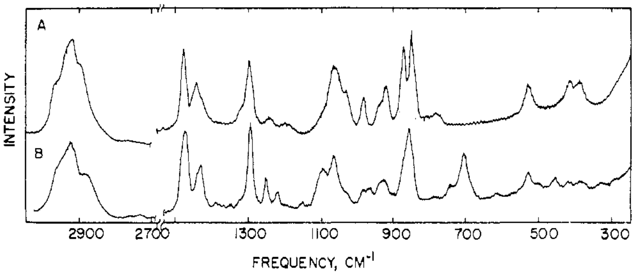


Figure 2.—Raman spectra of (A) 2.8 *M* 1,3-propanediol and (B) 2 *M* $B(OH)_4^-$ + 4 *M* 1,3-propanediol. In both spectra the region above 2700 cm^{-1} is run at *ca.* one-third the sensitivity used for the lower region.

TABLE II

RAMAN FREQUENCIES AND ASSIGNMENTS FOR THE MONOBORATE–1,2-ETHANEDIOL CHELATE[a]

Freq, cm^{-1}	Assignment	Freq, cm^{-1}	Assignment
~2970 s, p	a_2 and b_1 CH str	~1065 m, dp	b_2 ring str
~2880 vs, p	a_1 and b_2 CH str	942 s, p	a_1 ring breathing
1482 s, dp	a_1 and b_2 CH_2 def	~885 m, p (?)	a_1 or b_2 ring str
1370 mw, p	a_1 CH_2 wag	764 mw, p	a_1 ring str (B–O)
1355 w, dp	b_2 CH_2 wag	~720 vw	CH_2 rock (?)
1235 ms, dp	a_2 CH_2 twist	623 m, dp	b_2 in-plane ring bend
1134 w, p (?)	a_1 or b_2 ring str	407 m, p	a_1 in-plane ring bend

[a] Abbreviations are the same as in Table I.

TABLE III

RAMAN FREQUENCIES AND ASSIGNMENTS FOR THE MONOBORATE–1,3-PROPANEDIOL CHELATE[a]

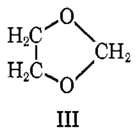
Freq, cm^{-1}		Assignment (expected bands)
~2945 vs, dp		CH str (4 a′ + 2 a″)
2881 vs, p		
~1475 m, dp		CH_2 def (2 a′ + a″)
1433 ms, dp		
1391 w, dp		CH_2 wag (a′ + 2 a″)
1375 vw, dp		
1349 vw, dp		
1252 m, dp	a″	CH_2 twist (a′ + 2 a″)
1221 mw, dp	a″	
1150 w, dp	a″	ring str (3 a′ + 3 a″)
1093 ms, p	a′	
966 mw, dp	a″	
857 s, p	a′	
707 ms, p	a′	
613 w, p	a′	ring def (4 a′ + 2 a″)
~570 vw, p	a′	
497 m, dp	a″	
455 m, dp	a″	
383 m, p	a′	
~329 w, p	a′	

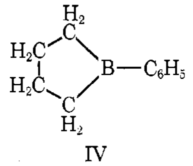
[a] Abbreviations are the same as in Table I.

which together can be explained only on the basis of the ring formation originally postulated by Hermans. First, it is evident that boron remains four-coordinate in the reaction products, presumably with a pseudotetrahedral environment, since no feature attributable to three-coordinate boron systematically appears near 875 cm^{-1} and a polarized band is found only moderately displaced in frequency from the 744-cm^{-1} a_1 band of $B(OH)_4^-$. Observing this band in one of two distinct frequency regions irrespective of the polyol's molecular mass (*ca.* 765 cm^{-1} for the 1,2-diols and 1,2,3-propanetriol and *ca.* 720 cm^{-1} for the 1,3-diols) is understandable if rings are formed and the band's position depends on their size. Second, spectra of the monoborate–polyol solutions are unchanged with time, even up to several months in some cases, thus demonstrating that extensive polymerization does not slowly occur. Third, all new bands located in the 1200–1400-cm^{-1} region for these solutions (involving CH_2 wagging and twisting motions) are markedly narrower and more intense than the corresponding bands for the unreacted polyols. This spectral sharpening is like that which often characterizes liquid-to-solid transformations[22] and, in the present study, must result from a decrease in number of possible rotational isomers accompanying ring formation. This observation argues against polyol bridging and unidentate polyol binding in these solutions, because such modes of attachment are not expected to restrict very greatly the polyol's rotational freedom.

