



CRYSTAL-CHEMISTRY OF BORATES *

Boron presents two kinds of coordination, triangular and tetrahedral. A crystal-chemical classification is described founded in the number of atoms characteristics of the fundamental building block. Also some examples are given in this paper.

(*) Communication presented at VII Congresso Iberoamericano de Cristalografía, Coimbra, September 1981.
Manuscript received 29.3.1982.

Boron, like silicon is found very abundantly in nature in the form of oxygenated compounds. Structural studies of silicates have shown that, in almost all these compounds, the silicon is surrounded by a tetrahedral group of four oxygen atoms, and, according to this, they may be classified by the ratio O:Si. The borates might be expected to be based in BO_3 coordination groups, so that classification might be made in a similar way to that of silicates. In fact, the oxygenated chemistry of boron is much more complex, since the boron has been found not only with triangular coordination, but also with coordination index four. The borates in which all the boron atoms have coordination three, correspond to the simple previous outline, but, due to the two different coordination indices found in many of these compounds, there is no simple connection between the ratio O:B and the type of complex in the crystal.

It has not yet been understood what determines the coordination index of the boron in a particular compound. For example, in the α -metaboric acid, and also in calcium and potassium metaborates, all the boron atoms have triangular coordination, while both groups BO_3 and BO_4 exist in the monoclinic form of the metaboric acid. On the other hand, in zinc metaborate, and in another form of metaboric acid, γ -metaboric, all the boron atoms have coordination index four.

Recognition of this fact, as the result of structural studies, has led to revision of many formulas. For example, the structural formula of colemanite, $\text{Ca}_2\text{B}_6\text{O}_{11} \cdot 5\text{H}_2\text{O}$, is $\text{CaB}_3\text{O}_4(\text{OH})_3 \cdot \text{H}_2\text{O}$; bandilite is not $\text{CuCl}_2 \cdot \text{CuB}_2\text{O}_4 \cdot 4\text{H}_2\text{O}$, but $\text{CuClB}(\text{OH})_4$, and even borax, $\text{B}_4\text{O}_7\text{Na}_2 \cdot 10\text{H}_2\text{O}$, provides us with a good example of revision of a familiar chemical formula, since its structural formula is $\text{Na}_2(\text{B}_4\text{O}_5(\text{OH})_4) \cdot 8\text{H}_2\text{O}$. On the other hand, zinc metaborate had always been formulated as $\text{Zn}(\text{BO}_2)_2$, yet the true formula is $\text{Zn}_4\text{O}(\text{BO}_2)_6$.

All these facts give a great interest to the study of the stereochemistry of boron.

We are now going to summarise some of the structural characteristics of the borates studied up to now in those aspects referring to the coordination of boron.

ORTHOBORIC ACID AND ORTHOBORATES

ORTHOBORIC ACID

In orthoboric acid, the plane $B(OH)_3$ molecules are joined by hydrogen bridges, forming layers.

ORTHOBORATES

The first X-ray studies established the plane form of the BO_3^{3-} ion, proving that the $InBO_3$, $ScBO_3$ and a form of the YBO_3 have the structure of calcite, and that the $LaBO_3$ has that of aragonite.

Similary, the ion BO_3^{3-} is present exclusively in cobalt, magnesium and zinc orthoborates. It is certain that, due to the stoichiometry of these compounds, orthoborate can not have any other anionic grouping than one based on BO_3 triangles.

PYROBORATES

Two rather different forms from pyroborate ion have been found in the corresponding salts of Mg and Co, although the grouping consists of two BO_3 triangles sharing a vertex. The essential difference lies in the angle formed by the BO_3 planes; in the $Co_2B_2O_5$, the angle is 7° and the two planes are rotated in the opposite direction, whereas in the $Mg_2B_2O_5$, the angle between the planes of the BO_3 groups is $22^\circ 19'$.

METABORIC ACID AND METABORATES

METABORIC ACID

The situation is more complex in this type of compounds, due to the existence of coordination indices three and four for the boron atom. For example, the structure of the form γ of metaboric acid consists of a cubic network in which the boron is coordinated wholly tetrahedrally: the β - HBO_2 , crystallizes in the monoclinic systems and the boron has double coordination, triangular and tetrahedral, whereas the α - HBO_2 contains exclusively BO_3 triangles sharing two vertices, and forming rings of six members in combining three of these BO_3 groups.

METABORATES

In metaborates cyclical and in chain ions have been found. The hexagonal ring formed for three BO_3 triangles, forms the cyclical anion $B_3O_6^{3-}$ of sodium

and potassium metaborates which could, therefore, be written as $Na_3B_3O_6$, and $K_3B_3O_6$ respectively. BaB_2O_4 has the same unit.

In the metaborates, ions in infinite chain may exist; this is the case with calcium metaborate, in one of its forms, which contains chains of BO_3 triangles sharing the vertices, which is the analogous chain with piroxene SiO_3^{2-} .

