Cage Structures for Polyborate Ions

Abstract. *Conventional concepts of chemical bonding appear inadequate to explain the structures of the anhydrous polyborates. A cage-type structure with occluded oxide ion is proposed for the octaborate, hexaborate, and tetraborate ions. The proposed structure is discussed in terms of the composition, x-ray diffraction patterns, and nuclear magnetic resonance spectra of the sodium polyborates.*

Proposed structures for anhydrous polyborate ions (*1*) remain unsubstantiated (*2, 3*). I now suggest a possible cage structure.

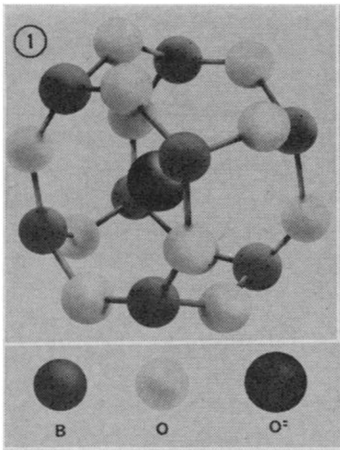
From conventional concepts of chemical bonding a variety of anhydrous polyborate salts can be assumed. However, only three sodium polyborate salts exist: disodium tetraborate ($Na_2B_4O_7$, mp 742.5°C), disodium hexaborate ($Na_2B_6O_{10}$, mp, incongruent, 766°C), and disodium octaborate ($Na_2B_8O_{13}$, mp 816°C) (*4*). Also, most reliable composition studies (*1*) show that polyborates of other metals exist only as tetraborates, hexaborates, and octaborates.

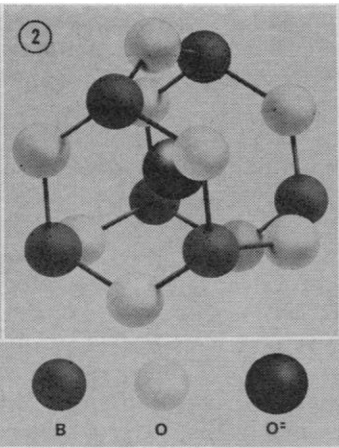
The difficulty of resolving the polyborate structure seems to revolve around diverse views as to boron coordination behavior. These diverse views indicate that the structures of polyborate ions might not be analogous with those of any known complex ions. I have therefore investigated the feasibility of cage-type structures for $B_8O_{13}^{--}$, $B_6O_{10}^{--}$, and $B_4O_7^{--}$ ions. These proposed structures (Figs. 1 to 3) are conceived as B_8O_{12}, B_6O_9, and B_4O_6 cages, each having an occluded oxide ion.

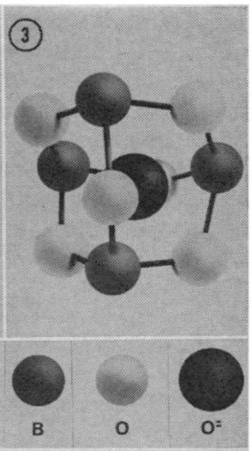
The argument for the proposed cage structures of the polyborate ions is based principally on the following experimental information: (i) the phase diagram study of the sodium oxide-boron oxide system by Morey and Merwin (*4*), which discloses the exclusive existence of disodium octaborate, disodium hexaborate, and disodium tetraborate in the polyborate composition range; (ii) Biscoe and Warren's (*5*) x-ray diffraction data on sodium polyborates; and (iii) the nuclear magnetic resonance (NMR) investigations of Krogh-Moe (*6*) and Bray and O'Keefe (*7*), which negate the commonly held belief that the oxide ion coordinates with a BO_3 group forming the BO_4 species with tetrahedrally arranged oxygens around the boron atom.

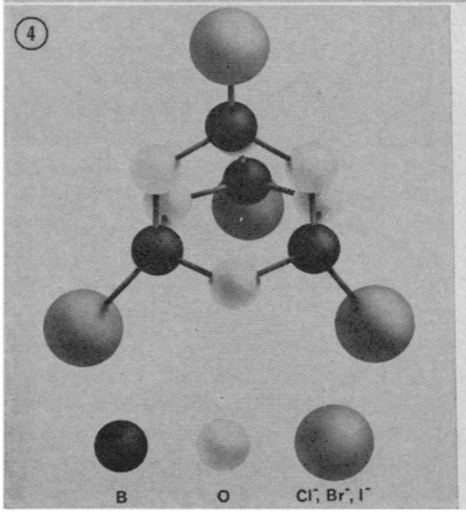
From the symmetrical arrangement of the cage-forming atoms, one can either derive the separations between the nearest boron and oxygen pairs, if the bond lengths between B and O were given, or, conversely, one can calculate the B–O bond lengths, knowing what the above separations are. Should both the given and the derived data agree with those determined experimentally by Biscoe and Warren (*5*), the cage structures might be further supported. Then the determining radius could be estimated for the oxide ion occluded in the cage. To meet the above objectives, several relevant cage parameters were calculated by applications of trigonometric laws.