There is quite good agreement between the monoborate–polyol chelate frequencies and spectra of related ring systems, especially for the five-membered case, thus providing still further support of the proposed structure. In the following discussion, attention will be focused on the simplest chelates involving 1,2-ethanediol and 1,3-propanediol, but comparisons among all the systems also will be made. The question of complex stoichiometry will be treated in a later section, specifically for the 1,2-ethanediol system. At present, it suffices to note that because only minor frequency shifts occur as the concentration ratio of monoborate to polyol is changed, there appears to be negligible vibrational coupling between the chelate rings in any complex containing more than one polyol per boron. Therefore, simple 1:1 models, excluding the exocyclic –OH groups, will be adopted below.

Five-Membered Chelate.—Considered to be nearly planar, the nine-atom five-membered chelate belongs to the point group C_{2v} and generates the vibrational representation $\Gamma_{vib} = 7\ a_1 + 4\ a_2 + 4\ b_1 + 6\ b_2$ (all modes Raman active; *x* axis chosen perpendicular to the plane of the ring). The frequencies and assignments given in Table II may be compared with those for 1,3-dioxolane (III), a related molecule which Barker,


III


IV

et al.,[23] also treated on the basis of C_{2v} symmetry, although recent nmr evidence indicates some puckering.[24]

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[24] R. U. Lemieux, *Can. J. Chem.*, **40**, 1955 (1962).

Among the Raman bands assigned by these authors for 1,3-dioxolane, the following strong ones correspond closely in both frequency and intensity to bands listed in Table II: 2972 (a_2 and b_1 antisymmetric C–H stretches), 2894 (a_1 and b_2 symmetric C–H stretches), 1481 (a_1 and b_2 CH_2 deformations), 1210 (a_2 CH_2 twist), and 939 cm^{-1} (a_1 ring breathing). Similarly, Greenwood and Wright[25] attributed an intense infrared band at *ca.* 930 cm^{-1} to the breathing mode of the five-membered ring in phenylboracyclopentane (IV). In the present study, the unexpected depolarization of the 1482-cm^{-1} band and polarization of the 2970-cm^{-1} band probably arise from band overlap and/or symmetry lowering (to point group C_s, for example) brought about by slight ring puckering in solution. Bands assigned to CH_2 wagging vibrations ($a_1 + b_2$) are observed in the predicted frequency region; however, those due to the b_1 CH_2 twisting mode and both CH_2 rocking modes ($a_2 + b_1$) cannot be distinguished with certainty from bands of unreacted 1,2-ethanediol. The questionable spectral feature at *ca.* 720 cm^{-1} might be associated with one of the CH_2 rocking modes, although it is far removed from the corresponding bands at 800 and 884 cm^{-1} for 1,2-ethanediol.[13] The polarized 764-cm^{-1} peak is absent in the published Raman spectrum of 1,3-dioxolane[23] and therefore can confidently be assigned to an a_1 ring vibration involving predominantly B–O stretching. The nature of this vibration will be discussed more fully in a later section after the stoichiometry of the complexes is established. Of the three bands reasonably assigned to the remaining ring-stretching vibrations ($a_1 + 2\ b_2$), those at *ca.* 885 and 1134 cm^{-1} are of uncertain symmetry, since their degree of polarization could be in error owing to their low intensity and/or location. Both b_2 ring-stretching modes involve antisymmetric B–O stretching which, based on analogy with $B(OH)_4^-$, is expected to contribute only very weakly to the Raman intensity. The peaks at 407 and 623 cm^{-1} must be assigned to the two in-plane ring-bending vibrations, a_1 and b_2, respectively; they are considered too strong to have arisen from exocyclic B–OH deformations. The magnitude of the frequency difference between them is similar to that observed for the boracyclopentane ring[25] (a_1 at 601 cm^{-1}, b_2 at *ca.* 870 cm^{-1}), though much larger than for 1,3-dioxolane (a_1 at 658 cm^{-1}, b_2 at 671 cm^{-1}). Apparently, inclusion of boron in the ring is responsible for this large frequency separation; only the a_1 mode involves appreciable movement of boron. Finally, as in the case of 1,3-dioxolane, Raman bands due to the out-of-plane ring deformations ($a_2 + b_1$) of the five-membered chelate are not observable owing to their weakness and/or low frequency.