On the other hand, CaB_2O_4 phase (III) of high pressure contains the unit $B_6O_{12}^{6-}$, consisting of the grouping of four BO_4 tetrahedrons and two BO_3 triangles, sharing among them all its vertices.

In an extreme situation, containing exclusively BO_4 tetrahedrons, there are the metaborates: $Zn_4O(BO_2)_6$, CuB_2O_4 , CaB_2O_4 phase (IV) of high pressure, and $LiBO_2$ (III).

OTHER BORATES

The borates whose stoichiometry is not included in the above sections, contain, apart from the ions cited above, other complex anions resulting from the combination of BO_4 tetrahedrons and BO_3 triangles.

Thus, a tetrahedron and four triangles sharing the four vertices of the first polyhedron, and in turn sharing a vertex among themselves, give rise to the ion $B_5O_{10}^{5-}$, which is part of the structure of potassium pentaborate, KB_5O_8 .

Two BO_4 groups and two BO_3 give rise to the unit B_4O_9 found in borax, $B_4O_7Na_2 \cdot 10H_2O$. The same anionic unit exists in cadmium and zinc diborates, CdB_4O_7 , ZnB_4O_7 .

The combination of two BO_4 tetrahedra and one BO_3 triangle gives rise to the ion $[B_3O_4(OH)_3]_n^{2n-}$, found in colemanite, meyerhofferite and inyoite minerals, which are members of a series originally formulated as $Ca_2B_6O_{11} \cdot nH_2O$:

		Structural formula
$Ca_2B_6O_{11}$		
$\cdot 5H_2O$	Colemanite	$Ca B_3O_4(OH)_3 \cdot H_2O$
$\cdot 7H_2O$	Meyerhofferite	$Ca B_3O_3(OH)_5 \cdot H_2O$
$\cdot 9H_2O$	(synthetic)	$Ca B_3O_3(OH)_5 \cdot 2H_2O$
$\cdot 11H_2O$	(unknown)	
$\cdot 13H_2O$	Inyoite	$Ca B_3O_3(OH)_5 \cdot 4H_2O$

Having seen it in this way it seems desirable to attempt a more coherent classification of borates.

PROPOSED PRINCIPLES FOR CLASSIFICATION OF BORATES

TENYSON in (1963) [1] presented a crystal-chemical classification of borates based on their analogy with silicates, using the terms nesoborates, soroborates, inoborates (chains), phylloborates (sheets) and tektoborates (three-dimensional network). This classification could be used if the number of boron atoms in the essential ring were stated as well as the proposed name. For example inyoite is a soroborate with $n=3$ and borax is a soroborate with $n=4$.

EDWARDS and ROSS in (1960) [2] formulated their classification on the basis that «the relation of the tetrahedral boron to the total boron is equal to the relation of the charge of the cation to the total boron», which is equivalent to saying that each $B(OH)_4$ tetrahedron introduces a negative charge when it enters in a polyanion. Unfortunately this postulate falls down for all hexaborate polyanions and for partially hydrated polyanions.

LIMA DE FARIA and FIGUEIREDO in (1976) [3] in a general classification of inorganic structures, include borates within the latter, grouped according to chains, sheets and frameworks. Finally HELLER in (1970) [4] and CHRIST and CLARK in (1977) [5] base their classification on the number of boron atoms in what they call the fundamental building block which seems in principle a good idea for classifying borates.

DEFINITION OF MODULES OF FUNDAMENTAL CONSTRUCTION AND RESULTING POLYANIONS

Obviously the units making up the polyanions are triangles and tetrahedra: BO_3 and BO_4 . Each such unit may appear isolated in the structure. Defining n as the number of atoms characteristic of the fundamental building block, n would be equal to 1 for these simple units. Using a simple notation we can distinguish the cases of isolated triangles $1:\Delta$ and isolated tetrahedra $1:T$. Each unit may be combined with others of its class to form pairs (dimers), chains, sheets or three-dimensional network (T only). The notation will then be $2:\Delta$ or $2:T$ for isolated pairs, $1:\Delta$ or $1:T$ to indicate chains, $1:\Delta_2$ or $1:\Delta_3$ for sheets, and $1:\Delta_3$ for three-dimensional networks.

TRIBORATES

The true polyanions in which triangles and tetrahedra may exist together begins with $n=3$. The tribo-

rate module is illustrated in fig 1 and may be completed with triangles or tetrahedrons in four forms with notations $3:3\Delta$, $3:2\Delta + T$, $3:\Delta + 2T$, $3:3T$.

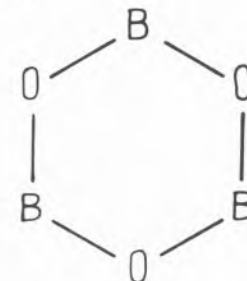
The following may be cited as examples:

$3:3\Delta$ α -metaboric acid and the anhydrous sodium and potassium borates $Na_3B_3O_3$ and $K_3B_3O_3$.

$3:2\Delta + T$ ameginite, β form of metaboric acid and CsB_3O_3 .

