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The structure and classification of complex borates

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The review is devoted to systematic analysis of polyborate structures based on the recognition of fundamental building blocks. A wide range of inorganic polyborates are analyzed. The approach makes it possible to identify the place of new compounds among previously investigated ones, to compare their structures and to reveal structural features in order to substantiate the properties of novel materials and to optimize their search.
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1. Introduction

Inorganic borates known to date form a large class of chemical compounds. These include various metal compounds whose anionic fragments comprise boron atoms coordinated to three or four oxygen atoms to form BO_3 triangles and BO_4 tetrahedra. Dual coordination fashion of boron atoms underlies a unique position of borates among other classes of inorganic compounds including silicates, phosphates, nitrates and carbonates. Usually, borate structures have complex architectures composed of the basis triangles and tetrahedra, which makes them structurally similar to organic compounds. Borates were first discovered as natural minerals that most often have simple structures of boron – oxygen anions.

Inorganic synthesis of new borates aimed to design advanced materials is carried out under conditions that resemble environmental conditions to one or another extent. For instance, borates suitable for optical applications (in particular, second harmonic generation) as well as those exhibiting luminescent, magnetic and other properties were synthesized. Most borates were synthesized hydrothermally; this method simulates natural exogenous and low-temperature endogenous mineralization conditions. Boron atoms in these compounds are constituents of boron – oxygen tetrahedra and triangles. A large number of borates were obtained from high-temperature melts. Such compounds have rather simple structures with mainly triangular coordination of boron atoms and contain no bound water. A feature of borates synthesized at high temperatures and pressures consists in mainly tetrahedral coordination of most boron atoms, which relates these borates to silicates.

Structural classifications of borates are more complicated than those of silicates owing to dual coordination fashion of boron atoms and a wide variety of boron – oxygen radicals.† The best known and most widely used classification was proposed by C.L.Christ and J.P.Clark.[1] Having admitted the validity of borate classification by analogy with silicates,‡ they put forward a new criterion, *viz.*, the fundamental building block (FBB), *i.e.*, an independent boron – oxygen unit composed of boron polyhedra. The notation of a FBB represents a character string which includes the total number of boron atoms in the block and

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† A boron-oxygen radical is a group of boron and oxygen atoms representing the anionic constituent (part) of a borate structure.
‡ Silicates are classified into six subclasses including isolated tetrahedral, ring, chain, ribbon, layered and framework structures.

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the symbols Δ for the BO_3 triangle and T for the BO_4 tetrahedron. The FBB constituents are put in braces, the boron – oxygen polyhedra specified in the Δ/T terms are put in square brackets; and the number of infinity signs placed as subscripts at the end of the character string denotes a 1D, 2D or 3D anionic radical. Depending on the number of boron polyhedra, there are mono-, di-, tri-, tetra-, penta- and hexaborate blocks. Most researchers have used this approach to analysis and classification of borate structures for decades.

Burns *et al.*[2] proposed a new classification system for borate structures with the recognition of three-membered rings of boron – oxygen polyhedra as the most stable structural fragments. Their classification is based on analysis of the types and fashion of the condensation of such fragments into complex radicals that are described using additional symbols specifying the type of connection of the boron – oxygen polyhedra. Namely, the symbol $<\ldots>$ denotes a ring of boron – oxygen polyhedra, while the symbols '–' and ' = ' separating two rings indicate the number of shared polyhedra (one or two, respectively), and the symbol □ denotes a tetrahedron. For instance, the character string $<\Delta 2\square> - <2\square\Delta>$ describes a pentaborate unit that can be treated as a result of condensation of two three-membered rings. The structural divisions proposed by Christ and Clark[1] are discarded and the structural classifications of borates available prior to publication of the study by Burns *et al.*[2] thus appear outside the new system.

Most synthetic inorganic compounds have natural prototypes, *viz.*, natural minerals. Strunz[3] developed a classification system for all minerals including borates. It is based on the recognition of FBBs according to Christ and Clark.[1] The groups of mono-, di-, tri-, tetra-, penta- and hexaborates include compounds built up of units containing the same number of boron polyhedra and variable number of BO_3 triangles and BO_4 tetrahedra; the number of boron atoms in the notation specifies affiliation to a certain group. Within each group, compounds are classified with respect to the extent of condensation of a given block with subdivision into soro- (isolated groups), ino- (chain), phyllo- (layered) and tecto- (framework) units. Borates with anionic radicals described by more complex notations are treated as mega- or polyborates.

The classification by Strunz[3] was refined and extended in yet another study[4] that appeared to be in-demand. The classical approach used in this revealed structural-genetic series in each group of borates and described structural transitions in each series. As to polyborates, only a few examples of their structures were presented without detailed analysis.

Our review was inspired by the wish to continue efforts[4] to classify polyborates and by the study of Wei *et al.*,[5] who noticed that two types of borate clusters (more exactly, building blocks) are rare to occur since it is difficult to realize Pauling's fifth rule. This opinion was strengthened by two references.[6,7] Pauling's fifth rule is also called the principle of parsimony. According to this rule, the number of essentially different types of constituents of a stable structure tends to be small, which limits the diversity of inorganic compounds (see, *e.g.*, Ref. 8). Advances in inorganic synthesis suggest that this rule holds only for very simple structures (as applied to borates, mainly for those obtained at high temperatures).

In this review, we use the approach by Christ and Clark[1] to systematically analyze the structure of polyborates. A clear-cut division is made between condensed complex borates whose structures are made up of same-type building blocks containing more than six boron atoms and polyborates composed of two and more different types of building blocks. The structures of recently synthesized different-composition borates are considered and their classification and crystal chemical characteristics are refined.

2. The structure of borates: a crystallographic description

The term 'polyborates' (identical term is 'megaborates') was proposed by Christ and Clark[1] and Strunz.[3] Borates known by the time of publication of those studies mainly included compounds whose structures were composed of same-type blocks. Recently synthesized borates are significantly different from them in this respect and demonstrates diversity of blocks in one structure. Using the classification of Burns *et al.*,[2] one can lose key structural fragments, *e.g.*, a basis ring radical, and the possibility to reveal structural similarity between compounds. This method[2] is mathematical (rather abstract) in character and inappropriate for the determination of the polarity and arrangement of structural fragments, *i.e.*, the basis features underlying the properties of compounds and the possibility of further search. This approach is used to study not only borates, but also, *e.g.*, borophosphates.[9] An attractive feature of the method is its simplicity; in particular, there is no need for detailed analysis of various projections to reconstruct the 3D structure. The authors of a monograph[10] devoted to high-temperature crystal chemistry of borates considered a number of phases using a hybrid characterization technique and the methods of Christ and Clark[1] and Burns *et al.*;[2] in the latter case, the emphasis was placed on bridging oxygen atoms that act as anchors for structural blocks and are used for monitoring their temperature-induced deformations.

Progress in theory and experimental techniques has made it possible to solve a wide variety of new structures, and the problem of characterizing the complexity of crystal structures became relevant.[11,12] However, in the case of materials science research it is more important to correctly assess the results of synthesis bearing in mind further analysis of the structure and comparison with the known compounds rather than to characterize the complexity of structures *per se*.

Table 1 presents selected structural data for borates that exemplify the classification system of Christ and Clark.[1] It also lists structural data for compounds that at first glance can be treated as polyborates since corresponding notations include more than six boron atoms. However, anionic radicals of these compounds are built up of same-type blocks and therefore one deals with condensed borates belonging to corresponding groups (see above) rather than polyborates. Structural data for polyborates built up of different-type blocks are listed in Table 2. They are classified from structures composed of combinations of hexaborate blocks with different-type (penta-, tetraborate, *etc.*) blocks to structures containing combinations of penta-, tetra-, tri- and diborate blocks with simpler different-type blocks. This approach allows one to unambiguously characterize the structure of the anionic radical of any polyborate and to correctly compare and classify the structures.

Table 1. Selected parameters of borate structures with same-type FBBs.

Chemical formula	Space group	Lattice constants		Boron – oxygen radical		Ref.
		linear dimensions /Å	angles /deg	type	notation	
			Hexaborates			
$Sr_2[B_{12}O_{18}(OH)_4]\cdot 6\,H_2O$ (tunellite)	$P2_1/c$	$a = 9.934$, $b = 8.213$, $c = 14.390$	$\beta = 114.0$	Layer	$6[3\Delta + 3T]_{\infty\infty}$	13
$Ho[B_6O_9(OH)_3]$ (see [a])	$R3c$	$a = 8.385$, $c = 20.710$		Framework	$6[3\Delta + 3T]_{\infty\infty\infty}$	14
$(Li_{5.5}Fe_{0.5})FePb[B_6O_{12}]_2$	$R\bar{3}$	$a = 13.71$, $c = 6.554$		Chain	$6[3\Delta + 3T]_{\infty}$	15
			Pentaborates			
$BaB_5O_8(OH)\cdot H_2O$ (tunellite)	$P\bar{1}$	$a = 6.781$, $b = 6.901$, $c = 9.737$	$\alpha = 102.55$, $\beta = 91.51$, $\gamma = 119.72$	Layer	$5[3\Delta + 2T]_{\infty\infty}$	16
$Na_2[B_4O_6(OH)_2]\cdot 3\,H_2O$ (kernite)	$P2_1/c$	$a = 7.017$, $b = 9.158$, $c = 15.677$	$\beta = 108.9$	Chain with shared tetrahedron	$4:\{5[2\Delta + 3T] - 1T\}_{\infty}$	17
$Na_2Ba_2[B_{10}O_{17}(OH)_2]$	$A2$	$a = 9.362$, $b = 6.678$, $c = 11.46$	$\beta = 93.48$	Layer	$10:\{2 \times 5[2\Delta + 3T]_{\infty\infty}\}$	18
$Na_2Cs_2[B_{10}O_{17}]$ (see [b])	$C2/c$	$a = 21.711$, $b = 6.446$, $c = 10.952$	$\beta = 105.997$	"	$10:\{2 \times 5[3\Delta + 2T]_{\infty\infty}\}$	19
$LiBa_2[B_{10}O_{16}(OH)_3]$	$P\bar{1}$	$a = 6.732$, $b = 11.369$, $c = 11.581$	$\alpha = 119.31$, $\beta = 90.11$, $\gamma = 73.08$	"	$10:\{2 \times 5[2\Delta + 3T]_{\infty\infty}\}$	20
$Ag_2Cs[B_{15}O_{24}]$	$P2_12_12$	$a = 17.811$, $b = 22.218$, $c = 5.132$		Highly corrugated layer	$15:\{3 \times 5[4\Delta + 1T]_{\infty\infty}\}$	21
$Ba_5[B_{20}O_{33}(OH)_4]\cdot H_2O$	$P2$	$a = 9.362$, $b = 6.713$, $c = 11.709$	$\beta = 95.09$	Layer	$20:\{2 \times 10(5[3\Delta + 2T] + 5[2\Delta + 3T])_{\infty\infty}\}$	18
$Rb_3[B_7O_{12}]$	$P\bar{1}$	$a = 6.603$, $b = 6.632$, $c = 30.085$	$\alpha = 91.19$, $\beta = 91.78$, $\gamma = 119.29$	Double layer	$14:\{2 \times 5[3\Delta + 2T] + 4[2\Delta + 2T]_{\infty\infty}\}$	22
$(Nd_{0.952}Na_{0.075})Nd[B_9O_{15}.(OH)Cl_{0.85}]\cdot 2.65\,H_2O$	$P2/n$	$a = 10.699$, $b = 6.405$, $c = 23.154$	$\beta = 92.55$	"	$9:\{(5[2\Delta + 3T])_{\infty} + (4:3[1\Delta + 2T] + [1\Delta])_{\infty}\}_{\infty\infty}$	23
$Cs_3[B_{13}O_{21}]$	$C2/c$	$a = 23.064$, $b = 13.367$, $c = 24.464$	$\beta = 90.288$	Layer	$13:\{2 \times 4[3\Delta + 1T]_{\infty\infty} + 5[4\Delta + 1T]_{\infty}\}_{\infty\infty}$	24
			Tetraborates			
$CuTm_2[B_4O_{10}]$	$P2_1/c$	$a = 4.522$, $b = 7.200$, $c = 9.292$	$\beta = 90.16$	Layer	$4:[4T]_{\infty\infty}$	25

Table 1 (continued).

Chemical formula Ref.	Space group	Lattice constants		Boron – oxygen radical		
		linear dimensions /Å	angles /deg	type	notation	
			Triborates			
$Ba_2[B_6O_9(OH)_4]$	$P2_1$	$a = 6.828$, $b = 8.706$, $c = 8.441$	$\beta = 100.65$	Layer	$6{:}\{2 \times 3[2\Delta + 1T]\}_{\infty\infty}$	26
$Sr_3B_6O_{11}F_2$ (see [c])	$P2_1$	$a = 6.558$, $b = 8.511$, $c = 9.673$	$\beta = 101.21$	Framework	$6{:}\{2 \times 3[1\Delta + 2T]\}_{\infty\infty\infty}$	27, 28
$LiBa[B_9O_{15}]$ (see [d])	$R\bar{3}c$	$a = 10.982$, $c = 17.067$		"	$3 \times 3[2\Delta + 1T]_{\infty\infty\infty}$	29
$[Ni(en)_2]_6[(VO)_{12}O_6]$. $.B_{18}O_{39}(OH)_3] \cdot 5\,H_2O$	$R\bar{3}c$	$a = 20.824$, $c = 21.050$		Isolated rings	$18{:}\{6 \times (3[1\Delta + 2T])\}$	30
$Ba_2KZn_3[(B_3O_6)(B_6O_{13})]$	$P\bar{1}$	$a = 7.052$, $b = 7.125$, $c = 18.803$	$\alpha = 93.4$, $\beta = 90.7$, $\gamma = 119.6$	Isolated groups	$9{:}\{3[3\Delta] + 6(2 \times 3[2\Delta + 1T])\}$	31
$Ba_4Na_2Zn_4[(B_3O_6)_2(B_{12}O_{24})]$	$P\bar{1}$	$a = 7.029$, $b = 7.069$, $c = 17.501$	$\alpha = 91.92$, $\beta = 96.46$, $\gamma = 119.72$	The same	$18{:}\{6(2 \times 3[3\Delta]) + 2 \times 6(3[2\Delta + 1T] + 3[2\Delta + 1T])\}$	32
$Na_{11}[B_{21}O_{36}]Br$	$C2/c$	$a = 15.722$, $b = 8.951$, $c = 24.089$	$\beta = 100.788$	Layer	$21{:}\{2 \times 6(3[2\Delta + 1T] + 3[1\Delta + 2T])_{\infty\infty} + 9(3 \times 3[2\Delta + 1T])\}_{\infty\infty}$	33
			Diborates			
$Pb_2[B_4O_5(OH)_4](OH)_2 \cdot H_2O$	$C2$	$a = 9.441$, $b = 8.370$, $c = 6.425$	$\beta = 179.0$	Layer	$4{:}\{2 \times 2[1\Delta + 1T]\}_{\infty\infty}$	34

Note. The isostructural compounds listed below have boron – oxygen radicals of the same type and notations as those of the borates specified.

[a] This borate is isostructural to compound $Gd[B_6O_9(OH)_3]$.[13]

[b] This borate is isostructural to compounds $Na_2Tl_2[B_{10}O_{17}]$ and $Cs_2K_2[B_{10}O_{17}]$.[19]

[c] This borate is isostructural to compounds $Ba_3B_6O_{11}F_2$ and $Pb_3B_6O_{11}F_2$.[27, 28]

[d] This borate is isostructural to compound $K_3[B_9O_{15}]$.[29]

Table 2. Selected structural data for polyborates.

