

**BORATE STRUCTURES FORMED AT AMBIANT PRESSURES:  
EQUALLY BONDED O ATOMS AS A KEY TO UNDERSTAND THE APPORTION OF  
BO<sub>3</sub> TRIANGLES AND BO<sub>4</sub> TETRAHEDRA**

by

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The anion complexes of borates, formed at ambient pressures, are characterized by BO<sub>3</sub> triangles and/or BO<sub>4</sub> tetrahedra. which may be isolated or linked in different ways by means of shared O atoms. Borates formed at high pressure are, however, built up of only BO<sub>4</sub> tetrahedra (or one gets there in steps with increasing pressure, e.g. CaB<sub>2</sub>O<sub>4</sub>).

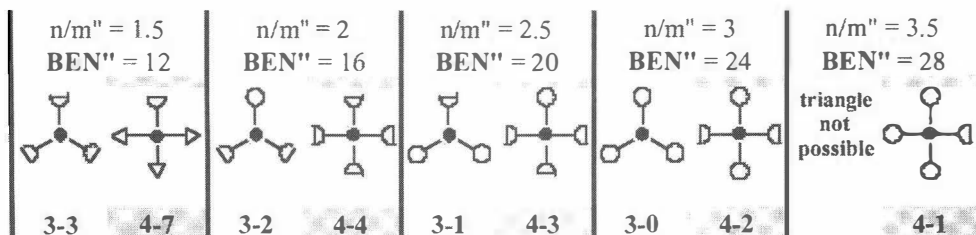
Comparing alkali borates formed at ambient pressures previous investigators had noted that the more alkali in the compound the more BO<sub>4</sub> tetrahedra occur. For other borates the partition of triangles and tetrahedra seemed arbitrary. Here will be given explanations.

The anion complex in a borate can be constructed with base triangles and/or base tetrahedra. Base polyhedra are the smallest building units consisting each of one central atom surrounded by anions, i.e. here 3 or 4 O atoms, respectively, the anion count being different depending if it is endstanding (1) or shared with other base polyhedra (1/2, 1/3). The base triangles and tetrahedra, for which the graphs are shown below, can be characterized by their anion to central atom ratio ( $\cong n/m$ ", here it is the O/B ratio) and the **Base polyhedron Electron Number** ( $\cong \mathbf{BEN}''$ "), i.e. sum of the number of electrons for all central atom - anion bonds (2c2e) and lone-electron pairs (1c2e) on the anions which have completed octets. In the last line of the figure are given two-numeral codes of the base polyhedra with the coordination number of the central atom, on the left, and, on the right, the total number of bonds the anions extend to central atoms of other base polyhedra. One should take note that isoelectronic base triangles and base tetrahedra, i.e. those with some  $n/m$ " and  $\mathbf{BEN}''$ ", have different numbers of anion bonds to other base polyhedra.

The partition of base triangles and base tetrahedra in the anion complexes of borates, formed at ambient pressures, can be explained based on the following hypothesis:

**The anion complex is preferably built with base triangles (if the O/B ratio permits), but precedence takes that all O atoms have the same number of O-(B,H) bonds, whenever possible.**

This condition, attributable to entropy requirements, can be satisfied, if needed, by changing an appropriate number of base triangles into isoelectronic base tetrahedra, where, as seen in the figure, the anions extend a larger number of bonds to other base polyhedra.



$1.5 \leq O/B_{a.c.} < 2$  ( $12 \leq BEN''_{a.c.} < 16$ ): An anion complex (a.c.) constructed with base triangles alone would contain a mixture of 3-3 and 3-2 base triangles in the ratio  $(2 - O/B_{a.c.}) : (O/B_{a.c.} - 1.5)$ . But this combination of base triangles has both endstanding and shared O atoms. By changing all 3-2 base triangles into isoelectronic 4-4 base tetrahedra all O atoms in the structure are now shared, i.e. equally bonded to two B atoms.