$3:\Delta + 2T$ is the most frequent in isolated forms, chains, sheets and framework; inyoite; meyerhofferrite and colemanite.

$3:3T$ nifontovite.



$n = 3$

Fig. 1

TETRABORATES

For $n=4$ we have the same two cases whose modules are represented in fig. 2, 4-1 and 4-2 which can be completed with triangles and tetrahedra giving the respective polyanions.

The tetraborate unit 4-1: $2\Delta + 2T$ was first found in the structure of borax. Other forms also completely hydrated have the same structure, tincalconite; hungchaoite, in all these cases the polyanion is isolated.

The same polymerized unit is found in kernite forming chains.

The unit 4-2: $4T$ is found isolated in borcarite.

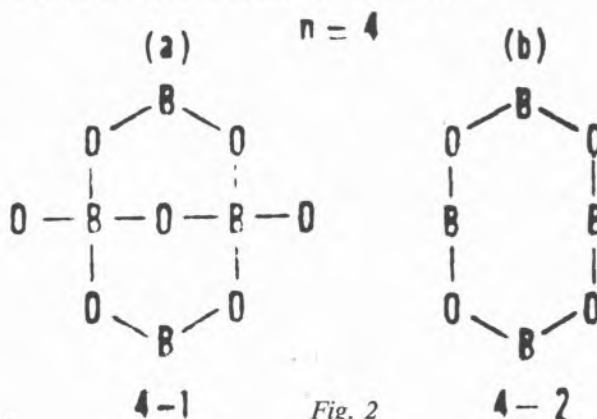


Fig. 2

PENTABORATES

The pentaborate module can be seen in fig. 3. The pentaborate unit $5:4\Delta+T$ was found many years ago by Zachariasen in the structure of synthetic potassium borate $K[B_5O_6(OH)_4] \cdot 2H_2O$. The corresponding mineral santite has the same structure.

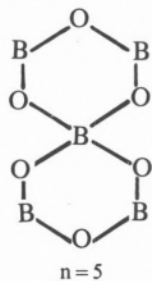


Fig. 3

HEXABORATES

The hexaborate module is shown in fig. 4 and may be completed in four different ways giving place to the hydrated forms $6:3\Delta+3T$, $6:6T$, $6:2\Delta+4T$,

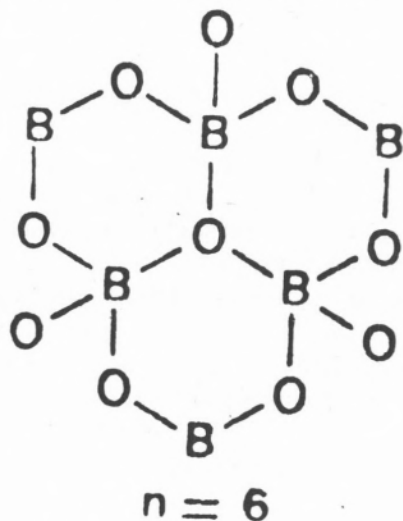


Fig. 4

$6:\Delta+5T$. These structures are made up of isolated polyanions, chains and sheets. One of the most well-known is the tunelite $6:3\Delta+3T$ whose units link up forming sheets. Chains of $3\Delta+3T$ have found in aristarainite and isolated units in rivadavite.

$$\underline{n > 6}$$

So far only one borate with $n > 6$ is known. This has $n = 9$, fig. 5, and is found modified in the structure of the preobranzhenskite.

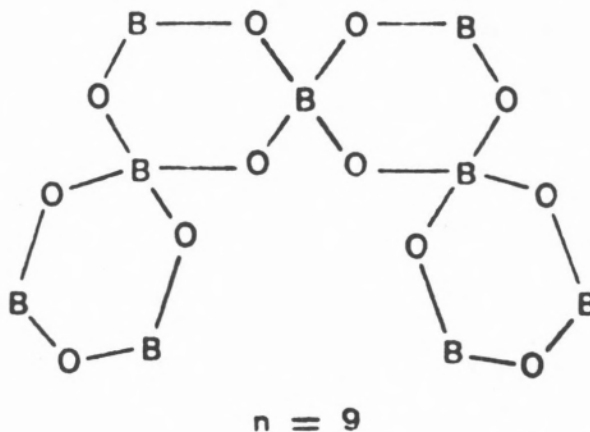


Fig. 5

REFERENCES

- [1] C. TENNYSON, *Fortshr. Mineral.*, **41**, 64-91 (1963).
- [2] J. O. EDWARDS, V. F. ROSS, *J. Inorg. Nucl. Chem.*, **15**, 329-337 (1960).
- [3] J. LIMA DE FARIA, M. O. FIGUEIREDO, *J. Sol. Stat. Chem.*, **16**, 7-20 (1976).
- [4] G. HELLER, *Fortschr. Chem. Forschung.*, **15**, 206-280 (1970).
- [5] C. L. CHRIST, J. R. CLARK, *Physc. and Chem. of Minerals*, **2**, 58-88 (1977).