Chemical formula	Space group	Lattice constants		Boron–oxygen radical		Ref.
		linear dimensions /Å	angles /deg	type	notation	
			Hexa- + monoborates			
$Li_3[B_8O_{12}(OH)_3]$	$P\bar{6}2c$	$a = 8.930$, $c = 15.996$		Layer	$18{:}\{3\times(6[3\Delta+3T]-[1\Delta])+[1\Delta]\}_{\infty\infty}$	35
$Mg_3[B_7O_{13}]Cl$ (boracite)	$F\bar{4}3c$	$a = 12.99$		Framework	$7{:}\{6[6T]+[1\Delta]\}_{\infty\infty\infty}$	36
γ-$Li_4[B_7O_{12}]Cl(Br)$	$F\bar{4}3c$	$a = 12.141$		"	$7{:}\{6[3\Delta+3T]+[1\Delta]\}_{\infty\infty\infty}$	37
$Mn_3[B_7O_{13}]Cl$	$Pca2_1$	$a = 8.678$, $b = 8.689$, $c = 12.296$		"	$7{:}\{6[6T]+1\Delta\}_{\infty\infty\infty}$	38
$Pb_3[B_9O_{16}](OH)\cdot B(OH)_3$ (see [a])	$P31c$	$a = 10.07$, $c = 8.53$		"	$10{:}\{9(6[6T]+3\times[1\Delta])_{\infty\infty\infty}+[1\Delta]\}$	39
$NaBa_3[B_9O_{16}](OH)\cdot B(OH)_4$ (see [b])	$P1$	$a = 10.253$, $b = 10.286$, $c = 8.769$	$\alpha = 90.17$, $\beta = 89.80$, $\gamma = 120.02$	"	$10{:}\{9(6[6T]+3\times[1\Delta])_{\infty\infty\infty}+[1\Delta]\}$	40
$Pb_6[B_{12}O_{24}]\cdot H_2O$	$R\bar{3}m$	$a = 11.4326$, $c = 17.385$		Isolated rings	$12{:}\{[6T]+6\times[1\Delta]\}$	41
$Pb_6(Li_{0.648}Na_{0.192})[B_{12}O_{24}]\cdot I_{0.84}\cdot 0.168\,H_2O$	$R\bar{3}m$	$a = 11.472$, $c = 17.229$		The same	$12{:}\{[6T]+6\times[1\Delta]\}$	42
$Zn_6[B_{12}O_{24}]\cdot 6.72\,H_2O$	$R\bar{3}m$	$a = 11.410$, $c = 17.156$		"	$12{:}\{[6T]+6\times[1\Delta]\}$	42
$Na_8[B_{12}O_{20}(OH)_4]\cdot H_2O$ (see [c])	$P2_1/c$	$a = 8.7096$, $b = 11.9176$, $c = 9.4686$	$\beta = 96.0$	"	$12{:}\{[6T]+6\times[1\Delta]\}$	42
$Li_3KB_4O_8$	$R\bar{3}$	$a = 9.211$, $c = 19.705$		"	$12{:}\{[6T]+6\times[1\Delta]\}$	43
$LiNa_2Sr_8[B_{12}O_{24}]F_6Cl$	$R\bar{3}$	$a = 9.677$, $c = 24.30$		"	$12{:}\{[6T]+6\times[1\Delta]\}$	43
$Li_3NaBa[B_6O_{12}]$	$R\bar{3}$	$a = 9.462$, $b = 18.71$		"	$12{:}\{[6T]+6\times[1\Delta]\}$	44
$Ca_9[B_{26}O_{34}(OH)_{24}]Cl_4\cdot 13\,H_2O$ (pringleite)	$P1$	$a = 12.746$, $b = 13.019$, $c = 9.693$	$\alpha = 102.0$, $\beta = 102.0$, $\gamma = 85.6$	"	$12{:}\{[6T]+6\times[1\Delta]\}$	45
$KGd[B_6O_{10}(OH)_2]$	$P\bar{6}2m$	$a = 4.524$, $b = 12.096$		Layer	$6{:}\{[4T]+2\times[1\Delta]\}_{\infty\infty}$	46
$KHo[B_6O_{10}(OH)_2]$	$P\bar{3}1m$	$a = 4.524$, $b = 12.096$		"	$6{:}\{[4T]+2\times[1\Delta]\}_{\infty\infty}$	46
			Hexa- + diborates			
$NaSr_7Al[B_{18}O_{36}]$ (see [d])	$R\bar{3}c$	$a = 11.356$, $c = 36.655$		Isolated rings	$18{:}\{[6T]+6\times[2\Delta]\}$	47
$Ba_{0.975}[B_6O_9(OH)(O_{0.975}Br)\cdot B_2O(OH)_3]$	$P2_1/n$	$a = 7.945$, $b = 13.859$, $c = 10.04$	$\gamma = 90.08$	Layer	$8{:}\{6[3\Delta+3T]+2[2\Delta]\}_{\infty\infty}$	18
$Pb[B_6O_{10}(OH)\cdot B_2O(OH)_3]$	$P2_1/n$	$a = 7.91$, $b = 9.979$, $c = 14.030$	$\beta = 90.36$	"	$8{:}\{6[3\Delta+3T]+2[2\Delta]\}_{\infty\infty}$	13
$Sr[B_6O_{10}(OH)\cdot B_2O(OH)_3]$	$P2_1$	$a = 9.909$, $b = 8.130$, $c = 9.737$	$\beta = 107.46$	"	$8{:}\{6[3\Delta+3T]+2[2\Delta]\}_{\infty\infty}$	13

Table 2 (continued).

Chemical formula	Space group	Lattice constants		Boron – oxygen radical		Ref.
		linear dimensions /Å	angles /deg	type	notation	
			Hexa- + diborates			
$La[B_6O_{10}(OH)\cdot B_2O(OH)_4]$ (see [e])	$P2_1/n$	$a = 9.86$, $b = 7.94$, $c = 14.131$	$\beta = 90.0$	Layer	$8:\{6[3\Delta+3T]+2[\Delta+T]\}_{\infty\infty}$	48
			Hexa- + triborates			
$Nd[B_6O_{10}(OH)\cdot B_3O_3(OH)_4]$ (see [f])	$P2_1/n$	$a = 9.871$, $b = 7.716$, $c = 16.696$	$\beta = 90.0$	Layer	$9:\{6[3\Delta+3T]+3[\Delta+2T]\}_{\infty\infty}$	48
$Ba_2[B_6O_9(OH)_2][B_3O_3(OH)_4].$ $.(OH)\cdot 4\,H_2O$	$Pmn2_1$	$a = 10.168$, $b = 16.232$, $c = 7.554$		Alternating layers of hexa- and triborate blocks	$9:\{6[3\Delta+3T]_{\infty\infty}+3[2\Delta+1T]_{\infty\infty}\}$	5
			Hexa- + mono- + diborates			
$La_4[B_{22}O_{36}](OH)_6\cdot 13\,H_2O$ (see [g])	$I23$	$a = 18.111$		Cluster	$22:\{6[3\Delta+3T]+3\times2[2\Delta]+[1\Delta]+3\times3[2\Delta+1T]\}$	49
			Hexa- + mono- + triborates			
$Li_9Ba[B_{15}O_{27}](CO_3)$	$R\bar{3}1c$	$a = 8.8599$, $c = 15.148$		Framework	$15:\{12(6[6T]+6\times[1\Delta])+3[3T]\}_{\infty\infty\infty}$	50
			Hexa- + di- + pentaborates			
$Ba_{5.5}B_{13}O_{22}(PO_4)(OH)_3$	$P2_1/c$	$a = 6.891$, $b = 13.629$, $c = 25.581$	$\beta = 90.04$	Double layer	$2\times13:\{6[3\Delta+3T]_{\infty}+5[1\Delta+4T]_{\infty}+2[1\Delta+1T]\}_{\infty\infty}$	50
			Penta- + monoborates			
$Li_6Rb_5[B_{11}O_{22}]$	$C2$	$a = 11.625$, $b = 7.101$, $c = 13.744$	$\beta = 106.87$	Isolated groups	$11:\{2\times5[3\Delta+2T]+[1\Delta]\}$	51
$Na_8Rb[B_{21}O_{36}]$ (see [h])	$I\bar{4}$	$a = 15.057$, $c = 6.580$		The same	$21:\{4\times5[3\Delta+2T]+[1T]\}$	52
$Cs_3[B_7O_{12}]$	$C2/c$	$a = 59.911$, $b = 11.520$, $c = 34.525$	$\beta = 101.052$	Three layer-thick sheets	$24:\{2\times(5[3\Delta+2T])_{\infty\infty}+(5[2\Delta+3T]_{\infty}+$ $+5[2\Delta+3T]_{\infty}+4\times[1T])_{\infty\infty}\}$	53
$La[B_5O_8(OH)_2]\cdot 1.5\,H_2O$	$P2_1/n$	$a = 6.447$, $b = 10.580$, $c = 12.590$	$\gamma = 89.92$	Framework	$5:\{4[\Delta+3T]_{\infty\infty}+[1\Delta]\}_{\infty\infty\infty}$	54
$Mg_3[B_{11}O_{15}(OH)_9]$ (preobrazhenskite)	$Pbcn$	$a = 8.441$, $b = 8.680$, $c = 19.741$		Corrugated layer	$11:\{9(2\times5[2\Delta+3T]-[1T])+2\times[1T]\}_{\infty\infty}$	55
			Penta- + diborates			
$LiSr_4[B_{11}O_{20.5}(OH)]$	$P\bar{1}$	$a = 6.468$, $b = 8.451$, $c = 14.881$	$\alpha = 101.21$, $\beta = 93.96$, $\gamma = 90.67$	Double layer and isolated groups	$12:\{2\times5[2\Delta+3T]_{\infty\infty}+[2\Delta]\}$	56

Table 2 (continued).

Chemical formula	Space group	Lattice constants		Boron – oxygen radical		Ref.
		linear dimensions /Å	angles /deg	type	notation	
			Penta- + diborates			
$Ca_2Fe[Cl \mid B_9O_{13}(OH)_6]Cl \cdot 4\,H_2O$ (penobsquisite)	$P2_1$	$a = 11.62$, $b = 9.407$, $c = 8.726$	$\beta = 98.58$	Framework	$9{:}\{5[2\Delta + 3T]_\infty + 2 \times 2[1\Delta + 1T]_\infty\}_{\infty\infty\infty}$	57
β-$Tl_2B_2O_7$	$P\bar{1}$	$a = 6.742$, $b = 13.225$, $c = 13.389$	$\alpha = 119.093$, $\beta = 92.288$, $\gamma = 91.012$	"	$12{:}\{5[2\Delta + 3T] + 5[2\Delta + 3T] + 2[2\Delta]\}_{\infty\infty\infty}$	58
			Penta- + triborates			
α-$Na_2[B_8O_{13}]$	$P2_1/a$	$a = 6.507$, $b = 17.796$, $c = 8.277$	$\beta = 96.6$	Framework	$8{:}\{5[4\Delta + 1T] + 3[2\Delta + 1T]\}_{\infty\infty\infty}$	59
β-$Na_2[B_8O_{13}]$ (see [i])	$P2_1/c$	$a = 11.936$, $b = 7.801$, $c = 10.558$	$\beta = 99.846$	"	$8{:}\{5[4\Delta + 1T] + 3[2\Delta + 1T]\}_{\infty\infty\infty}$	60
			Penta- + tetraborates			
$NaCa_2[B_9O_{14}(OH)_4] \cdot 2\,H_2O$ (studenitsite)	$P2_1/b$	$a = 11.503$, $b = 10.53$, $c = 12.58$	$\beta = 99.5$	Layer	$9{:}\{5[2\Delta + 3T]_\infty + 4[2\Delta + 2T]\}_{\infty\infty}$	63
$Na_6[B_{13}O_{22.5}]$	$Iba2$	$a = 33.359$, $b = 9.554$, $c = 10.644$		Framework	$13{:}\{5[3\Delta + 2T] + 2 \times 4[2\Delta + 2T]\}_{\infty\infty\infty}$	64
			Penta- + mono- + diborates			
$Ca_{16}(Mg,Li,\square)_2[B_{13}O_{17}(OH)_{12}]_4 \cdot Cl_6 \cdot 28\,H_2O$ (walkerite)	$Pba2$	$a = 15.5484$, $b = 22.672$, $c = 8.772$		Framework	$13{:}\{2 \times 2[1\Delta + 1T]_\infty + 9(2 \times 2[1\Delta + 1T]_\infty + + 5(4[2\Delta + 2T] + [1T]))_{\infty\infty}\}_{\infty\infty\infty}$	65
$Rb_{18}Mg_6[B_5O_{10}]_3[B_7O_{14}]_2F$ (see [j])	$C2/c$	$a = 11.058$, $b = 19.70$, $c = 31.01$	$\beta = 90.134$	Isolated groups	$12{:}\{5[4\Delta + 1T]\} + \{2 \times 3[2\Delta + 1T] + [1\Delta]\}$	66
			Penta- + mono- + triborates			
$Rb_5[B_{19}O_{31}]$ (see [k])	$C2/c$	$a = 18.211$, $b = 11.519$, $c = 13.310$	$\beta = 95.63$	Framework	$19{:}\{2 \times 5[4\Delta + 1T] + 2 \times 3[2\Delta + 1T] + + 2 \times [1\Delta] + [1T]\}_{\infty\infty\infty}$	67
$Sr_2[B_{16}O_{26}]$	$P\bar{1}$	$a = 6.7415$, $b = 13.225$, $c = 13.389$	$\alpha = 119.093$, $\beta = 92.288$, $\gamma = 91.012$	"	$16{:}\{5[4\Delta + 1T] + 3 \times 3[2\Delta + 1T] + 2 \times [1\Delta]\}_{\infty\infty\infty}$	69
$Sm_3[B_{13}O_{22}(OH)_3](OH) \cdot 3\,H_2O$	$P2/c$	$a = 10.715$, $b = 6.419$, $c = 29.937$	$\beta = 98.168$	Layer	$13{:}\{(4[2T + 2\Delta])_\infty + 9(5[2\Delta + 3T])_\infty + + 4(3[2\Delta + 1T + 1\Delta)_\infty)\}_{\infty\infty}$	70
			Penta- + mono- + tetraborates			
$La_4[B_{14}O_{27}]$	$C2/c$	$a = 11.208$, $b = 16.42$, $c = 25.37$	$\beta = 100.12$	Framework	$14{:}\{2 \times (4[1\Delta + 3T])_{\infty\infty} + 5{:}(4[2\Delta + 2T] + + [1\Delta])\}_{\infty\infty\infty}$	71

Table 2 (continued).

Chemical formula	Space group	Lattice constants		Boron – oxygen radical		Ref.
		linear dimensions /Å	angles /deg	type	notation	
			Penta- + di- + tetraborates			
$AgSr[B_7O_{12}]$	$C2/c$	$a = 6.642$, $b = 11.536$, $c = 21.980$	$\beta = 92.52$	Double layer	$14:\{2\times4[2\Delta+2T]_{\infty\infty}+6(4[2\Delta+2T]+2[2\Delta])_{\infty}\}_{\infty\infty}$	72
			Tetra- + monoborates			
$Pb_6[B_{10}O_{21}]$	$P\bar{1}$	$a = 6.833$, $b = 7.010$, $c = 11.125$	$\alpha = 85.9$, $\beta = 102.0$, $\gamma = 119.6$	Isolated groups	$10:\{2\times(4[2\Delta+2T]+[1\Delta])\}$	73
			Tetra- + mono- + triborates			
$Rb_2[B_4O_7]$ (see [l])	$P\bar{1}$	$a = 9.860$, $b = 10.653$, $c = 6.649$	$\alpha = 103.4$, $\beta = 101.4$, $\gamma = 89.1$	Framework	$8:\{4[2\Delta+2T]+3[2\Delta+1T]+[1\Delta]\}_{\infty\infty\infty}$	74, 75
			Tri- + monoborates			
$Cs_3Zn_6[B_9O_{21}]$	$Cmc2_1$	$a = 8.4268$, $b = 19.210$, $c = 14.541$		Isolated groups	$6:\{3[3\Delta]+3\times[1\Delta]\}$	7
$SrBi_2[B_4O_{10}]$	$P\bar{1}$	$a = 6.819$, $b = 6.819$, $c = 9.812$	$\alpha = 96.09$, $\beta = 109.11$, $\gamma = 101.94$	The same	$4:\{3[2\Delta+1T]+[1\Delta]\}$	76
$Li_4Cs_3[B_7O_{14}]$	$P3_121$	$a = 6.931$, $c = 26.799$		"	$7:\{2\times3[2\Delta+1T]+[1\Delta]\}$	77
$Ba_4K_2Zn_5[(B_3O_6)_3(B_9O_{19})]$	$P2_1/n$	$a = 7.162$, $b = 38.772$, $c = 12.360$	$\beta = 90.26$	"	$18:\{9(3\times3[3\Delta])+9(3[2\Delta+1T]+3[\Delta\Delta\Delta]+3[2\Delta+1T])\}$	78
$Ag[BO_2]$	$Pbcn$	$a = 8.441$, $b = 8.680$, $c = 19.741$		Chain	$4:\{3[1\Delta+2T]+[1\Delta]\}_{\infty}$	79
$BaBi_2[B_4O_{10}]$	$P2_1/c$	$a = 10.150$, $b = 6.362$, $c = 12.485$	$\beta = 102.87$	"	$4:\{3[3T]+[1\Delta]\}_{\infty}$	80
β-$Dy_2[B_4O_9]$	$P\bar{1}$	$a = 6.162$, $b = 6.428$, $c = 7.485$	$\alpha = 102.537$, $\beta = 97.084$, $\gamma = 102.446$	Ribbon	$8:\{2\times3[3T]+[1\Delta]+[1\Delta]\}_{\infty}$	81
$Cs_2Cd_3[B_{16}O_{28}]$ (see [m])	$C2/c$	$a = 21.486$, $b = 7.685$, $c = 13.369$	$\beta = 91.705$	Layer	$4:\{3[1\Delta+2T]+[1\Delta]\}_{\infty\infty}$	82
$Na_3[B_7O_{12}]$	$P\bar{1}$	$a = 6.638$, $b = 8.249$, $c = 8.836$	$\alpha = 95.875$, $\beta = 100.680$, $\gamma = 99.688$	Framework	$7:\{3[2\Delta+1T]+3[1\Delta+2T]+[1\Delta]\}_{\infty\infty\infty}$	19
$Ba_2[B_{10}O_{17}]$	$P\bar{1}$	$a = 6.7128$, $b = 9.8698$, $c = 9.9998$	$\alpha = 76.860$, $\beta = 83.200$, $\gamma = 73.332$	Ribbon	$10:\{8(2\times(3[1\Delta+2T]+[1\Delta]))_{\infty}+2\times[1\Delta]\}_{\infty\infty\infty}$	83

Table 2 (continued).