Application: Predicted (and observed) ratios of 3-3 base triangles to 4-4 base tetrahedra in alkali borates without hydroxyl groups: -  $B_2O_3$  (1:0),  $CsB_9O_{14}$  (8:1),  $KB_5O_8$  (4:1),  $Na_2B_8O_{13}$  (3:1),  $K_5B_{19}O_{31}$  (14:5),  $CsB_3O_5$  (2:1),  $Li_3B_7O_{12}$  (4:3),  $K_2B_4O_7$  (1:1).

If the anion complex has hydroxyl groups the base polyhedra must have as many endstanding O atoms as there are hydroxyl groups for forming O-H bonds. Thus for a given B/O ratio the partition of base triangles and tetrahedra will vary depending on the number of OH groups.

Example:  $(NH_4)_3B_{15}O_{20}(OH)_8 \cdot 4H_2O$ : A complex with  $O/B = 28/15$ , constructed alone with base triangles, would consist of four 3-3 and eleven 3-2 base triangles, the latter with one endstanding anion. Eight endstanding O atoms are needed for the eight OH groups. If the remaining three 3-2 base triangles are changed to isoelectronic 4-4 base tetrahedra, then all O atoms have two bonds, i.e. five O to 2B and eight O to 1B and 1H. In this way one can explain why the complex is constructed of four 3-3, eight 3-2 and three 4-4 base polyhedra.

$O/B = 2$  ( $BEN'' = 16$ ): For borates without hydroxyl groups are available 3-2 base triangles (with one endstanding and two shared O atoms) and 4-4 base tetrahedra (where all anions are shared). Based on the preferred equi-bonding of O atoms one might expect to find only 4-4 base tetrahedra. However, the expected quartz-like structure of the anion complex would – given the small radius of B ( $r_B = 0.25 \text{ \AA}$ ) – not leave enough space for the cations. Thus in the borates without hydroxyl group occur only 3-2 triangles.

Mixtures of 3-2 triangles and 4-4 tetrahedra occur, however, in borates with hydroxyl groups. The triangle to tetrahedron ratio is as above determined by the number of hydroxyl groups in the formula. All O atoms have two bonds either to two B atoms or one B and one H.

Examples             $Ag_2B_4O_6(OH)_2 \cdot H_2O$             Two 3-2 triangles and two 4-4 tetrahedra  
                           $KB_5O_6(OH)_4 \cdot 2H_2O$             Four 3-2 triangles and one 4-4 tetrahedron

$O/B = 2.5$  ( $BEN'' = 20$ ): Pyroborates without hydroxyl groups, such as suanite  $Mg_2B_2O_5$ , are constructed with 3-1 base triangles. An incentive to change to the isoelectronic 4-3 base tetrahedra is lacking as also there the O atoms have unequal bonding.

**O/B = 3 (BEN" = 24):** In borates without hydroxyl groups, such as kotoite  $Mg_3B_2O_6$ , occur 3-0 base triangles where all O atoms are endstanding, participating on one O-B bond.

In borates with hydroxyl groups, such as vimsite  $CaB_2O_2(OH)_4$ , two of the endstanding O per base polyhedron are used for the two OH groups. These O atoms have two bonds (1 to B and 1 to H). To allow two bonds also for the remaining O atom the 3-0 base triangle changes into the isoelectronic 4-2 base tetrahedron.

**O/B = 3.5 (BEN" = 28):** Base triangles with  $O/B > 3$  do not exist, thus only 4-1 base tetrahedra will occur. The anion complex is similar to that found in sorosilicates. The six endstanding O are bonded to H atoms and the seventh bridging O atom to two B atoms. Thus all O atoms extend two bonds. A mineral example is pentahydroborite  $CaB_2O(OH)_6 \cdot 2H_2O$ .

**O/B = 4 (BEN" = 32):** These borates are fully hydroxylated, as for example frovolite  $CaB_2(OH)_8$ . As anion complex can exist only an isolated tetrahedron (4-0 base tetrahedron) where all four endstanding O atoms extend a bond to an H atom.