The cage concept requires that any of the peripheral oxygens can have only four equidistant, nearest-oxygen neighbors, and any of the borons can have three equidistant, nearest-boron neighbors. On the other hand, Biscoe and Warren (*5*) estimated that, irrespective of the ratio of Na_2O to B_2O_3 in the polyborate range, there are between five to six oxygens at a distance of about 2.45 Å from each oxygen. At the same time, they ascribe values of 2.7 to 3.1 Å to the distances between the nearest boron pairs. The latter distances amount to twice the B–O bond lengths they found and impose an exceptional condition that the covalent (interbond) angle of oxygen should be about 180°. But this angle is known to range only between 100° and 118° ± 3° (*8*). Besides, Biscoe and Warren find the calculated area for the B-to-B peak "too small to allow it to show on the distribution curve." Thus both the nearest O-to-O and









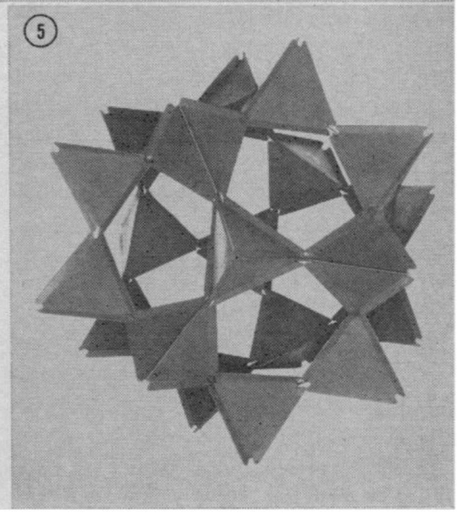


Fig. 1. $B_8O_{13}^{--}$ ion depicted as a B_8O_{12} cage with occluded oxide ion. Fig. 2. $B_6O_{10}^{--}$ ion depicted as B_6O_9 cage with occluded oxide ion. Fig. 3. $B_4O_7^{--}$ ion depicted as a B_4O_6 cage occluded oxide ion. Fig. 4. B_4O_6 cage with halide ions (Cl^-, Br^-, I^-) coordinated external to boron atoms. Fig. 5. Dodecahedral structural unit suggested for the compact ionic network of disodium tetraborate. The tetraborate ion cages, with surrounding four sodium ions, are represented by tetrahedra.

Table 1. Calculated θ (B–O–B) and φ (O–O–O) angles between the lines from polyborate cage centers to nearest pairs of cage-forming boron and oxygen atoms, and calculated distances of B and O atoms from polyborate cage centers.

Polyborate ion	Angles		Distance (Å) of	
	θ	φ	B atom	O atom
Octaborate	70°32′	60°00′	2.12	2.45
Hexaborate	81°48′	69°05′	1.87	2.16
Tetraborate	109°28′	90°00′	1.50	1.73

Table 2. Normalized covalent radii of boron and oxygen atoms, and determining radii allowed for oxide ion occluded in polyborate cage. Results in angstroms.

Polyborate ion	Covalent radius (of atoms)		Determining radius for occluded oxide ion
	Boron atom	Oxygen atom	
Octaborate	0.75	0.67	1.37
Hexaborate	.76	.68	1.11
Tetraborate	.79	.71	0.71

B-to-B distances may be actually about the same, and hence contribute cumulatively to the peak intensity at 2.45 Å in their x-ray diffraction patterns. With this assumption, the B–O bond lengths for the respective cages were calculated as follows: first, the angles θ and φ between the lines from the cage centers to the nearest-neighbor-pairs of boron and oxygen atoms were calculated (Table 1). Then, by means of these angles, and from the nearest-neighbor-pair distances of 2.45 Å, the distances from the boron and oxygen atoms to the cage centers were derived (Table 1). From these 2 and the half-values of the θ angles, the bond lengths between the boron and oxygen atoms of the cages were obtained. The calculated B–O bond lengths in angstroms, namely 1.42 for octaborate ion, 1.42_6 (averaged) for the equimolar mixture of octaborate and hexaborate, and 1.50 for tetraborate, agree well with Biscoe and Warren's experimental data of 1.42 for the equimolar mixture and 1.48 for tetraborate.

Since the B–O bond lengths are longest in the tetraborate and shortest in the octaborate, the covalent radii of boron and oxygen atoms can be regarded as increasing proportionately. These radii, normalized with respect to the covalent radii of boron and oxygen atoms listed in the periodic table of elements (*9*), are given in Table 2.

