191. *The Stereochemistry of Polyborate Anions and of Borate Complexes of Diols and Certain Polyols.*

By Johannes Dale.

The possible monocyclic and condensed cyclic structures for the complex polyborate anions have been deduced from steric considerations. Among these, a possible tetrameric urotropine-like cage structure $[B_4O_6(OH)_4]^{4-}$ is suggested for the crystalline hydrates of sodium metaborate.

Monocyclic sodium borate complexes of several 1,2- and 1,3-diols, a spiran-type bisdiol monoborate complex of pinacol, a spiran-type bisborate complex of pentaerythritol, and tridentate cage complexes of 1,1,1-trishydroxymethyl-ethane and *cis*-cyclohexane-1,3,5-triol, have been obtained crystalline from aqueous solution, and their structures proved by a study of thermal dehydration curves. The differences in stability between complexes and corresponding cyclic esters of the various types of diols and polyols are explained by stereochemical arguments.

cis- and *trans*-Cyclohexane-1,3-diol are readily separated by using the fact that the *cis*-isomer forms a distillable cyclic ester with boric acid, whereas the *trans*-isomer forms a polymer.

In the preceding paper the preferential formation of alkali borate complexes with one of the isomers in several sets of stereoisomeric 1,2- and 1,3-diols was reported and its use in the separation of such isomers was described without discussing in detail the structures of the complexes. Some of these complexes crystallized from water to give well-developed crystals which have now been investigated by chemical analysis, and, what is especially important from the structural point of view, by studying the dehydration curves recorded in a thermobalance to distinguish accurately between loosely bound water of crystallization and water bound structurally as hydroxyl groups on the boron atom. Simple stereo-chemical considerations led to an explanation of why 1,2-diols in general form more stable borate complexes than 1,3-diols, and to the prediction and subsequent isolation of stable cage structures, or tridentate complexes (which, however, had already been postulated by Mills, Angyal, and McHugh [1] from the ionophoretic behaviour of certain inositol isomers).

Before discussing these structures in detail we shall consider the structures of the

[1] Angyal and McHugh, *Chem. and Ind.*, **1956**, 1147; *J.*, 1957, 1423.

complex inorganic polyborate anions by a stereochemical analysis of boron compounds * similar to conformational analysis of cyclohexane derivatives.[2] There is some confusion about the structure of inorganic borates, not only in text-books, but even in recent publications,[3] in contrast to structural developments in borane and silicate chemistry. Also, it is now possible to check the results by recent accurate structure determinations of some borate minerals.[4-6]

To begin with, a few facts about the chemical behaviour of boric acid need be restated: (1) Boric acid behaves in aqueous solution exclusively as a monobasic acid;[7] hydrated salts with more than one cationic charge per boron atom are unknown. This means that boric acid acts, not as a proton donor, but as a Lewis acid, accepting the electron pair of the base (*e.g.*, OH⁻) to form a tetrahedral anion.[7,8] (2) The weakness of boric acid is explained by its reluctance to sacrifice the mesomeric stabilization in its planar trigonal form (B–O distance [5] 1·37 Å) to assume the tetrahedral structure where no mesomerism is possible (B–O distance [5] 1·48 Å). (3) The low energy difference between structures with trigonal and tetrahedral boron and their ready interconversion explains the practically instantaneous establishment of equilibria in condensation and hydrolysis of boric acid and borates,[7,9] as well as in the formation and hydrolysis of boric acid esters.[10] (Of course, to complete an esterification, time may be required because water has sometimes to be removed from an equilibrium which, although reached instantaneously. may be unfavourable.) (4) In dilute solutions practically no polyions exist.[7]

Inorganic Polyborate Anions.—In condensations under dehydrating conditions the planar boric acid molecule has an obvious tendency to form a six-membered planar ring, α-metaboric acid [11] (I), not only because the OBO angle of 120° fits accurately, but also because the second valency from the oxygen has to form a 120° angle in the same plane to allow one electron pair in a π-orbital on the oxygen to overlap maximally with the vacant π-orbital on the boron atom. The ring thus becomes quasi-aromatic; and it may be noted that α-metaboric acid is isoelectronic with phloroglucinol.

The simple borate anion (III) with its tetrahedral OBO angle of 109·5°, which has been shown by *X*-ray analysis to be present in some double-salt minerals,[12,13] and by Raman spectroscopy to be the anion in solutions of sodium metaborate,[8] would fit well in a planar five-membered ring, which, however, is out of question because of the required boron–oxygen alternation. In the condensed six-membered ring (VI) which, as in the cyclohexane molecule, must be expected to assume the puckered chair conformation since there is no longer any mesomeric restriction on the oxygen atoms, the ring as such will be non-strained, but three of the six substituent hydroxyl groups must become axial and thereby cause a repulsive strain, which, however, can be relieved by condensing on another borate anion to form a urotropine- or adamantane-like cage structure (IX). This structure is probably present in the crystalline hydrates of sodium metaborate for the following reasons: (1) Infrared studies in progress in this laboratory show that the spectra are different from that of the simple ion (III) present [12,13] in teepleite, $NaB(OH)_4,NaCl$; the spectra are more complex and show resemblances with that of urotropine. (2) The

* [*Added in proof.*] A different approach to the structural analysis of polyborates has meanwhile been published by Edwards and Ross (*J. Inorg. Nuclear Chem.*, 1960, **15**, 329).