Complete spectral assignments cannot readily be made for the 1,2-propanediol– and 1,2,3-propanetriol–monoborate systems; nevertheless, inspection of their frequency listings (Table I) reveals many similarities to the five-membered chelate spectrum just discussed. In the case of the triol, this illustrates that the polyol functions like a 1,2-diol in reacting with $B(OH)_4^-$ to form a five-membered ring, in accord with the known greater stability of five- *vs.* six-membered borate chelates.[3] As anticipated, vibrations of the ring methylene groups are little affected by substitution on carbon. Probably because of its somewhat isolated position, the B–O ring stretch is relatively free from coupling and likewise insensitive to substitution, appearing at 766 cm^{-1} for the diol and 768 cm^{-1} for the triol. However, other bands are altered by attachment of $-CH_3$ or $-CH_2OH$ to the ring, the most dramatic example being the intense ring-breathing vibration at 942 cm^{-1}. This peak either becomes much weaker and obscured by nearby bands or is shifted to 864 and 856 cm^{-1} for $-CH_3$ and $-CH_2OH$ substitution, respectively. The former explanation appears preferable, since Barker, *et al.*,[26] observed similar intensity diminution of the ring-breathing band in 4-substituted 1,3-dioxolanes and attributed the polarized band at *ca.* 830 cm^{-1} to stretching of the C–C link between ring and substituent. In any event, the ring-breathing vibration clearly will not be a useful indicator of the ring size of borate chelates involving complex polyols.

The spectral effect caused by ring substitution at boron was determined for a solution containing 3.5 *M* 1,2-ethanediol and 0.8 *M* benzeneboronate, $C_6H_5B(OH)_3^-$, the latter known to function like $B(OH)_4^-$ toward polyols[27] and found to exhibit its symmetric B–O stretch at 692 cm^{-1}. Numerous bands were observed which match those found for the monoborate–1,2-ethanediol chelate, including the strong, polarized ring-breathing vibration at 941 cm^{-1} (also intense for 2-substituted 1,3-dioxolanes[26]). In contrast, the only feature in the 700–800-cm^{-1} region is now located at 715 cm^{-1}, rather than 764 cm^{-1}, but is similarly attributable to the B–O ring stretch. Note that the upward frequency shift from 692 to 715 cm^{-1} approximately equals that found for $B(OH)_4^-$, from 744 to 764 cm^{-1}; apparently incorporation into a five-membered ring has the same perturbing influence on both boron anions.

Six-Membered Chelate.—The six-membered ring is expected to exist in the chair form, like 1,3-dioxane,[28] and belong to the point group C_s. On this basis, the 12-atom unit generates the vibrational representation $\Gamma_{vib} = 17\ a' + 13\ a''$ (all modes Raman active). Spectral comparison with the related molecule 1,3-dioxane is only of limited value since detailed assignments are not available for this compound, although its Raman spectrum was first recorded many years ago.[29] In Table III, the intense peak at 857 cm^{-1} is attributed to ring breathing since it is located in the vicinity of the strongest band observed for 1,3-dioxane, at 834 cm^{-1},[29] which can only be assigned to the same vibration. The remaining bands for the monoborate–1,3-propanediol chelate were assigned using known CH_2 group frequencies and reasonable estimates of the ring vibrational frequencies based on reported assignments for 1,4-dioxane.[30] It is evident that all CH_2 vibrations are not represented, presumably owing to low intensity and extensive band overlap. For the same reasons, several polarization data may be in doubt. With regard to the ring motions, however, five of the expected six stretches ($3\ a' + 3\ a''$) can be accounted for, as can all six deformations ($4\ a' + 2\ a''$), thus lending support to the proposed ring model. The appearance at 707 cm^{-1} of a

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[25] N. N. Greenwood and J. C. Wright, *J. Chem. Soc.*, 448 (1965).