Chemical formula	Space group	Lattice constants		Boron–oxygen radical		Ref.
		linear dimensions /Å	angles /deg	type	notation	
			Tri- + mono- + diborates			
α-$Bi_2[B_8O_{15}]$	$P2_1$	$a = 4.314$, $b = 22.150$, $c = 6.469$	$\beta = 105.49$	Ribbon	$8{:}\{4(3[3\Delta]+[1\Delta])+2\times2[1\Delta+1T]\}_\infty$	84
β-$Bi_2[B_8O_{15}]$	$P\bar{1}$	$a = 4.316$, $b = 6.461$, $c = 22.485$	$\alpha = 87.094$, $\beta = 86.538$, $\gamma = 74.420$	"	$8{:}\{4(3[3\Delta]+[1\Delta])+2\times2[1T+1\Delta]\}_\infty$	84
			Di- + monoborates			
$Pb_4Zn_2[B_{10}O_{21}]$	*Pbcn*	$a = 14.606$, $b = 17.490$, $c = 13.296$		Layer	$20{:}\{2\times(2\times2[1\Delta+1T]+2\times2[1T+1T])_\infty+4\times[1\Delta]\}_{\infty\infty}$	85
$Ba_2Li[B_5O_{10}]$	$P2_1/m$	$a = 4.414$, $b = 14.576$, $c = 6.697$	$\beta = 104.26$	Ribbon	$5{:}\{2\times2[1\Delta+1T]_\infty+[1\Delta]\}_\infty$	86
$Li_5Cs_2[B_7O_{14}]$	*Ama*2	$a = 21.278$, $b = 13.630$, $c = 4.428$		Ribbon and chain	$10{:}\{2\times(2[1\Delta+1T]+[1\Delta])_\infty+2[2\Delta]\}_\infty$	87

Note. The isostructural compounds listed below have boron–oxygen radicals of the same type and notations as those of the borates specified.

[a] This borate is isostructural to compound $(Pb,Ba)_3[B_9O_{16}](OH)\cdot B(OH)_3$.[40]

[b] This borate is isostructural to compound $LiBa_3[B_9O_{16}](OH)\cdot B(OH)_4$.[40]

[c] This borate is isostructural to compound $Ag_6[B_{12}O_{18}(OH)_6]\cdot 3\,H_2O$.[42]

[d] This borate is isostructural to compound $Sr_8Mg[B_{18}O_{36}]$.[47]

[e] This borate is isostructural to compounds of the general formula $M[B_6O_{10}(OH)\cdot B_2O(OH)_4]$, where M = Ce, Pr, Nd.[48]

[f] This borate is isostructural to compounds of the general formula $M[B_6O_{10}(OH)\cdot B_3O_3(OH)_4]\cdot H_2O$, where M is a rare-earth element.[49]

[g] This borate is isostructural to compounds of the general formula $M_4[B_{22}O_{36}](OH)_6\cdot 13\,H_2O$, where M = Ce, Pr, Nd, Sm, Eu, Gd.[49]

[h] This borate is isostructural to compound $Na_8Cs[B_{21}O_{36}]$.[42]

[i] This borate is isostructural to compounds $Ag_2[B_8O_{13}]$, $LiNa[B_8O_{13}]$ and β-$LiK[B_8O_{13}]$.[61, 62]

[j] This borate is isostructural to compound $Cs_{18}Mg_6[B_5O_{10}]_3[B_7O_{14}]_2F$.[66]

[k] This borate is isostructural to compound $K_5[B_{19}O_{31}]$.[68]

[l] This borate is isostructural to compound $K_2[B_4O_7]$.[75]

[m] This borate is isostructural to compound $Rb_2Cd_3[B_{16}O_{28}]$.[82]

Note that Tables 1 and 2 do not include structural data for all borates studied to date. They present data for those compounds that clearly illustrate the principles of our classification and description of the structure of the anionic radical and have the most interesting structures.

In the last decade, the number of synthesized borates and studies on the structure and properties of these compounds abruptly increased. One can say that systematic search for new compounds with specified properties involves combining various metals as cations with anionic borate complexes. The structures of borates are regularly complicated, which makes their description and determination of crystal chemical characteristics of the new phases difficult. In the early 2000s the most complex borate anions were reported by a research group from France [19, 24, 53, 58] and best characterized within the framework of the classical approach by Christ and Clark.[1] Recently, most results in this field have been obtained by researchers from P.R.China [44, 47, 53, 78, 83] and USA.[49, 50, 56]

3. Hexaborates and polyborates with hexaborate block

We begin with analyzing the structures whose anionic radicals are built up of the most complex hexaborate block having a number of subtypes. We will demonstrate the difference between hexaborates and polyborates with hexaborate and other blocks.

3.1. The 6[3Δ + 3T] block

The 6[3Δ + 3T] block is the most abundant in the structures of hexaborates. It was found in individual form and in the form of a chain radical in certain minerals; this block is typical of structures belonging to a large family of layered hexaborates.[4] The structure of tunellite $Sr_2[B_{12}O_{18}(OH)_4]\cdot 6H_2O$ (Fig. 1)[13] contains layers comprised of same-type hexaborate blocks. Therefore, tunellite is a condensed hexaborate with the boron–oxygen radical described as $6[3\Delta + 3T]_{\infty\infty}$ rather than a polyborate. Layers in the structures of borates $Pb[B_6O_{10}(OH)\cdot B_2O(OH)_3]$,[13] $Ba_{0.975}[B_6O_9(OH)(O_{0.975}Br)\cdot B_2O(OH)_3]$[18] and $Sr[B_6O_{10}(OH)\cdot B_2O(OH)_3]$[13] also comprise the 6[3Δ + 3T] blocks; they are similar to the layers in tunellite but contain branchings. In these borates the polyborate radical is composed of two types of blocks, *viz.*, the hexaborate block and a diborate one (two triangles that share a vertex of a tetrahedron in the hexaborate block); the notation for this boron–oxygen radical is $8:\{6[3\Delta + 3T] + 2[2\Delta]\}_{\infty\infty}$.

The structures of compounds $M[B_6O_{10}(OH)\cdot B_2O(OH)_4]$ (M is a rare-earth metal)[48] also contain layers comprising hexa- and diborate blocks; however, the latter consists of a triangle and a tetrahedron rather than two triangles. The notation for the boron–oxygen radical is $8:\{6[3\Delta + 3T] + 2[1\Delta + 1T]\}_{\infty\infty}$. In layers, $Nd[B_6O_{10}(OH\cdot B_3O_3(OH)_4]$ and $M[B_6O_{10}(OH)\cdot B_3O_3(OH)_4]\cdot H_2O$ (see Ref. 48) are composed of the hexaborate blocks and three-membered rings consisting of a triangle and two tetrahedra, so the notation of the layers has a more complicated form $9:\{6[3\Delta + 3T] + 3[1\Delta + 2T]\}_{\infty\infty}$. In the structure of $Ba_2[B_6O_9(OH)_2][B_3O_3(OH)_4](OH)\cdot 4H_2O$ (Fig. 2) hexaborate layers and isolated triborate layers are alternately arranged along the *b* axis; the notation is $9:\{6[3\Delta + 3T]_{\infty\infty} + 3[2\Delta + 1T]\}$. In the structure of

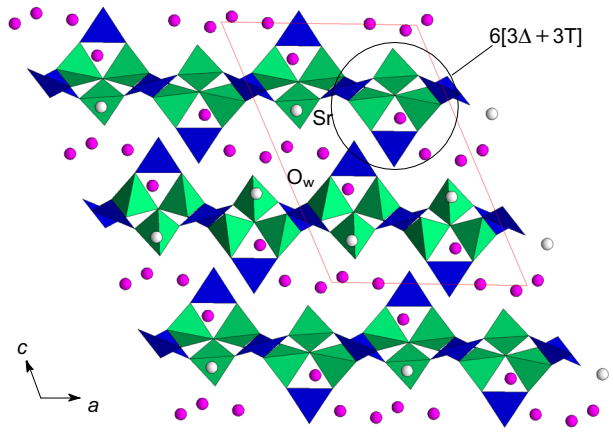


Figure 1. Crystal structure of tunellite $Sr_2[B_{12}O_{18}(OH)_4]\cdot 6H_2O$: *ac* projection (see §).[13]

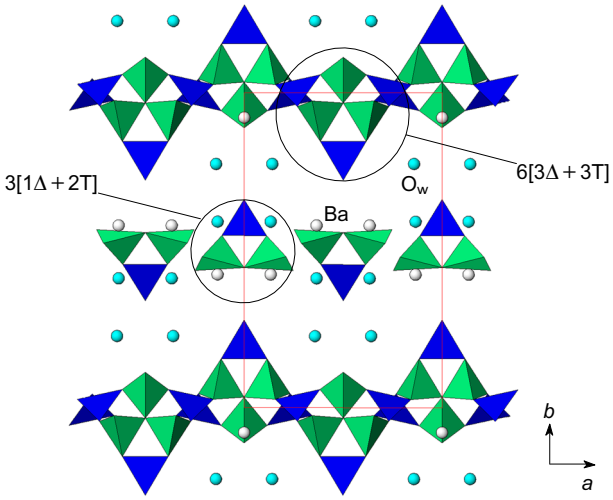


Figure 2. Crystal structure of $Ba_2[B_6O_9(OH)_2][B_3O_3(OH)_4](OH)\cdot 4H_2O$: *ab* projection.[5]

$Li_3[B_8O_{12}(OH)_3]$ (see Ref. 35) three hexaborate blocks form a three-membered ring with the loss of one triangle in every block; the rings are linked into a layer by additional triangles. The boron–oxygen radical is described as $18:\{3x(6[3\Delta + 3T] - [1\Delta]) + [1\Delta]\}_{\infty\infty}$.

3.2. The 6[6T] block

The hexaborate blocks in boracites $Mg_3[B_7O_{13}]Cl$ (Ref. 36) and $Mn_3[B_7O_{13}]Cl$ (Ref. 38) have similar configurations, but they consist entirely of the [6T] tetrahedra. The hexaborate blocks are linked into a framework using tetrahedra and triangles, *e.g.*, $7:\{6[6T] + [1\Delta]\}_{\infty\infty\infty}$. Earlier, these borates were treated as heptaborates;[3] however, they should

§ All figures were compiled by the authors using structural data taken reported in the references cired (see particular Figure Captions). The strucures are presented in different (most important) projections. Anionic boron-oxygen radicals ar represented by polyhedra and the fundamental building blocks (FBBs) are specified. In each Figure, shown are the unit cells and the FBBs constituting the anionic radicals (circumscribed by circles or ellipses).

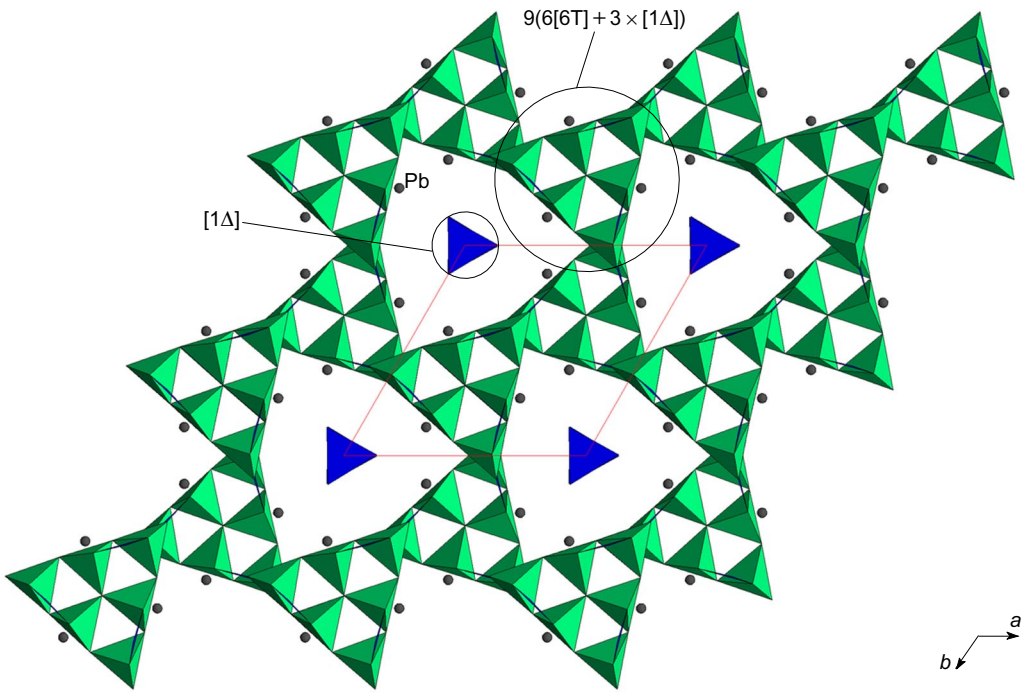


Figure 3. Crystal structure of $Pb_3[B_9O_{16}](OH)\cdot B(OH)_3$: *ab* projection.[39]

be classified as polyborates since they consist of two types of blocks. In formal nonaborates $Pb_3[B_9O_{16}](OH)\cdot B(OH)_3$ (Fig. 3), $NaBa_3[B_9O_{16}](OH)\cdot B(OH)_4$ and $LiBa_3[B_9O_{16}](OH)\cdot B(OH)_4$ (Ref. 40) the hexaborate blocks consist of six tetrahedra and are featured by three triangles at vertices; therefore, actually one deals with polyborates. Six 9(6[6T] + 3 × [1Δ]) blocks form a ring while the rings are linked into a framework with large voids occupied by isolated BO_3 triangles or BO_4 tetrahedra. This approach allows one to reveal a family of structurally similar polyborates and compare their structures.

3.3. The 6[3Δ + 3T] ring

This quite an unusual hexaborate block was for the first time found in the structure of γ-$Li_4[B_7O_{12}]Cl(Br)$.[37] It differs from the hexaborate units considered above by the absence of the central oxygen atom. The block consists of 6[3Δ + 3T] rings linked into a framework through additional BO_3 triangles assuming a cubic symmetry and belongs to polyborates described by the character string $7{:}\{6[6T] + [1\Delta]\}_{\infty\infty\infty}$. The structures of trigonal $Ho[B_6O_9(OH)_3]$ (Fig. 4) and some other related rare-earth borates also include hexaborate blocks linked into a framework described as $6[3\Delta + 3T]_{\infty\infty\infty}$; as a consequence, these compounds belong to hexaborates rather than polyborates.