[2] Barton and Cookson, *Quart. Rev.*, 1956, **10**, 44.
[3] *E.g.*, Carpéni, *Bull. Soc. chim. France*, 1949, 344, 742; 1950, 1280.
[4] Morimoto, *Mineral. J. Japan*, 1956, **2**, 1.
[5] Christ, Clark, and Evans, *Acta Cryst.*, 1958, **11**, 761.
[6] Clark, *Acta Cryst.*, 1959, **12**, 162.
[7] Ingri, Lagerström, Frydman, and Sillén, *Acta Chem. Scand.*, 1957, **11**, 1034.
[8] Edwards, Morrison, Ross, and Schultz, *J. Amer. Chem. Soc.*, 1955, **77**, 266.
[9] Edwards, *J. Amer. Chem. Soc.*, 1953, **75**, 6151.
[10] Hermans, *Z. anorg. Chem.*, 1925, **142**, 83.
[11] Tazaki, *J. Sci. Hiroshima Univ.*, 1940, *A*, **10**, 55; *Struct. Rep.*, **8**, 211.
[12] Fornaseri, *Periodica Mineral. Rome*, 1949, **18**, 103; 1950, **19**, 157; *Struct. Rep.* **12**, 263.
[13] Collin, *Acta Cryst.*, 1951, **4**, 204.

" tetrahydrate " of sodium metaborate loses water easily,[14] to form the " dihydrate " which on further dehydration [14,15] yields the " hemihydrate " whose tetrameric formula fits the cage structure (IX).   (3) The unit cell of the " dihydrate " contains four boron atoms.[14]

Although none of these indications is proof of the cage structure, it is interesting that the last point at least definitely excludes the sterically unfavourable cyclic ion (VI), and that the corresponding " monohydrate " has never been observed.[14]
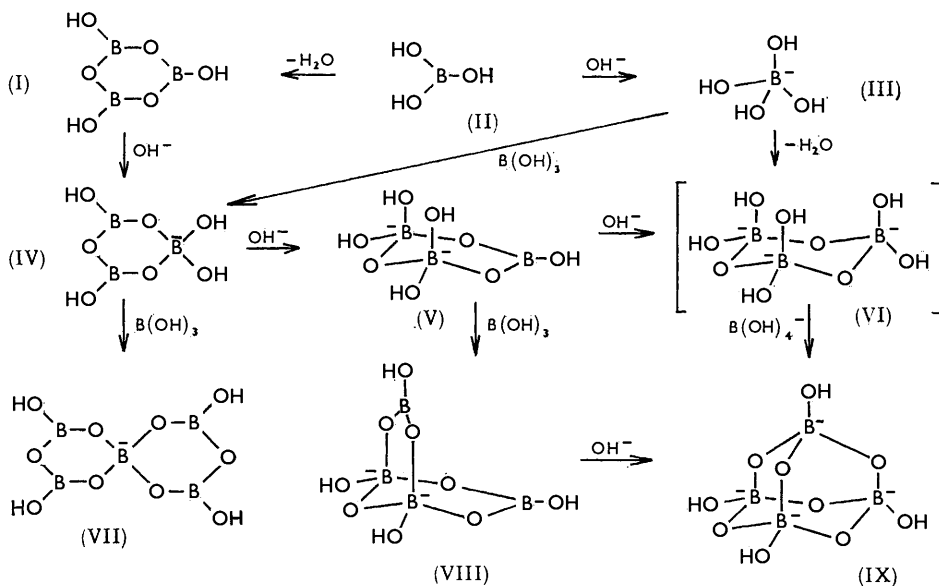
The annexed scheme also shows the structural relation between the various " mixed " polyborate anions.   It is important that in all precisely determined crystal structures the number of tetrahedral boron atoms in a polyborate ion is equal to the number of cationic charges, the excess of boron atoms being trigonal planar.   Starting from the α-metaboric acid (I), by neutralizing one boron atom the ion (IV), probably planar, is obtained.   This may be the ion present in the so-called " triborate " of lithium [16] and has been considered from an analysis of titration curves to be the most important polyborate ion in sodium borate solutions.[7]   By condensing on two more molecules of boric acid, the spiran structure (VII) is obtained, which, probably because of its higher symmetry, favours crystallisation, to give pentaborates, whose structure was established long ago by X-ray diffraction of the potassium salt.[17]   Here again, the so-called " tetrahydrate " loses its two molecules of water of crystallization rather easily.[18]   Also, nuclear magnetic resonance studies [19] confirm the presence of two molecules of water and four hydroxyl groups bound in the ion.*