[26] S. A. Barker, E. J. Bourne, R. M. Pinkard, and D. H. Whiffen, *ibid.*, 807 (1959).

[27] J. P. Lorand and J. O. Edwards, *J. Org. Chem.*, **24**, 769 (1959).

[28] E. L. Eliel and M. C. Knoeber, *J. Amer. Chem. Soc.*, **90**, 3444 (1968).

[29] M. J. Murray and F. F. Cleveland, *J. Chem. Phys.*, **12**, 156 (1944).

[30] F. E. Malherbe and H. J. Bernstein, *J. Amer. Chem. Soc.*, **74**, 4408 (1952).

polarized band attributable to B–O ring stretching, rather than near 765 cm^{-1}, illustrates the dependence of this vibrational mode on ring size.

Inspection of Table I reveals that the effect of methyl substitution on the six-membered ring is like that for the five-membered chelate. Thus, in the spectrum of the 1,3-butanediol–monoborate solution the ring-breathing band could be hidden under the 851-cm^{-1} band of unreacted diol and the intense, polarized band at 829 cm^{-1} attributed to stretching of the C–C bond between the ring and methyl substituent. Of course vibrational coupling could alter this explanation and in reality shift the ring-breathing mode to 829 cm^{-1}. The only new peak in the 700–800-cm^{-1} region is now found at 732 cm^{-1} and is assigned to B–O ring stretching. Although this vibration is higher in frequency than for the unsubstituted six-membered ring, it falls well below the average position (766 cm^{-1}) for the five-membered chelates.

Of the possible spectral criteria for establishing the ring size of monoborate–polyol complexes, none appears so generally useful as the position of the band assigned to B–O ring stretching. Its dependence on ring size places it in two distinct frequency regions, both relatively free from interfering bands. This Raman correlation should be applicable to the elucidation of structure in a variety of polyhydroxy systems, although if favorably oriented 1,2- and 1,3-diol groups are both present, $B(OH)_4^-$ probably will react only with the former as in the case of 1,2,3-propanetriol.

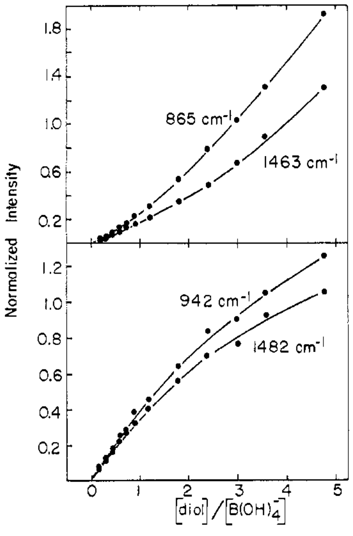

Figure 3.—Normalized Raman intensity *vs.* formal ratio $[diol]/[B(OH)_4^-]$ for the 1,2-ethanediol–monoborate system; constant $[B(OH)_4^-] = 1.5\ M$.

Equilibria in the Monoborate–1,2-Ethanediol System.—Quantitative Raman intensity studies were made on the simplest monoborate–diol system in order to identify the important equilibria in concentrated aqueous solution. The first study involved a series of 12 molar ratio solutions containing constant total $[B(OH)_4^-] = 1.5\ M$ and total [diol] ranging from 0.25 to 7.2 *M*. In all instances, heights of resolved bands were measured and normalized with the 980-cm^{-1} band of SO_4^{2-} as internal standard. Results are displayed in Figure 3 for the 865- and 1463-cm^{-1} bands of unreacted 1,2-ethanediol and the 942- and 1482-cm^{-1} bands of the chelate. Other chelate bands show similar intensity variation, for example, those at 764, 1065, 1235, and 2970 cm^{-1}. The broad curvature of the plots indicates weak complexation but, unfortunately, neither the number of species nor their identity is revealed. However, the molar ratio data allow calculation of a (unreacted diol concentration) and hence $\bar{n}$ (the average number of diol molecules reacted per monoborate ion). The height of the 865-cm^{-1} band was chosen as a measure of a, even though a shoulder at *ca.* 884 cm^{-1} grows in as [diol] is increased. After resolution, the 865-cm^{-1} band maintains the same half-width and depolarization ratio in all spectra. Furthermore, with an independent series of 1,2-ethanediol solutions the normalized 865-cm^{-1} band height increases linearly with concentration over the range 0.40–4.0 *M*.