3.4. The [6T] ring

The structures of $Pb_6[B_{12}O_{24}]\cdot H_2O$ (Fig. 5), $Na_8[B_{12}O_{20}(OH)_4]$, $Ag_6[B_{12}O_{18}(OH)_6]\cdot 3\,H_2O$, $Zn_6[B_{12}O_{24}]\cdot 6.72\,H_2O$ (Ref. 42), $Li_3KB_4O_8$ (Ref. 43), $Pb_6(Li_{0.648}Na_{0.192})[B_{12}O_{24}]I_{0.84}\cdot 0.168\,H_2O$ (see Ref. 42), $LiNa_2Sr_8[B_{12}O_{24}]F_6Cl$,[43] $Li_3NaBa[B_6O_{12}]$,[44] and pringleite $Ca_9[B_{26}O_{34}(OH)_{24}]Cl_4\cdot 13\,H_2O$ (Ref. 45) are composed of

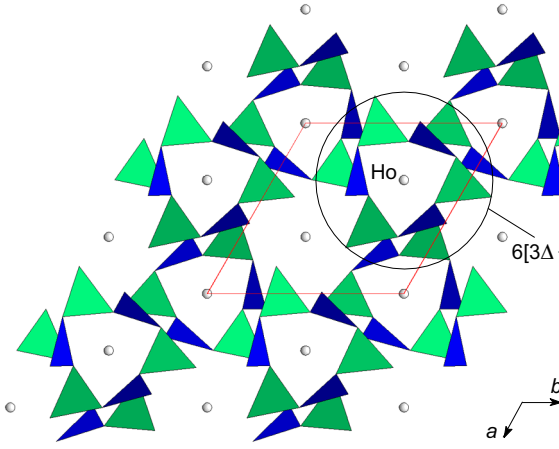


Figure 4. Crystal structure of $Ho[B_6O_9(OH)_3]$: *ab* projection.[14]

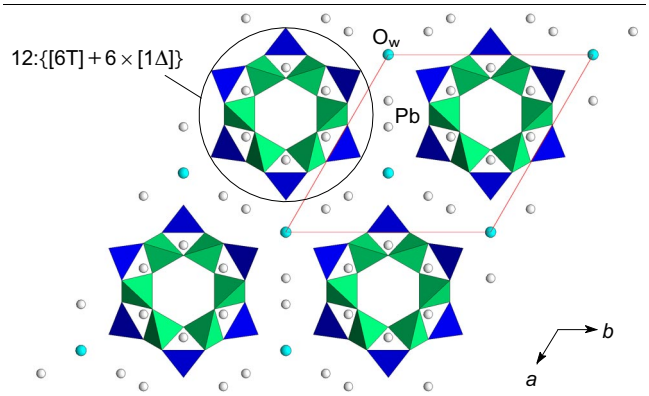


Figure 5. Crystal structure of $Pb_6[B_{12}O_{24}]\cdot H_2O$: *ab* projection.[41]

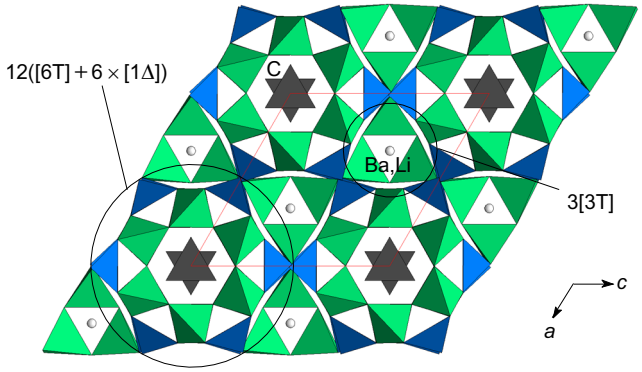


Figure 6. Crystal structure of $Li_9Ba[B_{15}O_{27}](CO_3)$: *ac* projection.[50]

isolated six-membered rings of tetrahedra and six boron triangles attached to them at vertices and can be described as 12:{[6T] + 6 × [1Δ]}. One can distinguish tri- and diborate blocks in the complex dodecaborate ring, so exact classification is debatable; however, the most appropriate building block is the ring of six tetrahedra.

The structure of $Li_9Ba[B_{15}O_{27}](CO_3)$ (Fig. 6) includes similar dodecaborate rings and isolated triborate rings with CO_3 triangles located in the rings. Thus, this complex polyborate contains a complex dodecaborate radical and an additional triborate radical. Overall, the boron – oxygen radical is described as 15:{12([6T] + 6 × [1Δ]) + 3[3T]}$_{\infty\infty\infty}$.

In other layered polyborates, $KGd[B_6O_{10}(OH)_2]$ and $KHo[B_6O_{10}(OH)_2]$, the anionic radical is built up of six-membered rings of boron – oxygen tetrahedra and boron – oxygen triangles attached to the rings in polar orientation.[46] Positions of the triangles are statistically occupied. Although the structures of both compounds include same-type radicals, these borates exhibit fundamentally different properties since the structure of $KHo[B_6O_{10}(OH)_2]$ is centrosymmetric while that of $KGd[B_6O_{10}(OH)_2]$ is acentric.

The structures of borates $NaSr_7Al[B_{18}O_{36}]$ and $Sr_8Mg[B_{18}O_{36}]$ contain[47] isolated rings of six tetrahedra with two triangles attached to each tetrahedron to eventually compose three-membered rings of tetrahedra and triangles described as 18:{[6T] + 6 × [2Δ]}. This polyborate radical can also be treated as resulting from condensation of six triborate rings; in this case, the notation is 18:{6 × 3[1T + 2Δ]}.

The structure of $La_4[B_{22}O_{36}](OH)_6 \cdot 13\,H_2O$ includes rings 6[3Δ + 3T] containing an additional triangle (Fig. 7). Three diborate blocks consisting of two triangles each are attached to vertices of the ring tetrahedra along the perim-

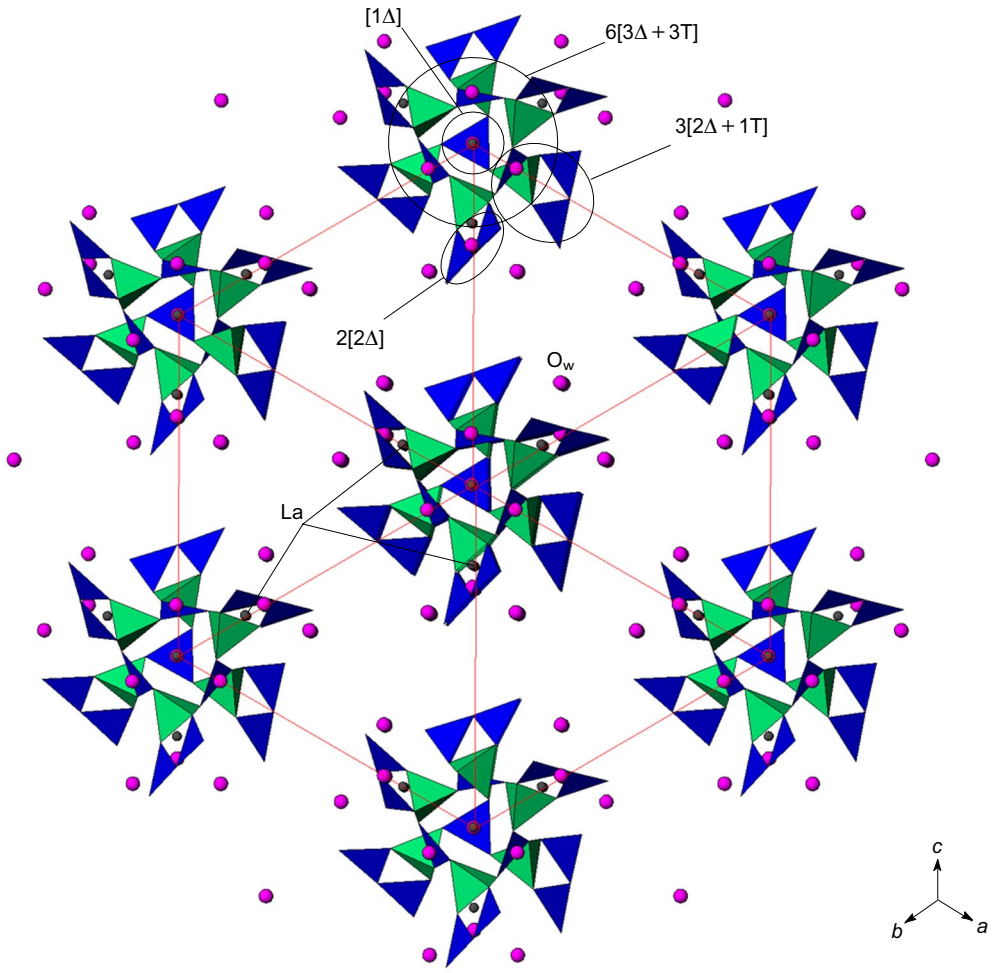


Figure 7. Crystal structure of $La_4[B_{22}O_{36}](OH)_6 \cdot 13\,H_2O$: projection on the plane normal to the 3-fold axis.[49]

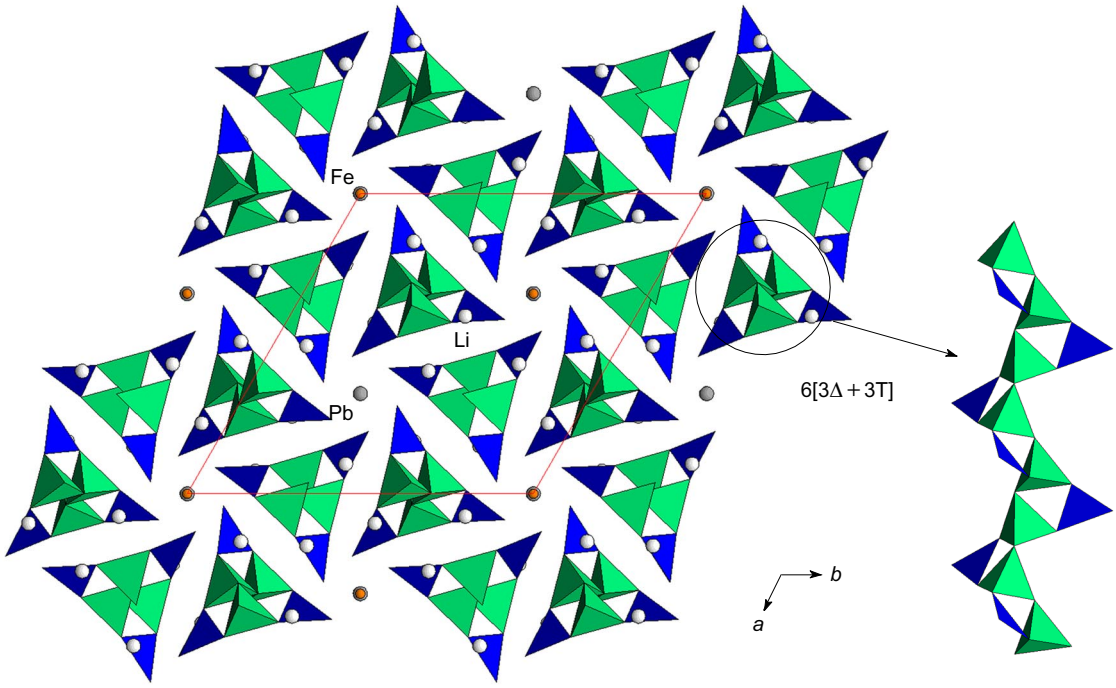


Figure 8. Crystal structure of $(Li_{5.5}Fe_{0.5})FePb[B_6O_{12}]_2$: *ab* projection.[15]

eter to form complex isolated units, namely, clusters denoted as 22:{6[3Δ + 3T] + 3 × 2[2Δ] + 1[Δ] + 3 × 3[2Δ + + 1T]}. The formation of the boron–oxygen radical can also be interpreted as condensation of six triborate blocks involving additional triangles with the formation of a cluster with encapsulated hexaborate ring. In this case the Christ and Clark notation is 22:{6 × 3[2Δ + 3T] + + 3 × [1Δ] + [1Δ]}

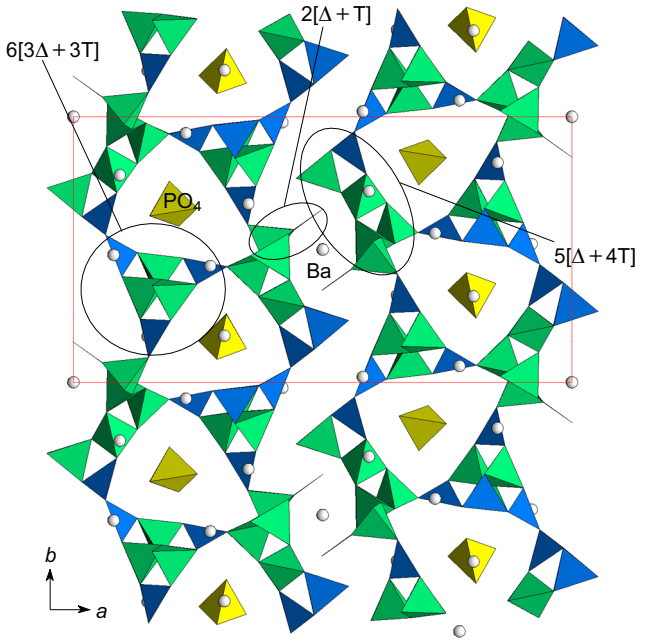


Figure 9. Crystal structure of $Ba_{5.5}B_{13}O_{22}(PO_4)(OH)_3$: *bc* projection.[50]

3.5. The 6[3Δ + 3T] chain

Isolated hexaborate blocks in the structures considered above have a symmetry axis 3. In these structures triborate rings are connected in the same plane. However, triborate blocks can also be linked along the screw axis 3_1 to form chains. This occurs in, *e.g.*, the structure of $(Li_{5.5}Fe_{0.5})FePb[B_6O_{12}]_2$ (Fig. 8) where helical chains were found for the first time. In the complex borate $Ba_{5.5}B_{13}O_{22}(PO_4)(OH)_3$, double layers are composed of three types of blocks,[50] *viz.*, hexa-, penta- and diborate ones $(2 \times 13:\{6[3\Delta + 3T]_\infty + 5[\Delta + 4T]_\infty + 2[\Delta + T]\}_{\infty\infty})$. Hexaborate blocks form a helical chain as described above. Penta- and diborate blocks connect chains into double layers; large voids in these structures are occupied by PO_4 tetrahedra (Fig. 9).

These examples show that the structures of most polyborates with the hexaborate block represent combinations of this block with the simplest mono- and diborate units. No examples of combination of hexa- and tetraborate blocks are available and there is only one example of a combination of hexa- and pentaborate blocks (see Fig. 9).

4. Pentaborates and polyborates with pentaborate block

Different number of triangles and tetrahedra is possible for pentaborate blocks. In this Section we will consider the structures of pentaborates and polyborates with pentaborate block and other additional units. There are three types of pentaborate blocks in these structures.

4.1. The 5[4Δ + 1T] block

The 5[4Δ + 1T] block is typical of the structures of borates containing large alkali metal (K, Rb, Cs) atoms, NH_4^+ ion and Ag atom. The chemical formula of the borate $Ag_2Cs[B_{15}O_{24}]$ includes 15 boron atoms. However, this

compound is a condensed pentaborate rather than polyborate. Its structure consists of three independent identical pentaborate units that form corrugated layers described as 15:{3 × 5[4Δ + 1T]}$_{\infty\infty}$ (Fig. 10). In polyborates α-$Na_2[B_8O_{13}]$,[59] β-$Na_2[B_8O_{13}]$ (Fig. 11),[60] $Ag_2[B_8O_{13}]$,[61] $LiNa[B_8O_{13}]$,[62] and β-$LiK[B_8O_{13}]$ (Ref. 62), the 5[4Δ + 1T] pentaborate blocks are combined with the 3[2Δ + 1T] triborate blocks to form chains, which are in turn linked into a framework 8:{5[4Δ + 1T] + + 3[2Δ + 1T]}$_{\infty\infty\infty}$.

The structures of compounds $M_{18}Mg_6[B_5O_{10}]_3[B_7O_{14}]_2F$ (M = Rb, Cs)[66] contain two types of isolated borate units represented by the 5[4Δ + 1T] pentaborate block and a complex structural fragment composed of two triborate blocks and an additional triangle. In the crystal structure, these units are connected through MgO_4 tetrahedra. The notation for the boron–oxygen radical is 12:{5[4Δ + 1T]} + + {2 × 3[2Δ + 1T] + 1[Δ]}.