When now the simple ring is doubly neutralized it has to be bent and the resultant dinegative ion (V) possesses some degree of instability because of its two axial hydroxyl

* [*Added in proof.*]   Recently, the ion (IV) has been found to be the structural unit in the three-dimensional network of anhydrous cæsium triborate (Krogh-Moe, *Acta Cryst.*, 1960, **13**, 889), and the ion (VII) the basic unit in the network structure of anhydrous potassium and rubidium pentaborate (Krogh-Moe, *Arkiv Kemi*, 1959, **14**, 439).

[14] Menzel and Schulz, *Z. anorg. Chem.*, 1943, **251**, 167.
[15] Krc, *Analyt. Chem.*, 1951, **23**, 806.
[16] Filsinger, *Arch. Pharm.*, 1876, **208**, 211.
[17] Zachariasen, *Z. Krist.*, 1937, **98**, 266.
[18] Rosenheim and Leyser, *Z. anorg. Chem.*, 1921, **119**, 1.
[19] Smith and Richards, *Trans. Faraday Soc.*, 1952, **48**, 307.

groups. In spite of this, X-ray structural work has shown the dinegative ion (V) to be present in several borate minerals,[5,6] but, perhaps significantly, only combined with the dipositive calcium ion. The repulsive strain may be somewhat relieved by making the ring more planar (although thereby introducing ring strain), but the degree of departure from planarity cannot be read off with certainty from the published drawings of these structures. However, the strain in form (V) can be relieved completely by adding one molecule of boric acid to form the very stable tetraborate ion (VIII). It is therefore not surprising that it is this ion which is the most preponderant dinegative ion in sodium borate solutions,[20] and not the triborate ion (V) as proposed originally.[7] The structure of sodium tetraborate " decahydrate " (borax) has been determined [4] and found to contain the ion (VIII), and it is interesting that this salt, as well as the " pentahydrate," can be easily dehydrated to the " dihydrate " stage,[21] while further dehydration is slow and produces a glass. By neutralizing the two remaining boron atoms in (VIII), the two fused rings must assume the chair form, a sterically impossible situation except when an oxygen bridge is formed by loss of water to give again the cage structure (IX).

It should be emphasized that it is not possible for steric reasons to add further atoms or groups to form new condensed rings on the final polyborate structures (VII), (VIII), and (IX). Of course, the structural elements can be combined into chains linked by oxygen bridges, but this does not create any new stable, compact, and rigid elements. Thus, polymeric chains of the ring (V) are found in some calcium borate minerals [5] and, by combining different structural elements, possible structures can be suggested for the rare " octaborate " $Li_2B_8O_{13},6H_2O$,[16] and the unstable $K_2B_5O_9H,3H_2O$ [22] if the anions are written in the form $B_4O_4(OH)_5^-$ and $B_5O_5(OH)_7^{2-}$ respectively.*

Borate Complexes of Diols and Polyols.—The striking steric similarity between the combination trico-ordinated boron–oxygen and olefinic or aromatic carbon on the one hand, and between tetraco-ordinated boron–oxygen and saturated carbon on the other hand, enables the stereochemistry of the diol–borate complexes to be considered in a completely analogous manner.

The sodium borate complexes of the 1,2- and 1,3-diols described in the preceding paper crystallized in general from water as simple 1 : 1 compounds with three molecules of water of crystallization. A precipitation of a crystalline spiran-type bisdiol monoborate complex was observed only in the case of pinacol, presumably because of the very high symmetry of this complex anion (X). The 1,3-diols must be expected to form borate complexes having six-membered non-planar cyclohexane-like ring systems. Proof of the puckered chair form with two types of substituent, axial and equatorial, was obtained from the observation that racemic pentane-2,4-diol with one axial methyl group forms a slightly less stable complex than the diequatorial *meso*-isomer, and that when the axial group is phenyl no complex is formed at all with the racemate. Further, 2,4-dimethylpentane-2,4-diol forms an ester with boric acid,[10] although it is somewhat unstable because of a single methyl–methyl axial interaction, but it gives no complex;[10] instead the ester is hydrolyzed when alkali is added, since there would have been three axial interactions in the complex (methyl–methyl and twice methyl–hydroxyl) (see XI and XII). Similarly, we have now found that *cis*-cyclohexane-1,3-diol forms a cyclic boric ester (XIII), but no complex (XIV) with sodium borate.