Figure 4 displays the resulting formation curve for the monoborate–1,2-ethanediol system. The approach to $\bar{n} = 2$ at high values of a appears very likely, showing that for the highest complex $[diol]/[B(OH)_4^-] = 2$. The possibility that the curve approaches $\bar{n} > 2$ is extremely remote, in view of an earlier argument against polyol bridging and unidentate polyol binding in these solutions.

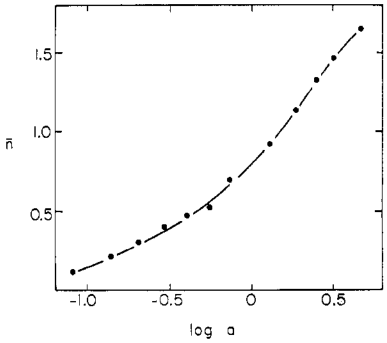

Figure 4.—Plot of $\bar{n}$ (average number of reacted diol molecules per $B(OH)_4^-$) *vs.* log a (a is unreacted diol concentration) for the 1,2-ethanediol–monoborate system; constant $[B(OH)_4^-] = 1.5\ M$, [diol] = 0.25–7.2 *M*.

To determine if the 1:1 complex exists to any measurable extent, a second study involving a series of 11 solutions was designed according to the method of continuous variations, with a fixed sum of stoichiometric concentrations $[diol] + [B(OH)_4^-] = 4.0\ M$ and the formal ratio $[diol]/[B(OH)_4^-]$ varied from 0.43 to 5.7. Plots of resolved band height (normalized using SO_4^{2-}) at 942, 1235, and 1482 cm^{-1} *vs.* formal ratio exhibit a single broad maximum at $[diol]/[B(OH)_4^-] \approx 1.5$. Unequivocal species identification with these data is not possible, although the extreme breadth of the curves indicates weak complexation while the nonintegral peak position suggests the presence of more than one species. If only a single species were present, the plots should maximize at an integral formal ratio corresponding to the stoichiometry of the complex.[31]

Collectively, then, Raman intensity data support the existence of 1:1 and 2:1 complexes in the concentrated aqueous 1,2-ethanediol–monoborate system. The molar ratio data (a and $\bar{n}$) are not sufficiently accurate, however, to allow *simultaneous* determination of both overall equilibrium molarity quotients, β_1 (= [1:1 com-

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[31] F. J. C. Rossotti and H. Rossotti, "The Determination of Stability Constants," McGraw-Hill, New York, N. Y., 1961, p 47.

plex]/[B(OH)$_4^-$][diol]) and β_2 (= [2:1 complex]/[B(OH)$_4^-$][diol]^2), using a graphical method.[32] Alternatively, these quotients can be obtained as follows. First, the reasonable assumption is made that in solutions of low $\bar{n}$ (≤ 0.5) only the 1:1 complex exists in significant concentration. The relationship $1/\bar{n} = 1/\beta_1 a + 1$ should then hold for these solutions;[33] a plot of $1/\bar{n}$ *vs.* $1/a$ should have a slope of $1/\beta_1$ and an intercept of unity. The line in Figure 5 is a least-squares fit to the six points with $\bar{n} \leq 0.5$, weighted to pass through the theoretical intercept. The slope yields $\beta_1 = 1.8 \pm 0.2\ M^{-1}$ (estimated error limits). In order to achieve the best fit to the experimental formation curve (Figure 4) using this value of β_1, β_2 must equal $0.65 \pm 0.15\ M^{-2}$. These values of β_1 and β_2 (measured at 30°) agree very well with those determined by a pH method for more dilute solutions at 35°, $\beta_1 = 1.87\ M^{-1}$ and $\beta_2 = 0.893\ M^{-2}$.[3] This is not altogether surprising, since equilibrium quotients for reactions involving no change in charge type are expected to be insensitive to changes in ionic strength. A likely extension of this result is the prediction that equilibrium quotients for other concentrated monoborate–polyol systems are also comparable to those for more dilute aqueous solution.