Since the distance of the boron atom from the cage center is shorter than that of the oxygen atom and the covalent radius of the boron atom is larger than that of the oxygen atom (Table 2), the difference between the cage-radial distance of the boron atom and its covalent radius should be the determining radius for the occluded oxide ion in the cage.

The proposed polyborate-ion cages require that each boron atom of the cage should have within its neighborhood four oxygen atoms, but obviously not in tetrahedral configuration. In the tetraborate ion, all four oxygens should be equidistant from boron atoms (at 1.50 Å). In hexaborate and octaborate ions, three oxygen atoms should be equidistant from boron atoms, and the fourth oxygen should lie at the estimated 1.87 and 2.12 Å distances, respectively (see Table 1). At the same time, the angle between the lines from boron atom to the occluded and the adjoining peripheral oxygen atoms should change from one polyborate ion to another (Table 3) (*10*). The above picture is in accord with the deductions made by Bray and O'Keefe (*7*) from their NMR studies on borate glasses.

The B_8O_{12} cage could readily occlude the oxide ion with its normal ionic radius of 1.40 Å, and thus might present a special case of a clathrate ion (Table 2). On the other hand, the occlusion of the oxide ion in the B_4O_6 cage would necessitate reduction of its radius to 0.71 Å. This radius reduction actually can be corroborated both theoretically and experimentally as follows. (i) It is recognized that the radius of an atom or ion that has donated one electron pair to another atom or ion is reduced by approximately 0.20 Å. However, inside the B_4O_6 cage, owing to the favorable proximity of four boron atoms, the oxide ion should be capable of donating simultaneously all four pairs of its outer-shell electrons to the surrounding boron atoms. Hence, conceivably, the ion's original 1.40 Å radius might be reduced by 4×0.20 Å, that is, even to 0.60 Å. (ii) Biscoe and Warren (*5*) estimate that each B–O bond length in BO_4 units should be 1.50 Å. In this case, the normalized radius of each oxygen atom in the unit would be 0.71 Å, which agrees precisely with the calculated data given for the tetraborate ion in Table 2. (iii) Recent NMR investigations (*11*) show that in lead tetraborate, PbB_4O_7, which incidentally is isomorphous with SrB_4O_7 (*12*), the fraction of boron atoms with four coordinated oxygens is 1. This means that all boron atoms form BO_4 units—a fact explainable only by the concept of an oxide ion occluded in the B_4O_6 cage. Thus the hexaborate-cage ion, being intermediate in size between the octaborate and the tetraborate, should be likewise structurally plausible.

Table 3. Calculated for polyborate cages: angles α (O–B–O) between the lines from boron to adjoining oxygens, one peripheral and one occluded; and (interbond) covalent angles β (B–O–B) of peripheral oxygens. β is equal to 2 × [180° − α − (θ/2)].

Polyborate ion	Angles	
	α	β
Octaborate	85°00′	119°28′
Hexaborate	80°29′	117°16′
Tetraborate	70°32′	109°28′

Table 4. Distances (angstroms) of sodium ion from polyborate cage centers. (*A*) calculated on the basis of the Biscoe and Warren data; (*B*) calculated as the sum of distance of boron atom from the cage center and radii of sodium ion and covalent boron atom.

Disodium polyborate	*A*	*B*	(*A* − *B*)
Octaborate	3.94	3.82	+ 0.12
Hexaborate	3.57	3.58	− 0.01
Tetraborate	2.94	3.24	− 0.30

The concept of polyborate ion cages suggests that each sodium ion should be shared between two cages. At the same time, for electrostatic balance, every polyborate ion cage would have to be surrounded by four other cages, separated from each one by one sodium ion. According to Biscoe and Warren (*5*), each sodium ion in all its polyborate salts is equidistant, at 2.40 Å, from six oxygens. One may then assume that any sodium ion would probably be located somewhere on a line from the cage center through the midpoint between three equidistant (at 2.45 Å) cage oxygens.

In order for the above equidistance condition to hold in disodium octaborate, the sodium ions should then be located in front of boron atoms. In hexaborate- and tetraborate-ion cages, on the other hand, three equidistant oxygens are also present in the faces containing $(B–O)_3$ rings. The hexaborate cage has two such rings and the tetraborate four. Although it is apparent that the sodium ion could be readily allocated opposite the $(B–O)_3$ ring, in disodium hexaborate at least two sodium ions should be found in front of two boron atoms (as in the case of disodium octaborate). The latter condition could be fulfilled only if the separation between the boron atom and the sodium ion were not smaller than the sum of the radii of both (on the assumption of 2.40 Å separations of sodium ion from three oxygens of one cage).