It should be mentioned that this ester (XIII) is formed less easily than those of other secondary 1,3-diols; thus, only the diol is extracted from an aqueous solution of the diol and boric acid. This can be understood if it is assumed that the *cis*-diol exists normally in the diequatorial conformation, at least in polar solvents, and has to become diaxial to react. The diequatorial conformation is indicated by X-ray data for the solid;[23] on

[20] Sillén, *Quart. Rev.*, 1959, **13**, 146.
[21] Menzel, Schulz, Sieg, and Vogt, *Z. anorg. Chem.*, 1935, **224**, 1.
[22] Carpéni, *Compt. rend.*, 1954, **239**, 1500.
[23] Furberg and Hassel, *Acta Chem. Scand.*, 1950, **4**, 597.

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the other hand, the infrared spectrum [24] indicates an internally hydrogen-bonded diaxial conformation in dilute solution in carbon tetrachloride. *trans*-Cyclohexane-1,3-diol forms only a polymer with boric acid; therefore, by distilling off the cyclic ester of the *cis*-isomer, or rather a mixed ester with 1-hexanol (see p. 930), a mixture of the two isomers
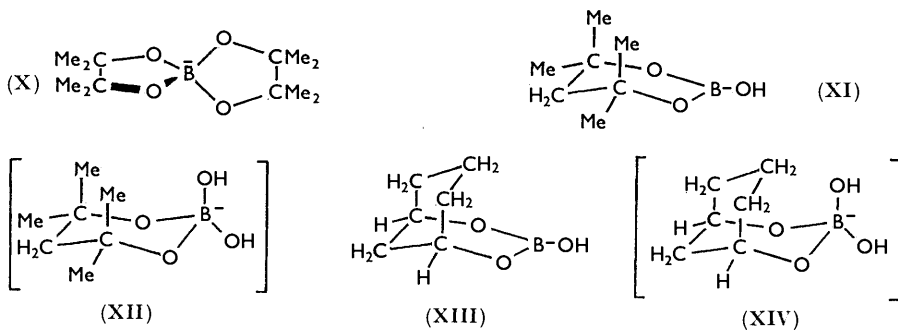
can be easily separated. This novel method is especially useful in this case, as the borate-complex method evidently cannot be used, and separation by fractional crystallization is extremely slow and tedious.[25]

Several complexes of 1,2-diols have been prepared earlier by Hermans [10] and by Maan,[26] but, except for phenylethylene glycol,[10] they were all from cyclic diols. We have now isolated sodium borate complexes of the unsubstituted cyclic diols, *cis*-cyclopentane- and *cis*-cyclohexane-1,2-diol, and of the isomeric butane-2,3-diols. The essentially planar structure of the five-membered ring system is indicated by the fact that the cyclopentanediol forms a much stronger complex then the cyclohexanediol, and that the racemic butane-2,3-diol, with *trans*-disposition of the methyl groups, forms a much stronger complex than the *meso*-isomer with two methyl groups on the same side. It is also interesting that pinacol (2,3-dimethylbutane-2,3-diol) not only forms an ester,[10] but, as already mentioned, has now been found to form *also* a complex when alkali is added. This shows that there are no interacting groups as close as in the axial positions of the six-membered ring. Further indications of the planar structure are the existence of stable *cis*-cyclohexane- and *cis*-cyclopentane-1,2-diol complexes even with methyl substituents in the 1-position,[26] and the fact that only with the larger phenyl groups do the complexes become too unstable to be isolated.[26] If in the latter case the interaction with the hydroxyl group on the boron atom is removed by making boron trigonal, a stable ester would result, as in fact found with 1-phenylcyclopentane-1,2-diol.[26]

At first it seemed surprising that complexes with 1,2-diols were more stable than those with comparable 1,3-diols, when on the other hand the converse is true for the corresponding esters. Thus, secondary 1,2-diol esters deposit boric acid in water, whereas secondary 1,3-diol esters are usually formed directly by mixing the diol and boric acid together in water solution. However, if the structural requirements of the planar boric acid (or ester) system are considered, it is seen that to form a five-membered ring the angles, especially the BOC angles, have to be drastically reduced from the 120° required for maximal meso-meric interaction, thereby forcing the oxygen into sp^3-hybridization. When, therefore the tetrahedral anion is being formed, there is less mesomeric energy to lose and the strain can be completely removed. The possibility of forming, with tetrahedral boron, a ring structure which cannot be easily formed with trigonal boron, is therefore the driving force in the acidity increase of boric acid in the presence of 1,2-diols. In a six-membered ring both configurations of boron can be accommodated without strain; hence, there is no
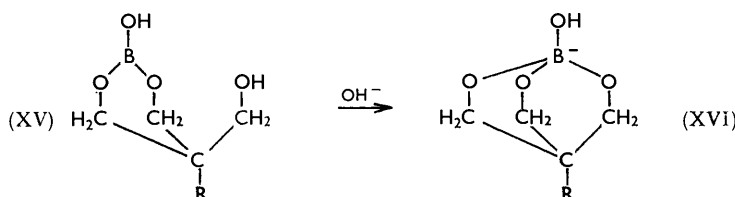
[24] Kuhn, *J. Amer. Chem. Soc.*, 1952, **74**, 2492.
[25] Rigby, *J.*, 1949, 1586.
[26] Maan, *Rec. Trav. chim.*, 1929, **48**, 332.

such strong driving force towards formation of a borate anion in the presence of 1,3-diols and the acidity of boric acid is not increased to a measurable extent.