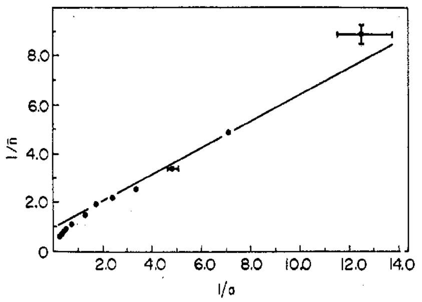

Figure 5.—Plot of $1/\bar{n}$ *vs.* $1/a$ for the 1,2-ethanediol–monoborate system; constant [B(OH)$_4^-$] = 1.5 *M*, [diol] = 0.25–7.2 *M*. The straight line is a least-squares fit to the six points having $\bar{n} \leq 0.5$, weighted to have an intercept of unity.

In the 1,2-ethanediol–monoborate system, the relative intensities of bands due to the ring remain essentially constant for both 1:1 and 2:1 species (*i.e.*, throughout the molar ratio series of solutions). The only evidence of interaction between the rings of the 2:1 complex is found in the region below 650 cm^{-1}, where the band assigned to b_2 in-plane bending gradually moves from 623 cm^{-1} (half-width of 35 cm^{-1}) for a solution containing 2.0 *M* B(OH)$_4^-$ and 4.0 *M* diol to 636 cm^{-1} (half-width of 22 cm^{-1}) as the total diol concentration is increased to *ca.* 12 *M*. Smaller changes are seen for the 407-cm^{-1} peak. The 764-cm^{-1} B–O stretching band appears to remain unaltered, although small changes would tend to be obscured by overlap of the 744-cm^{-1} B(OH)$_4^-$ band. Therefore, despite the existence of the 2:1 complex, the absence of major band splittings in solutions with high diol concentration justifies earlier use of the 1:1 model for purposes of assignment.

Several additional comments should be made concerning the band assigned to B–O ring stretching. For a D_2O solution containing 1.0 *M* monoborate and 2.0 *M* 1,2-ethanediol, in which both 1:1 and 2:1 complexes exist, bands of equal intensity appear at 704 and 737 cm^{-1} in addition to a weak shoulder remaining at *ca.* 760 cm^{-1}. The 704-cm^{-1} band is the symmetric B–O stretch of unreacted B(OD)$_4^-$, as determined in a separate experiment. The residual at *ca.* 760 cm^{-1} must arise from the 2:1 complex which has no –OH groups and perhaps from a small amount of undeuterated 1:1 complex. Appearance of the 737-cm^{-1} band, obviously shifted from 764 cm^{-1} upon deuteration, indicates that the 764-cm^{-1} band involves stretching not only of the B–O bonds within the ring but also of the B–OH groups in the 1:1 complex. If for this complex two distinct bands were present due to symmetric stretching of the cyclic and exocyclic B–O bonds, one would expect them to be polarized and to be of comparable intensity. The fact that this condition is not observed implies that the two types of B–O bond have nearly the same energy of vibration. The existing situation resembles that found with the methyl metaborate ring,[34] for which it is not possible to distinguish cyclic from exocyclic B–O stretching vibrations in the infrared spectrum.

Acknowledgment.—The author is grateful to K. W. Littlepage for valuable technical assistance.

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[32] Reference 31, p 92.

[33] Reference 31, p 86.

[34] D. W. Aubrey, M. F. Lappert, and H. Pyszora, *J. Chem. Soc.*, 1931 (1961).