If the calculations would not invalidate the above condition, the argument for the hexaborate cage structure might have added support. Consequently, the differences between alternatively calculated distances, indicated as *A* and *B* in Table 4, for sodium ions from the respective cage centers were calculated. The derived distances denoted by *B* are self-evident. The data used for deriving the distances denoted by *A* were (i) the sodium ion–oxygen atom separation equal to 2.40 Å; (ii) the oxygen distance from cage center (Table 1); and (iii) the angle between the lines from the cage center to the adjoining peripheral boron and oxygen atoms (that is, $\theta 2$, Table 1). From the data in Table 4, for disodium octaborate, the difference +0.12 Å attests that the sodium ions would not be sterically hindered in their allocation opposite boron atoms of the cage. For disodium hexaborate, the difference −0.01 Å is so small that it can be ignored, and thereby the necessary condition for some sodium ions allocated in front of boron atoms may be validated. Finally, for disodium tetraborate the large negative difference −0.30 Å rules out the above possibility.

The suggested structures of polyborate ions, and the possible allocations of cations around them, may afford a basis for the interpretation of the unresolved ionic networks in the polyborate salts. For example, for disodium tetraborate the most compact structural unit in the ionic network may be the dodecahedral one (Fig. 4). In the model shown, each tetrahedron represents the B_4O^{--} cage ion with a shared sodium ion at each corner.

The formation of polyborate salts is associated with considerable volume reduction with respect to the original volumes of boron oxide and metal oxide (*13*, p. 213). This effect is absent in polysilicate formation (*13*, p. 201). Eversteijn, Stevels, and Waterman (*14*) hold that the above difference may be due to different structural transformations in boron oxide and silicon dioxide networks, caused by the cation of the metal oxide. They admit, however, that more experimental and theoretical work would be required to confirm (or reject) their conjecture.

Formation of the suggested cage-type polyborate ions may readily account for this phenomenon (*15*).

The tendency of boron oxide to form cage structures might also account for different solubilities of boron oxide in molten sodium halides. In molten sodium fluoride (mp 992°C), boron oxide is completely soluble (*16*). In other sodium halides, its solubility diminishes with the increase in atomic number of the halide (*17*). Moreover, Harrison (*18*) shows that molten sodium chloride dissolves boron oxide as the B_4O_6 species, which may be cage-structured (*19*). The chloride ion, with an ionic radius of 1.81 Å (*9*), would be too large to fit inside the B_4O_6 cage even if its radius could be reduced by 4×0.20 Å, thus becoming 1.00 Å (upon donation of four pairs of its electrons to the four boron atoms of the cage). However, up to four chloride ions could be coordinated external to boron atoms (Fig. 5). This coordination could make possible some dissolution of covalent boron oxide in the ionic medium of molten sodium chloride. The tendency of halide ions to form complexes with the B_4O_6 cages should diminish with the decrease in negative-charge density of the halide ion. Accordingly, the solubility of boron oxide is smaller in molten sodium bromide than in sodium chloride, and is the lowest in sodium iodide (*17*). Also, with the increase in the vibrational energy of the complexes of boron oxide-halide ion, fewer halide ions should tend to coordinate with the B_4O_6 cages. Hence, the solubility of boron oxide in molten sodium halides (other than fluoride) diminishes with a rise in temperature (*17*).

The complete solubility of boron oxide in molten sodium fluoride, on the other hand, may be attributed to the small ionic radius, 1.36 Å (*9*), of the fluoride ion. Hence it should be feasible for this ion, by donating four electron pairs to four boron atoms, to become occluded by the B_4O_6 cage. The heretofore stoichiometrically inexplicable formation of $B_4O_6F^-$ ions might thereby be clarified.

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Mars: New Absorption Bands in the Spectrum

Abstract. *New absorption bands have been found in the near-infrared spectrum of Mars by Fourier spectroscopy. They are tentatively identified in part as due to reduced gases in the Martian atmosphere.*

During the 1965 opposition of Mars, spectra were obtained at the Observatoire de Haute-Provence, France, by means of Fourier-transform spectroscopy. The Michelson interferometer used is described and samples of typical spectra of Mars and Venus, together with solar spectra for comparison, are given in (*1*); the complete spectra are being prepared for publication.

The Mars spectra were obtained from 5700 to 6950 cm^{-1} (1.44 to 1.75 μ) with a resolution of about 1 cm^{-1}, and from 4050 to 4550 cm^{-1} (2.20 to 2.47 μ) with a resolution of about 4 cm^{-1}. They are reproducible and include the expected telluric and solar lines.

The Mars spectra were obtained mainly in order to measure absorption by lines in the 1.6-μ CO_2 bands to enable more precise estimation of the surface pressure. The CO_2 bands did indeed appear in the spectra, with the lines in the low-frequency branches resolved, but they were severely overlapped by unexpected absorption fea-