The fact that pentaerythritol was the only compound, containing the 1,3-diol structure and no 1,2-diol structure, which was known to raise the acidity of boric acid to the same degree as 1,2-diols,[27] together with the fact that the dimethyl ether of pentaerythritol does not show this effect,[28] led us to the belief that a cage structure with three hydroxyl groups linked to the same boron atom might be involved. The driving force would then be found in the fact that the trigonal boron atom cannot link more than two of these hydroxyl groups, and only by becoming a tetrahedral anion would it be able to close the bridge to form the favourable cage structure (XV —→ XVI).*

$$
(XV) \quad
\begin{array}{c}
\text{OH} \\
| \\
\text{B} \\
\diagup \quad \diagdown \\
\text{O} \qquad \text{O} \qquad \text{OH} \\
| \qquad\quad | \qquad\quad | \\
\text{H}_2\text{C} \qquad \text{CH}_2 \qquad \text{CH}_2 \\
\diagdown \qquad\quad \diagup \\
\text{C} \\
| \\
\text{R}
\end{array}
\xrightarrow{\text{OH}^-}
\begin{array}{c}
\text{OH} \\
| \\
\text{B}^- \\
\diagup \;\; | \;\; \diagdown \\
\text{O} \;\; \text{O} \;\; \text{O} \\
| \qquad | \qquad | \\
\text{H}_2\text{C} \;\; \text{CH}_2 \;\; \text{CH}_2 \\
\diagdown \qquad \diagup \\
\text{C} \\
| \\
\text{R}
\end{array}
\quad (XVI)
$$

This idea was supported by Brown and Fletcher's finding [29] that 1,1,1-trishydroxymethylpropane does not give a cage structure with boric acid, but only a polymer. We have now found that the same is true of 1,1,1-trishydroxymethylethane, even in the presence of organic bases, but also that this triol raises the acidity of boric acid to about the same degree as pentaerythritol and gives a crystalline complex with sodium borate. The analysis gives an empirical formula of $C_5H_{16}BNaO_7$, and the compound loses three mol. of water below 47° whereafter no further weight loss occurs below 230°. Since, in general, in the simple ring systems with two hydroxyl groups on the boron atom an additional mol. of water starts to come off at a slightly higher temperature than the water of crystallization, this shows that only one hydroxyl group remains on the boron atom, thus proving the cage structure.

This cage structure can be considered as composed of three fused six-membered rings in the boat conformation, so an obvious extension was to make a complex with three fused rings in the chair conformation. α-Cyclohexane-1,3,5-triol (α-phloroglucitol), which has been shown by X-rays [30] to be the *cis*-isomer, was found to raise the acidity of boric acid to a similar degree and gave a crystalline complex with sodium borate. Again, above 48° (and below 300°) no further weight loss occurred, so that only one hydroxyl group remains on the boron atom, proving the urotropine-like cage structure (XVII). In contrast, the *trans*(β)-isomer gives no complex or increase in acidity. This incidentally furnishes, not only with a diagnostic tool for *cis*-cyclohexane-1,3,5-triol structures (cf. Angyal and McHugh [1]), as do other tridentate reactions to give, for example, phosphorous,[31] phosphoric,[31] thiophosphoric,[31] and orthocarboxylic esters,[32] but also provides a simple preparative method for separating such isomers. In the present case this is not of much use as the isomers are separable by crystallization,[33] but for non-crystalline derivatives the method should have potentialities.

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* In complete formal analogy the observation that the acidity of boric acid increases with concentration, or, more exactly, that polyborates are salts of stronger acids than the simple boric acid,[7] may be explained by the fact that condensed structures can be formed with tetrahedral boron, which for steric reasons cannot be formed with trigonal boron. Thus, the acidity of boric acid is increased not only in the presence of diols and polyols, but also in the presence of boric acid itself.