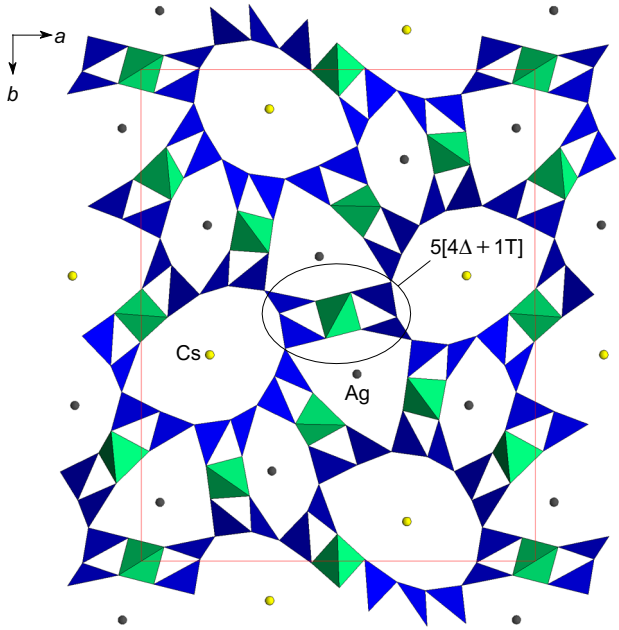


Figure 10. Crystal structure of $Ag_2Cs[B_{15}O_{24}]$: *ab* projection.[21]

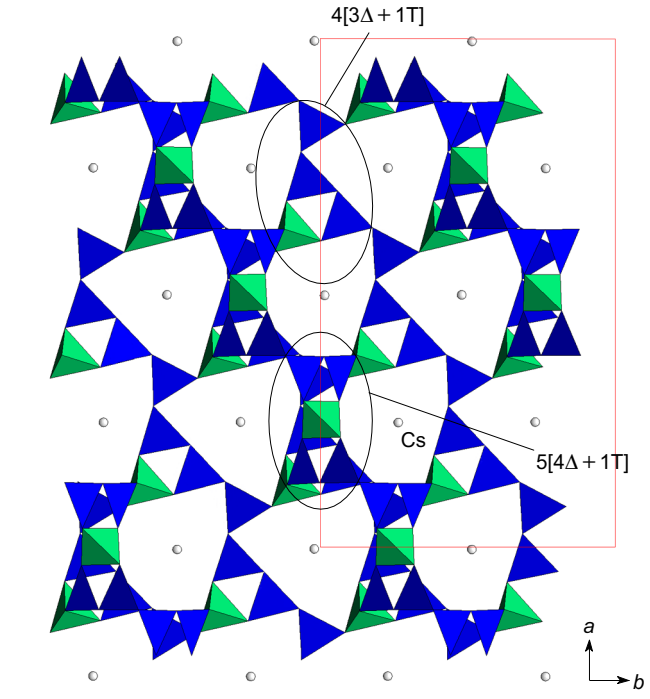


Figure 12. Crystal structure of $Cs_3B_{13}O_{21}$: *ab* projection.[24]

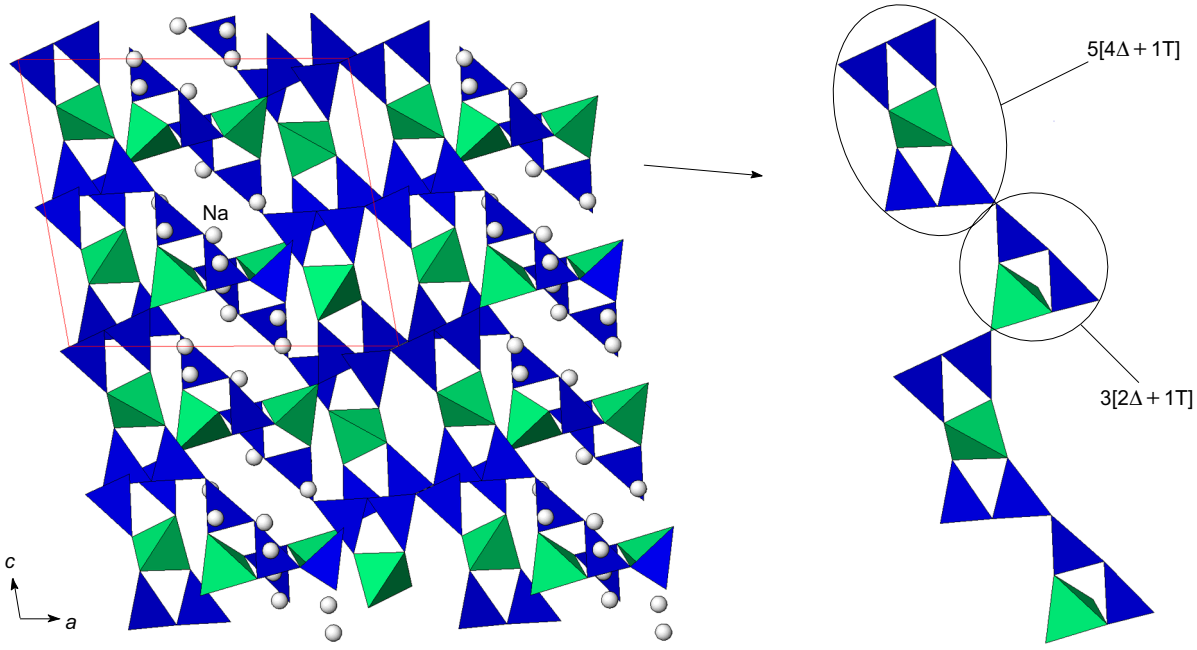


Figure 11. Crystal structure of β-$Na_2[B_8O_{13}]$: *ac* projection.[60]

In the structure of $Cs_3B_{13}O_{21}$ (Fig. 12) the polar layer consists of deficient pentaborate blocks 4[3Δ + 1T]. This layer is superimposed with chains of the 5[4Δ + 1T] pentaborate blocks. The complex layer is described as $13{:}\{2 \times 4[3\Delta + 1T]_{\infty\infty} + 5[4\Delta + 1T]_{\infty}\}_{\infty\infty}$.

The complex framework in the structures of $Rb_5[B_{19}O_{31}]$ (Ref. 67) and $K_5[B_{19}O_{31}]$ (Ref. 68) is composed of three types of blocks, that is, a penta-, a tri- and a monoborate one (additional triangle and tetrahedron). The notation for the framework is $19{:}\{2 \times 5[4\Delta + 1T] + 2 \times 3[2\Delta + 1T] + + 2 \times [1\Delta] + [1T]\}_{\infty\infty\infty}$.

The framework radical in the structure of $Sr_2[B_{16}O_{26}]$ (Ref. 69) is built up of one pentaborate block, three triborate blocks and two additional triangles bonded to one triborate block. The framework is denoted by $16{:}\{5[4\Delta + 1T] + 3 \times 3[2\Delta + 1T] + 2 \times [1\Delta]\}_{\infty\infty\infty}$.

4.2. The 5[3Δ + 2T] block

Compound $BaB_5O_8(OH)\cdot H_2O$ (Fig. 13) is a typical pentaborate where the 5[3Δ + 2T] blocks are linked to form corrugated layers.

The structure of $Na_2Tl_2[B_{10}O_{17}]$ (Ref. 19) contains double pentaborate layers $10{:}\{2 \times 5[3\Delta + 2T]_{\infty\infty}\}$; as a consequence, the number of boron atoms is doubled and equals 10.

Compound $Ba_5[B_{20}O_{33}(OH)_4]\cdot H_2O$ (Fig. 14) contains 20 boron atoms. Like two preceding compounds, it is a condensed pentaborate rather than polyborate. Layers in its structure are composed of two types of pentaborate blocks. Two layers are linked together at the shared vertices of the tetrahedra to form a double layer with large voids occupied by barium atoms. The double layer is described as $20{:}\{2 \times 10(5[3\Delta + 2T] + 5[2\Delta + 3T])_{\infty\infty}\}$.

Isolated units consisting of the pentaborate block in question and a monoborate block were found in the structures of $Li_6Rb_5[B_{11}O_{22}]$ (see Ref. 51) and $Na_8Rb[B_{21}O_{36}]$ ($Na_8Cs[B_{21}O_{36}]$).[52] They are described as

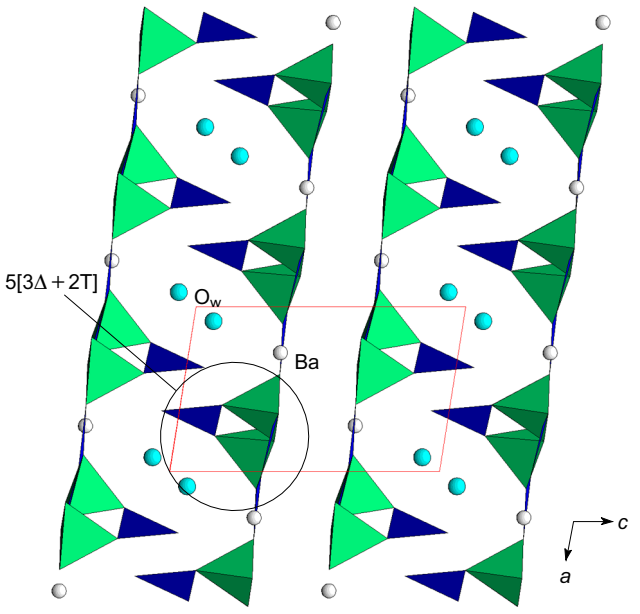


Figure 13. Crystal structure of $BaB_5O_8(OH)\cdot H_2O$: *ac* projection.[16]

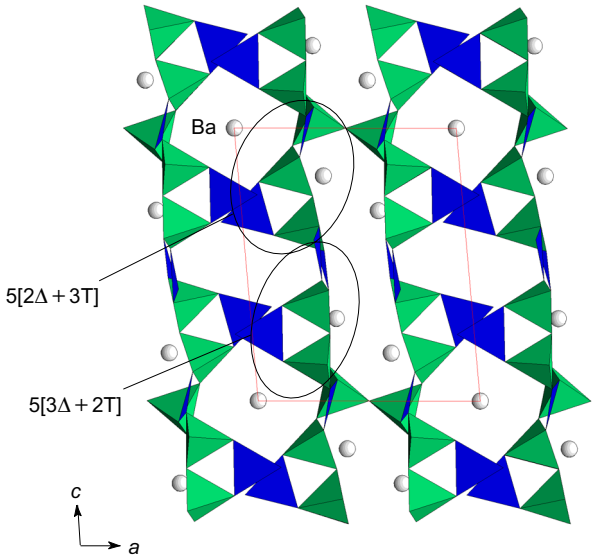


Figure 14. Crystal structure of $Ba_5[B_{20}O_{33}(OH)_4]\cdot H_2O$: *ac* projection.[18]

$11{:}\{2 \times 5[3\Delta + 2T] + 1[\Delta]\}$ and $21{:}\{4 \times 5[3\Delta + 2T] + 1[T]\}$, respectively.

The framework of the structure of $Na_6[B_{13}O_{22.5}]$ (Ref. 64) is built up of penta- and tetraborate blocks. The notation of the boron–oxygen radical is $13{:}\{5[3\Delta + 2T] + 2 \times 4[2\Delta + 2T]\}_{\infty\infty\infty}$.

The structure of $Rb_3[B_7O_{12}]$ (see Ref. 22) consists of triple layers composed of single sheets of borate polyhedra. The central sheet is formed by deficient pentaborate blocks and the upper and lower sheets are built up of pentaborate blocks. The triple layer is described as $14{:}\{2 \times 5[3\Delta + 2T] + + 4[2\Delta + 2T]\}_{\infty\infty}$.

4.3. The 5[2Δ + 3T] block

Although the chemical formula of $Na_2Ba_2[B_{10}O_{17}(OH)_2]$ (Ref. 18) includes 10 boron atoms, the compound is not a polyborate. Its structure consists of double pentaborate layers $10{:}\{2 \times 5[2\Delta + 3T]_{\infty\infty}\}$ with large voids occupied by barium atoms. Double layers of the 5[2Δ + 3T] blocks are also typical of the structure of $LiBa_2[B_{10}O_{16}(OH)_3]$.[20]

Considering the structure of $LiSr_4[B_{11}O_{20.5}(OH)]$ (Fig. 15), one also deals with double pentaborate layers described as $12{:}\{2 \times 5[2\Delta + 3T]_{\infty\infty} + [2\Delta]\}$. Large voids are occupied by isolated diborate groups (two triangles). In preobrazhenskite $Mg_3[B_{11}O_{15}(OH)_9]$,[55] there are two pentaborate blocks 5[2Δ + 3T] with one tetrahedron being shared upon condensation. The pentaborate units are linked together to form a highly corrugated complex layer $11{:}\{9(2 \times 5[2\Delta + 3T] - [1T]) + 2 \times [1T]\}_{\infty\infty}$ through two additional tetrahedra.

The framework of penobsquisite $Ca_2Fe[Cl|B_9O_{13}(OH_6]Cl\cdot 4H_2O$ (Fig. 16) is composed of two types of chains with mutually perpendicular orientations, *viz.*, pentaborate chains based on the 5[2Δ + 3T] block are extended along the *b* axis while diborate chains based on the 2[1Δ + 1T] block are extended along the *c* axis. The anionic radical of penobsquisite is denoted by $9{:}\{5[2\Delta + 3T]_{\infty} + 2 \times (2[1\Delta + 1T]_{\infty})\}_{\infty\infty\infty}$.

The framework of β-$Tl_2B_2O_7$ (Ref. 58) is composed of two types of pentaborate blocks and a diborate

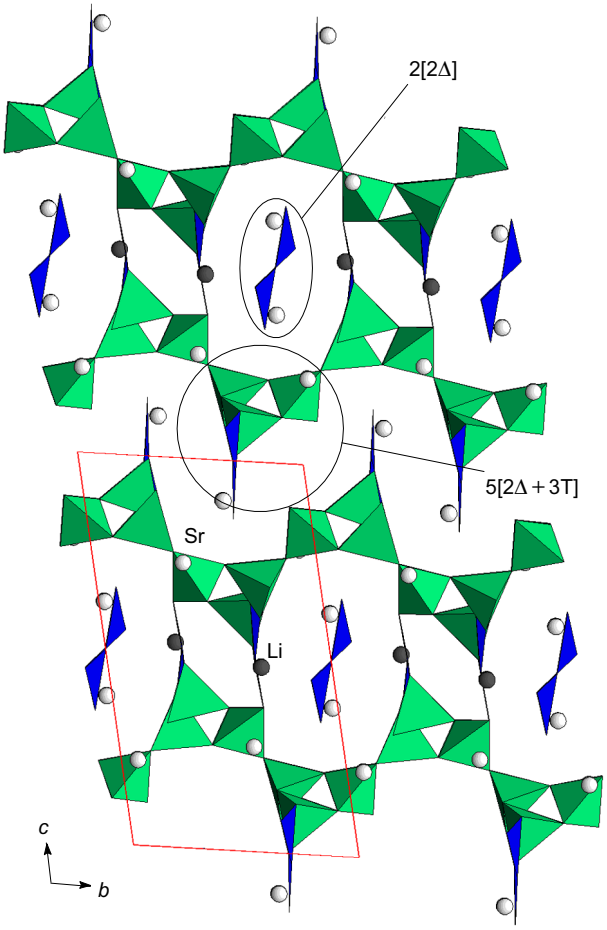


Figure 15. Crystal structure of $LiSr_4[B_{11}O_{20.5}(OH)]$: *bc* projection.[56]

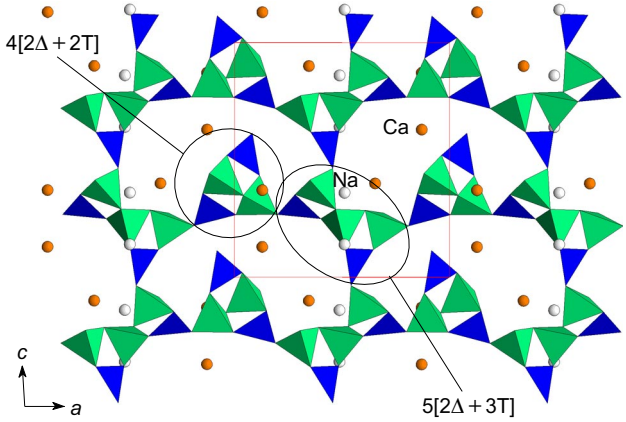


Figure 17. Crystal structure of studenitsite: *ac* projection.[63]

group (two triangles). Its notation is $12{:}\{5[2\Delta + 3T] + 5[2\Delta + 3T] + 2[2\Delta]\}_{\infty\infty\infty}$.

In the studenitsite $NaCa_2[B_9O_{14}(OH)_4]\cdot 2\,H_2O$ structure (Fig. 17), pentaborate chains aligned with the *c* axis form a framework through tetraborate blocks. The boron – oxygen radical is described as $9{:}\{5[2\Delta + 3T]_\infty + 4[2\Delta + 2T]\}_{\infty\infty}$.

In the $(Nd_{0.925}Na_{0.075})Nd[B_9O_{15}(OH)Cl_{0.85}]\cdot 2.65H_2O$ structure,[23] there are sheets consisting of two identical layers. Two types of chains can be distinguished in each layer, *viz*., a classical pentaborate chain and a chain with incomplete pentaborate block that lacks the fifth triangle. The incomplete pentaborate block can also be treated as a combination of the triborate block and an additional triangle; then, the complex anionic radical of the polyborate is described as $9{:}\{(5[2\Delta + 3T])_\infty + (4{:}3[2T + 1\Delta] + [1\Delta])_\infty\}_{\infty\infty}$. Isolated sheets consisting of two layers were distinguished in the $Sm_3[B_{13}O_{22}(OH)_3](OH)\cdot 3\,H_2O$ structure (Fig. 18). They are similar to those found in Nd-borate.

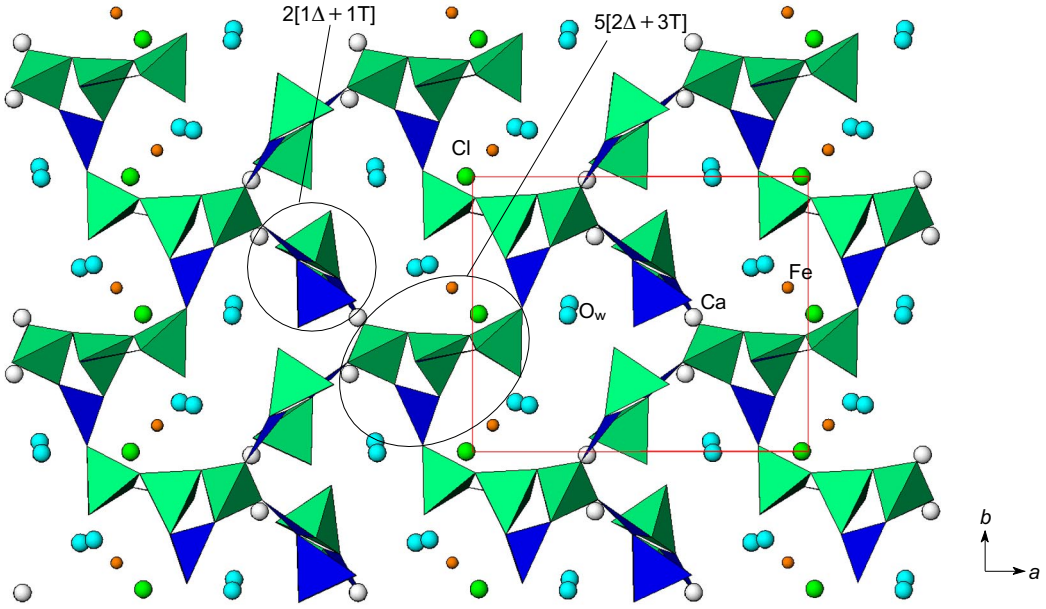


Figure 16. Crystal structure of penobsquisite: *ab* projection.[57]

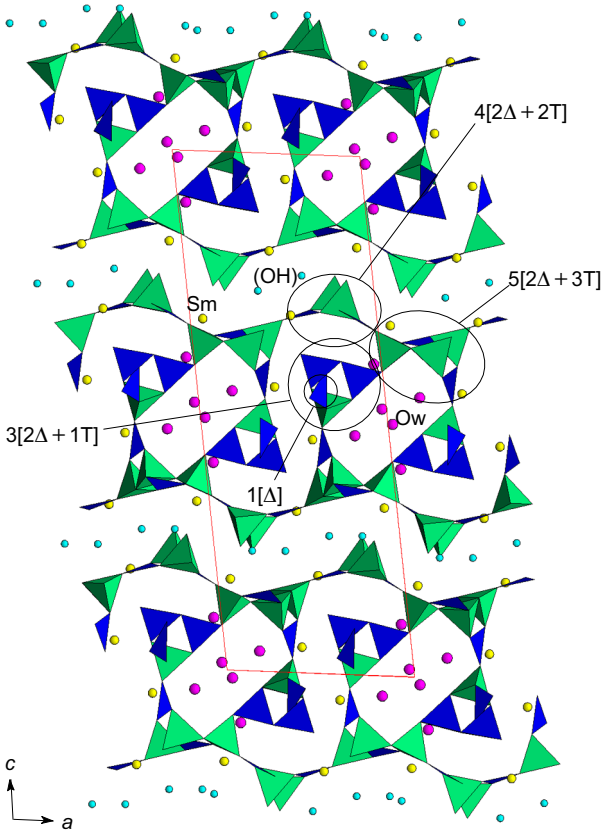


Figure 18. Crystal structure of $Sm_3[B_{13}O_{22}(OH)_3](OH)\cdot 3\,H_2O$: *ac* projection.[70]

The Sm-borate layer represents a complicated version of the Nd-borate layer since it has an additional branching from the triborate block and an additional triangle. The Christ and Clark notation for the anionic radical of Sm-polyborate is $13{:}\{4[2T + 2\Delta]_\infty + 9{:}(5{:}[2\Delta + 3T]_\infty + 4{:}(3[2\Delta + 1T] + 1\Delta)_\infty)\}_{\infty\infty}$.

There are structures in which blocks of four boron polyhedra can be distinguished; however, these blocks are neither topologically nor condensationally tetraborate, being similar to pentaborate ones. This is particularly clearly seen upon their condensation into a layer. Such structures will be treated as incomplete or deficient pentaborate structures, with a lack of one BO_3 triangle or BO_4 tetrahedron.

The chemical formula of kernite $Na_2[B_4O_6(OH)_2]\cdot 3\,H_2O$ includes four boron atoms; therefore, this mineral was treated as tetraborate for long. The projection of the kernite structure (Fig. 19) clearly demonstrates that the chain radical contains no tetraborate blocks, being composed of pentaborate blocks 5[2Δ + 3T]. One tetrahedron is shared by two pentaborate blocks in the chain and the number of tetrahedra in the chemical formula decreases by unity; it follows that the structure should be treated as pentaborate.

The anionic part of the structure of $LaB_5O_8(OH)_2\cdot 1.5\,H_2O$ (Fig. 20) is formed by nonpolar corrugated layers built up of deficient pentaborate block 4[1Δ + 3T]. The layers are linked into a framework through

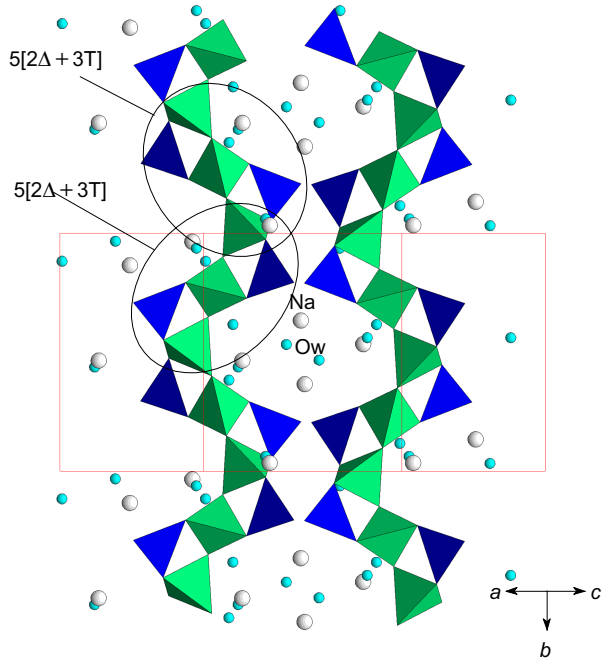


Figure 19. Crystal structure of kernite: projection on the diagonal plane.[17]

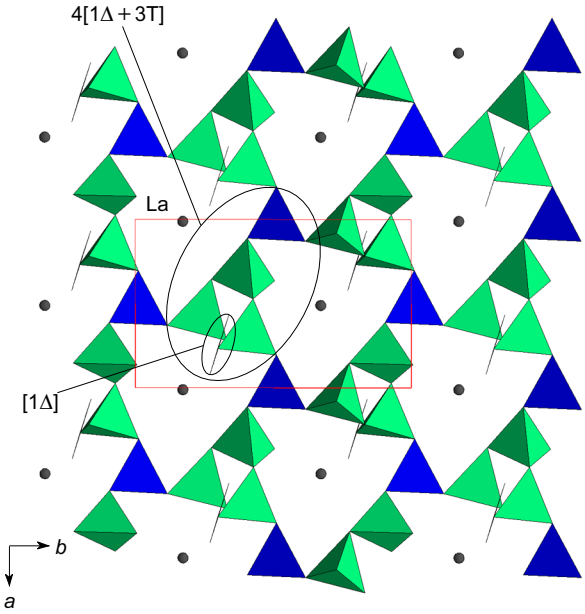


Figure 20. Crystal structure of $La[B_5O_8(OH)_2\cdot 1.5\,H_2O$: *ab* projection of a layer.[54]

additional monoborate triangles and the framework is described as $5{:}\{4[1\Delta + 3T]_{\infty\infty} + [1\Delta]\}_{\infty\infty\infty}$.

Considering the structure of $La_4[B_{14}O_{27}]$,[71] one can distinguish double layers consisting of incomplete pentaborate blocks 4[1Δ + 3T] lacking one triangle. The double layers are linked into a framework through tetraborate blocks and additional triangles. The notation for the boron–oxygen radical is $14{:}\{2\times(4[1\Delta + 3T])_{\infty\infty} + 5(4[2\Delta + 2T] + [1\Delta])\}_{\infty\infty\infty}$.

In the structure of $AgSr[B_7O_{12}]$ (Ref. 72) double layers consisting of deficient pentaborate blocks are connected through chains of tetra- and diborate blocks. The anionic part of the structure is described as $14:\{2\times 4[2\Delta+2T]_{\infty\infty}+(4[2\Delta+2T]+[2\Delta])_{\infty}\}_{\infty\infty}$.

The framework of walkerite $Ca_{16}(Mg,Li,\square)_2[B_{13}O_{17}(OH)_{12}]_4Cl_6\cdot 28\,H_2O$ (Ref. 65) consists of diborate chains that simultaneously constitute the layer and held the layers together. Within the layer, the diborate chains are connected through incomplete pentaborate block 4[2Δ + 2T] and isolated tetrahedron. The framework is described as $13:\{2\times 2[1\Delta+1T]_{\infty}+9(2\times 2[1\Delta+1T]_{\infty}+5(4[2\Delta+2T]+[1T]))_{\infty\infty}\}_{\infty\infty\infty}$.

Polyborates with pentaborate blocks form a wide variety of structures where these blocks are combined with the simplest monoborate blocks (see Table 2).

5. Tetraborates and polyborates with tetraborate block

Natural and synthesized tetraborates are much less abundant than penta- and hexaborates. Only two tetraborate blocks are known, *viz*., 4[4T] and 4[2Δ + 2T].

5.1. The 4[4T] block

An example of a simple tetraborate whose layered radical is formed by the 4[4T] block is provided by the structure of $CuTm_2[B_4O_{10}]$ (Fig. 21).

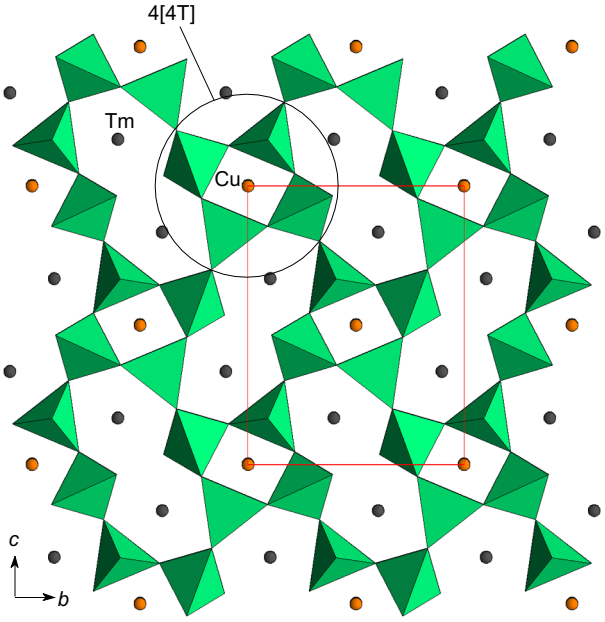


Figure 21. Crystal structure of $CuTm_2[B_4O_{10}]$: *bc* projection.[25]

5.2. The 4[2Δ + 2T] block

In the structure of polyborate $Pb_6[B_{10}O_{21}]$ (Fig. 22) one can distinguish a 4[2Δ + 2T] tetraborate block to which an additional BO_3 triangle is attached. This structural fragment is connected to the same fragment through terminal vertices of triangles to form isolated units $10:\{2\times(4[2\Delta+2T]+[1\Delta])\}$.

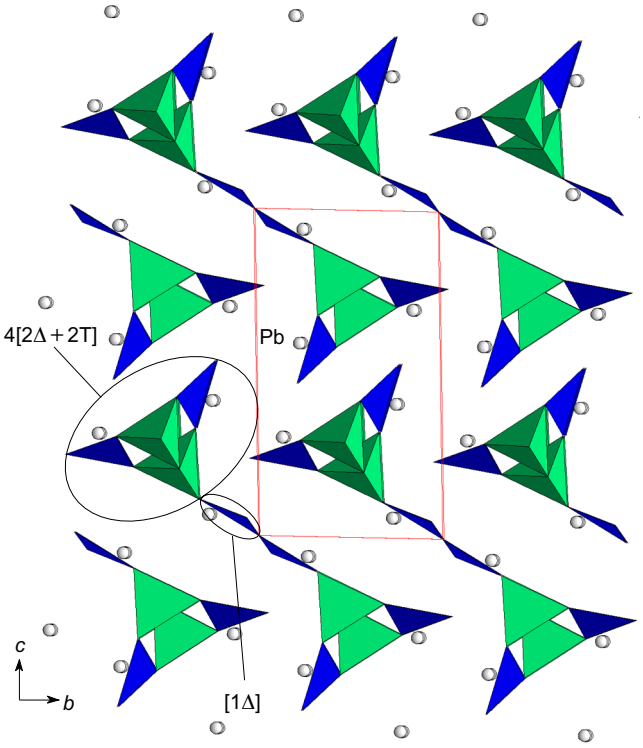


Figure 22. Crystal structure of $Pb_6[B_{10}O_{21}]$: *bc* projection.[73]

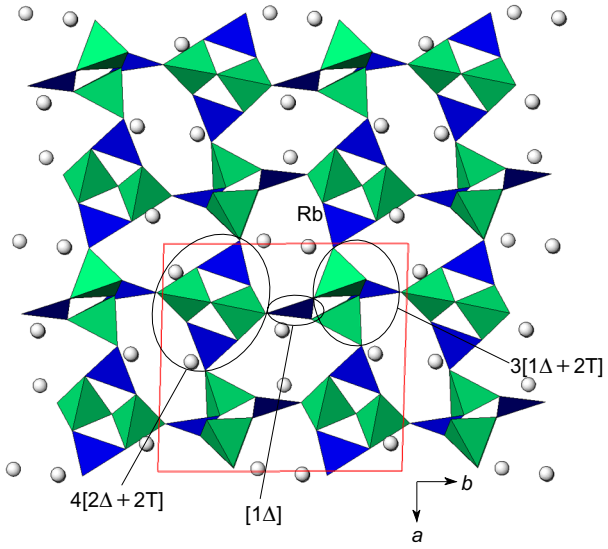


Figure 23. Crystal structure of $Rb_2[B_4O_7]$: *ab* projection.[74]

In the structures of $Rb_2[B_4O_7]$ (Fig. 23) and $K_2[B_4O_7]$ (Ref. 75) tetraborate units are combined with additional triborate triangles to form a framework $8:\{4[2\Delta+2T]+3[2\Delta+1T]+[1\Delta]\}_{\infty\infty\infty}$.

6. Triborates and polyborates with triborate block

6.1. The 3[1Δ + 2T] block

Hexaboron compounds $M_3B_6O_{11}F_2$ (M = Sr, Ba, Pb)[27,28] represent condensed triborates rather than hexaborates.