[27] Boëseken and Van Rossem, *Rec. Trav. chim.*, 1911, **30**, 392.
[28] Orthner and Freyss, *Annalen*, 1930, **484**, 131.
[29] Brown and Fletcher, *J. Amer. Chem. Soc.*, 1951, **73**, 2808.
[30] Andersen and Hassel, *Acta Chem. Scand.*, 1948, **2**, 527; 1951, **5**, 1349.
[31] Stetter and Steinäcker, *Chem. Ber.*, 1952, **85**, 451.
[32] Stetter and Steinäcker, *Chem. Ber.*, 1953, **86**, 790; 1954, **87**, 205.
[33] Lindemann and Baumann, *Annalen*, 1930, **477**, 78.

When finally it was tried to isolate the complex of pentaerythritol, only an amorphous precipitate, probably a polymer, was obtained from a very concentrated solution when equimolar quantities were used. When a large excess of sodium borate was used, a crystalline complex was obtained which, however, proved to be of the bis-type having the spiran structure (XVIII). Apparently, the free hydroxyl group in the tridentate complex,

(XVII)   (XVIII)
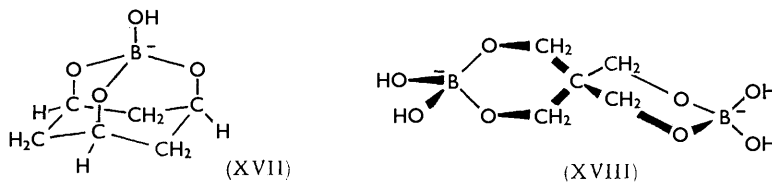
which undoubtedly must be the main species in solution, renders it too soluble, so that other less soluble species, even when present as minor constituents, may crystallize instead. Caution is therefore needed when drawing conclusions as to the composition of a borate solution from the substances precipitated.

EXPERIMENTAL

Preparation and Analysis of Sodium Borate Complexes.—The sodium borate complexes were, except when otherwise stated, prepared by heating equimolar quantities of the diol (or polyol) and sodium metaborate in water containing a little extra sodium hydroxide to prevent precipitation of borax. After cooling, the crystals were filtered off and wiped on filter paper. When the complexes crystallized as very thin leaflets, this method was not very efficient, as shown by unsatisfactory analyses. The complexes were analyzed by potentiometric titration, first with hydrochloric acid to determine sodium, then with sodium hydroxide in the presence of mannitol to determine boron. Ordinary combustion analysis was used to obtain the values for carbon and hydrogen. Finally, the dehydration curve in air of samples of about 100 mg. was recorded on a Stanton thermobalance modified to obtain a rate of temperature rise as slow as to require about 6 hr. to reach 200°. Usually, the transparent crystals became white and opaque when the water of crystallization was lost, but did not melt below 330°. The dehydration was completely reversible at least up to about 120°, so that the dried sample picked up exactly the lost quantity of water when exposed to the atmosphere.

meso-*Pentane*-2,4-*diol.*—The *complex* crystallized as thin flakes (Found: C, 26·55; H, 8·15; B, 4·7; Na, 10·15. $C_5H_{18}BNaO_7$ requires C, 26·8; H, 8·1; B, 4·8; Na, 10·3%). Between 50° and 105° it lost rapidly 24·0% of its weight ($3H_2O$ requires 24·1%); up to 150° there was a less rapid loss of about 8% ($1H_2O$ requires 8·0%); and above 150° the weight loss continued at a still somewhat slower rate. The dried complex (100°) was insoluble in ether, chloroform, benzene, or tetrahydrofuran, but soluble in hot xylene or pyridine, apparently with dehydration to give polymers since gels were formed on cooling.

Racemic Pentane-2,4-*diol.*—The *complex* was obtained as irregularly shaped crystals (Found: C, 26·3; H, 8·3; B, 4·7; Na, 10·2%). Between 50° and 100° it lost rapidly 24·1% of its weight; up to 140° the loss was less rapid and amounted to about 8·5%; it then continued at a still slower rate at higher temperatures.

meso-*Butane*-2,3-*diol.*—The *complex* crystallized from relatively concentrated solutions as thin flakes (Found: C, 23·15; H, 7·8; B, 5·0; Na, 10·7. $C_4H_{16}BNaO_7$ requires C, 22·9; H, 7·7; B, 5·15; Na, 10·95%). It lost rapidly 25·6% of its weight ($3H_2O$ require 25·7%) between 55° and 95°; above this temperature a much slower loss continued without stop.