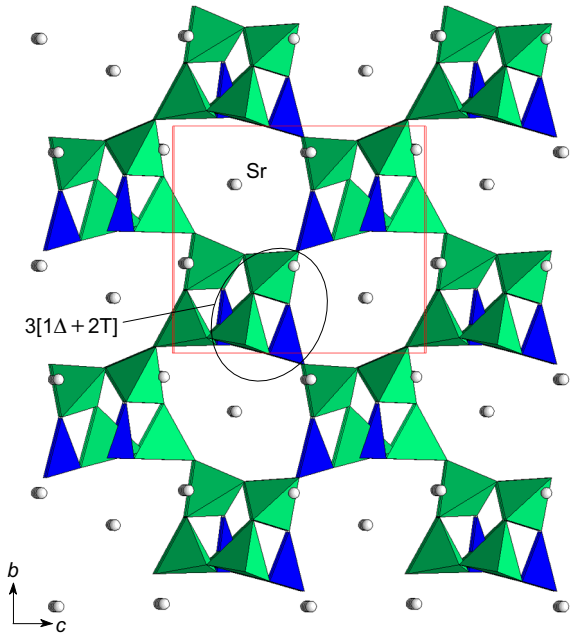


Figure 24. Crystal structure of $Sr_3B_6O_{11}F_2$: *bc* projection.[27]

Triborate blocks in their structure are connected in pairs and then linked into a framework $6:\{2 \times 3[1\Delta + 2T]\}_{\infty\infty\infty}$ (Fig. 24).

The $[Ni(en)_2]_6[(VO)_{12}O_6B_{18}O_{39}(OH)_3] \cdot 5H_2O$ structure (en is ethylenediamine)[30] contains isolated twelve-membered rings of six triborate blocks $18:\{6 \times (3[1\Delta + 2T])\}$.

Compound $Na_{11}[B_{21}O_{36}]Br$ (Fig. 25) also belongs to condensed triborates. The anionic part of its structure consists of double layers composed of two types of triborate blocks, $3[2\Delta + 1T]$ and $3[1\Delta + 2T]$. The layers are connected to each other through groups of three triborate blocks. The boron–oxygen radical is described as $21:\{2 \times 6(3[2\Delta + 1T] + 3[1\Delta + 2T])_{\infty\infty} + 9(3 \times 3[2\Delta + 1T])\}_{\infty\infty}$.

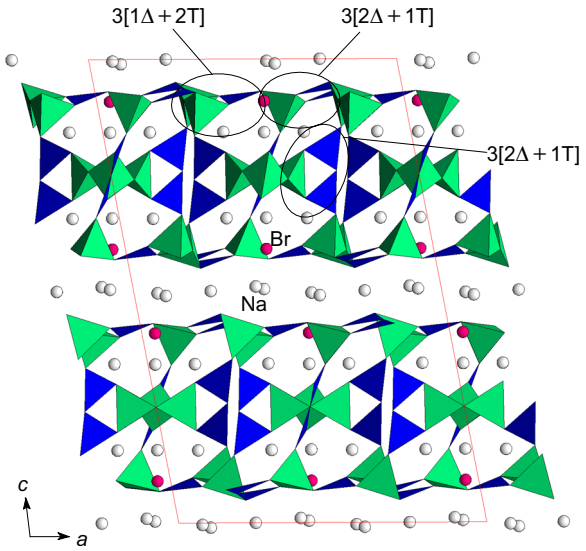


Figure 25. Crystal structure of $Na_{11}[B_{21}O_{36}]Br$: *ac* projection.[33]

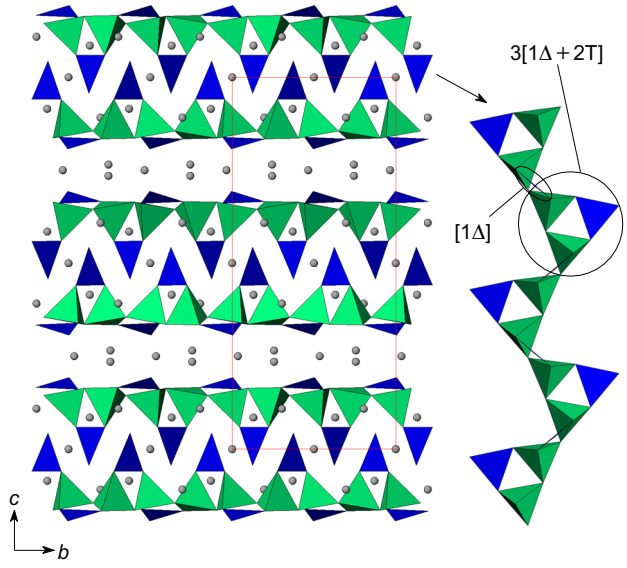


Figure 26. Crystal structure of $Ag[BO_2]$: *bc* projection.[79]

Chains in the structure of polyborate $Ag[BO_2]$ (Fig. 26) consist of triborate groups $3[1\Delta + 2T]$; an additional triangle is attached to the terminal vertices of two tetrahedra. The Christ and Clark notation for the boron–oxygen radical is $\{3[1\Delta + 2T] + [1\Delta]\}_{\infty}$.

In the structure of $Cs_2Cd_3[B_{16}O_{28}]$ (Ref. 82), chains of triborate blocks formed using additional BO_3 triangles are interlinked into a polar layer $4:\{3[1\Delta + 2T] + [1\Delta]\}_{\infty\infty}$.

In the structure of $Na_3[B_7O_{12}]$ (Ref. 19), the framework is composed of two types of triborate blocks connected through additional triangles. The anionic radical is described as $7:\{3[2\Delta + 1T] + 3[1\Delta + 2T] + [1\Delta]\}_{\infty\infty\infty}$.

In the structure of $Ba_2[B_{10}O_{17}]$ (Fig. 27), one can distinguish ribbons consisting of two chains of triborate blocks

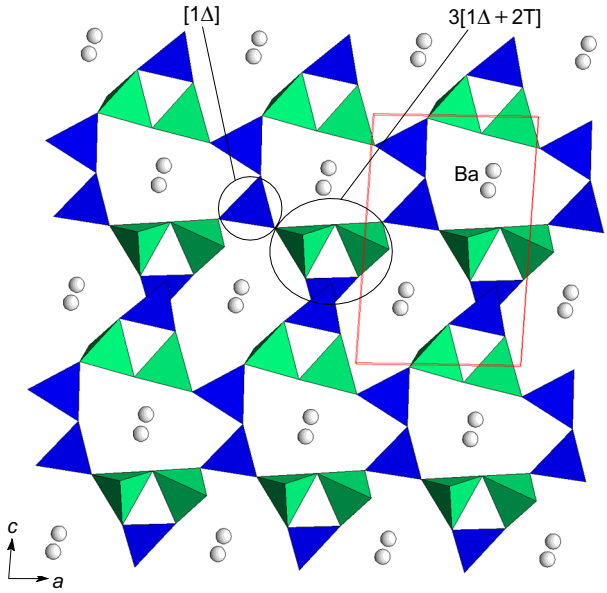


Figure 27. Crystal structure of $Ba_2[B_{10}O_{17}]$: *ac* projection.[83]

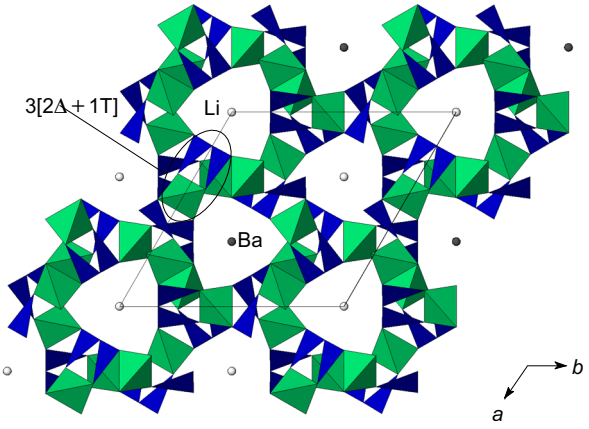


Figure 28. Crystal structure of $LiBa[B_9O_{15}]$: *ab* projection.[29]

and triangles and extended along the *b* axis. Along the *c* axis, the ribbons are linked by additional triangles into a framework $10:\{8:(2\times(3[1\Delta+2T]+[1\Delta]))_\infty+2\times[1\Delta]\}_{\infty\infty\infty}$.

6.2. The 3[2Δ + 1T] block

The structure of $Ba_2[B_6O_9(OH)_4]$ (see Ref. 26) contains condensed triborate layers $6:\{2\times3[2\Delta+1T]\}_{\infty\infty}$. The framework of $LiBa[B_9O_{15}]$ (Fig. 28) also consists of only triborate blocks $3\times3[2\Delta+1T]_{\infty\infty\infty}$, which form large voids occupied by lithium and barium atoms.

Isolated fragments comprising a triborate block and a BO_3 triangle can be distinguished in the structure of polyborate $SrBi_2[B_4O_{10}]$.[76] The boron–oxygen radical is described as $4:\{3[2\Delta+1T]+[1\Delta]\}$.

The anionic part of the structure of $Li_4Cs_3[B_7O_{14}]$ (Fig. 29) represents isolated units consisting of two triborate blocks connected by an additional triangle. The notation of the boron–oxygen radical is $7:\{2\times3[2\Delta+1T]+[1\Delta]\}$.

The structure of compound $Ba_2KZn_3[(B_3O_6)(B_6O_{13})]$ (Fig. 30) contains layers consisting of pairs of 3[2Δ + 1T] triborate blocks sharing the vertices of BO_4 tetrahedra and isolated triborate blocks 3[3Δ]. Taking account of anionic

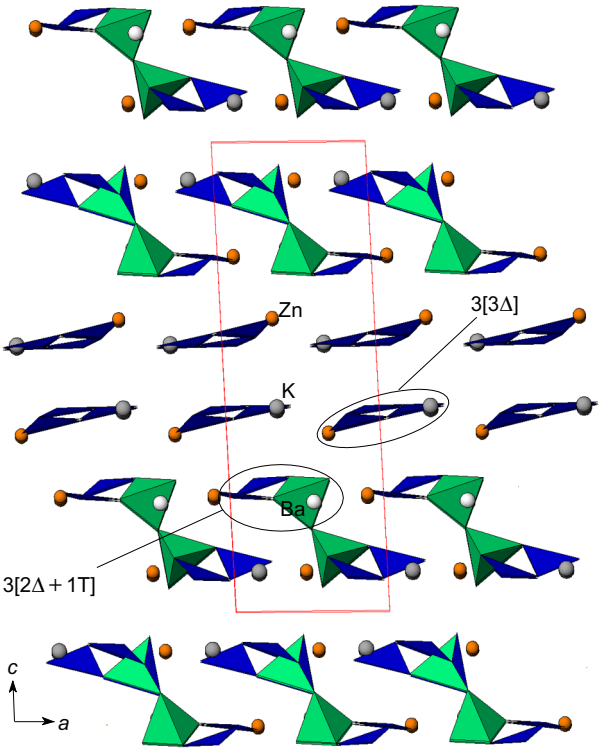


Figure 30. Crystal structure of $Ba_2KZn_3[(B_3O_6)(B_6O_{13})]$: *ac* projection.[31]

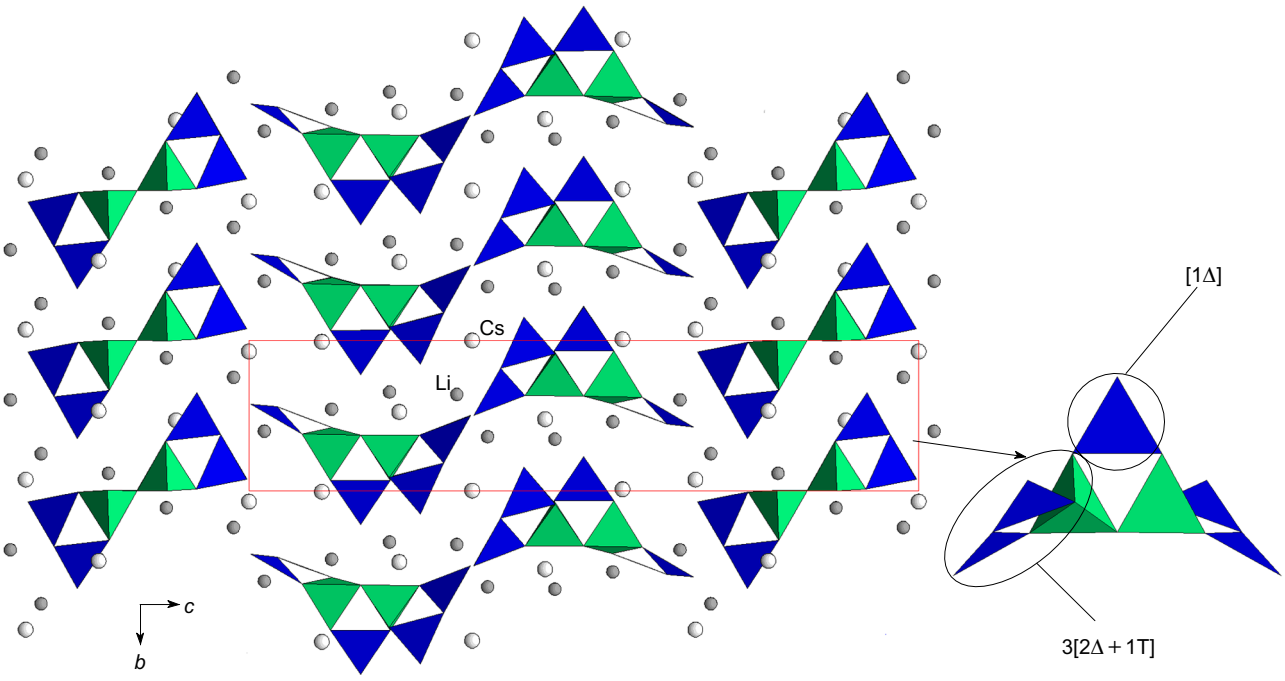


Figure 29. Crystal structure of $Li_4Cs_3[B_7O_{14}]$: *bc* projection.[77]

layers of ZnO_4 tetrahedra, one deals with mixed-metal anionic radical. The complex boron–oxygen radical is described as 9:{3[3Δ] + 6(2 × 3[2Δ + 1T])}.

The structure of $Ba_4Na_2Zn_4[(B_3O_6)_2(B_{12}O_{24})]$ (Ref. 32) also has isolated fragments consisting of four triborate blocks 3[2Δ + 1T] and, like in the preceding structure, isolated triborate groups 3[3Δ]. The Christ and Clark notation for the complex boron–oxygen radical is 18:{6(2 × 3[3Δ]) + 2 × 6(3[2Δ + + 1T] + 3[2Δ + 1T])}. Taking into account anionic layers of ZnO_4 tetrahedra and the boron-containing blocks, one gets a mixed-metal anionic radical. Both compounds, $Ba_2KZn_3[(B_3O_6)(B_6O_{13})]$ and $Ba_4Na_2Zn_4[(B_3O_6)_2(B_{12}O_{24})]$, should be treated as triborates rather than polyborates.

Compound $Ba_4K_2Zn_5[(B_3O_6)_3(B_9O_{19})]$ (Fig. 31) has the most complicated structure among the barium borates considered here. Two triborate blocks 3[2Δ + 1T] are connected by linear isolated groups consisting of three BO_3 triangles 3[ΔΔΔ]. Two out of three triborate blocks 3[3Δ] are located as in the structures of $Ba_2KZn_3[(B_3O_6)(B_6O_{13})]$ and $Ba_4Na_2Zn_4[(B_3O_6)_2(B_{12}O_{24})]$ while the third block resides in large voids of the layered structure. The compound in question can be classified as polyborate. The boron–oxygen radical is described as 18:{9(3 × 3[3Δ]) + 9(3[2Δ + 1T] + + 3[ΔΔΔ] + 3[2Δ + 1T])}.