Racemic Butane-2,3-*diol.*—The *complex* crystallized as thick oblong hexagonal plates (Found: C, 23·0; H, 7·9; B, 5·2; Na, 10·9%). Between 70° and 130° It lost rapidly 25·8% of its weight, with little further loss to 145°, above which temperature the loss continued slowly with no stop.

cis-*Cyclopentane*-1,2-*diol.*—The *complex* crystallized as irregular plates (Found: C, 26·95; H, 7·5; B, 5·05; Na, 10·2. $C_5H_{16}BNaO_7$ requires C, 27·05; H, 7·3; B, 4·9; Na, 10·35%). Between 50° and 90° it lost rapidly 24·3% of its weight ($3H_2O$ require 24·4%), with little further loss to 125°, whereafter slow loss continued without stop.

cis-*Cyclohexane*-1,2-*diol.*—The *complex* was obtained from concentrated solutions as very

thin shiny flakes (Found: C, 29·9; H, 7·8; B, 4·6; Na, 9·7. $C_6H_{18}BNaO_7$ requires C, 30·5; H, 7·7; B, 4·6; Na, 9·75%). It lost rapidly 21·6% of its weight between 53° and 90° ($3H_2O$ require 22·9%). Above 90° a slow loss continued without stop.

Pinacol.—A complex was precipitated very slowly on mixing equimolar quantities of pinacol and sodium borate. It proved to be the bisdiol borate, and was later found to crystallize more easily when twice as much pinacol was used. The very concentrated solution had to be filtered hot to remove some oil droplets (pinacolone?), and on cooling, the 2 : 1 *complex* crystallized as large, but extremely thin, leaflets which broke easily to give a powder. It contained four mol. of water of crystallization (Found: C, 43·1; H, 9·8; B, 3·2; Na, 7·0. $C_{12}H_{32}BNaO_8$ requires C, 42·6; H, 9·55; B, 3·2; Na, 6·8%). Between 40° and 80° it lost rapidly 20·9% of its weight ($4H_2O$ require 21·3%), but no more up to 170°. Above 170° a slow loss started. Titration of the complex with hydrochloric acid had to be carried out slowly as the hydrolysis was very slow compared with that of the other simple complexes.

1,1,1-Trishydroxymethylethane.—The *complex* crystallized as very long flakes which broke easily (Found: C, 27·1; H, 7·35; B, 5·0; Na, 10·3. $C_5H_{16}BNaO_7$ requires C, 27·05; H, 7·25; B, 4·9; Na, 10·35%). It lost rapidly 24·0% of its weight between 35° and 47° ($3H_2O$ require 24·4%), then no more up to 230°. Above this temperature a rapid loss started.

α-Cyclohexane-1,3,5-triol.—The *complex* of the α-(*cis*-)isomer (for the preparation see below) crystallized as oblong flakes (Found: C, 30·8; H, 7·1; B, 4·7; Na, 9·65. $C_6H_{16}BNaO_7$ requires C, 30·8; H, 6·9; B, 4·6; Na, 9·8%). Between 35° and 48° it lost rapidly 22·8% of its weight ($3H_2O$ require 23·1%), then no more up to 300°, whereafter rapid weight loss occurred.

Pentaerythritol.—Using equimolar quantities of pentaerythritol and sodium metaborate, gave an amorphous precipitate from concentrated solutions. This was filtered off and pressed

between filter paper, but had to be dried in air at 20° to reach a constant weight. Analysis showed it to be a 1 : 1 *complex*, probably polymeric (see inset) containing six mol. of water of crystallization (Found: C, 20·9; H, 7·8; B, 4·05; Na, 8·2. $C_5H_{20}BNaO_{10}$ requires C, 21·9; H, 7·4; B, 3·95; Na, 8·4%). It lost rapidly 39·2% of its weight between 30° and 80° ($6H_2O$ require 39·5%), whereafter a slow loss continued without stop.

When substantially more than two moles of sodium borate were used per mole of penta-erythritol, thin needles crystallized already from much more dilute solutions. Analysis showed it to be the *diborate* (*i.e.*, the 1 : 2 complex) containing twelve mol. of water of crystallization (Found: C, 12·6; H, 7·55; B, 4·4; Na, 9·45. $C_5H_{36}B_2Na_2O_{20}$ requires C, 12·4; H, 7·45; B, 4·45; Na, 9·5%). If heated quickly, the crystals melt above 75°, then solidify again as the water evaporates. If they are heated slowly, no melting occurs below 350°. On the thermo-balance the complex lost rapidly 36·4% of its weight between 40° and 65° ($10H_2O$ require 37·1%); between 65° and 95° it lost more slowly 7·4% ($2H_2O$ require 7·4%); and above 95° a still slower loss continued without stop.

The infrared spectra of the two complexes are very similar, and different from that of the borate complex of 1,1,1-trishydroxymethylethane; hence, a tridentate cage structure is excluded.

Attempts to prepare Borate Complexes of 1,1,1-Trishydroxymethylethane in the Presence of Amines.—(a) *Tributylamine.* Molar quantities of the triol, boric acid, and tributylamine were heated together, rapidly becoming homogeneous. In less than 1 hr. the theoretical amount of water had distilled off. After cooling, a solid mass was deposited. The supernatant liquid (pure tributylamine) was decanted. The solid was non-volatile, burned with a green flame, and must be a polymeric triol borate. When heated it fused, giving a hard brittle glass, soluble with decomposition in water and acids.

(b) *Pyrrolidine.* When the much stronger base pyrrolidine was used and the water removed by azeotropic distillation with chloroform, the expected quantity of a homogeneous yellow solid was obtained after removal of the solvent *in vacuo*. It was tough when hot, and brittle when cold, soluble in water (with decomp.) and chloroform, but insoluble in benzene, and burned with a green flame. Surprisingly, attempts to sublime or distil the expected compound $Me·C(CH_2·O-)_3B \longleftarrow HNC_4H_8$ only led to decomposition of the solid, so either the B $\longleftarrow$ N link is thermally unstable, or the base is linked differently to a triol borate polymer instead of to the tridentate complex.

Preparation of Cyclohexane-1,3,5-triol (Phloroglucitol).—Phloroglucinol (100 g.) in absolute ethanol (100 ml.) containing Raney nickel (15 g.) and sodium hydroxide (0·5 g.) was hydrogenated at a constant pressure of 140—150 atm. The uptake started at 90° and was essentially complete

at 125° in 30 min. The products were worked up and the isomers separated as described by Lindemann and Baumann.[33] The yield of the *cis*-isomer (α-phloroglucitol; m. p. 185°) was 26%, and of the *trans*-isomer (β-phloroglucitol; m. p. 145°) 20%. Yields of 60% of α and 10% of β have been reported [31] for a similar hydrogenation carried out at 50°/1 atm.

When it was tried to prepare a sodium borate complex of the *trans*-isomer, very pure unchanged triol crystallized on cooling.

Separation of cis- *and* trans-*Cyclohexane-*1,3-*diol.*—The crude cyclohexane-1,3-diol was prepared by catalytic hydrogenation of resorcinol under the conditions reported by Clarke and Owen,[34] but with Raney nickel furnished by Fluka AG. The reaction was much faster and complete in 30 min., and the quantity of cyclohexanol formed was negligible. The diol distilled at 118—122°/7 mm. (yield 71%; n_D^{20} 1·4980). The liquid diol mixture (58 g.) was heated with trihexyl borate (204 g.), and the liberated hexan-1-ol (86 g.) distilled off at 153°. On further distillation, *in vacuo*, the mixed ester, *cis*-cyclohexane-1,3-diol hexyl borate (83·1 g.), n_D^{21} 1·4390, passed over at 107—120°/0·8 mm. Then the temperature started to rise and the index of refraction dropped to 1·4275 (trihexyl borate has n_D^{21} 1·4260). At the same time the polymeric borate of the *trans*-diol started to separate.

cis-Cyclohexane-1,3-diol was isolated by dissolving the distilled mixed ester in concentrated alkali, extracting the solution with ether (no sodium borate complex was formed), and distilling the extract. Hexan-1-ol distilled first, then the *cis*-diol (40 g., 70%) at 100—104°/0·5 mm. After recrystallization from acetone the diol melted at 82—83°.

The *trans*-cyclohexane-1,3-diol was isolated similarly from the residue, which contained some trihexyl borate. The *trans*-diol (15·6 g., 27%) distilled at 130—142°/6 mm. and, recrystallized from acetone, had m. p. 118—120°.

Separation is also possible if the hexanol is replaced by pentanol, but it is more difficult to get a clear separation by distillation of the mixed ester and the excess of tripentyl borate. This is necessary, as the last portion of the liquid is hard to remove completely from the polymer and therefore should not contain the *cis*-isomer.

cis-*Cyclohexane-*1,3-*diol Borate.*—When a solution of the *cis*-diol and boric acid in water was extracted with ether, no borate was obtained but only the pure diol. Similarly, an attempt at partial hydrolysis of *cis*-cyclohexane-1,3-diol hexyl borate by the addition of one mol. of water failed to yield the simple cyclic ester; instead, boric acid was precipitated.

A mixture of *cis*-cyclohexane-1,3-diol and boric acid was then heated in benzene and the water formed was removed azeotropically. When the calculated quantity of water had been collected, the excess of boric acid was filtered off, the solution concentrated, and hexane added. A mixture of a powder and needles was obtained. The rest was evaporated, and sublimed with difficulty *in vacuo*. This sublimate was also heterogeneous and was recrystallized from hexane, giving long thin needles of the *diol borate*, m. p. 165—180° when determined slowly (Found: B, 7·5; $C_6H_{11}BO_3$ requires B, 7·6%). On a Kofler bank it first melted at 105—110°, then solidified and remelted at 180° as the *anhydride* (Found: B, 8·4. $C_{12}H_{20}B_2O_5$ requires B, 8·2%).

When the borate was treated with alkali, no precipitate was formed but the diol separated as an oil.

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[34] Clarke and Owen, *J.,* 1950, 2103.