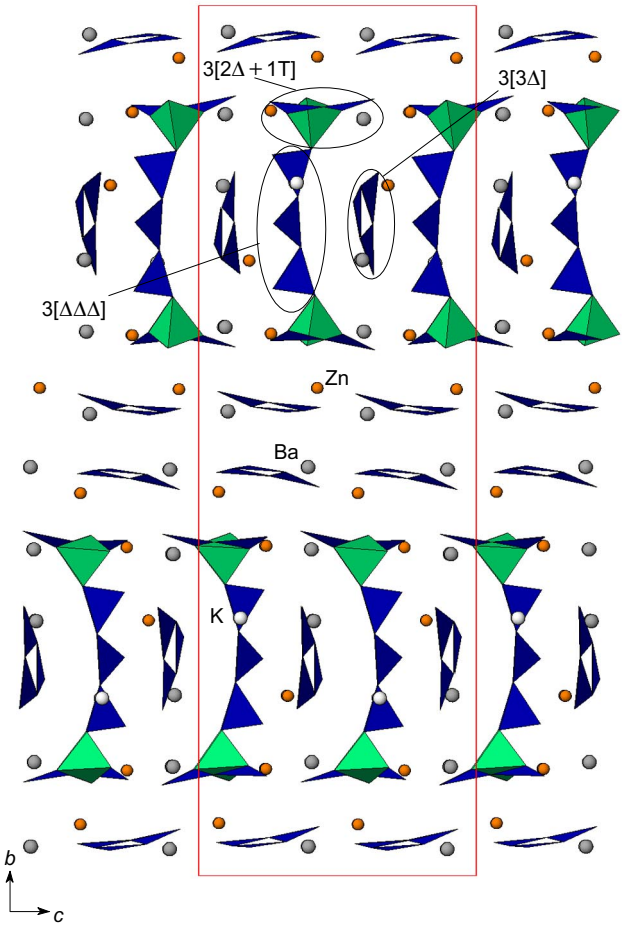


Figure 31. Crystal structure of $Ba_4K_2Zn_5[(B_3O_6)_3(B_9O_{19})]$: *bc* projection.[78]

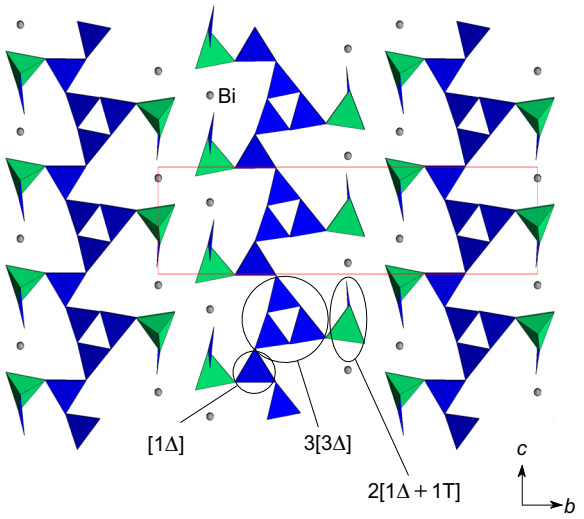


Figure 32. Crystal structure of β-$Bi_2[B_8O_{15}]$: *bc* projection.[84]

6.3. The 3[3Δ] block

The structure of $Cs_3Zn_6[B_9O_{21}]$ (Ref. 7) exhibits isolated triborate blocks and isolated triangles connected by ZnO_4 tetrahedra to form mixed Zn-B-O layers. The notation for the boron–oxygen radical is 6:{3[3Δ] + 3 × [1Δ]}.

Triborate blocks in β-$Bi_2[B_8O_{15}]$ (Fig. 32) are linked by additional triangles to form chains. Attachment of diborate groups (triangle and a tetrahedron) to apices of the chain triangles leads to formation of a ribbon described as $8:\{4(3[3\Delta] + [1\Delta]) + + 2 \times 2[1T + 1\Delta]\}_\infty$.

6.4. The 3[3T] block

In the structure of $BaBi_2[B_4O_{10}]$ (Fig. 33) triborate block consisting of three tetrahedra are connected by monoborate units (triangles) to form a bent chain $4\{3[3T] + [1\Delta]\}_\infty$.

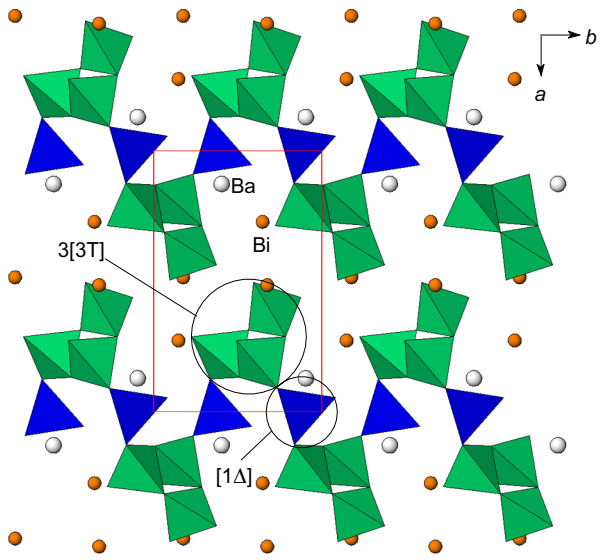


Figure 33. Crystal structure of $BaBi_2[B_4O_{10}]$: *ab* projection.[80]

Ribbons in the structure of polyborate β-$Dy_2[B_4O_9]$ are composed of 3[3T] triborate blocks and two additional triangles and are described as $8{:}\{2\times3[3T]+[1\Delta]+[1\Delta]\}_\infty$.[81]

7. Diborates and polyborates with diborate block

The structure of $Pb_2[B_4O_5(OH)_4](OH)_2\cdot H_2O$ (Fig. 34) is typical of diborates. It consists of 2[1Δ + 1T] blocks connected to form bent chains extended along the *b* axis; in turn, the chains form a layer. Large voids in the layer and the inter-layer space are filled with lead atoms, hydroxyl groups and water molecules.

The anionic part of the structure of $Ba_2Li[B_5O_{10}]$ (Fig. 35) represents ribbons composed of two diborate chains and an additional triangle and is described as $5{:}\{2\times2[1\Delta+1T]_\infty+[1\Delta]\}_\infty$.

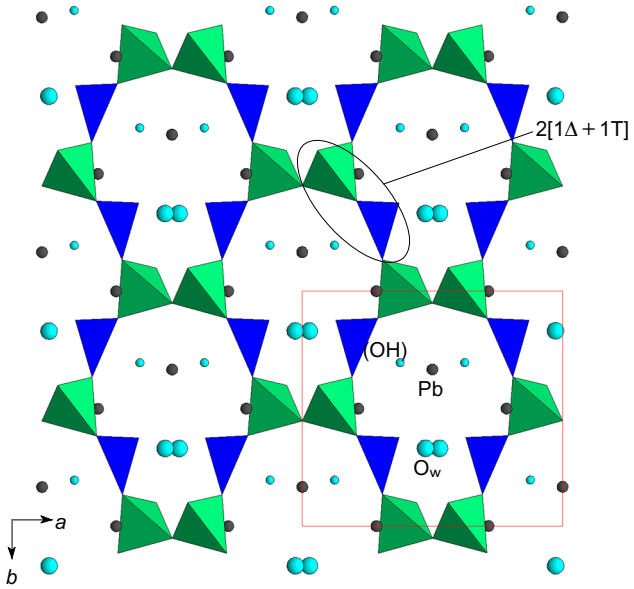


Figure 34. Crystal structure of $Pb_2[B_4O_5(OH)_4](OH)_2\cdot H_2O$: *ab* projection.[34]

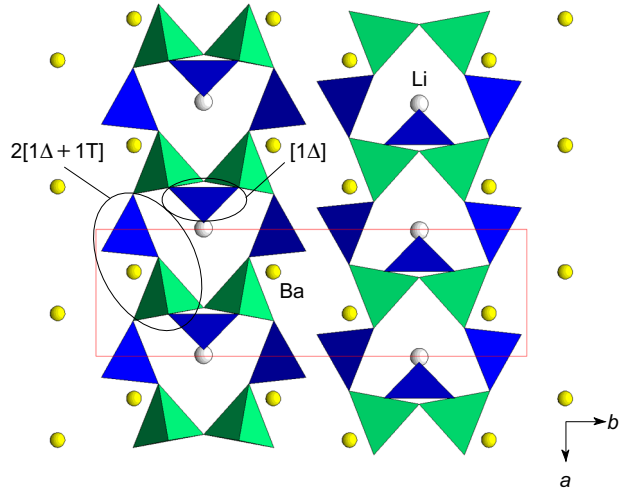


Figure 35. Crystal structure of $Ba_2Li[B_5O_{10}]$: *ab* projection.[86]

Ribbons can also be distinguished in the structure of $Pb_4Zn_2[B_{10}O_{21}]$.[85] In this case chains are composed of two types of diborate blocks, [1Δ + 1T] and 2[1T + 1T]. Two chains are interconnected to form a ribbon to which an additional BO_3 triangle is attached as in the structure of $Ba_2Li[B_5O_{10}]$. Ribbons linked at vertices of BO_4 tetrahedra form corrugated layers arranged parallel to the *ab* plane. The notation of the layer is $20{:}\{2\times(2\times2[1\Delta+1T]+2\times2[1T+1T])_\infty+4\times[1\Delta]\}_{\infty\infty}$. Layers are linked by ZnO_4 tetrahedra to form a mixed framework.

The structure of $Li_5Cs_2[B_7O_{14}]$ (Fig. 36) contains two types of isolated diborate chains. One chain is composed of diborate blocks (triangle and tetrahedron) and additional triangles are attached to the chain tetrahedra. The other chain consists of B_2O_5 blocks (two triangles). The anionic boron–oxygen radical is described as $\{2\times(2[1\Delta+1T]+[1\Delta])_\infty+2[2\Delta])_\infty$.

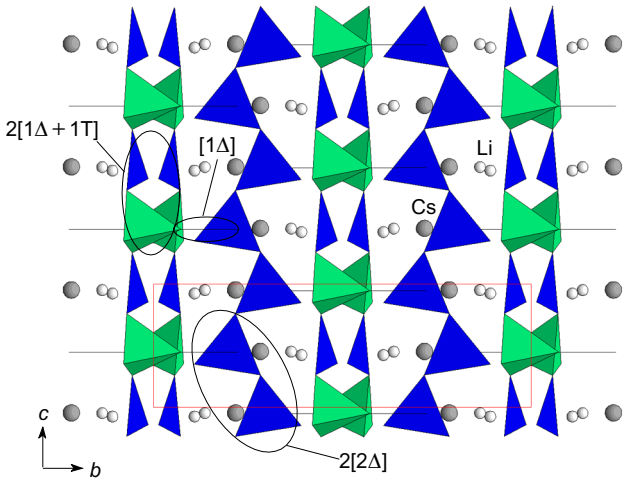


Figure 36. Crystal structure of $Li_5Cs_2[B_7O_{14}]$: *bc* projection.[87]

Among the polyborate structures considered above, the of $Cs_3[B_7O_{12}]$ structure (Fig. 37) is the most complicated. The anionic part consists of three-layer thick boron–oxygen sheets and was characerized[53] using the method of Christ and Clark.[1] We will follow the authors of original communication[53] and make some corrections. The first and third layers (L_1 and L_3, respectively) are identical and consist of 5[3Δ + 2T] pentaborate blocks only. The second layer, L_2, is composed of chains of 5[2Δ + 3T] pentaborate blocks with two different orientations, with the chains being connected by additional tetrahedra. The notation for the three-layer system is $24{:}\{2\times(5[3\Delta+2T])_{\infty\infty}+(5[2\Delta+3T]_\infty+5[2\Delta+3T]_\infty+4\times[1T])_{\infty\infty}\}$. From the standpoint of the method of Christ and Clark[1] this very complicated polyborate structure is composed of only two types of FBBs, *viz.*, penta- and monoborates condensed into layers and thick multilayer sheets.

8. Conclusion

Our analysis of the structure of borates is first of all necessary for correct structure determination in order to relate the structure of crystals to their properties and to properly classify the borates under study. The method in question has long been known; however, it was not used systematically. Many researchers use the approach of Burns

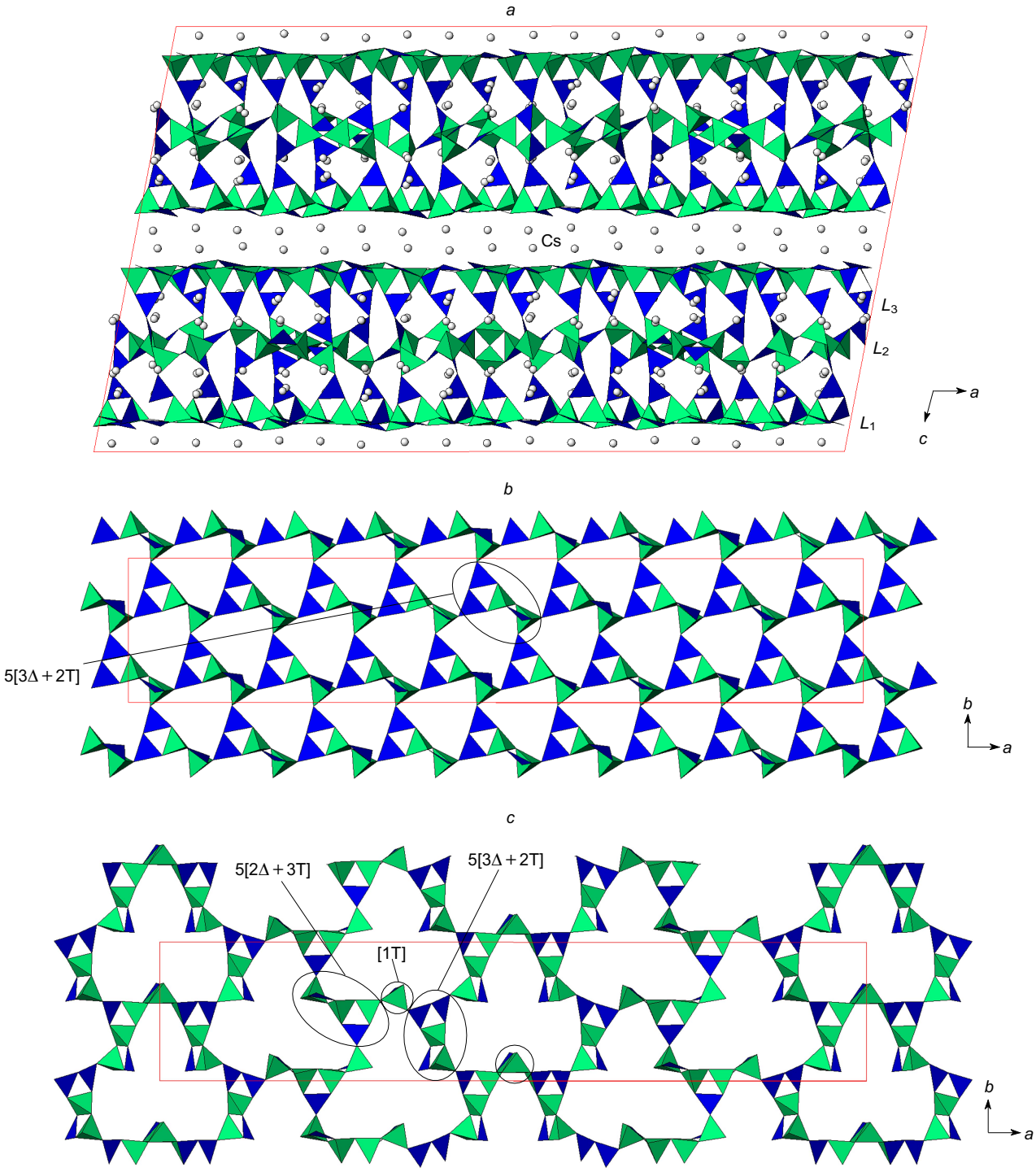


Figure 37. Crystal structure of $Cs_3[B_7O_{12}]$: *ac* projection of three-layer thick boron-oxygen sheets (*a*), *ab* projection of layer L_1 (*b*) and *ab* projection of layer L_2 (*c*).[53]

et al.,[2] which often fails to perform correct analysis and leads to fundamental errors in the structural description and to the loss of structural similarity. In this review we applied the method of Christ and Clark [1] to characterize the anionic radical in all borates studied and thus to obtain the best description of their structural features.

An analysis of original publications showed that the principle of parsimony, even if it is valid for a particular rational (optimum) structure of any crystal, does not limit the diversity of constituent structural blocks in borate anionic radicals. Modern complex initial systems used to synthesize new phases demonstrate various anionic boron–oxygen architectures built up of different sets of fundamental building blocks. All recent studies on new borates show that these compounds belong to polyborates that require a correct structural characterization.

Many borate crystals have technological applications. Modern studies on the synthesis of borates are aimed to

obtain advanced materials. In the case of targeted synthesis based on the structural studies of the available compounds, it is of paramount importance to reveal structural units (building blocks) and to determine their features (in particular, polarity and methods of jointing in the structure). This can be done with certainty using the approach considered in this review. It allows one to distinguish structural families among new complex borates and to reveal the structural features of compounds that underlie the optimum properties of crystals.

Summing up, the material presented in this review is necessary for proper classification of new compounds and for further optimization of the synthesis of promising phases.

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